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The Beginnings of Piezoelectricity

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THE BEGINNINGS OF PIEZOELECTRICITY

A Study in Mundane Physics

by

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Springer

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LIST OF ABBREVIATIONS

DSB	*Dictionary of Scientific Biography,* ed. Charles C. Gillispie, 16 vols., New York: Charles Scribner's Sons, 1970–1980
AHES	*Archive for History of the Exact Sciences*
Ann. Phy	*Annalen der Physik und Chemie*
Göttingen Abhandlungen	*Abhandlungen der Königlichen Gesellschaft der Wissenschaften zu Göttingen*
HSPS	*Historical Studies in the Physical (and Biological) Sciences*
Leipzig Abhandlungen	*Abhandlungen der mathematisch-physischen Classe der Königl. Sächsischen Gesellschaft der Wissenschaften zu Leipzig*
OLP	*Œuvres de Pasteur,* ed. Pasteur Vallery-Radot, 7 vols., Paris: Masson, 1922
OPC	*Œuvres de Pierre Curie,* Paris: Gauthier-Villars, 1908
TMPP	William Thomson, *Mathematical and Physical Papers,* 6 vols., Cambridge: Cambridge University Press, 1882–1911

INTRODUCTION

Most scientific research is, so to say, “mundane”; it is painstaking labor that requires much time, effort, study, skill, and indeed ingenuity, but it rarely involves revolutionary path-breaking, fundamental issues of Nature and her behavior or the attention of a wide audience and the concomitant glamor. The adjective “mundane” in this context should imply neither dullness nor diminution. Creativity and originality come out of this kind of research not less than from the more glorious studies. The daily basis on which much scientific work is carried out makes it neither less important nor less creative. Romantic notions of the isolated genius who exposes the great secrets of Nature by revelation, like the legendary story of Archimedes jumping out of the bath, are not confirmed by detailed studies. Despite what might sometimes be thought, mundane science can be an intriguing intellectual and practical enterprise, which, like the more glamorous stories in the history of science, involves among other things originality, surprises, and controversies.

This book is a study of a branch of mundane physics at the end of the nineteenth century. It discusses the discovery of a particular phenomenon—the generation of electricity by mechanical strain and of mechanical strain by electricity in crystals—named piezoelectricity, and the development of its research. How was piezoelectricity developed and why did it develop this way rather than in other ways? These are the basic questions of this study and their answers are sought through a thorough examination of the field’s history. To understand the particular development of the field, I have looked at the practice of physicists—in the ways they chose their subjects of research and carried them out, on their background and on the reasoning that led to hypotheses, theories, models, experiments, discoveries, and mistakes. I reconstruct the physicists’ reasons to investigate particular questions in particular ways. It is a historical rather than a rational reconstruction. The general approaches of “research programs” toward science and logical derivations are important, but the role of personal motivations, academic positions, scientific traditions, and contingent circumstances cannot be ignored.

Many historical studies have been dedicated to the discovery of novel effects and phenomena. Following the discovery of a new basic phenomenon and the emergence of a novel field, much less attention was dedicated to the early development of physical research. This book follows the history of piezoelectricity after the discovery of the effect to its consolidation into an accepted body of experimental and theoretical knowledge. This process seems to recur in the establishment of novel scientific subfields and thereby, knowledge. The mere discovery of an effect (in piezoelectricity that pressure induces electric polarity in crystals) was not enough to establish a scientific subfield. It could have been left as merely another curious experimental fact unconnected to any other. A subfield emerged only with subsequent study of the observed effect and related phenomena under various conditions, which resulted in the knowledge of their characteristics and laws. Such study is neither self-evident nor inevitable. The subsequent study depended both on the phenomenon and on a few scientists interested in issues that it raised; the interest stemming from their own theoretical experimental, or occupational concerns, and their earlier works. The emergence of a new subfield requires a basic consensus on the phenomena that it encompasses and their characteristics. As this history shows, such a consensus evolved via experimental study, theoretical arguments, and controversy. Its evolution was part of a process of consolidation that the new field underwent in the first two decades after its discovery. At the end of this process piezoelectricity encompassed an accepted body of knowledge consisting in experimental findings and a mathematical theory that accounted for them. Still, many issues were left open and were the subject of disagreement between scientists. That the subfield of piezoelectricity was compatible with the general concepts and laws of contemporary science enabled its consolidation. Discordance with the accepted truths of physics would probably have precluded a consensus on the theory. Apparently this process, which I examine here, characterizes non-revolutionary fields.

The historiography of nineteenth century physics has concentrated on the main developments in central theories that had implications in several branches of the field and continued to be important for later physics. The basic questions of thermodynamics and the kinetic theory of heat and electromagnetism have enjoyed a major attention from historians. Yet these questions occupied only a part (although significant) of physical research at the time. Many physicists were often occupied with various other questions that were only partly or indirectly connected to these issues. Many fields of research and developments of nineteenth century physical science have not been subject to an adequate historical analysis. This is true in particular of the research of the "gross matter" phenomena, like elasticity, the physics of crystals and dielectrics, and researches that had no direct impact on the study of other fields. Piezoelectricity represents both kinds of understudied fields. Therefore, its history offers an additional perspective on late-nineteenth century physics. This perspective reveals important but until now obscure developments like that of the concept and application of symmetry in physics (which involved subjects like crystallography, optics, elasticity, and heat conductivity). It turns attention to understudied fields and developments in nineteenth century physics like elasticity or pyroelectricity. The history of piezoelectricity also provides an additional view on subjects that have attracted more historical research like electromagnetism and thermodynamics by discussing their application in the research of a "gross matter" phenomenon. It shows how various approaches and theories were conceived and applied to a particular problem by working physicists. The examination of the practice of physicists provides meaning to notions like acceptance or rejection of theories. It reveals the elements of different theories that the physicists adopted or rejected and how they applied them. In other words, it shows the significance of particular views to physical research. This research examines the application of known theories like the thermodynamic potentials. The historians paid much more attention to their formulation and origins than to their application. However, their application was crucial to their influence on physical practice. Without it they would have been only slogans or issues of scientific faith.

Justifiably, historians have looked for the roots of the revolutions in physics at the beginning of the twentieth century. Thus, physical questions that led to the subsequent revolutionary events have gained more attention than those that did not. By focusing on the relativistic and quantum revolutions, historians have given more emphasis to breaks in the development of physics than to the continuity. Piezoelectricity displays another path from nineteenth to twentieth century physics, a path characterized by continuity rather than by rupture. This path was shared by various branches of physics that experienced only minor changes as a result of the upheaval in the fundamental laws of nature. Perhaps (but this is a speculation that lies beyond the scope of this research) the technological application of these branches was more significant to their development in the twentieth century than the revolutions in physics.

Piezoelectricity was mundane physics. Yet, it is only one example of mundane physics, not necessarily a representative one. One cannot derive general laws about the development of mundane science from it. This is far from my aim. This history of the beginnings of piezoelectricity is a "case study" in the sense that it is a detailed study of scientific work. It is not, however, a sample of general behavior like the way a quartz crystal is studied in a piezoelectric experiment. The development of piezoelectricity was unique, resulting from the specific combination of individuals, scientific questions, knowledge, and working conditions that were involved. From this unique development one can still cautiously draw historical lessons. Some features of this history are typical of similar cases or have parallels in other developments. Still, they certainly do not form a historical law. The first and foremost interest of the book is the particular history of the emergence of piezoelectricity *per se*. It is particular both because it involved one instead of another development, and because this development was shaped by a combination of causes that has not and could not have been repeated. The history of science, like any other branch of history and unlike natural science, is about particulars. Yet when dealing with local history, as in this study, historians usually aim beyond the particular examples discussed. From practices, methods, approaches, views, and devices employed in one local case, historians explore beyond its proximate. This is also my aim here.[1]

Beyond the interest in the study of mundane "gross matter" phenomena, there are good specific reasons to draw historians and philosophers of science to the early history of piezoelectricity. Though almost unknown outside the professional community, piezoelectric devices are today ubiquitous. Virtually everyone in the West

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[1] On the tension between the local and the general in the history of science see Peter Galison, *Image and Logic: A Material Culture of Microphysics*, Chicago: The University of Chicago Press, 1997, pp. 59–63.

possesses at least one device based on piezoelectric technology. Most of us carry at least one piezoelectric device a few millimetres from the skin. I refer, of course, to the wristwatch. All quartz watches and clocks are based on piezoelectricity. The piezoelectric resonator is the basis for most electronic time keepers and regulators. Thus, most electronic devices contain such a resonator, which utilizes the two basic effects of piezoelectricity: the induction of electricity by changes of pressure and the converse induction of strain by changes in the electric field in crystals. Yet, time keeping is but one application of the phenomenon, and its scientific study continues unabated: about 1400 papers dealing with some aspect of the phenomena were published in the year 2004.[2] Transducers, sensors, actuators, pumps, motors, and "smart structures" are only some of the central devices that employ the piezoelectric effect. Electric communication, medical diagnostics, computers, industrial sensors, and microelectromechanical (MEMS) devices are a few examples for the application of the piezoelectric effect.

The scientific significance of piezoelectricity is not limited to technological applications. Discovered in 1880 and thoroughly studied in the following decade and a half, the phenomenon is an early example of complex matter physics that went beyond elasticity and optics. Piezoelectricity is a phenomenon of crystals, i.e., arranged complex matter. It does not appear in simple or randomly arranged materials; its properties are dependent on the structure of the crystal. Piezoelectricity is a reciprocal phenomenon of energy conversion from one kind (elastic) to another (electric). By relating elasticity and electricity in complex matter, it had interesting bearings on their appearance, nature, and the relationship between them in crystals and in general.

Piezoelectricity was discovered by two young physicists—Jacques and Pierre Curie. They detected the so-called direct effect: the induction of electric polarization by variation of pressure. It immediately became a subject of research by its discoverers and soon by others. The converse effect, i.e., the creation of strain by electric field, however, was discovered only a year later following a theoretical prediction. In the first 15 years of research the basic properties of the phenomenon were observed and a theory that embraced these properties was successfully formulated, elaborated, and refined. By 1895, piezoelectric research attained a firm body of both empirical and theoretical knowledge. The theory of 1895 is still the basis of current piezoelectric theory. It explains the mechanism of devices like the piezoelectric resonator. Yet, at the time, no one predicted future practical application of the phenomenon. Only 20 years later during the First World War, did the phenomenon begin to be exploited outside the laboratory, in a search for a device to detect German submarines. The sonar, the direct product of this research, was put into use only after the war had ended.

Experiments were the focus of piezoelectric research in the first years after its discovery. Physicists studied various properties of the new phenomena, like the relations between stress, direction, and the resultant electric effect in several crystals. A way to understand the effect was suggested in 1881 by the Curies, which, however,

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[2] Science Citation Index Expanded™ cites 1960 papers that mention piezoelectricity in their abstract. Random sample shows that about 30% of them only use piezoelectric instruments and do not study the phenomenon itself.

did not provide a detailed account of the phenomena. Yet, in 1889 Röntgen revealed experimental results that disagreed with that explanation. In the following year, Woldemar Voigt introduced a mathematical theory that accounted for all the experimental data and predicted further phenomena. By its applicability to all crystals under any stress, Voigt's was a general theory. Its formulation divides the early history of piezoelectricity into two successive phases, which I call a pretheoretical and a theoretical phase. The term "pretheoretical" designates a field that is not accounted for by a comprehensive theory, i.e., a theory that describes most observable behaviors in the field, while "theoretical" designates a field that is accounted for by such a theory. This is not to say that the theory had no role in the pretheoretical phase. Even during that phase, theoretical thinking and speculations had a significant role.

A theory designates quite different things in different contexts and by different authors. One is to refer to the part of science that is not empirical, i.e., which is beyond the relations observed in the laboratory. In another, more restricted sense, a theory is a set of laws or assumptions that describes a scientific field or its part in a way that accounts for central phenomena in the field, whether qualitatively or quantitatively. In this work I use the noun theory in the more restricted sense, while I employ its adjective and adverb in a more general way in reference to ideas that are not completely rooted in the experiment. Voigt's was not only a theory in the restricted sense but a rigorous elaborated mathematical one. Rigorous by the fact that its several conclusions derived from a few assumptions, elaborated as central consequences of it that had empirical significance were spelt out, and mathematical in its formulation and quantitative predictions.[3] Since it was also general, it directed both the theoretical and the empirical research in the theoretical phase, no such theoretical idea had a similar role in the pretheoretical phase. Experimentation took the lead in that phase. A combination of experiment and speculations, models, partial explanations, and theoretical derivation from other branches characterized the pretheoretical phase. It seems typical of young fields. A theoretical phase is closely related to a mathematical formulation that enables extensive predictions from a limited number of assumptions. Thus, it seems to characterize the more quantified branches of physical science since the end of the eighteenth century. A pretheoretical phase, on the other hand, does not require any rigorous theory and therefore, mathematics and quantitative rules.

Mathematization and the comprehensiveness of the theory made almost any further research, either experimental or theoretical, related to the general theory. As shown below the division into two phases appears in almost every aspect: the type of experiments performed, the reasons for their performance, the theoretical speculations suggested, the relation between theory and experiment, the scientists who contributed to the field, and, of course, the elaboration of the mathematical theory itself. The new phase also meant a renewed interest in the field as a glance at the annual number of contributions to the field (Figure 1) shows.[4] Differences between the two phases in

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[3] In the following I use these terms. In particular I use elaborated theory to designate one that includes relations derived from its basic assumptions especially with reference to applications in different conditions.

[4] One should not over-interpret the particulars of the graph; it is mainly intended to demonstrate general tendencies in the interest in the field. The graph is based on table A.2.

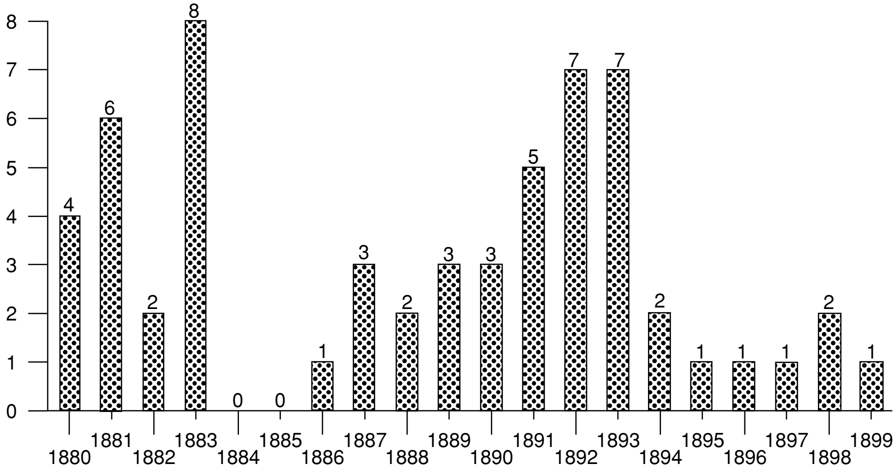

Figure 1: Annual number of publications on piezoelectricity: 1880–1899.

piezoelectricity might be more conspicuous than in other fields, but I presume that the division characterized a process of maturation of many mathematical physical branches throughout the last two centuries.

The turn from a study dominated by experimental research to one directed by comprehensive mathematical theory might be a characteristic of the growth of new non-revolutionary physical fields in physics after the middle of the nineteenth century. The history of pyroelectricity, a related phenomenon discovered at the middle of the eighteenth century, suggests that earlier, experiments and sporadic hypotheses could dominate a field for a long period. Pyroelectricity gained a mathematical theory only in the account given by Voigt to piezoelectricity.

The early history of piezoelectricity until the consolidation of the field circa 1895 raises intriguing historical questions, which I examine in this study. An interesting question about almost any new field concerns its emergence. How and why the phenomenon was discovered and how its knowledge developed from that point? Although scientific discovery has been extensively discussed by historians and philosophers of science, the discovery of piezoelectricity seems to defy common classification. It was not an accidental discovery; the Curies had looked for the phenomenon. Yet, it was neither an empirical confirmation of an established theory, nor a result of any ‘crisis state;’ it followed neither the use of a new instrument nor experimental method.[5] Nevertheless, contingency, theoretical derivations and speculations, and experimentation all played their part in the discovery. The story of this discovery demonstrates the tension between logical and physical necessity on the one hand and contingency on

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[5] On categories of discovery see for example, Thomas S. Kuhn, “The Function of Measurement in Modern Physical Science,” in *The Essential Tension*, Chicago: The university of Chicago Press, 1977, pp. 178–224, on p. 204. Kuhn also mentions discovery of “quantitative specification of what is qualitatively already known,” which is clearly irrelevant to the qualitative discovery of piezoelectricity.

the other, a tension that characterizes much of the history of science. This tension continued to be manifested in the subsequent research of the phenomenon, especially in the pretheoretical phase when contingent causes and traditions independent of theory shaped much of its experimental study.

Piezoelectricity involved several scientific subdisciplines: elasticity, electromagnetism, physics of crystals, and crystallography. Various approaches and ideas common either to the physics of the time (e.g., thermodynamics), or to a particular subdiscipline (e.g., considerations of symmetry current in crystallography and the physics of crystals) shaped the research in the field. This influence is apparent from the discovery of the phenomenon, which was based on knowledge, attitudes, experimental procedures, and theories from these fields. It turns out, therefore, that the discovery of piezoelectricity was a product of familiarity with more than one subdiscipline. Acquaintance with a few subdisciplines might also have been a key for other discoveries. Various theories and subdisciplines continued to be relevant for the study of the new phenomena. Even after the field had obtained a systematic theory of its own, it was not isolated but had interesting interactions with various connected theories (e.g., electromagnetism) and approaches (e.g., thermodynamics). This history examines the relations and interactions between the various approaches and theories relevant to the study of piezoelectricity. These include the central approaches of contemporary physics. Thereby, it throws light on the central issues of contemporary physics and suggests a picture of physics at the end of the nineteenth century. In particular, it displays the use and application of the new thermodynamic concepts and formulations.

Among the relations discussed here, the relationship between the mechanistic-molecular approach on the one hand and the thermodynamic-phenomenological on the other is especially interesting. According to the molecular approach, phenomena should be explained in terms of molecules, atoms, and their interactions. On the other hand, according to Woldemar Voigt, who developed the phenomenological theory of piezoelectricity, in such a theory, "a small number of principles, i.e., rules derived from experience and ascribed hypothetical general validity, support an edifice of mathematical conclusions that yields the laws of the phenomena in the field concerned."[6] Phenomenological theories aimed at describing the phenomena and their relations as found empirically by using a minimal number of laws. They did not aim at explaining the relations between the phenomena on the basis of another effect or process (hence regarded as more basic) but only at describing them. Molecular theories or continuum models like the vortex atom, in contrast, aimed precisely at such an explanation by invoking various hypotheses that could not be derived from empirical knowledge. The phenomenological approach accepted only hypotheses grounded on empirical results, either of the particular phenomena examined or of a larger field.[7]

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[6] Woldemar Voigt, "Phänomenologische und atomistische Betrachtungsweise," E. Warburg, ed., *Die Kultur der Gegenwart*, dritter Teil, dritte Abteilung erster band - *Physik* (Berlin, 1915), 714–731, on 716.

[7] In adopting the term phenomenological theories from the physicists of the epoch I do not apply the term as it is sometimes used especially by philosophers. Thus a few clarifications might be helpful. First, the phenomena accepted by this approach were the results of experiments rather than the readings of indicators in the laboratory, e.g. they described a relation between pressure and charge, voltage or

The phenomenological approach did not require direct reduction to magnitudes and entities observable in the laboratory. In the later part of the nineteenth century, the laws of elasticity and the basic laws of electrostatics (i.e., Coulomb's law in its various forms and the relationships between electric charge, voltage, force, and moment) were conceived as expressing true verified relations. Therefore, physicists employed these laws in elaborating phenomenological theories for particular branches like piezoelectricity. Similarly, they used entities like polarization that are not directly measured.

Piezoelectricity was first explained by a molecular model, but in 1890 it was superseded by Voigt's phenomenological theory, which was, like virtually all of its kind, expressed with continuous differential equations. Subsequently, it guided most research in the field, but physicists continued to propose molecular models and preferred it to molecular suggestions. This development from an explanatory to a descriptive theory seems to contradict the logical order from a description of phenomena to their explanation.[8] Moreover, the transition from molecular to continuum theory runs against the current of the time toward corpuscular theories in physics. The two most famous examples are the kinetic theory of gases and statistical mechanics for the science of heat, and the advent of the "ions" followed by the electron in electromagnetism. Contemporary developments in spectral analysis, the theory of anomalous dispersion, electrolysis and discharge are less known examples of the same current.[9] The success of corpuscular theories was only partial, however. Even the famous achievement of reducing heat to motion encountered difficulties, most famously in attempted explanations of the second law of thermodynamics.

Nonetheless, contemporaries regarded the theories of discrete matter as successful. At the end of the century most physicists believed in a molecular-atomistic structure of matter, even though they interpreted it in different ways. The critical response to the opposition well demonstrates the view of the majority. In 1895, the German Scientific Society invited Georg Helm to present his criticism of the mechanical-atomistic view at its annual meeting. "The meeting was an unmitigated disaster" for the opposition. Eminent scientists attacked the speaker. Most physicists in the audience conceived the assumption of atoms or molecules as indispensable. Shortly after, Wilhelm Ostwald,

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polarization rather than between a mass and a declination of a needle; these indicators were translated into experimental results by theories that were by then already well accepted. (In that the use of 'phenomenological laws' here agrees with that of Nancy Cartwright. However, unlike Cartwright, here the term phenomenological is not restricted to laws but is employed also for theories: Nancy Cartwright, *How the laws of physics lie*, Oxford: Oxford University press 1983, 1–3). Second, in my use of the term "Phenomenological theories" I do not confine the theory to empirical regularities. Phenomenological theories can be based on various assumptions and principles that are not derived from the empirical data of the **specific** theory, like the principle of energy conservation and considerations of symmetry. Both were assumed in piezoelectric phenomenological theory. Terms like "macroscopic" or even "continuum" theory would not do, since they do not exclude assumptions about hidden entities or mechanisms (notice that phenomenological theory does not exclude the use of analytical concepts like energy or entropy).

[8] Yet historically the later theory described phenomena unaccounted for by the earlier theory.

[9] John L. Heilbron, *A History of the Problem of Atomic Structure from the Discovery of the Electron to the Beginning of Quantum Mechanics*, PhD. Dissertation, University of California, Berkeley, 1964, pp. 16–24, Olivier Darrigol, *Electrodynamics from Ampère to Einstein*, Oxford: Oxford University Press, 2000, pp. 265–294.

the leading German antagonist to atomistic-mechanical explanation, regrettably observed: “Repeatedly one hears and reads that no other understanding of the physical world is possible except that based on the “mechanics of atoms”; matter and motion seem the final concepts to which the manifold of natural phenomena must be reduced.” Even if Ostwald exaggerated the commitment of physicists to atomistic theories, and neglected the will of most to admit additional concepts like force and tension to the two mentioned, he was correct in pointing out the general preference of atomistic-molecular theory.[10] Still, some physicists preferred to base their accounts on overall principles, occasionally on those of thermodynamics, while others did not regard mechanical concepts as final. A few physicists, especially in Britain, favored reduction of atoms and molecules to singularities in a continuous medium.[11] Another small group considered an electromagnetic reduction of physics; yet, that did not deny the centrality of corpuscles.[12] Nevertheless, as the response to Helm’s address displays, the growing explanatory power of corpuscular theories was generally recognized. Despite the general tendency toward molecular theories, piezoelectricity was accounted for by a continuum theory. Even after virtually all had accepted the atomistic assumption toward the end of the first decade of the twentieth century, no satisfactory molecular theory was suggested for piezoelectricity. Voigt’s phenomenological theory still prevailed.

This book studies the reasons for the peculiar development of piezoelectric theory. Why did the phenomenological become the dominant theory of the field? Why was none of the molecular models proposed after the introduction of Voigt’s theory accepted? On the other hand, why did physicists continue to propose molecular explanations? Many protagonists did not view these different approaches as contradictory. Furthermore, most physicists did not follow a rigorous philosophical system. Their ideas on science rarely follow a logical derivation from basic principles; they are better characterized as *Weltanschauung* or world-view (i.e., a collections of positions not necessarily systematic) than as philosophy. These views of science were shaped primarily by scientific education and experience of the scientists rather than by elaborated philosophies of science.[13] The relinquishing of the molecular models of piezoelectricity did not originate in a rejection of molecularism, nor were the later attempts at a molecular theory derived from a realist rejection of continuum

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[10] Heilbron, *Problem of Atomic Structure*, 16–24, 41–43, quotations on p. 42. Ostwald himself also mentioned interactions between atoms. Later evidence convinced Ostwald by 1909 that “we have experimental proof for the discrete or grainy nature of matter” (*ibid.*, p. 44).

[11] William Thomson and Joseph Larmor are two representatives of this approach.

[12] The influence of and commitment to the “electromagnetic view of nature” was more limited than that occasionally attributed to it by the secondary literature. Hardly a handful of physicists was committed to the view. See Shaul Katzir: “On ‘the Electromagnetic World-View’: a comment on an article by Suman Seth,” *HSPS* 36 (2005) 189–92. On that view see Russel McCormmach, “H. A. Lorentz and the electromagnetic view of nature,” *Isis* 61 (1970), 459–97.

[13] For example, “Einstein could learn from [the textbook of] Drude [a student of Voigt] the principle of the economy of thought and the critical attitude toward mechanism. Drude’s phenomenology excluded any picture of ether process.” Darrigol, *Electrodynamics*, p. 373. On physicists loose employment of philosophical doctrines see for example Mara Beller, *Quantum Dialogue: The Making of a Revolution*, Chicago: The University of Chicago Press, 1999, pp. 3–5.

theory. A close look at the particular developments in the field is required to answer the questions posed above. Attempts to explain the appearance of piezoelectricity by molecular models reveals tension between basic hypotheses about the building blocks of nature and more complex phenomena. This is an early manifestation of the problem of reducing physics to the emerging atomic and later subatomic physics.

Experiments played various and changing roles in the early history of piezoelectricity. Its history provides a good opportunity to observe these functions of experiments, their varying uses and designs, and their changing relation with theory and assumptions in a pretheoretical and a theoretical phase of research. Although this is not a study of experimental culture, a few experiments that were important to the subsequent history of the subject are closely examined. In the pretheoretical phase most experiments were qualitative. Following the introduction of a quantitative theory, exact measurements became central. German physicists distinguished between these two laboratory activities, which they called "measuring physics" and "experimental physics", respectively. "Measurements" were carried out to obtain precise quantitative data, while "experiments" did not necessarily involve quantitative information. Qualitative or approximate quantitative results were usually sufficient for the latter kind of laboratory activities, which were still the majority. Exactitude was needed in "measuring physics," which aimed not only at accurate results but also at exact values that were required for the determination of constants of nature. Since precise quantitative values were often based on mathematical theory, exact measurements were usually carried out by theoretical or mathematical physicists in Germany, while "experimental physics" was dominated by experimental physicists.[14] Both kinds of laboratory activities played significant, though somewhat different, roles in the history of piezoelectricity. The choice between these methods reflected both the successive stages of study and the personal tendency of the experimentalist.

During the nineteenth century, exact numerical values and precise results became increasingly important in physics. By the second half of the century, exact quantitative measurement using precision instruments had become a distinctive and essential practice of physics. Later, they gained even more importance.[15] This makes exact measurements and their development an important subject for historical inquiry. One issue discussed here is the role of the exact measurements of piezoelectricity.[16] One aim of "measuring physics" was the determination of constants, and such constants were often considered as means to higher ends. Another almost obvious goal was the confirmation of mathematical theory that could not be tested qualitatively. Yet, as I show below, these were not the only roles of quantitative experiments. Moreover, historical

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[14] Christa Jungnickel and Russell McCormmach, *Intellectual Mastery of Nature: Theoretical Physics from Ohm to Einstein*, Volume 2, Chicago: The university of Chicago Press, 1986, p. 120.

[15] Thomas S. Kuhn, "Mathematical versus Experimental Traditions in the Development of Physical Science," in *The Essential Tension,* pp. 31–65.

[16] On the roles of experiment in science see for example Allan Franklin, *The Neglect of Experiment*, Cambridge: Cambridge University Press, 1986; *id.*, *Experiment, Right or Wrong*, Cambridge: Cambridge University Press, 1990; *id.,* 'The Roles of Experiment,' *Physics in Perspective* 1 (1999), 35–53. D. C, Gooding, T. Pinch, and S. Schaffer (eds), *The Uses of experiment: studies in the natural sciences*, Cambridge: Cambridge University Press, 1986 and M. Heidelberger and F. Steinle (eds), *Experimental Essays - Versuche zum Experiment*, Baden-Baden: Nomos, 1998.

understanding of exact measurement at the end of the nineteenth century requires more than a recognition of their roles. The practice of such measurements and their relations to other experiments, measurements, and theories should also be studied.

At least since the period discussed here the ability of experiment to test theories was doubted. Experiments, the argument went, are theory laden, and thus cannot be used to test particular theoretical claims.[17] Indeed experiments involve theory, but as the discussion below shows, theory is only one component of their complexity. Seemingly paradoxical, the recognition of this complexity leads to the conclusion that experiments can test some theoretical claims. In the following (also see Chapter 5) I show that experiments as well as their interpretation depended on material apparatus, various levels of theory and experimental analysis, contingent circumstances, and at least in one case on previous experimental results. Earlier, empirical results determined the evolution of an experiment and its conclusion.

"Measuring physics" was a German concept, and indeed Germans were most prominent in the quest for exact numerical results at the time. Nevertheless, even in a field dominated by Germans, like piezoelectricity, precise measurements and determinations were also carried out by French scientists. The French and German methods, however, were very different, suggesting the existence of disparate traditions in their approach to precise experiments and their physical and mathematical analysis. Their alternative methods of determining piezoelectric constants demonstrate the differences between two experimental traditions. National differences can also be seen in other realms, for example, in the type and nature of explanations suggested by physicists from different countries. The history of piezoelectricity supplies intriguing and partly contradictory evidence for the perplexing character of "national styles" at the end of the nineteenth century. Even the case of the exact measurements shows that nationality was not the decisive factor in determining scientific approach. Affiliation with a particular school or tradition was more important. German experimentalists shared the attitude of their colleagues across the Rhine rather than of their compatriot theoreticians. Still, German experimentalists also adopted techniques and attitudes of German measuring physics, in particular its use of mathematical analysis to reduce experimental error. This step displays a combination of different experimental traditions, and point out an important stage in the mathematization of experimental physics.

Despite all these, and other interesting historical questions associated with the early history of piezoelectricity, it lacks a historical discussion. For more than 120 years since its discovery, the field has received, at best, only cursory expositions in texts on physics and in discussions on certain famous scientists who contributed to it (e.g., Pierre Curie, Pierre Duhem, Röntgen, and William Thomson).[18] The developments in the study of piezoelectricity were not examined. As a field of static electricity it was not treated by scholars of late-19th century electrodynamics and is not mentioned

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[17] Pierre Duhem, *The Aim and Structure of Physical Theory*, tran. Philip P. Wiener, Princeton: Princeton University Press, 1954.

[18] Among these most detailed are the two biographies of Pierre Curie: Loïc Barbo, *Pierre Curie 1859–1906: Le rêve scientifique*, Paris: Belin, 1999 and Anna Hurwic, *Pierre Curie*, Paris: Flammarion, 1995.

in general histories of the subject like those of Whittaker and Darrigol.[19] Even the basic historical plot concerning the contributors to the field, their central contributions and the dates thereof have not been set down. The elementary aim of this work is to fill this gap and relate the story of the development of the field with its changes and turning points, in its historical context. Although science has a very wide and rich history, many studies are concentrated on a small number of (indeed important) developments. By merely relating the history of a field that has not been studied, this book suggests novel historical evidence relevant to known issues in the history and philosophy of science. Yet, as stated above, my goal here is in a sense more concrete and wider. I wish to explore beyond the local history of piezoelectricity to practices and characteristics of late-nineteenth century physics.

A historian needs documents to reconstruct the history of piezoelectricity on the issues raised above. In this case, the principal and almost only source are original scientific publications. Unfortunately, I could not find relevant archival documents such as correspondence, notebooks or drafts. This is probably connected to the peripheral character of the subject,[20] to the period and to personal habits of work. Notwithstanding the possible gains from archival sources, published contributions to physics from the end of the nineteenth century contain highly valuable historical information beyond the scientific content of theories and experiments. Physics papers at that period varied in length and style: from short two to four pages notes in the *Comptes rendus* of the French Academy of Science to papers stretching anything between five and 60 pages in the leading scientific journals,[21] to a couple of hundreds of pages in proceedings of scientific societies. Research papers were long enough to include "extra-scientific" details, like stated motives for the work and its short history. Moreover, they were mostly written in the first person, and allowed a tone personal enough to mention such issues. "Extra scientific" issues usually appear in the introduction or conclusions of the papers, or in footnotes. The latter are an important source for the historian. Reasons to do particular research or take a particular approach are not always spelt out, but are often implied in the scientific publications. Except for Röntgen's 1889 experiment, the central reasons for carrying out the major steps in the history discussed can be inferred from published sources. These sources also include secondary documents like recollections and obituaries by colleagues and students that fill in a few more details. However, most of the information comes from published scientific papers. Of course, such public sources that reports on most events in retrospect (e.g., descriptions of experiment are usually, but not always, written after they were done) do not supply all the relevant information. Still, they reveal quite a lot including motivations of the participants, changes in their research, and even failures and mistakes.

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[19] Edmund Whittaker, *A History of the Theories of Aether and Electricity*, New York: Humanities Press, 1973, Vol. 1 (originally published in 1953), Olivier Darrigol, *Electrodynamics from Ampère to Einstein*, Oxford: Oxford University Press, 2000.

[20] Nothing even slightly resembling the effort of "Archive for the History of Quantum Physics" has been undertaken for piezoelectricity.

[21] These are journals like the German *Annalen der Physik und Chemie*, the British *Philosophical Magazine* and the French *Journal de physique.*

THE STRUCTURE OF THE BOOK

The structure of this book follows the division of the early history of piezoelectricity into two phases. The first part (Chapters 1–2) relates the discovery and the following developments in the field to the introduction of Voigt's theory in 1890, developments that led to its formulation. These chapters discuss theoretical and experimental developments together, as they were closely interrelated during the pretheoretical phase. The second part (Chapters 3–5) deals with the history of the field in the theoretical phase. This part is thematically divided into three chronologically parallel chapters that discuss explanatory models of the phenomena, the elaboration of the general theory, and experimentation. In this story the reader is presented with a complex and unfamiliar history of a chapter of physics that is not widely known. To obtain an overview, the reader might like to consult Appendix 4, which offers a few tables of events set out by categories.

The first chapter traces the origin of the discovery of piezoelectricity and its background in the study of pyroelectricity, which had been known since the eighteenth century. In Appendix 1, I show that other earlier observations that were later linked to piezoelectricity had neither significant historical nor scientific links to the later discovery. After suggesting what led to the discovery, the chapter continues to discuss the research and findings in the field up until 1883. These include the discovery of the converse effect. At that time the first wave of research ended, central properties of the phenomena were discovered and its basic interpretation suggested. Chapter 2 traces the development of mathematical description of the phenomena from 1887, when Czermak suggested a quantitative account of piezoelectricity in quartz. This attempt, however, was not only partial but also inaccurate. The road to the more elaborate and valid mathematical theory of Voigt passed through Röntgen's qualitative experiment of 1889. Both are discussed in this chapter, which explains the reasons for the adoption of the phenomenological theory and rejection of the molecular explanation.

Attempts to explain piezoelectricity continued after the introduction of the general theory. Chapter 3 discusses such theories including some suggested before 1890. It answers what led to their construction, what were their assumptions, how well they accounted for the observations and why none of them was adopted. Chapter 4 traces the elaboration of the mathematical theory during the early 1890s. It focuses on the thermodynamic formulation of the theory and its significance. Relations to other theories like Maxwell's electromagnetism are also discussed. The last chapter examines the experimental work in the 1890s. The discussion of exact measurements, which dominated that research, is the focus of this chapter. It ends with an examination of later connected measurements of J. Curie and Röntgen that shed more light on methods of exactitude under question. The conclusions discussed the meaning and implications of the pretheoretical and theoretical phases and the shift from the one to the other, after they were separately examined in the previous chapters. The relations between the research done in different countries—the issue of national style—receive an explicit treatment in the conclusions' second section. Lastly, the tension between the molecular and the phenomenological theories is discussed again in light of the findings of the previous three chapters.

CHAPTER 1

THE DISCOVERY OF THE PIEZOELECTRIC EFFECT

THE APPEARANCE OF THE EFFECT

> The crystals that have one or more axes with dissimilar ends, i.e., the hemihedral [semi-symmetrical] crystals with oblique faces, possess a particular physical property of giving rise to two electric poles of opposite signs at the extremities of these axes when they undergo a change in temperature: This phenomenon is known as *pyroelectricity*.
>
> We have found a new method for developing polar electricity in these same crystals, which consists of subjecting them to variations in pressure along their hemihedral axes.[1]

With these sentences the young brothers Jacques and Pierre Curie announced their discovery of the piezoelectric effect to the French Academy of Science on August 2, 1880.[2] Nearly four months previously, on April 8, Jacques Curie reported to the French Society of Mineralogy that with the collaboration of Pierre, they had discovered that a compression of asymmetric crystals along their hemihedral axes produces electric polarization. Decompression of the same crystals in the same directions generated an electric effect with a reverse sign. Amorphous materials, on the contrary, did not show any electric effect due to pressure.

The Curies compared the unknown phenomenon and its properties to the known phenomenon of pyroelectricity, which appears in the same crystals. Examining six crystal species (tourmaline, zinc blende, boracite, topaz, calamine, and quartz) the brothers found that in all the electric effect of compression is like that of cooling and that of decompression is like that of heating regarding the directions and signs of the produced charge. However, they did not find any correspondence between the strength of the effects of heating and of pressure. They added that the elastic constants of these

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[1] Jacques et Pierre Curie, "Développement, par pression, de l'électricité polaire dans les cristaux hémièdres à faces inclinées," *OPC*, pp. 6–9, on p. 6. Page numbers in parentheses in this chapter refer to *OPC*.

[2] An electrification by pressure had been already observed by Haüy and A.C. Becquerel at the beginning of the nineteenth century. However, the effect they observed was not piezoelectricity, but was probably a kind of contact electricity. Though their findings found their way to a few textbooks, they did not influence the discovery of piezoelectricity and its study. I discuss this historical episode and its relation to piezoelectricity in Appendix 1.

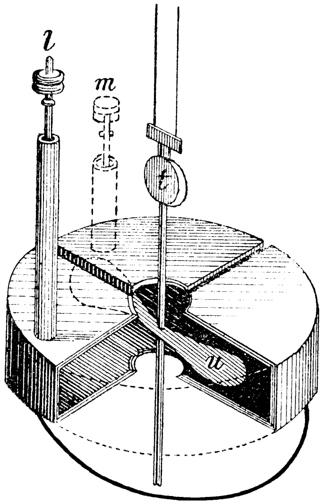

Figure 1.1: Thomson's quadratic electrometer: the two opposing quadratic sections are electrically connected and isolated from the adjacent quadrats. Usually, they are connected to two different parts of the circuit through l and m, while the needle u is electrified by a third source. The needle is suspended without electric contact with the sections and is turned by the electric force exerted by the quadrants against a torsion of a platinum wire. Its deviation is observed by the motion of t, and is approximately proportional to the voltage difference between the sectors. (from Graetz, note 4)

crystals are known to be positive (except calamine whose coefficient was unknown).[3] Thus, heating these crystals causes a thermal expansion, while **decompression** causes mechanical expansion of the same sort. The agreement between the phenomena of pressure and of variation in temperature, led them to regard both as manifestations of effects due to contraction and expansion. "Whichever be the determining cause [they wrote], every time that a nonconducting hemihedral crystal with inclined faces contracts, there is a formation of the electric poles in a certain direction; every time that the crystal expands, the release of electricity takes place in opposite direction" (p. 8).

The experiments that the brothers carried out to reach these results were relatively simple. A crystal specimen was placed between two copper plates perpendicular to its hemihedral axis. The plates, isolated electrically from the environment, were placed in a vice by which the specimens were compressed and released. The Curies connected the plates in two different arrangements to a Thomson quadrant electrometer, which was probably the most popular instrument for measuring electrical tension. In this instrument a cylindrical brass container is (electrically) divided into four quadrants; the opposite quadrants (or sectors) are connected by a wire; an aluminum vane (referred to as a needle) inside the container is free to move by the electric influence of the quadrants against torsion, while its position is optically marked outside (Figure 1.1).[4]

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[3] J. et P. Curie, "Développement par compression de l'électricité polaire dans les cristaux hémièdres à faces inclinées," *Bulletin de la société minéralogique de France*, 3 (1880): 90–93.

[4] Leo Graetz, "Elektroskope und Elektrometer," Adolph Winkelmann, ed., *Handbuch der Physik*, Breslau: Eduard Trewendt, 1895, *3, part 1*, 59–67.

In the first arrangement they connected the two plates separately to the two couples of opposite quadrants and electrified the needle. This was the common use of Thomson's electrometer, which showed the difference in electric tension (in arbitrary scale) between the adjacent quadrants, and thus the copper plates at the edges of the crystals. In another arrangement "one could also record each electricity separately; for that it is sufficient to connect one of the copper plates to the earth, and the other to the [electrometer's] needle and the two pairs of sectors were charged by a battery" (p. 7).[5] This arrangement, however, could not be used for quantitative measurement. The Curies were first interested in qualitative questions. Clearly, they designed these experiments to observe the electric effect of pressure on hemihedral crystals. This was not an accidental discovery.

The observation of the electric tension followed common practice at the time. In particular, it resembles the measurement method that Charles Friedel employed in his research on pyroelectricity a year earlier, which is mentioned by the Curies.[6] Jacques Curie was Friedel's assistant at the mineralogy laboratory at the Paris Faculty of Science (the Sorbonne). The delicate part in these experiments was the cutting of the crystals along their crystallographic axes, with two parallel faces perpendicular to the examined axis. However, crystal prisms cut in such a way were available from manufacturers and were in use in several mineralogical laboratories like the one in which the Curies worked.[7] Thus, they probably used readymade prisms and did not have to cut their crystals themselves. The other parts of their apparatus (in this and later experiments) were standard laboratory devices.

The brothers carried out their early experiments on piezoelectricity in Friedel's laboratory. Like his brother, Pierre was an assistant at the Parisian Faculty of Science. During that winter Pierre worked with Paul Desains at the latter's laboratory of physics on the length of "caloric waves" which was soon to be called heat radiation. In June they communicated a joint paper on this subject to the Academy of Science. However, Jacques and Pierre's work on piezoelectricity had started earlier, as they reported about it in April 1880. Thus, until the summer Pierre worked simultaneously with Desains on heat radiation and with his brother on piezoelectricity.[8] Probably

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[5] *Ibid.*, p. 91; The second arrangement could not be used for quantitative measurement. This was not a problem for the Curies in this experiment.

[6] Curie, "Développement par compression," (*Bulletin Minéralogique*) p. 92. Charles Friedel, "Sur la pyroélectricité dans la topaze, la blende et le quartz," *Bulletin de la société minéralogique de France*, 2 (1879), pp. 31–34 more on that publication below.

[7] Manufactures offered both standard and custom-made crystal prisms. At least in Germany that was very common, as revealed from a list of instrument-makers and their catalogues in a basic textbook like Paul Groth's *Physikalische Krystallographie - und Einleitung in die krystallographische Kenntniss der wichtigeren Substanzen* (Leipzig, Wilhelm Engelmann, 1885, on pp. 695–99). The Curies needed only standard prisms, but when Röntgen needed more special specimens cut according to specific instructions he bought them from *Hrn. Steeg und Reuter* from the optic institute at Homburgh v.d. Höhe; W.C. Röntgen, "Ueber die durch electrische Kräfte erzeugte Aenderung der Doppelbrechung des Quarzes," *Ann. Phy.*, 18 (1883), pp. 213–228, on p. 216, id., "Electrische Eigenschaften des Quarzes," *Ann. Phy.*, 93 (1890): 16–24, on p. 16.

[8] According to Anna Hurwic, Pierre Curie's biographer, Pierre joined the research of his elder brother probably at the beginning of July, after the publication of his paper on June 28. Thus she assumes that the brothers obtained their results in a short time and rushed to publish them at the beginning of

in the summer Jacques and Pierre Curie returned with full force to their study of piezoelectricity, submitting two papers to the Academy of Science in August.

In these communications they reported on the piezoelectricity of four additional species of crystals known to be pyroelectric, which were not mentioned in their April publication.[9] From the 10 species that they examined, they now reached generalizations about the relations between crystallographic structure and the generation of electricity by alternation of pressure or temperature. Restating a rule that had been formulated by Haüy for pyroelectricity, they concluded that due to contraction the positive pole is always at that end of the axis at which the angle between the axis and the crystal's face is more acute.[10] Comparing the crystal axes excited by pressure to those that were not, they found rules for the appearance of the electric effect. In 1882 they summarized them clearly in terms of the symmetry of the crystal:

> For a direction to have the properties of an electric axis in a crystal, it is necessary that this crystal lacks the same element of symmetry as that missing in an electric field pointed along this direction, this is to say: 1. that it [the crystal] has no center; 2. that it has no plane of symmetry perpendicular to the direction in question; 3. that it has no axis of symmetry of an even order perpendicular to this direction. These conditions are necessary, and the experiment shows that they are sufficient in the case of crystals.[11]

In the following six months Jacques and Pierre Curie continued to examine the properties of the new phenomenon they had discovered. Their early qualitative experiments demonstrated the existence of the new phenomenon analogical to the known pyroelectricity and showed its connection to the symmetry of crystals. The Curies did not further pursue the relations between piezoelectricity and the structure of crystals. This would be done a few years later by Hankel, Röntgen and others. Instead, they turned to systematic quantitative experiments to reveal the rules that govern the development of charge by pressure. What led them to this study? First, similar rules had been discovered for pyroelectricity by Gaugain twenty-five years earlier.

August; Hurwic, *Pierre Curie*, pp. 37–39. This reconstruction fails to consider the brothers' first paper on piezoelectricity from April, published in the *Bulletin Minéralogique*. Hurwic refers to this publication as the first publication but fails to notice its date. Another biographer Loïc Barbo also dates the work on piezoelectricity to August without reference to the earlier paper, *Pierre Curie 1859–1906: Le rêve scientifique*, Paris: Nelin, 1990, p. 45. In that they follow Marie Curie in her preface to *OPC* (p. xv), who dates the discovery of piezoelectricity after his collaboration with Desains, and the other editors of this volume, who neither included nor mentioned the brothers' first paper.

[9] A few of these crystals are not regarded today as pyroelectric, but as piezoelectric. Every piezoelectric crystal shows tertiary pyroelectricity, which is a secondary effect of piezoelectricity. Due to this effect non-pyroelectric crystals like quartz were regarded as pyroelectric. Walter Guyton Cady, *Piezoelectricity: An Introduction to the Theory and Applications of Electromechanical Phenomena in Crystals*, New York: Dover Publications, Inc., 1964, pp. 699–700.

[10] J. et P. Curie, "Sur l'électricité polaire dans les cristaux hémièdres à faces inclinées," *Œuveres,* pp. 10–14, on p. 13–14 (communicated to the French Academy on August 16). The latter rule was formulated somewhat differently, referring to solid angles for pyroelectricity by Haüy more than 50 years before. See Antoine César Becquerel, *Traité expérimental de l'électricité et du magnétisme*, Tome II, Paris: Pirmin Didot frères, 1834, p. 68.

[11] J. et P. Curie, "Phénomènes électriques des cristaux hémièdres a faces inclinées," *Journal de Physique théorique et appliquée*, 1 (1882): 245–251, on p. 247. According to this description a tension difference can exist also in other directions, but only as a result of the electric tension along an electric axis.

The strong link that they found between the two phenomena suggested that laws of electric generation of the two phenomena should be analogous. Second, quantitative rules were the preferred way to formulate physical relations at the end of the nineteenth century. Quantitative rules for pyroelectricity were formulated by Gaugain only a century after its discovery; the rules for piezoelectricity were formulated a year after its discovery. This exhibits the quantification of the study of electricity during the nineteenth century. Third, such rules could throw light on the Curies' explanatory model of the phenomenon.

After leaving the *École polytechnique* for political reasons in 1830 and directing various metallurgic establishments, Jean-Monthée Gaugain returned to Paris in 1851 to study electricity and to teach, without being admitted to the permanent faculty of any institute. Generation of electricity and its relation with other agents occupied much of his early work, and apparently led him to study pyroelectricity.[12] In 1856 he "performed a very large number of experiments" on more than 30 tourmaline specimens in various cases of heating and cooling. His experiments surpassed all previous ones in accuracy and attention to experimental errors. They were the first thorough quantitative measurements made in order to reach general rules about the dependence of the effect's intensity on external conditions like the change in temperature and the dimensions of the crystal. But Gaugain did not determine any absolute magnitudes, he only determined the relative ones. This was sufficient for his end. With these observational data he established three empirical laws:

[A] The quantity of electricity developed by a single prism is proportional to its section and independent of its length.

[B] The quantity of electricity that tourmaline develops while its temperature decreases by a determined number of degrees is independent of the time that the cooling took.

[C] The quantity of electricity that tourmaline develops while its temperature increases by a determined number of degrees is precisely the same as that which results from an equal decrease of temperature.

Points A and B imply that the amount of electricity developed is constant for every degree of temperature change regardless of the absolute temperature and the total change in temperature.[13]

Almost 30 years earlier, in 1828, Antoine César Becquerel used an electrometer to produce the first quantitative electric measurements on a specimen under cooling to support his claims about pyroelectricity. The early quantitative measurements of Becquerel and little later of James Forbes enabled them to study the dependence of the phenomenon on the dimensions of the specimens. Becquerel remarked that long tourmaline crystals do not show an electric effect, a claim challenged by Forbes. In his experiments, Forbes observed variations in the effect's intensity (i.e., electric charge)

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[12] Poggendorf's *Biographisch-literatisches Handwörterbuch zur Geschichte der exacten Wissenschaften*, Bd. 3, p. 497.

[13] J. M. Gaugain, "Mémoire sur l'électricité des tourmalines," *Annales de chimie et de physique*, 57 (1859): 5–39, quotes on pp. 21 and 5–6. Due to various reasons like conductivity, which Gaugain explicated, these laws are valid only in a finite range of temperatures.

between longer and shorter specimens, but attributed it mainly to internal differences between specimens. He further cut one specimen in a ratio of 1:3 and found that both parts had similar intensities. Thus, the length has no influence on the intensity of the effect. The surface area of the crystal, however, was found to have a clear influence on the intensity—the larger the area, the larger the effect.[14] However, Forbes had still failed to gain a mathematical relation between the surface area and the electric effect, which Gaugain succeeded in finding two decades later.

Like Gaugain, the Curies examined only one species of crystal—tourmaline. The choice of tourmaline was natural, since it has strong pyro- and piezoelectric effects and was the paradigmatic crystal in the pyroelectric research. As they sought quantitative rules, their new experiment reached higher precision than the earlier one. The pressure was applied by wooden lever (where weights were probably loaded on the other side) rather than by a vice. One of the two copper plates bordering the crystal was connected to a Thomson electrometer's needle, while the other was grounded.[15] In grounding the plate they followed Gaugain, who had observed that this had increased the deviation of his electroscope in the pyroelectric measurements.[16] Each time they put one prism of tourmaline between the (isolated) copper plates perpendicular to its principal axis. They used different prisms with lengths which varied from 0.5 mm to 15 mm for the same surface area, and surfaces which varied from 2 mm^2 to 1cm^2. Applying various weights, they had enough experimental data to determine the basic rules of the development of electricity by pressure in tourmaline.[17]

Jacques and Pierre Curie did not publish detailed results of their observations. They were content to announce the rules to the Academy of Science in January 1881. These, they wrote, are five:

I. The two ends of tourmaline release equal quantities of electricity of opposite signs.
II. The quantity released by a certain increase of pressure is of the opposite sign and equal to that produced by an equal decrease of pressure.
III. This quantity is proportional to the variation of pressure.
IV. It is independent of the tourmaline's length.
V. For a same variation of pressure [*sic*] per unit of surface area, it is proportional to the area.

From the last two rules follows an important conclusion that "For a same variation of pressure the quantity of electricity released is independent of the dimensions of the tourmaline" (pp. 15–16). These laws are formulated for the "quantity of electricity," i.e., the electric charge generated by a change of pressure on the crystal's surface, as detected by the electrometer. Since the laws are only relative, the absolute magnitude of the charge is unimportant and, therefore, one can rely on the electrometer's

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[14] James D. Forbes, "An account of some Experiments on the Electricity of Tourmaline, and other Minerals, when exposed to Heat," *Philosophical Magazine*, 5 (1834):133–143.

[15] Stabilization of the needle was not a problem, since they could keep the pressure for a long time until vibrations virtually damped away.

[16] Gaugain, "électricité des tourmlines," p. 6.

[17] J. et P. Curie, "Lois du dégagement de l'électricité par pression dans la tourmaline," *OPC*, pp. 15–17.

measurement of tension, which is proportional to the charge (the capacity is constant), since "the capacity of the copper plates . . . was always negligible relative to the capacity of the electrometer" (p. 16). Later physicists would prefer to refer to the electric polarization (dipole moment density also called an electric moment), which is an intrinsic quality of the crystal. By "pressure" the Curies referred to the total pressure, that is, the force, or weight in their experiment, rather than to force per unit of area. It is simple to show that their conclusion also holds true for stress and polarization in place of weight and charge. The brothers concluded that these laws are the same as those for pyroelectricity. This equivalence is explained by their hypothesis that "the contraction or expansion along the tourmaline axis" causes both phenomena. Previously, they had implied that the phenomena are caused by contraction and expansion; following the agreement of the qualitative rules they made this causal claim explicit (p. 17). Shortly afterwards, they examined quartz and found that its electrification by pressure follows the same rules.[18]

According to the empirical laws formulated by the Curies, the electrical effect of a variation in pressure on crystals is linear. Thus, every crystal has a characteristic coefficient (or coefficients), which shows the amount of electric charge produced by increase or decrease in pressure. After convincing themselves of the validity of this relation, the brothers carried out an experiment to measure these coefficients of tourmaline and quartz in the first half of 1881. This points to an additional step in quantifying the phenomena, which surpassed Gaugain's pyroelectric measurements that yield only relations but failed to give them numerical values. In their previous experiments they measured only the electric tension, which they knew to be proportional to the charge, but did not know the coefficient of proportion (which is the capacity of the system). To determine the magnitudes of the coefficients, they had to establish an exact quantitative relation between electric tension and charge.

To this end, the Curies designed a new experimental apparatus based on the one they had used previously (Figure 1.2).[19] A crystal bar was placed between two copper plates perpendicular to its hemihedral (semi-symmetric) axis. One plate (A) was connected to the ground, the other (B) was connected to a cylindrical capacitor (C) and to a sector of Thomson's electrometer, whose other sector was connected to a "Daniell cell" (D)—a battery of a known and steady potential of 1.12 V (while the needle is charged). Its other pole was connected to the earth. They exerted known weights on the crystal directly by a bracket (*potence*),[20] and replaced standard cylindrical capacitors until the charged needle of the electrometer stabilized at its zero point between the two sectors. At this point the electric potential in the two sectors was even, and thus

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[18] They mentioned this examination only in June 1882 (J. et P. Curie, "Phénomènes électriques," p. 248), but their presentation of the piezoelectric laws as valid for crystals in general and their determination of quartz coefficient already in July 1881, suggest that they had performed experiments on quartz before. See J. et P. Curie, "Les cristaux hémièdres à faces inclinées comme sources constances d'électricité," *OPC*, pp. 22–25.

[19] J. et P. Curie, "Les cristaux hémièdres."

[20] Before the end of 1881 they applied pressures on quartz both in the direction of a (hemihedral) electric axis and perpendicular to that direction. The found that in a square bar both induce electric charge of the same quantity (and of an inverse sign) at the ends of a polar axis.

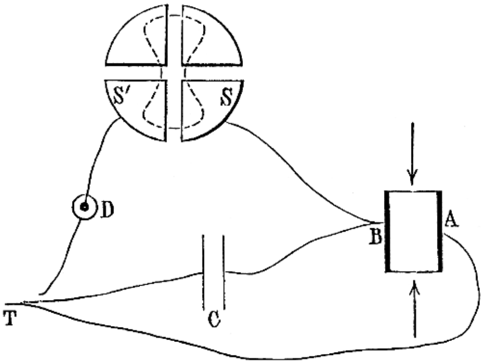

Figure 1.2: Curies' experimental measurement of piezoelectric constants (from "Phénomènes électriques," *Journal de Physique*, 1 (1882): 248.).

equal to that of the known Daniell cell. Next, they removed the external capacitor (C) and correspondingly some weights until the needle stabilized again at its zero point, i.e., until the voltage on the plate was again that of one Daniell. The difference in the quantity of charge between the two cases was clearly due to the difference in the weight that pressed the crystal. Since the voltage is the same, the charge difference is a multiplication of the known voltage by the difference in the capacities, which is the capacity of the cylindrical capacitor ($\Delta Q = V\Delta C$). Thus, they immediately deduced the charge developed per variation of a weight or force unit.

By determining only differences in quantities the Curies bypassed complicated measurements of the capacity of the system. Instead, they needed to know only the capacity of a known condenser. They used "a cylindrical condenser made up of two [close] pieces [plates], with which one can eliminate the error due to its boundaries [*extrémités*]," and calculated their capacity from their dimensions by unspecified method.[21] In their construction of a "null experiment" in which they kept the electrometer's needle at zero, the Curies eliminated errors not only in reading the needle's deviation, but more significantly, in translating its deviation into units of voltage. Thus, the data analysis in their experiment was simple and did not require any complicated mathematics. I will return to the issue concerning other determinations of the same constants in Chapter 5. Keeping the voltage low (a few volts) during most parts of the experiment gave the additional benefit of reducing electric leakage.

They found the piezoelectric constant for quartz and tourmaline to be 0.062 (esu/kg) and 0.053 (esu/kg), respectively. In units later used that is correspondingly 6.3×10^{-8}, and 5.4×10^{-8} (statcoulomb/dyne) (pp. 22–25).[22] These values

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[21] J. et P. Curie, "Phénomènes électriques," *Journal de Physique*, p. 250, footnote.

[22] Apparently the precision of the results was determined by the precision of the calculation of capacity (including three significant digits). So the difference in the number of digits between tourmaline and quartz is arbitrary. The Curies did not publish any estimation of the error in the experiment. On the attitude towards error and precision in piezoelectric measurements see chapter 5 below.

are less than 10% lower than the current ones, probably due to imperfections in the examined crystals. The brothers made further determinations of the coefficients' values. A year later in 1882 they published slightly modified results for quartz—0.063 electrostatic units—making it closer to current values, but in 1889 they returned to the earlier value of 0.062.[23] Jacques Curie continued measuring the coefficient of quartz in the same "null experiment" method at least until the end of the first decade of the twentieth century determining a value of 6.9×10^{-8}, a value that is equal to the current one.[24]

The brothers were quick to find practical applications to their empirical work. They showed that the new device, which apparently was planned to measure the coefficients of the new phenomena, could be utilized for measuring electric magnitudes. In the same article in which they published the values of the coefficients, they explained how, after determining the piezoelectric coefficient of a crystal its piezoelectric effect can be used to measure capacity, electrostatic force and most importantly charge. In this way the piezoelectric coefficient is used to calculate other magnitudes (pp. 24–25). In particular it enabled the application of "null experiments" in various electric measurement, when the piezoelectric quartz was used to balance an electric effect under study. This was the first in a series of measuring instruments based on the piezoelectric effect that the brothers developed.[25] Both utilized these instruments in later research. Invention and construction of physical instruments were common among French physicists, especially among experimentalists. The practice of the Curie Brothers can be seen as part of this French tradition.[26]

The research of Jacques and Pierre Curie, two young assistant physicists, 25 and 21, respectively, at the time of their first experiment, is impressive. They discovered a

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[23] *Ibid.*. pp. pp. 249–51.id., "Dilatation électrique du quartz," *OPC*, pp. 35–55, (originally published in 1889) p. 36. From their figure in the 1882 publication and from description of Jacques Curie's later measurements it seems that at least from the end of 1881 the brothers measured quartz coefficient by the transverse effect (i.e. applying pressure perpendicularly to the electric axis). Marie Curie, *Traité de radioactivité*, Paris: Gauthier-Villars, 1910, Vol 1: pp. 104–5. On the transverse effect see below p. 41.

[24] M. Curie, *radioactivité*, pp. 104–5. Cady, *Piezoelectricity*, pp. 216–9, 227. On this experiment see below chapter 5, p. 215.

[25] On these meters see P.H. Ledecoer, "Nouveaux électromètres à quadrants apériodiques," in *OPC*, pp. 564–586 and J. Curie., "Quartz piézo-électrique" *Ibid.* pp. 554–563. The latter is an extract from his dissertation written in 1889, in which he utilized this device in measuring dielectric coefficients and low currents with the null method. Pierre and Marie Curie later employed it in the study of radioactivity. The brothers' interest in application of their discovery to scientific instruments is evident. They continued to develop such instruments after they had ended their joint research of the phenomena in 1883, collaborating with instrument-makers like Bourbouze. Pierre Curie continued to develop scientific instruments during his later career. Yet, neither they nor others applied the phenomenon to non-scientific devices for use outside the laboratory until the first World War.

[26] Many French physicists insisted that the physicists themselves should construct their own physical instruments. Yet, in the actual construction of the instruments they, like the Curies, were helped by instrument makers. Christine Blondel, "Electrical Instruments in 19th Century France, between Makers and Users," *History and Technology*, 13 (1997):157–182, especially pp. 171–173. See also Elizabeth Garber, *The Language of Physics: The Calculus and the Development of Theoretical Physics in Europe, 1750–1914*, Boston: Birkhäuser, 1999, p. 314.

new phenomenon and carried out a systematic experimental study of it, which yielded quantitative relations that characterize it. Their research reveals a clear influence of the study of pyroelectricity, which they explicitly linked to piezoelectricity already in their first publication on their work and thoughts. They discovered the effect in a deliberate attempt to detect it in axes known to become polarized due to pyroelectricity and further carried out experiments with pressure to complement those carried out before with heating and cooling. Moreover, three weeks after the publication of the piezoelectric laws, the Curies suggested a common explanation for both pyro- and piezoelectricity. To understand their explanation and more importantly to evaluate the contribution of pyroelectric study to the discovery of piezoelectricity, I should briefly trace the history of pyroelectricity.

A BRIEF HISTORY OF PYROELECTRICITY

In 1880, when piezoelectricity was discovered, pyroelectricity had already been known and studied for over a century. While piezoelectricity was discovered in the laboratory in a deliberate attempt to observe an electrical effect of pressure, pyroelectricity was known through casual encounters with heated tourmaline. The attractive power of heated tourmaline was known before it became a subject of scientific study; that the phenomenon is electric, however, was discovered only experimentally, based on an electric theory.[27] It is not known when and by whom the attractive power of heated tourmaline was first discovered. However, we do know that it was introduced to Europe circa 1700.[28] Probably, the first published description of the phenomenon appeared in a book by Johan Georg Schmidt in 1707.

> The ingenious Dr. Damius [he wrote] . . . told me that in the year 1703 the Dutch first brought from Ceylon in the East Indies a precious stone called tourmaline, turmale, or trip, which had the property of not only attracting the ashes from the warm or burning coals, as the magnet does iron, but also repelling them again . . . and I have no doubt that if heated, it would attract other things besides ashes.[29]

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[27] My account of the history of pyroelectricity relates only major developments. The persons involved, their motivations and works are only patly presented. This brief history makes extensive use of Sidney B. Lang "History of Pyroelectricity," Chapter II in his *Sourcebook of Pyroelectricity*, London: Gordon and Breach Science Publishers, 1974, pp. 85–153. Lang's is the most comprehensive history of pyroelectricity until 1900, and includes in addition more than a hundred bibliographical references.

[28] Various references in ancient and mediaeval literature suggest the possibility that the phenomenon was observed in the West long before. However, even if the attraction of tourmaline was known before (which is doubtful) it was forgotten and had no practical tradition. No one knew how to identify the stone or stones mentioned in the books. Thus, previous encounters with the phenomenon in the West had no effect on the history of the phenomenon. For a discussion of ancient and mediaeval possible references to tourmaline see *ibid.,* pp. 85–93.

[29] Quoted in translation from *ibid.,* pp. 96. It appears originally in Immer Gern Speculirt (pseudonym of J. G. Schmidt), *Curiöse Speculationes bey Schlaflosen Nächten*, Chemnitz and Leipzig, 1707, pp. 269–70.

The curious new phenomenon attracted considerable interest in Europe. Its properties were discussed in scientific circles and in various books on natural facts and curiosities. However, it was not connected to electricity. In 1747, Carl Linnaeus was apparently the first to relate the attraction and repulsion by tourmaline with electricity. However, this was only a speculation. Linnaeus relied on unreliable verbal information and did not observe the "electric stone" himself. Thus, he even claimed that the stone exhibits this behavior "when neither heated by motion nor by friction."[30] It was only nine years later that Franz U. T. Aepinus discovered that this was indeed an electric phenomenon.

Toward the end of 1756 the mineralogist Johan Gottlob Lehmann drew the attention of the physicist Aepinus to the stone that attracts and repels small bodies. It is not clear whether Lehmann himself suggested this to be an electric effect. Whatever the case, Aepinus quickly recognized that the phenomenon is electric and that it differs from "the usual kind of electric phenomena," in which the body possesses the same kind of electric properties over its entire surface. In his experiments, he heated tourmaline in hot water and examined its electricity **after** it was taken out of the water. He discovered that two opposite ends of the tourmaline show opposite electric behavior simultaneously. In view of his Franklinian view of electricity, he concluded that the crystal acquires a surplus and a shortage of electricity at its opposite poles. He regarded that as a corroboration of the Franklinian theory of one electric fluid. This view was shared by the British electricians Benjamin Wilson and John Canton, who made further experiments on tourmaline. However, they were not the only ones. "Once Aepinus' discovery became known to the electrical investigators of western Europe, it aroused great interest." The interpretation by plus and minus electricity, however, was not accepted everywhere. In France, electricians accounted for the phenomena in terms of Nollet's system of electricity, which assumed electric atmospheres and different effluent and affluent flows, apparently, with less success.[31]

Aepinus thought that the new electric effect was due to heat, i.e., to the high temperature of the crystal. He disregarded the decrease in the specimens' temperature during his observations. Yet, he noticed that the process of heating and its uniformity is important, since in cases of uneven heating the poles were reciprocal to that of their "natural" state caused by uniform heating. That the effect is due to a temperature change rather than heat was first realized by John Canton three years later. Tourmaline, he wrote, will "both emit and absorb the electrical fluid, *only* by the increase, or diminution of heat." He further observed that "it will, while heating, have the electricity of one of its sides positive, and that of the other negative, this will likewise be the case when it is taken out of boiling water, and suffered to cool; but the side that was positive while it was heating, will be negative while it is cooling, and the side that

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[30] Quoted in *ibid.,* pp. 103.

[31] R.W. Home, "Aepinus, the Tourmaline Crystal, and the Theory of Electricity and Magnetism," *Isis*, 67 (1976): 21–30. (Reprinted with the same pagination in *id.*, *Electricity and Experimental Physics in 18th Century Europe*, Variorum, 1992), especially pp. 23–26, quotations from p. 24, 25. John L. Heilbron, *Electricity in the 17th and 18th Centuries: A study in early Modern Physics*, Mineola: Dover, 1999, pp. 280–86, 328–29, 387–88.

was negative, will be positive."[32] In a later experiment he showed that the positive and negative charges are of equal magnitude. Canton also corroborated an earlier assumption that the properties of tourmaline are independent of its external shape, by showing experimentally that when broken into three pieces, tourmaline maintains the direction of its polar axis and its properties. In 1760 Canton discovered that other precious stones can also be electrified by a change of temperature. Thus, the phenomenon is not restricted to tourmaline. Wilson soon carried out a more extensive experimental study of various mineral species. He concluded that, like tourmaline, their electric properties depend on internal quality rather than on external shape.[33]

The study of electricity in crystals gained a new and distinctive stimulus in the work of René-Just Haüy, who devoted his studies to the structure and properties of crystals. He conducted several studies on the subject from 1785 until his death in 1822, which included research on the electrification of crystals by variation in temperature. Following Coulomb's view of magnetism, and the analogy between that phenomenon and pyroelectricity, which had been expressed already by Aepinus (see below), he suggested to "consider each molecule of heated tourmaline as a small electric body, whose one end is in a positive state and the other in a negative state."[34] In 1801, after he had formulated a general theory of crystal structure, Haüy related this hypothesis to the crystallographic characteristics of the crystals. He identified the polar electric bodies with the "integrated molecules." Since every piece of tourmaline keeps the electric properties of the whole, he regarded the assumption as "highly plausible." In Haüy's crystallography the integrated molecules (*molécules intégrants*) are the elementary building blocks of the crystal, shaped according to their crystal system. The molecules, which are joined to each other to construct a continuous material body without any gaps, form a series of positive and negative poles. Yet, only the outer ones have an external effect, since the others balance the effects of each other.[35] Haüy continued studying the relation between the structure of the crystal and its electrical activity in various crystals and later found that asymmetric crystals, whose number of faces at both ends is not equal (hemihedral), are electrified by temperature change while symmetric crystals are not.[36] In 1840 Gabriel Delafosse, a former student of Haüy, emphasized the significance of symmetry in the physics of crystals. By connecting the polarity of the crystal's molecules to their structure he qualified

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[32] John Canton, "An attempt to account for the regular diurnal Variation of the horizontal magnetic Needle; and also for its irregular Variation at the Time of an Aurora Borealis," *Philosophical Transactions*, 51 (1759 read on Dec. 13): 398–445, the quotation and the whole discussion of tourmaline on pp. 403–4. Canton first announced his discovery in "a letter to Mr. Urban" in *The Gentleman's Magazine*, of September 1759 pp. 424–25 (signed by Noncathoni).

[33] Joseph Priestley, *The History and Present State of Electricity, with Original Experiments*, London 1767 (reprinted New York, 1966), Vol. I. pp. 377–79.

[34] R. J. Haüy, "Des observations sur la vertu électrique que plusieurs minéraux acquièrent à l'aide de la chaleur," *Journal d'histoire naturelle*, 1 (1792):449–461, on p. 461.

[35] René-Just Haüy, *Traité de minéralogie*, Paris, 1801, Tome III, pp. 44–58. Christine Blondel, "Haüy et l'électricité: De la démonstration-spectacle à la diffusion d'une science newtonienne," *Revue d'histoire des sciences* 50 (1997): 265–282.

[36] Lang, "History," p. 117.

his teacher's molecular assumption—only molecules which are not symmetrical can be polarized electrically.[37]

Though the basic phenomenon of pyroelectricity was known since Canton, many observations remained perplexing for a long time. We know today that the observed electricity is a complex effect of uniform and nonuniform heating and the conductivity of the crystal and its environment. Since the discovery of the phenomena, researchers had notions of the influences of these variables, but a complete theoretical account of them (especially of different modes of temperature changes) was given only following the discovery of piezoelectricity. As early as the 1760s Aepinus and Wilson disputed over the behavior of large crystals under nonuniform heating. The question whether the effect is caused only by a variation of temperature, and whether it persists after the specimen reaches its final temperature was more important for the understanding of the phenomena. Antoine César Becquerel in 1828 and Forbes in 1834 still saw a need to restate that the effect depends on variation of temperature and not on absolute temperature. Moreover, while measuring the intensity of the electric effect during cooling both found that the effect reaches its maximum *before* the specimen reaches its final temperature. Forbes thus claimed, in contrary to David Brewster's earlier claim, that tourmaline maintains its electric state **only** when its temperature is changing.[38] Perhaps since the development of the charge in time involved too many variables, after these experiments the attention of the researchers turned to other questions like the appearance of the phenomenon in various crystals, and its relation to their structure.

Brewster, who coined the term pyroelectricity in 1824, tested its appearance in a lengthy list of minerals, using a special device designed for this aim. In 1836, Gustav Rose studied the effect's directions in various kinds of tourmaline specimens from different regions. Later he collaborated with Peter Riess in a study of the pyroelectric properties of a few other minerals. Beginning with his 1839 dissertation, Wilhelm Gottlieb Hankel made pyroelectricity his area of expertise. To the earlier studies of the distribution of electricity on crystal surfaces by heating or cooling, Hankel added a few experimental techniques, some quantitative, that enabled him to improve on previous results. With these techniques he examined the properties of pyroelectricity in many crystal species.[39]

Aepinus had already called attention to the uniqueness of pyroelectricity—the only phenomenon that generates an electrified matter with two opposite poles, i.e., an electric dipole that cannot be divided into two separate monopoles. The polarity of tourmaline led him to an analogy between pyroelectric matter and magnets, which are always dipolar. According to his own testimony, he "was struck at the time, . . . by the utmost similarity between this stone [tourmaline] and the magnet . . . So, spurred on by this opportunity and by a brighter gleam of hope, I began afresh and more diligently,

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[37] Gabriel Delafosse, "Recherches sur la cristallisation considerée sous les rapports physiques et mathématiques," *Mémoires présentés par divers savants à la acadèmie royal des sciences*, 8(1843): 641–690, on pp. 665–668. The paper was submitted already in 1840.

[38] Forbes, "Experiments on the Electricity of Tourmaline."

[39] Lang, "History" p. 119–23.

to explore the similarity of the magnetic and electrical forces."[40] Not surprisingly, the analogy continued to appeal to later physicists who pondered over the hidden source of the phenomena. Haüy assumed that like Coulomb's molecular magnets the "*molécules intégrantes*" are polar. Thus, like a magnet, a pyroelectric crystal is composed of tiny dipoles. Brewster, who claimed that tourmaline maintains its electricity, compared it with a magnet. Even Forbes, who thought that tourmaline does not maintain its polarity as magnets do, used the analogy.[41]

Michael Faraday's new concepts of electricity in nonconductors, themselves encouraged by magnetic analogy, supplied an alternative theoretical scheme for the interpretation of dipolar electricity in crystals. In an encyclopedia article on pyroelectricity published in 1860, William Thomson, the active and young (but already established) Glasgow professor of natural philosophy, utilized Faraday's concept of electric polarity to suggest his hypothesis of the source of the phenomena.

> The most probable account that can be given of the pyroelectric quality of dipolar crystals [Thomson wrote] is, that these bodies intrinsically possess the same kind of *bodily electro-polarization* which Faraday . . . has clearly proved to be temporarily produced in solid and liquid nonconductors, and that they possess this property to different degrees at different temperatures. The inductive action exercised by this electro-polar state of the substance, on the matter touching the body all round, induces a superficial electrification which perfectly balances its electric force on all points in the external matter . . . When the temperature of the substance is changed, its electro-polarization changes simultaneously, while the masking superficial electrification follows the charge only by slow degrees—more or less slow according to the greater or less resistance offered to electric conduction in the substance or along its surface.[42]

Thomson's suggestion resembles Haüy's hypothesis and can be regarded as an elaboration of it. Yet, the suggestion differs in two important aspects. Thomson did not commit himself to any assumption on the source or the exact location of the polarity inside the crystal. More importantly, for the first time he suggests that the polarity is permanent, i.e., that it exists even when the crystal and its parts seem to be electrically neutral. The analogy between polar electricity and polar magnetism was implicit in the electromagnetic theory. Since one could use mathematical relations derived originally for magnetism for the electric polarity, it became more informative. In 1878 when he republished his hypothesis, Thomson himself used this analogy to predict the existence of a converse pyroelectric (electrocaloric) effect, i.e., a temperature change due to electrification.

To sum up, circa 1880 when the Curies pondered about the source of pyro- and piezoelectricity, pyroelectricity was known to be associated with a change of temperature in hemihedral, i.e., asymmetric crystals. The appearance of electricity and its distribution were known to be closely linked to the structure of the crystal.

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[40] F.U.T. Aepinus, *Essay on the theory of Electricity and Magnetism*, translated by P. J. Connor, Princeton: Princeton University Press, 1979, on p. 238.

[41] Haüy, *Traité de minéralogie*; Forbes, "Electricity of Tourmaline."

[42] William Thomson, "On the Thermoelectric, Thermomagnetic and Pyroelectric Properties of Matter," *TMPP*, 1: 315–316.

Haüy had done several experiments to study these relations in various species of crystal. Hankel, the expert in this kind of experimental work, was still active at the time. The phenomenon had neither a theoretical account nor a theoretical explanation, but Gaugain and Thomson took the first steps in both directions. Gaugain formulated quantitative laws about the development of an electrical charge in any pyroelectric crystal, which indicated that the magnitude of the effect depends only on the difference of temperature, the peculiar quality of the species of the crystal and its surface area. Following Haüy and others, William Thomson suggested interpretation of the effect in terms of internal polarity.

THE CURIES' MODEL

As mentioned above, three weeks after their publication of the piezoelectric laws, Jacques and Pierre Curie proposed a molecular explanation of the phenomenon in tourmaline. Their theory was based on previous suggestions on the source of pyroelectricity, and especially on Thomson's hypothesis of permanent inner electric polarization. Yet, although Thomson himself had discussed neither the source of the crystals' inner polarization nor a molecular hypothesis, the Curies attributed to him the assumption that the molecules of these crystals are always polarized.[43] Perhaps they were influenced by earlier molecular suggestions. Curiously, they did not mention the assumption of polar molecules of the crystallographic school of Haüy and Delafosse, to which Friedel was connected. Instead, they referred to A.C. Becquerel's and Forbes's "more or less vague" "hypotheses on the polarization of molecules," which they dated to 1825. However, as far as I have ascertained, neither of them mentioned polarized molecules, though Becquerel did assume a molecular source for the phenomenon.[44]

The Curies suggested that, like tourmaline, crystals are composed of polarized molecules, which are oriented in parallel layers toward the direction of a polar axis. "It is actually known [they wrote] that a cylinder made up of uniformly polarized molecules parallel to the generatrix [of the cylinder] can be replaced by two electric layers on the two bases" (p. 19). As Thomson suggested, they assumed that an electric charge on the crystals' surface neutralizes the exterior action of the inner polarization.[45] They further assumed that "between the two opposite sides of

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[43] J. et P. Curie, "Sur les phénomènes électriques de la tourmaline des cristaux hémièdres à faces inclinées," *OPC,* pp. 18–21. Thomson himself was an adherent of molecular views and suggested them in other contexts. Years later, in 1893, he adopted the Curies' assumption and referred to his original hypothesis as though it "assumed **molecular** polarization." William Thomson, "On the theory of Pyro-electricity and Piezo-electricity of Crystals," *TMPP*, 5: 325–332, on p. 325 (emphasis added). This mistake as been repeated by historians, e.g. Barbo, *Le Rêve Scientifique*, p. 47.

[44] A.C. Becquerel stated his ignorance of the source of pyroelectricity, but he thought that it depends on the distribution of the "electric fluids" in the crystals and the "grouping of their molecules," Becquerel, *Traité expérimental,* p. 70.

[45] J. et P. Curie, "les phénomènes électriques de la tourmaline." The Curies rejected a thermoelectric explanation and model suggested by Gaugain, who compared pyroelectric crystals to a thermoelectric battery with high resistance (made from bismuth and copper). According to such a model an electric

successive layers of molecules exists a constant difference of [electric] tension, which brings about a condensation of electricity that depends on the distance between two layers; if by some cause one changes this distance (variation of pressure or of temperature), the condensed quantity [of electricity on the layers and consequently on the bases] will change" (p. 20). They conceived this arrangement as a zinc-copper dry battery (Volta's element).[46] Considering the crystal as made of zinc-copper molecules they attained an expression for the charge on its base in terms of the "electromotive force of zinc-copper contact," the distance between successive layers and their surface area. They concluded that for a small variation in distance between the layers "the condensed electric quantity is proportional to the variation of the distance between two successive layers; it is proportional to the surface; it is independent of the number of layers and consequently, of the column's thickness. These laws are those provided by the experiments made on tourmaline" (p. 20).

Agreement with the experimental results is a necessary but not sufficient reason to view a model as "the most plausible." Jacques and Pierre Curie regarded their model as such, since they based it on the structure of crystals, as they conceived it. According to their view, the asymmetric form of the molecules, accepted since Haüy's time, can justify the hypothesis of electric tension between the opposing ends. The Curies had earlier found that in all crystals "the end corresponding to the more acute solid angle is negative by expansion [a result that Haüy had already found for pyroelectricity in 1792].[47] This constant relation is probably not accidental, and [they concluded] admitting the analogies between the molecular form and the hemihedral crystal form, one is led to remark that the acute end of a molecule always plays in relation to the opposite base of the successive molecule. The role of zinc in relation to copper in the analog example that we gave, namely it is constantly charged with positive electricity." (p. 21). Thus, molecules for Jacques and Pierre Curie here were the crystallographer's molecules rather than that of a chemist or a physicist... From 1801, they implicitly adopted Haüy's hypothesis of polar "integrated molecules." Like crystallographers and other physicists and chemists, they identified neither these molecules nor their parts with the atoms and molecules of physics and chemistry, although they shared

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tension should appear on heating, but, the Curies remarked, pressure should not yield an electric effect in this model. Second, they claimed that in contrast to their experiments this model predicts electric charge on the lateral surface of the tourmaline.

[46] Forbes, whom the Curies mentioned regarding molecular hypotheses, had suggested comparing pyroelectricity to a dry battery as early as 1834. Since A.C. Becquerel mentioned this comparison in his textbook, the Curies probably knew of it and it might have inspired their model (Becquerel, *Traité expérimental,* pp. 506–8). Forbes modelled tourmaline to "a series of isolated plates of glass arranged parallel to one another, suitably coated, and with the contiguous coatings connected by tinfoil." This, however, is far from the polarized layers suggested by the Curies. Moreover, Forbes was sceptical about the model. The "analogy [he wrote] supports the increase of the intensity with the diameter of the tourmaline; but when we come to consider the mode of charging it fails, and leaves us in great doubt as to whether the length of a crystal, if its structure be perfectly uniform, should have any influence or not." Forbes thought it does not, but the question was still open in the 1830s. James D. Forbes, "Experiments on the Electricity of Tourmaline." Unlike the Curies, Haüy considered the molecules as continuous rather than as forming separate layers.

[47] Haüy, "Des observations sur la vertu électrique," p. 454.

the assumption, accepted since Haüy, that the crystal's molecules are composed of more elementary molecules or atoms. The brothers implied that their model is valid for all piezoelectric crystals (crystals electrically polarized by pressure). However, it explains only uniaxial crystals and would not be easily adjusted to account for multiaxial crystals. Moreover, it follows from it that all piezoelectric crystals would be electrified by a uniform temperature change, a prediction that was found to be incorrect soon after.[48]

Jacques and Pierre's model reveals mechanical-molecular thought—an inclination to explain phenomena by hidden mechanisms based on concepts known from the physics of macro-bodies and the hypothesis of molecules. Simultaneously, it shows their interest in the connection between the symmetry of crystals and their physical properties. These were two separate currents in the scientific thought at the time. Among crystallographers and mineralogists and also in the earlier study of pyroelectricity, considerations of symmetry were more common than mechanical thinking. Even molecular-structural models, like those of Haüy or Forbes, were not mechanical—they did not involve any mechanical motion. While the Curies' molecular hypothesis was not hinted at in their previous publications, their concern with mechanical processes and the structure of crystals can be seen from their earlier publications on piezoelectricity. Contraction and expansion are mechanical concepts, which they used from the beginning to describe their findings. Moreover, these are the exact concepts needed to explain their findings along the lines proposed in their later model. This suggests that they were thinking about some version of the model immediately after discovering piezoelectricity, and plausibly also before its discovery. Thus, an analysis of the Curies' concepts suggests that their discovery originated from a mechanical model of pyroelectricity in which thermal deformations change the distances between polarized molecules and thus cause a change in their total polarization. Such a model was heavily based on Thomson's hypothesis of permanent polarization.

THE CAUSES OF THE DISCOVERY

So much did the Curies' concepts involve Thomson's hypothesis that Paul Langevin, a later student of Pierre Curie, presented the brothers' discovery as a verification of that hypothesis.[49] This is an exaggeration. Although the Curies inferred from Thomson that a change of pressure might also cause a change in the polarization of the crystal, this is not a consequence of the hypothesis. Moreover, neither Thomson nor anyone else had suggested this possibility in the twenty years that had passed since 1860, when he published it in *Nichol's Cyclopaedia of Physical Sciences*. No record of any attempt to detect the electric effect of pressure on crystals or to suggest its existence is known from that period. This absence cannot be

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[48] See below p. 59.

[49] Paul Langevin, "Pierre Curie," *Revue du mois*, 2 (1906), pp. 5–36, on pp. 30–31; Langevin explains the discovery in an anachronistic manner. Langevin's view was not expressed before 1883.

resolved by reference to the community's ignorance of the hypothesis, it had been well known even before Thomson republished it in the *Philosophical Magazine* (1878). It also found its way to the *opus magnus* of electromagnetism—Maxwell's *Treatise.*[50] Clearly, the implication that a change of pressure should also polarize crystals was not obvious. Indeed, it becomes a consequence of Thomson's hypothesis only if one assumes that the polarization of a crystal depends on the distances between inner electric poles. Then a change of pressure that causes expansion or contraction would consequently change the polarization. Thus, in order to assume that change of pressure would electrify crystals, the Curies had to first assume that pyroelectricity is caused by thermal deformation. This assumption does not necessarily follow from a molecular hypothesis.[51]

According to Langevin, Pierre Curie was concerned with questions of symmetry in physics in general, and in crystals in particular; this concern led him to the idea of the piezoelectric effect and its examination. Marie Skłodowska Curie, Pierre's later wife, agrees with Langevin that symmetry considerations guided her husband in his discovery of the effect. Indeed, Curie was engaged in the study of symmetry in physics since 1884. In the next decade he studied and formulated conditions of symmetry (or more exactly its lack) for the possible appearance physical phenomena, which are named after him. Both Langevin and Marie Curie claim that he had thought on this subject already in 1880, but had been slow to publish his ideas, as he was later with other subjects.[52] Langevin and Marie Curie based their description of Pierre Curie's scientific life on personal acquaintance with him. They might have even presented his own description. Yet, this does not eliminate the problem of this interpretation, which seems to read the history backward assuming that he had possessed insights on the topic in an earlier date but expressed it much later. However, Henri Poincaré had already suggested that Pierre Curie's study of piezoelectricity led him to that of symmetry, rather than the other way around.[53] This, I assume, is much more plausible. Indeed, symmetry played a role in Jacques and Pierre Curie's work. Yet, this was far from exceptional in the study of crystals. In this study physicists and mineralogists acknowledge the relation between symmetry and structure on the one hand, and the

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[50] Maxwell, A *Treatise on Electricity & Magnetism,* (first edition), Oxford, Clarendon Press, 1873, Vol. 1, pp. 59–60.

[51] Molecular interpretation of Thomson's hypothesis was not restricted to the Curies. For example, Edm. Hoppe assumed in 1877 that the molecules of pyroelectric materials are like a kind of magnets, Edmund Hoppe, *Geschichte der Elektrizität*, Leipzig: Johann Ambrosius Barth, 1884, p. 55.

[52] Langevin, "Pierre Curie," pp. 29–31, yet earlier in the same article Langevin claimed that the discovery of piezoelectricity led Curie to the study of symmetry (p. 10); Marie Curie, "Préface," *OPC* , pp. 9, v–xxii, on pp. xvii–xviii. A similar, though more cautious interpretation is given by Giuseppe Bruzzaniti in "Real History' as 'Dictionary' Reconstruction: A Historiographic Hypothesis for Pierre Curie's Scientific Undertaking," *Scienta*, 74 (1980): 643–661. Bruzzaniti views the research of piezoelectricity as a part of Pierre Curie's wider research programme of symmetry. On Curie's work on symmetry see Pierre Curie, "Sur la symétrie," *OPC*, pp. 78–113 (originally 1884), *id*., "Sur la symétrie dans les phénomènes physiques, symétrie d'un champ électrique et d'un champ magnétique," *OPC*, 118–141 (originally 1894) and Shaul Katzir, "The emergence of the principle of symmetry in physics," *HSPS,* 35(2004): 35–66.

[53] This is also the opinion of Curie's biographer Barbo who quotes Poincaré with approval, *Le rêve scientifique*, pp. 63–64.

physical phenomena on the other. Qualitative considerations of symmetry like the ones they used were common in the study of related phenomena. The brief history of pyroelectricity shows the centrality of general notions of symmetry in that study.[54] Symmetry also concerned Friedel[55] in whose mineralogical laboratory the Curies conducted their research. Thus, that they applied considerations of symmetry in these questions does not show that the brothers' research originated from a general concern for symmetry in physics.

The above-mentioned accounts of the discovery of piezoelectricity dedicate only a minor role to Jacques Curie. Since they were all written in essays on Pierre Curie, this should not be surprising. The later fame of Pierre in contrast with Jacques's quiet career in the provinces, probably added to this view.[56] Yet, contemporary evidence does not support this view. On the contrary, Jacques had more experience with pyroelectricity in particular and electricity in crystals in general as an assistant in Friedel's mineralogy laboratory since 1877. He assisted Friedel in his 1879 experimental study of pyroelectricity. In that research Friedel heated various crystals (including quartz and tourmaline) in one direction by attaching a hot hemisphere to one face of the crystal—a new technique that he had invented.[57] Jacques and Pierre referred to Friedel as their master in this subject.[58] Friedel's later collaboration with Jacques in a few joint papers on pyroelectricity, shows the close connection between his work and that of the brothers.[59] Friedel took part in a French mineralogical tradition that paid attention both to symmetry and to the molecular structure of crystals,[60] as the Curie brothers did in their study. Pierre, on the other hand, did not work on related subjects before his collaboration with Jacques. Still, all this does not make Jacques the true discoverer of piezoelectricity. It is difficult to separate the lives of Jacques and Pierre Curie during that period (1877–1882); separating their scientific lives is almost impossible. The brothers used to discuss their work and thoughts at

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[54] Yet symmetry considerations were applied systematically neither in the study of pyroelectricity nor in that of piezoelectricity. On the status and employment of symmetry consideration see below p. 79.

[55] Friedel, who made his major contributions in organic chemistry, studied with Pasteur in Strasbourg and later with Adolphe Wurtz in Paris, where he also studied mineralogy and was associated with Senarmont at the Ecole des mines. On the place of symmetry in the works of Pasteur and Senarmont see section 4 in chapter 2 below. Georges Lemoine, "Notice sur Charles Friedel," *Comptes rendus*, 131 (1900): 205–210; "Friedel Charles," *Encyclopaedia britannica*, 1911 edn. (http://49.1911encyclopedia.org/F/FR/FRIEDEL_CHARLES.htm).

[56] In 1883 Jacques Curie was appointed as lecturer of mineralogy at Montpellier. He stayed there until his death in 1941, except in the years 1887–1890 when he taught in Algeria and participated in a geological survey of the country. In 1888 he submitted a doctorate dissertation in physics to the Parisian faculty. However, in Montpellier he had to teach mainly mineralogy and geology, which apparently consumed most of his time. Y. Chatelain, "Curie (Jacques)," *Dictionnaire de biographie Française,* Tome 9, Paris, Librairie Letouzey et Ané, 1961, p. 1400.

[57] Friedel, "Sur la pyroélectricité." Friedel acknowledged J. Curie's help in 1879 in a later publication: J. Curie et C. Friedel, "Sur la pyro-électricité du quartz" *Comptes rendus*, 96 (1883): 1262–1269, 1390–1395.

[58] J. et P. Curie, "Développement par compression," (*Bulletin Minéralogique*) p. 92.

[59] Curie et Friedel, "Sur la pyro-électricité du quartz," id. "Sur la pyro-électricité dans la blende, la chlorate de sodium et la boracite" *Comptes rendus*, 97 (1883): 61–66.

[60] On this tradition see below chapter 2 p. 83, and "The emergence of the principle of symmetry in physics," *HSPS*, 35 (2004): 35–65, pp. 40–47.

length.[61] In such discussions it is impossible to decide who is the originator of an idea. Thus, the discovery of piezoelectricity was the fruit of the combined reflections of both minds. Friedel's 1879 pyroelectric experiment formed an immediate context for their discovery and was probably also a stimulus for it. It can explain why the phenomenon was discovered then rather than two decades earlier or later.

Yet Friedel's research was only a stimulus. The idea that a change of pressure along pyroelectric axes would excite electricity does not follow in any way from his research. One can search in vain in Friedel's publication for any hint on the mechanism that causes pyroelectricity, or the assumed induction of electricity by pressure. What can be found is a ground for speculations on the nature of pyroelectricity, based on disagreement between Friedel's and Hankel's results regarding the phenomenon in quartz, in particular about the relation between the effects of heating and cooling. Apparently, Jacques and Pierre Curie conceived their interpretation of pyroelectricity, which indicated the existence of piezoelectricity, by considering Friedel's results and the sources of this disagreement. I can only speculate on their path to the assumption that the phenomenon is a manifestation of thermal deformation. It might have been something like the following: the reliability of Hankel's observations (he was considered the expert on pyroelectric research) and the differences between the methods of heating and cooling used by the two experimentalists, probably suggested that the source of the disagreements lay in genuine differences in the behavior of quartz under different conditions. More specifically, these conditions were connected to the fact that Friedel heated the crystals in one direction, against Hankel who heated them from all directions. So, one could have assumed that pyroelectricity depends on the direction of heating and cooling. From that another step could have led the Curies to view the phenomenon as depending on deformation, rather than as a direct effect of heat.

To sum up, piezoelectricity was first detected in a deliberate attempt to observe the phenomenon, based on a theoretical notion of its existence.[62] I suggest that Friedel's pyroelectric research, which involved Jacques, introduced the Curies to the field. This

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[61] Hurwic, *Pierre Curie*, pp. 28–42.

[62] Since we do not have any written evidence of such an assumption before the discovery of the phenomenon a sceptic may claim that the experiment to detect the phenomenon was done without any definite assumption, as a kind of a naive question "does a change of pressure in crystals produce electricity?" Given the historical knowledge such a position cannot be totally refuted. However, I believe it is highly implausible. To begin, the question examined in the Curies' first experiment already assumes a connection to the hemihedral axes, and thus to either pyroelectricity or crystallography or both. They did not examine random axes, but only specific ones. Second, they were very quick to imply a theoretical frame for their findings, which suggested that they had considered it before constructing their experiment. Third, the Curies were not senior researchers with their own laboratory who could use their leisure and resources for whims or "Baconian experiments." On the contrary, they were young assistants who worked at different laboratories. That Pierre would have joined his brother for an experiment in whose chances of success he did not have reason to believe is doubtful. Moreover, they had to get access to a laboratory and scientific instruments (including crystal specimens) from Friedel. They most probably had to convince him that their experiment is not a shot in the dark. In my opinion these reasons make the sceptic's claim highly improbable. Lastly I wish to point out that my opinion that the discovery followed a theoretically rooted assumption leads to a plausible historical reconstruction.

research and probably the contradiction between its results and those of Hankel led them to thoughts and speculations about the source of pyroelectricity. Among these speculations was plausibly a view that the induced electric polarity is a secondary effect of contraction and expansion. That pressure should produce the same effect followed logically from that assumption. Friedel's work was only a trigger for the Curies. On the other hand, Thomson's hypothesis of permanent polarization was essential for their assumptions, which embraced Thomson's. Theoretical interests in symmetry and the molecular structure of crystals also played their part. Notwithstanding all these, mechanical thinking that reduces thermal effect to an elastic effect of deformation stood at the ground of the brothers' unique contribution to the understanding of pyroelectricity. This was a necessary component of their path to conceive pyroelectricity as an effect of deformation, which had not been previously suggested, and thus to the discovery of piezoelectricity. The Curies combined three distinctive approaches to science: considerations of symmetry, molecular assumptions, and mechanical explanations that characterized different disciplines (crystallography versus physics) and traditions. The discovery benefited from their position at a disciplinary boundary that enabled them to employ knowledge and ideas from various approaches. Apparently, in some cases acquaintance with various subdisciplines and approaches, especially with ones unfamiliar in a particular field, is potent to lead to discovery in that field.

PREDICTING A CONVERSE EFFECT

The *Encyclopædia Britannica*, 1972 edition, defines piezoelectricity as "the generation of electric charge in a substance by a mechanical stress that changes its shape, and a proportional change in the shape of a substance when voltage is applied."[63] However, Jacques and Pierre Curie's discovery and early experiments dealt only with the first part: "the generation of electric charge by a mechanical stress." This is termed the direct effect. They failed to examine the converse effect—that of electric voltage on the shape of crystals. This failure seems peculiar from a modern perspective such as the one given in the *Britannica*. A reciprocal effect of pyroelectricity was suggested by Thomson in his reprint of the inner polarization hypothesis in 1878,[64] on which the Curies based their explanation of piezoelectricity. Yet, they did not mention the possibility that a converse piezoelectric effect exists, and neither they nor other experimentalists tried to find such an effect. Indeed, an experimental detection of the converse effect was complex and delicate. Furthermore, due to these difficulties and lack of knowledge about the magnitude of the effect it had no clear chances of success. Still, such an experiment was feasible; not long after Lippmann had predicted the existence of the converse effect theoretically, the Curies themselves confirmed it experimentally.

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[63] Hans Jaffe, "Piezoelectricity," *Encyclopædia Britannica*, 1972 edition, Vol. 17, pp. 1062–1068, on p. 1062.

[64] Thomson, "Thermoelectric," p. 27.

Gabriel Lippmann earned his reputation (including the Nobel prize for physics in 1908) mainly from his experimental work, especially in developing new scientific instruments and laboratory techniques. In our story, however, he dons the theoretician's hat. From 1880 he was a professor of experimental physics at the Parisian Faculty of Science, in which the Curies worked. Three years later he became professor for mathematical physics. In 1881 Lippmann analyzed piezoelectricity in a study of electro-mechanical phenomena based on the conservation of electric charge (he called it electric quantity). A few years earlier, in 1876, he had claimed that this known conservation law should receive the status of a principle analogical to Carnot's principle in the "mechanical theory of heat." Carnot's principle determines "that the efficiency of the mechanical work of a heat machine is maximal" where the phenomenon is reversible and thus, the entropy does not change throughout a cycle. Similarly, the efficiency of the mechanical work of electricity, i.e., of an electric motor, is maximal in a reversible cycle. The constancy of the electric charge is a necessary and sufficient condition for such a cycle. Hence Lippmann considered this law as "the second principle of the theory of the electric phenomena," while the first principle was energy conservation.[65] Other contemporary scientists also took to this kind of study by analogy from the laws of heat to other subjects. Already since 1859 Gustav Zeuner had applied the equations of heat to study gravitation. In 1871 Ernst Mach employed the equations of entropy to express relations between two mechanical potentials (in analogy to heat and temperature). Lippmann's 1876 study of electricity is similar to Mach's earlier study of mechanics. Later in 1885, Arthur Joachim von Oettingen suggested a general and detailed analogy between heat energy and mechanical energy (pressure and volume, height and weight).[66]

Lippmann's interests in the relations between mechanical and electric phenomena did not begin with his formulation of a second principle of electricity. In 1873 he

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[65] G. Lippmann, "Extension du principe de Carnot à la théorie des phénomènes électriques. Équations différentielles générales de l'équilibre et du mouvement d'un système électrique réversible quelconque," *Comptes rendus* 81 (1876): 1425–1428. Lippmann proposed to solve the problem of efficiency of electric motors. The introduction of the first efficient electric motors three years earlier made the theoretical question of their efficiency a practical technological concern. The known relations between electric manufactures like Gramme, whose firm produced the first dynamos in France, and French scientists, suggest that Lippmann was motivated by the technological development. The relationship resembles the well-examined connection between the works of Carnot, Thomson and others on the theory of thermodynamics and the industry of heat motors. John L. Davis "Artisans and Savants," *Annals of Science*, 55 (1988): 291–314, on p. 307; Brian Bowers, "Electricity," in *An Encyclopaedia of the History of Technology,* edit by Ian McNeill, London: Routledge, 1990: 350–385. For a recent discussion of the relationship between thermodynamics and technology see Crosbie Smith, *The Science of Energy: A Cultural History of Energy Physics in Victorian Britain*, Chicago: The university of Chicago Press, 1998, Chapter 3 and passim.

[66] Georg Helm, *Die Energetik, nach ihrer geschichtlichen Entwickelung*, Leipzig: Veit, 1898, pp. 253–264. These analogies are similar to the use of thermodynamic potential functions in employing results of thermodynamics beyond the field of heat, and thereby in treating diverse subject with one method. However the analogies are less coherent and less general. They did offer not a genuine united yet abstract formalism, but more concrete expressions to particular problems. On the thermodynamic functions see below p. 157. Apparently, Lippman was critical towards the employment of potential functions, as suggested by his rejection of Duhem's PhD dissertation, which was a study of potential function (see below p. 110).

made his debut in the scientific community with a systematic experimental study of electro-capillarity in mercury. He discovered that this electro-mechanical phenomenon has a converse effect, and showed its reversibility.[67] In 1881 Lippmann set forth the theoretical consequences of the principle of conservation of charge, which he had stated five years earlier. With this, the principle of conservation of energy and a few empirical relations, he demonstrated the existence of several phenomena that connect electricity with mechanics (electric force of gas, electric expansion of glass, electro-capillarity, pyroelectricity). Some of these phenomena like electro-capillarity were already known; but others, like converse piezoelectricity, were unknown. Lippmann's paper shows the power of a general physical method based on principles in revealing natural behavior. This is a thermodynamic approach, which avoids hypotheses on the mechanism of the phenomena, like those the Curies or even those Thomson suggested for pyro- and piezoelectricity.[68] Lippmann's approach here is close to that of his German teachers Herman von Helmholtz and Gustav Kirchhoff with whom he studied in the mid-1870s. His relation with Kirchhoff connected him to Franz Neumann's school that would become important for piezoelectricity mainly through the contribution of Woldemar Voigt from 1890.

Lippmann's general approach enabled him to use the same basic equations for various phenomena, substituting the appropriate variables in every case. The key step in this analysis is to find two **independent** variables that determine the change in the electric charge in each situation. In piezoelectricity, these are the electric tension (or voltage), x, and the mechanical pressure, p. However, this is not enough. To analyze a cycle of piezoelectric effects, one has to consider a concrete but still general arrangement. Lippmann considered the extant example—a setting like that in the Curies' experiment.[69] Assuming that dm is the electric charge "received by" a metal frame A, which is joined to one of the crystal's ends,[70] he wrote the basic equation as:

$$dm = c\,dx + h\,dp \tag{1}$$

where c is the capacity of the frame and h a negative coefficient. From the principle of conservation of charge, a close integral of dm should equal zero, therefore equation (1) should be an exact differential. Hence,

$$\frac{\partial c}{\partial p} = \frac{\partial h}{\partial x} \tag{2}$$

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[67] Niels H. de V. Heathcote, *Nobel Prize Winners in Physics 1901–1950*, New York: Henry Shuman, 1953 pp. 65–69. I.B. Honley, "Gabriel Jones Lippmann," *DSB*, Vol. 8, pp. 387–8.

[68] The term thermodynamics is used here as was common at the time to denote the science based on the two thermodynamic laws and their generalizations. It is not applied here to the kinetic theory of gases, or to any other mechanical theory of heat.

[69] In a term that became popular following Einstein's theoretical work this can be called a thought experiment. It was not, however, new. Mathematical theory usually became meaningful only in concrete physical situations also before.

[70] Gabriel J., Lippmann, "Principe de la conservation de l'électricité ou second principe de la théorie des phénomènes électriques," *Annales de chimie et de physique*, 24 (1881): 145–177, on p. 164. The source of the charge is in "an electric reservoir of invariable potential."

A change in the crystal's energy (ε) is:

$$d\varepsilon = pdl - xdm \tag{3}$$

where l is the length of the crystal. Assuming that the change of length is linearly proportional to the voltage, he wrote its differential as a function of the latter and the pressure:

$$dl = adx + bdp \tag{4}$$

where a and b are coefficients. Lippmann inserted the right sides of equations (1) and (4) in (3). Under conservation of energy, equation (3) in its various formulations should be an exact differential. Lippmann implicitly assumed more than the general principle of energy conservation. He also assumed that the energy in the process can only transform between electrical and mechanical, and no energy is transformed or lost to other kinds like heat. He thus wrote:

$$\frac{\partial(cx - ap)}{\partial p} = \frac{\partial(hx - bp)}{\partial x} \tag{5}$$

Since *the length of the crystal* returns to its initial value when x and p do, equation (4) is also an exact differential, and yields an expression similar to equation (2). Using this relation, he arrived from equation (5) at an expression for a (the coefficient of expansion due to electric tension):

$$a = x\left(\frac{\partial h}{\partial x} - \frac{\partial c}{\partial p}\right) - h \tag{6}$$

The term in the brackets equals zero according to equation (2), therefore $a = -h$. Here h is the coefficient that shows the relation between the charge and the pressure, i.e., the piezoelectric coefficient, which the Curies found to be a constant. Hence, the coefficient a is also a constant, and is equal in magnitude and opposite in sign to the constant of direct piezoelectricity (the electric effect of pressure).

Following equation (4) the length l for a constant external pressure can be written as:

$$l = l_0 - hx \tag{7}$$

where l_0 is the crystal's initial length. The equation shows that the length of the crystal depends linearly on the electric tension, and that the effect of the electric tension on the length is inverse to that of the pressure in the direct piezoelectric effect. Lippmann supposed that "the frame A is applied to that base of the tourmaline that becomes positively electrified by pressure. [Therefore, h is negative] . . . Thus, if one electrifies a tourmaline with a positive charge at its base A, the crystal expands."[71] In that, Lippmann predicted the existence of the piezoelectric converse effect. His derivation

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[71] *Ibid.*, pp. 165–6. Later theoretical examinations showed that the sign of Lippmann's converse effect is sensitive to the exact arrangement of the experimental apparatus, since the independent variables he used are not truly independent piezoelectric variables. The relations between the electric charge and tension are not constants. Thus, the applicability of Lippmann's concrete argument is limited to specific cases.

is based on the general principles of conservation of energy and charge, but also on empirical data: the existence and linearity of the electric effect of pressure, the linear relation between pressure and deformation and the independence of these effects on the history of the crystal. Thus, his conclusions are based on the experimental discovery of the Curies. Moreover, Lippmann supposed more than he stated in these principles. Supposing that the energy is not lost to other kinds of effect in the process, he tacitly assumed that the phenomenon is reversible. Thus, Lippmann showed that converse piezoelectricity should exist if the electric energy gained in the direct effect does not transform into heat in a converse situation. Furthermore, once this assumption is accepted, the principle of conservation of electric charge is no longer required, although Lippmann made it his starting point for the whole analysis.[72] Importantly, Lippmann not only demonstrated the existence of a converse effect, but found its magnitude. According to equation (7), the coefficient that characterizes the effect of electric tension on length is equal in magnitude and contrary in direction to that of pressure on electric charge. The assessment of the effect's magnitude was useful for experimentalists, who now knew what kind of effect to look for. Perhaps the lack of such estimation prevented the Curies and others from searching for the converse effect earlier.

THE EXPERIMENTAL DETECTION OF THE CONVERSE EFFECT

The Curies' experiment

Lippmann's thermodynamic approach to piezoelectricity, which differs clearly from Jacques and Pierre Curie's mechanistic approach, did not prevent the brothers from adopting his conclusions. One did not need be a supporter of phenomenological theories to recognize the strength of Lippmann's argument. The brothers pointed out that Lippmann's result agrees with Lenz's law, according to which "the direction [of the effect] is always that in which the reciprocal phenomenon tends to oppose the production of the original phenomenon."[73] They calculated the change of length that one is likely to observe in the laboratory. A quartz or a tourmaline specimen of one

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[72] The principle of conservation of energy and the empirical laws Lippmann used are sufficient to show the existence of the converse effect and its magnitude. Since equation (3) is an exact differential (on Lippmann's assumptions), one can write:

$$\frac{\partial m}{\partial p} = -\frac{\partial l}{\partial x}$$

The Curies discovered a linear dependence of the charge in crystals on the pressure, so we may write $\partial m/\partial p = h$, where h is a constant. Therefore $\partial l/\partial x = -h$, and so $l = l_0 - hx$. Later textbooks, like that of Cady, use this reasoning (with more appropriate variables; Cady, *Piezoelectricity*, p. 182). Lippmann who was concerned with the conservation of charge principle used a longer procedure, which has an advantage in its applicability to additional phenomena.

[73] J. et P. Curie, "Contractions et dilations produites par des tensions électriques dans les cristaux hémièdres à faces inclinées," *OPC*, pp. 26–29, on p. 27. However, the relations between the converse phenomena are more complicated than Lippmann and Curie had first assumed, so Lenz's law cannot be applied so simply to the phenomena.

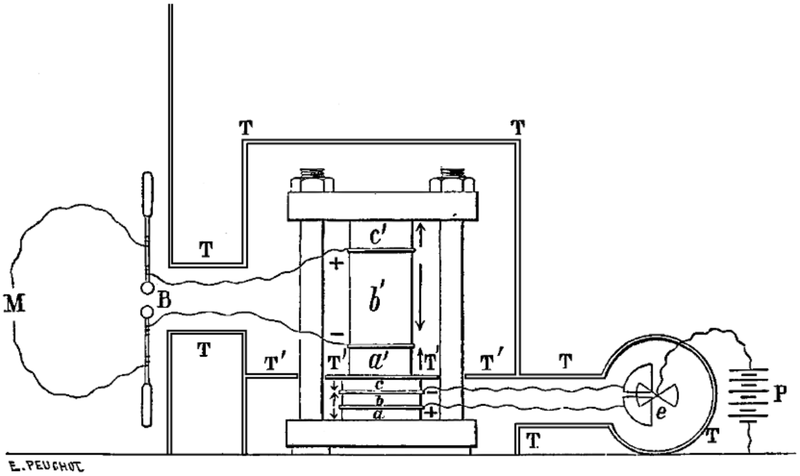

Figure 1.3: The first experiment to detect the converse effect (from J. and P. Curie, "Dilatation électrique du quartz").

centimeter (like the specimens they had) would expand (or contract) by about 1/2000 of a millimeter for the maximum potential possible between its ends.[74] This change of length could not have been detected optically. The brothers solved the problem by constructing an indirect experiment that measured changes in the crystal's length by the pressure that such an expansion generates, read by a manometer.[75] To this end they designed a special instrument for the measurement of pressure, based on the direct piezoelectric effect. The experimental apparatus they constructed was more complicated than those they had used before. Probably due to their earlier success, Desains, the director of the laboratory and his assistant director Jean-Louis, "Mouton placed a small room adjoining the physics laboratory at the disposal of the brothers so that they might proceed successfully with their delicate operations."[76]

The apparatus they constructed was divided into two electrically isolated systems (Figure 1.3). The phenomenon examined took place in the upper system, while the lower system was used to measure the pressure generated in the upper system by the direct piezoelectric effect. This manometer consisted of three strips of quartz (a, b and c) cut perpendicularly to their electric axes, which lay one on top of the other, with the electric axis of the middle strip in opposite orientation to that of the other two. Metallic plates were put between the strips of crystal and the strips were connected to two neighboring sectors of a quadrant electrometer. A change of pressure on the system electrified the two strips with opposite charges. Their earlier work on the direct effect showed that the deviation of the electrometer is proportional to the change of pressure. The structure of the apparatus' upper part was almost identical to that of

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[74] A spark would unload the plates when higher potential were applied.

[75] Notice that the length difference is the primary effect in Lippmann's reasoning, which is based on the Curies' primary variables. The primacy of the length agreed with the Curies' explanation of the source of the phenomenon.

[76] Marie Curie, *Pierre Curie*, The Macmillan Company, New York, 1923, p. 47.

the lower system, with the one important difference that the plates were subject to external electric tension rather than pressure. The metallic strips were connected to an electric source (Holtz's machine—M) that produced known potential difference between them. According to Lippmann's prediction, the potential difference generates contraction or expansion in the crystals (a′,b′,c′). A frame hindered this deformation and converted it to stress, which resulted in pressure measured by the lower system (p. 28).[77]

With all their ingenuity in constructing this apparatus, Jacques and Pierre Curie could not obtain quantitative results for the expansion of quartz due to electric tension. The apparatus consisted of too many components with various uncertain elastic coefficients that prevented the brothers from an exact determination of the assumed original change in length. In a short communication in December 1881, they only stated that a crude calculation showed the effect to be in the same order of magnitude as the theoretical prediction. Only in 1889 did they publish that their experiments had shown a rough linear ratio between the potential produced by the Holtz machine and the deviation of the electrometer. Since the former is the cause of the converse effect and the latter is proportional to the induced pressure, which itself is proportional to the expansion, this ratio indicated the linearity of the converse effect. Hence, it confirmed the theoretical expectation that, like the direct effect, the converse effect should also be linear (pp. 28–9, 41–3).

A year later, in November 1882, Jacques and Pierre Curie reported on a quantitative confirmation of Lippmann's prediction. This time they directly measured the change of the crystal's length rather than indirectly measuring the change in pressure. According to the Curies' view and Lippmann's reasoning, length rather than pressure was the independent variable. The key to their success was the use of the transverse effect in quartz in their new apparatus.

In their early experiments the Curies examined only the effect of pressure exercised on an electrical axis (x in Figures 1.4 and 1.5) on the polarization in the same axis. This is called the longitudinal effect. In 1881, Hankel was the first one to point out the transverse effect in which pressure in a direction perpendicular to an electrical axis (y in the figures) would also generate polarization in the electric axis. The Curies first mentioned it in a paper published in June of the following year, but they probably found it independently. They also measured its intensity.[78] According to Lippmann's

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[77] Jacques and Pierre Curie described this and other experiments in more details in the *Journal de Physique* in 1889: J. et P. Curie, "Dilatation électrique du quartz," on this experiment see *OPC* pp. 38–43.

[78] Wilhelm G. Hankel, "Über die Aktino- und Piezoelektrischen Eigenschaften des Bergkrystalles und ihre Beziehung zu den Thermoelektrischen," *Leipzig Abhandlungen*, 12 (1881): 459–547, on p. 542–3. Hankel's paper was sent to press in September and was available in Leipzig at the end of November. Yet due to its place of publication the Curies probably did not see it before they sent their own paper. Their paper presents previous experiments and conclusions to which it adds a few recent measurements that modified results of previous ones, rather than novelties, which they announced in communications to the Academy of Science. The existence of a transverse effect is their only novelty in this paper. A figure in the paper (fig. 1. here) suggests that they had applied the transverse effect in measuring the coefficient of quartz. Though the paper was published half a year after their qualitative confirmation of the converse effect, the effect is not mentioned in it at all. All these suggest that it was sent to print before the end of 1881. Jacques et Pierre Curie, "Phénomènes électriques des cristaux hémièdres," *Journal de physique,* on p. 247.

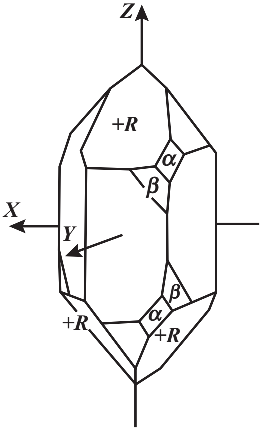

Figure 1.4: A quartz crystal with the three axes (adopted from Voigt, *Lehrbuch der Kristallphysik*).

argument, the direct transverse effect should also have a converse effect, i.e., an expansion along the y direction due to an electric tension along an electric axis (x). Unlike the longitudinal effect examined previously, the transverse effect depends on the crystal's dimensions, or more specifically, on the ratio between its length (mn in Figure 1.5) and its width (mm'). The higher the ratio, the stronger the effect.

Thus, for the converse effect the Curies reached the relation:

$$\delta = k\frac{l}{e}V \tag{8}$$

where δ is the change in length, k is the coefficient of the longitudinal effect, l the

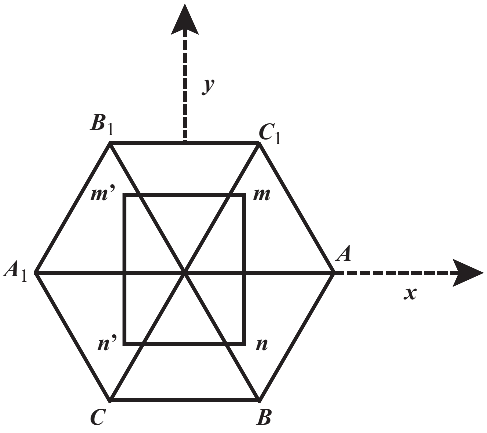

Figure 1.5: Quartz cut perpendicular to the principle axis (xy cut). AA_1 BB_1 CC_1 are its electric axes.

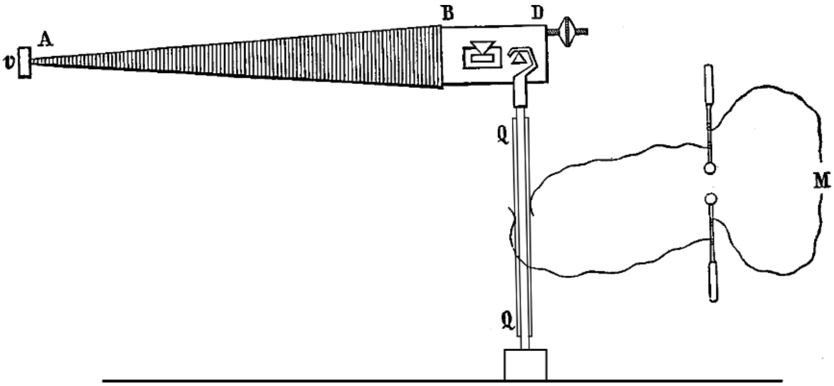

Figure 1.6: The Curies' second experiment to detect converse piezoelectricity, employing the transverse effect in quartz (from J. and P. Curie, "Dilatation électrique du quartz").

length, *e* the width and *V* the potential difference. This relation was given by the Curies in explaining the results of the experiment on the converse transverse effect. Clearly, they had also taken measurements on the direct effect before designing the experiment on the converse effect. They needed to know the relations on which they based their experiment before constructing it.

The transverse effect enabled a quantitative examination of the converse effect, which the Curies were unable to perform with the longitudinal effect. They explained that since the expansion in this case depends on the dimensions of the crystals they were able to generate larger deformations with the converse effect. They therefore cut specimens into long parallelepipeds, whose lengths were 11 and 60 times longer than their width. Each specimen was placed between two electrodes (QQ in Figure 1.6), parallel to its length, that exercised an electric field perpendicular to their electric axes. They were connected to a Holtz machine that generated an electric tension. The electrodes were a little shorter than the specimen so that the voltage differences between them could be higher than that permitted by the maximal charge possible over an air gap of the same width (higher voltage is discharged by sparks). Another, perhaps even more important, advantage of utilizing the converse effect was the possibility of leaving one end of the specimen free from any stress. Applying an electric field in the longitudinal direction, the electrodes disturb the free expansion of the specimen.[79] They connected the free end of the crystal to a lever (ABD in Figure 1.6) that amplified the expansion about 40 times. The lever's needle was observed through a microscope. They calculated the theoretical change in length for each crystal. Comparing the theoretical expansion with the observed, they found the latter to be about 4% higher. They explained the divergence by errors in reading through the microscope. For

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[79] Alternatively one could retain a gap between the electrode and the crystal, but then the value of the tension difference between the crystal's edges is uncertain.

such a delicate experiment this is evidently a good agreement, which justifies their conclusion that they had verified Lippmann's prediction.[80]

The measurement of the converse effect marks the end of the brothers' collective work. In November 1882 Pierre was nominated assistant (*prépaprateur*) at the newly established *École municipale de physique et de chimie industrielles*. In 1883, Jacques left to become a lecturer in mineralogy in Montpellier's Faculty of Science. With the termination of their intense collaboration they left the study of piezoelectricity. Jacques had enough time before leaving to Montpellier to study pyroelectricity in collaboration with Friedel, research that was tightly linked to piezoelectricity (below p. 82). However, they were occupied with new duties in their new positions. Pierre especially was preoccupied with the work of the school and lacked the resources for independent experimental research. Later, when they could find more time for scientific work, other, though related, scientific questions attracted their attention.[81] They continued to publish a few papers on piezoelectricity but those reflected mostly earlier works and a few improvements on electrometers based on the effect.[82]

Röntgen's and Kundt's experiments

In both experiments on the converse effect, the Curies exhibited ingenuity and skill, using known properties of piezoelectricity in examining unknown ones. Wilhelm Röntgen confirmed their results in a different method based on double refraction in quartz rather than on electric or elastic observations. Röntgen was then a young, active experimental physicist, a former student and protégé of August Kundt, who was regarded "as the most important 'experimental physicist' " in Germany.[83] In 1879, Röntgen undertook the "ordinary" professorship of physics at the small university of Giessen, after holding lesser positions in the University of Strasbourg, where Kundt was the ordinary professor and the head of a large institute for physics. Optics, and more specifically double refraction, was the central theme of Röntgen's studies since 1878, first in collaboration with Kundt and then alone. His interest in the physics of crystals can be traced back to an 1874 study of heat conductivity in quartz. He based his experiment on the properties of double refraction in crystals and his laboratory experience in manipulating polarized light. By the so-called piezo-optic effect, first observed by Brewster in 1815, stress or strain affects double refraction in crystals. Thus, a converse piezoelectric effect, which produces strain in the crystal, should

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[80] J. et P. Curie, "Déformations électriques du quartz," *OPC*, pp. 30–32. They published a longer and more detailed description of the experiment in their 1889 paper: *id.* "Dilatation électrique," pp. 44–49. In the later paper they also mentioned a third measurement on another parallelepiped, which was about 5% lower than the theoretical value. This is still a fair agreement.

[81] Until 1890 Pierre managed to make very little original work, then he turned to the study of magnetism. Jacques continued to work on crystals. In 1888 he submitted a dissertation (in Paris) on the specific induction and conductivity of crystals. At that time he participated in a geological survey of Algeria. Barbo, *Le rêve scientifique*, pp. 91–106, Y. Chatelain, "Curie (Jacques)," Louis Dulieu, *La faculté des sciences de Montpellier: de ses origines à nos jours*, Les presses universelles (n.p.), 1981.

[82] For example J. et P. Curie, "Dilatation électrique du quartz," originally published in 1889.

[83] Jungnickel and MCCormmach, *Intellectual Mastery of Nature*, Vol 2, p. 120.

have a similar effect on light. Röntgen designed experiments to observe this indirect effect of electric tension on the behavior of light. He found that the directions of influence of the electric field were as followed from the assumption that this is an effect of the pressures induced by converse piezoelectricity, concluding that the optical effect is an indirect effect of piezoelectricity.[84] Röntgen's method was simpler than those of the Curies, but it gave neither direct evidence nor quantitative results. He started working on his experiment in the fall of 1882, before the Curies published their quantitative confirmation of the converse effect. His method enabled him to examine the converse effect in various directions due to electric fields in various other directions. This ability, as shown below, would modify the development of piezoelectric research.

Röntgen used two identical quartz parallelepipeds placed one on top of the other with their optical, also called principal, axes (z in Figure 1.4) perpendicular to each other. A coherent beam of light passed perpendicularly to the optical axes of both parallelepipeds, and therefore underwent double refraction. When the crystal bars were free from external potential, the effects in the two bars counterbalanced each other, so the outcome was a united beam. A small deviation in the path of light in either bar would result in two beams (ordinary and extraordinary). To detect the extraordinary beam, Röntgen employed a Nichol's prism, through which only such a beam passes. He then placed one parallelepiped under an electric field oriented in the direction of a polar axis (x in Figures 1.4 and 1.5). The electric field was assumed to change the pressure in the crystal and by that to alter slightly the path of the doubled refracted beam. This slight deviation had no counterpart in the second crystal, which was free from electric influence. The output beam was therefore slightly polarized. Röntgen compared the influence of electric potential on double refracted light with the influence of mechanical stresses in the same direction. From this comparison he found the analogous mechanical effects of the various electric fields applied in the experiment, showing that inverse potentials produce inverse effects.[85]

Otto Glasser, Röntgen's biographer, claimed that Röntgen's joint research with Kundt in 1878–1879, led him to this experiment on piezoelectricity.[86] Indeed that research, which followed Kundt's interest and expertise in optics,[87] also examined

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[84] Röntgen explained that the converse piezoelectric effect should yield the phenomena he observed, but he did not refer to the possibility of a direct effect of the electric field on double refraction in quartz. This was done seven years later by Pockels. Later in quantitative experiments the latter measured the direct electro-optic effect and showed that the observed electro-optic effect in piezoelectric crystals is a mixture of a genuine direct electro-optic effect and an indirect piezoelectric effect. For details see the discussion in chapters 4 and 5. Nevertheless, Röntgen's claim that he confirmed the existence of the converse effect was justified, since his qualitative observations agreed with and even followed from the existence of a piezoelectric converse effect. To express it in other words, a failure to observe such an effect would have contradicted the existence of the converse effect.

[85] Röntgen W.C., "Durch electrische Kräfte erzeugte Aenderung der Doppelbrechung des Quarzes," More on Röntgen's research below.

[86] Glasser, however, does not support the claim with evidence. Otto Glasser, *Wilhelm Conrad Röntgen und die Geschichte der Röntgenstrahlen*, zweite Auflage, Springer, Berlin, 1958, pp. 74–80.

[87] Hans-Günter Körber, "Kundt, August Adolph," *DSB*, vol. 7, p. 526.

the influence of electricity (and magnetism) on polarized light, even if not in solids but in gas and vapor. Further, Kundt carried out research similar to Röntgen independently. Yet, Röntgen's independent work in Giessen is even closer to his study of piezoelectricity. There he studied the effect of electric field on double refraction in fluids (the Kerr effect). He claimed to discover this effect independently of Kerr a short time after the latter. Moreover, he used experimental techniques from this study in his research on piezoelectricity.[88] Röntgen himself, however, related his work on piezoelectricity to his 1880 research on the related phenomena of electrostriction: the deformation of dielectrics produced by electric stress. Its relation to piezoelectricity is obvious, and sufficient to draw Röntgen's attention to the novel phenomenon. Still, contemporary researchers did not confuse the two, since electrostriction is independent of the direction (sign) of the field and proportional to the square of the electric field, rather than linearly dependent on the field and its direction, as converse piezoelectricity.[89]

Following the discovery of the Kerr effect, Kundt and his junior colleague and former student Ferdinand Braun, Röntgen's successor as the extraordinary professor of physics in Strasbourg, designed an experiment examining the effect of an electric field on double refraction in quartz. Apparently, this was planned to follow Kundt's former work with Röntgen on similar effects in gases and vapors. However, the 'Holtz machine' that Kundt and Braun needed to produced electric tension for the experiment broke down so they had to postpone their experiment. Braun had left for Karlsruhe, so at the beginning of the winter of 1882–1883 Kundt returned alone to the experiment. Now he understood that a change in the double refraction of quartz should be connected to the piezoelectric effect and to Lippmann's argument for the converse effect rather than to Kerr's effect. According to Kundt, he was unaware of Röntgen's experiment on the same effect. Only after Röntgen's first publication did he hurry to publish his own results, which appeared right below Röntgen's in the *Annalen der Physik*.[90]

Kundt's method was simpler than Röntgen's. He used a parallelepiped square quartz; one edge of the square was parallel to a polar axis (x), while another was parallel to the optical axis (z). Unlike Röntgen, Kundt used a circularly polarized light, and examined the effect on light propagating in the direction of the optical

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[88] W.C. Röntgen, "Ueber die von Herrn Kerr gefundene neue Beziehung zwischen Licht und Elektricität," *Bericht der Oberhessischen Gesellschaft*, 19 (1880), pp. 1–16. *Id.* "Aenderung der Doppelbrechung des Quarzes," p. 218.

[89] *Ibid.*, p. 227, id., "Ueber die durch Elektricität bewirkten Form- und Volumenänderungen von dielektrischen Körpern," *Bericht der Oberhessischen Gesellschaft*, 20 (1881), pp. 1–22. The important role of the crystal form in the piezoelectric converse phenomenon prevented it from being confused with the phenomenon of electrostriction, as it is evident in Röntgen's work. Glasser's interpretation fails to incorporate this work of Röntgen. While Röntgen differentiated between the phenomena, a recent biographer of Röntgen - Albrecht Fölsing does refer to the earlier work as though it concerned inverse piezoelectric effect. Albrecht Fölsing, *Wilhelm Conrad Röntgen: Aufbruch ins Innere der Materie*, München: Carl Hanser, 1995.

[90] Röntgen's paper first appeared in *Bericht der Oberhessischen Gesellschaft*. A. Kundt, "Ueber das optische Verhalten des Quarzes im electrischen Felde," *Ann. Phy.*, 18 (1883): 228–233.

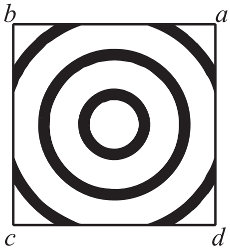

Figure 1.7: Circular rings of polarized light in quartz free from electric field.

axis, rather than in the direction of a polar axis. Under natural conditions, light in this direction does not suffer any change in its polarization. A polarized beam of light propagating parallel to the optical axis would keep its circular polarization. Sending light in the optical axis, Kundt placed the prism between electrodes that were either parallel or perpendicular to the polar axis. In 1875, Mach and Joseph Merten had shown that pressure makes quartz doubly refractive also for light travelling in the direction of the optical axis. Kundt expected to find a similar effect due to the piezoelectric influence of an electric field. Using an unspecified "polarization apparatus," he observed rings of light whose shape clearly showed its polarization. Free from an electric field the rings were circular (Figure 1.7). When he applied an electric field in the direction of a polar axis, he obtained an ellipse whose principal axis was either parallel or perpendicular to the polar axis, depending on the orientation of the field (Figure 1.8). Following the Curies' findings and Lippmann's theoretical ideas, he explained the results as due to a deformation in the polar axis. Electric fields perpendicular to the polar axis produced ellipses 45° to the left or to the right of that axis, according to the sign of the electric field (Figure 1.9). These, he explained, were due to compression in one of the quartz's two other polar axes and to expansion in the other. Thus, one axis became the ellipse's principal axis and the other its secondary axis. Kundt's observations displayed graphically the influence of electric fields on the optical properties of quartz. The experiment, Kundt claimed, gives "a very vivid demonstration (*anschauliche Darstellung*) to the Lippmann-Curies' discovery of the

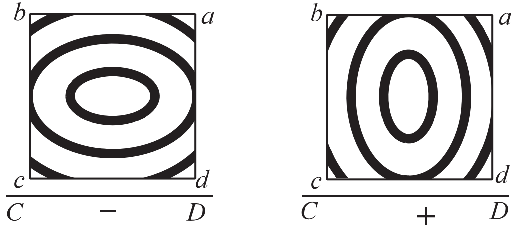

Figure 1.8: Elliptical rings due to electric field in the direction of a polar axis.

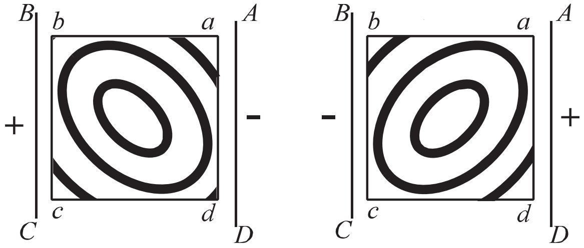

Figure 1.9: Elliptical rings due to an electric field in the *y* axis (perpendicular to a polar axis).

elastic deformation in hemimorphic crystals in electric fields." Like Röntgen, he did not refer to the possibility of a direct electro-optic effect.[91]

EARLY EXPERIMENTS AND THE EXAMINATION OF THE GEOMETRY OF PIEZOELECTRICITY

Röntgen was not the first experimentalist to enter the new field of piezoelectric research. Already in November 1880, three months after the publication of the discovery in the *Comptes rendus*, Hankel discussed it. Wilhelm Gottlieb Hankel was a senior experimental physicist, the head of the physical institute at Leipzig's university. Since 1839, he made pyroelectricity his own field; he established new standards of experimental precision in the field and carried more experiments than any other researcher. The link, already proclaimed by the Curies, between pyroelectricity and the newly discovered phenomenon, ensured his interest in it. He had, moreover, a special personal interest to defend his earlier results, challenged by the findings of Friedel and the Curies. No wonder he was quick to answer Friedel and his protégés, the Curies. In 1880, Hankel objected to the Curies' conclusion that the increase in pressure is always analogous to cooling. He claimed that in some crystals, like quartz, their effect is inverse. The core of the disagreement was the behavior of quartz in cooling; Hankel verified experimentally the brothers' findings on the electric effect of pressure, but he disagreed with Friedel's conclusions on the effects of heating and cooling, which the brothers repeated.[92] Friedel's experiment led Hankel to a new laboratory study of electric effects of heating and cooling in quartz in which he differentiated between the effect of radiation and that of "regular" heating and cooling by convention and conduction. In an 1881 publication, he named the former actino-electricity and the latter thermo-electricity, as he used to call pyroelectricity. Since, he did not find a general correlation between the electric

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[91] *Ibid.*, p. 232.

[92] W. Hankel, "Ueber die Entwickelung polarer Elektricität in hemimorphen Krystallen durch Aenderung des Druckes in der Richtung der asymmetrisch ausgebildeten Axen," *Berichte über die Verhandlungen der Königl. Sächs. Gesellschaft der Wissenschaften zu Leipzig*, 1880: 144–147.

effect of pressure and either that of radiation or of heat he gave it a special name—piezoelectricity.[93]

Hankel not only examined the electric effects of cooling, heating in special directions, and pressure in order to reveal the differences between their influence and to establish the existence of three different phenomena, but also to find particular properties of quartz crystals. In this he continued his earlier experimental work on pyroelectricity, both in the kind of questions asked and in methods, while, of course, piezo- and actino-electricity added new questions and methods. As in the earlier experiments, he measured electric tension using a gold-leaf electrometer of his own design (first described in 1850). Although others considered it less sensitive than Thomson's quadrant electrometer, Hankel referred to its high sensitivity.[94] Moreover, he put much skill and effort in eliminating experimental errors. To take two examples: in the pyroelectric measurements he constructed an apparatus that ensures measurement of the tension about 3 mm from the crystal surface, without touching it (a variation on an apparatus for the same end employed in 1868). For the piezoelectric experiment, he constructed a lever that enabled precise exertion of pressure by weights on the crystal, objecting that in the Curies' method (in stating the linearity of the effect) the intensity of the pressure was not completely determined. His measurements, nevertheless, confirmed the linear ratio between pressure (or more exactly weight) and tension found by the Curies. Unlike the Curies, he supplied the reader with the experimental data.[95]

Hankel calibrated the electrometer with a Daniell cell with which he had measured tension in known units. However, his experimental design did not enable measurement of charge, as the Curies did in determining the values of the piezoelectric constants. One reason for that was Hankel's uses of crystals in their natural shapes, rather than cutting them according to the effect under examination as other experimentalists did. This precluded him from arriving at quantitative rules, also for voltage, as numerical comparison between different directions and species became practically meaningless. Yet, while examining an influence on one direction, he also employed quantitative arguments. Hankel experimented with 143 natural and composite quartz specimens and reported on about 21. He showed more sensitivity than other students of piezoelectricity to the special properties of each specimen like its color and transparency, a sensitivity manifested in his detailed description of the experimental results for each specimen (comparing the Curies and later experimentalists who examined few specimens or only one). All these reveal an attitude closer to traditional crystallographical and physical study than that of the Curies and later researchers: an interest in the diversity of the phenomena in different species no less than in its generalization.

In an 1868 publication on pyroelectricity, Hankel showed that cooling divides quartz into six electric zones of negative and positive charges alternately. He concluded

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[93] The name is derived from the Greek word *piezein* - to press. Hankel, "aktino- und piezoelektrischen Eigenschaften des Bergkrystalles," p. 462.

[94] *Ibid.*, p. 478; Wilhelm G. Hankel, "Über die thermoelektrischen Eigneschaften des Bergkrystalles," *Leipzig Abhandlungen*, 8 (1868): 321–392; Graetz, "Elektroskope und Elektrometer."

[95] Hankel, *ibid.*, pp. p. 535–536, 542. The Curies examined tourmaline rather than quartz.

that quartz has three electric axes that coincide with the three known hemihedral axes, all in the plane perpendicular to its optical axis.[96] This conclusion agreed with the known hexagonal symmetry of quartz. Following the discovery of piezoelectricity, he looked for a similar effect due to pressure. Indeed, applying pressure on each axis separately, he found alternate signs in the electric tension at the six ends of the three hemihedral axes. He measured the electric tension only in the direction in which he pressed. In that case he found six electric zones. Yet, had he measured the tension in all edges due to pressure in one direction, he would have found only two zones.[97] The electric activity of the three hemihedral (polar) axes of quartz due to pressure had been already reported by Jacques and Pierre Curie, who also pointed out the sign of charge on each end.[98] Hankel added more detailed information including quantitative data (in arbitrary units) on the voltage in each pole and its surrounding surface due to a specific pressure. Yet, since he did not cut the crystals uniformly, he was unable to suggest a quantitative rule for the distribution of charge on the crystal's surface.

An interest in the detailed geometry of the electrical distribution, like the voltage in each edge, probably led Hankel to the discovery of the transverse effect in quartz (pressure in the *y* direction in Figure 1.5). Free from theoretical commitment on the common source of piezoelectricity and pyroelectricity, he examined the polarization in all directions including those perpendicular to the pressure and in the direction of the principal axis. In contrast to the Curies, he claimed to observe a small electric effect of pressure also in the principal axis (*z*). Yet, he admitted that due to the use of natural crystals, whose faces are not exactly parallel, his result was uncertain. Later experiments did not confirm this observation. As in his other experiments, he gave numeric results of his measurements of the transverse effect, but failed to offer a quantitative law. This, we have seen, had to wait to the Curies' experiment on the piezoelectric converse effect using a parallelepiped quartz bar. Still, Hankel formulated the qualitative rule according to which pressure perpendicular to an electric axis induces electricity with the inverse sign to that due to pressure in the direction of the axis.[99] In this and in other observations he showed the importance of examining the geometry of the effect, i.e., the results of pressures in various directions on electric tension in others. This examination was taken up by other experimentalists, notably by Röntgen.

The division of quartz into six piezoelectric zones was Röntgen's starting point in his experimental study of the phenomenon in the crystal. Unlike the Curies and Hankel, who had stated this division before, he based his description on the electric zones rather than on the electric axes. Since these zones have alternate electric charges, the lines between them should have no charge at all. Röntgen was most interested in these lines, which he named "axes of missing piezoelectricity" (*fehlender Piëzoelectricität*). In the middle, between two such axes lies an axis of maximum piezoelectricity, which

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[96] Hankel, "aktino- und piezoelektrischen Eigenschaften des Bergkrystalles," p. 483.

[97] *Ibid.*, pp. p. 537–547. Hankel made a special effort to apply the pressure in the direction of the axis between the edges.

[98] J. et P. Curie, "Sur l'électricité polaire," p. 11.

[99] Hankel, "aktino- und piezoelektrischen," pp. 542–3.

is a polar axis. Each axis of missing piezoelectricity thus forms angles of 30° with its two adjacent electric (polar) axes and is perpendicular to the third electric axis. So the crystallographic axis *y* in Figures 1.4 and 1.5 is an axis of missing piezoelectricity. Experimentally, locating the axes of missing piezoelectricity (whose ends are electrically neutral) was simpler than locating the polar axes (whose ends are electrified with highest intensity). In his first paper, sent in November 1882, Röntgen claimed that the angle between these axes is 60°. In the second part of his paper, sent in January 1883, he reported about experiments on both a circular quartz plate and quartz spheres. He pressed the crystal bars (differently in the two cases) and observed the electric tension between the two ends of the pressed axis with an electroscope. The experiment on the circular plate revealed exact intervals of 60° between successive zero charge points. In the experiment on a quartz sphere he found a deviation of no more than 2° and in its repetition with another sphere a larger deviation of 5°. He explained these deviations in deformations and irregularities in the crystal specimens. The discovery of the exact angle between the missing piezoelectric axes would have been almost impossible with natural crystals, like those Hankel used. The use of crystals shaped for the experimental purpose helped Röntgen to find a general spatial rule for their behavior.[100]

Röntgen probably performed the experiments on the exact location of the "missing piezoelectric axes" only after he had carried out experiments on the influence of electric fields on double refraction in quartz. In his earlier experiment on the converse effect, described above, he examined the influence of electric field in a polar axis on a beam of light propagating in the plane perpendicular to the optical (principal) axis. He soon used an identical apparatus, with two other quartz prisms, to measure the effect of electric fields directed in other directions on light propagating along a polar axis. In this experiment he ensured that the beam would propagate parallel to a polar axis rather than in an unspecific direction in the plane of these axes. Röntgen explained that he carried out this experiment to find directions of electric field that do not affect the double refraction. According to his account, the fact that the first experiment revealed effects of similar strengths, but of inverse directions for inverse potentials, suggested to him that fields in other directions should produce no effect on light. Since he understood the phenomenon as a secondary effect of piezoelectric deformation in the plane of the polar axes, his knowledge of Hankel's research and the latter's division of the quartz into six zones made the existence of such axes even more probable. Thus, the "missing piezoelectricity axes" and the optical axis were his first candidates for such axes. Indeed, he found no effect due to potential difference in these directions, while potential differences in other directions affected the double refraction of light propagating in a polar axis.[101] In view of the knowledge of the appearance of electric polarization by the direct effect, his results were predictable.

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[100] Röntgen, "Aenderung der Doppelbrechungen," pp. 214–5, 537–540. Röntgen made a special effort to press the crystals in the right direction through the centres of the plate and spheres. While in the experiment on the circular plate Röntgen applied the pressure only in perpendicular to the principal axis, in the ball he examined also other directions, finding the principal axis by its piezoelectric rather than its optic behavior.

[101] *Ibid.*, pp. pp. 220–224.

In his early experiments Röntgen examined the influence of electric fields on light propagating at the plane of the polar axes. He understood this as secondary effect of the converse piezoelectric effect in a polar axis, earlier observed with other method by Jacques and Pierre Curie. Next, he examined the influence of electric fields in various directions on light propagating in other directions, i.e., light whose double refraction is influenced by changes of pressure in other directions. Using the same method of compensating prisms, he first found that an electric field in a polar axis affects light propagating in the direction of the principal (optical) axis (whose wave plane is in the plane of the polar and the missing piezoelectric axes) and makes it doubly refracted. Kundt had observed the same effect a little earlier.[102] This observation was not surprising since the electric field was assumed to contract the quartz in the polar axis thereby changing the pressure in that axis, a change which was known to make the optical axis doubly refracted.

His later findings were more surprising. Röntgen examined whether an electric field in an axis of **missing** piezoelectricity has any influence on the refraction of light in quartz. With an optical analyzer he noticed that an electric field parallel to an axis of missing piezoelectricity altered the refraction of light directed 45° away from that axis. Surprised by the result, Röntgen applied another method similar to Kundt's to confirm his findings. He exercised an electric field in the direction of a missing piezoelectric axis perpendicularly to a center of a square plate and transmitted convergent light through it. Varying the direction of convergent light, he observed through a Steeg's polarization microscope a change from an original circle to an ellipse. The ellipse's principal axis was longest when light went 45° away from the axis of missing piezoelectricity.[103] Neither experiments on the direct effect nor pyroelectric experiments had shown any electric effect in the direction of axes of missing piezoelectricity.[104] Nor did theoretical ideas and models like that of the Curies anticipate any such influence. Consequently, Röntgen did not expect to find any effect of an electric field in such axes. Apparently, the examination was done as a regular experimental procedure of systematic examination of the influence of electric fields. In such a procedure one performs experiments even when expecting to find no effect. The observation of no effect is still a scientific fact worth publishing. In a similar manner, Röntgen examined the effect of electric fields in the direction of the principal axis and detected no effect. Röntgen probably wanted to confirm his notion that a missing piezoelectric axis has no piezoelectric activity. However, the experimental test revealed the opposite.[105]

The discovery had changed Röntgen's experimental program. To clarify the unexpected result of the optical experiments on the converse effect, he turned to electromechanical experiments on the direct effect. He carried out a series of experiments

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[102] Röntgen referred to this experiment (without its results) at the end of his first publication, *ibid.* p. 248; see in the second publication p. 549. On Kundt see above p. 47.

[103] *Ibid.*, pp. pp. 546–7.

[104] Kundt has found a similar result in his independent experiments on the converse effect described above on p. 47.

[105] This was not the first discovery unexpected by theoretical notions in the short history of piezoelectricity. The discovery of the transverse effect is an earlier example.

in which he systematically examined the electric effect of pressure on quartz in various directions. Röntgen's above-mentioned observations on the exact location of the missing piezoelectric axes were probably made then. In a second set of experiments he shaped a spherical quartz crystal, placed it under pressure in various directions and connected an electroscope to different points on its surface.[106] Thus, he observed the influence of pressure in one direction on the electricity in any direction. This was not done before. In all cases he found that the sphere is divided by a great circle that includes the two ends of the principal axis to two charged halves—one positive, the other negative. When he pressed the sphere in a polar axis, he found that the plane of the great circle that divided the sphere is perpendicular to the polar axis, i.e., the plane contains a missing piezoelectric axis. When he pressed the sphere in an axis of missing piezoelectricity (that is, perpendicular to a polar axis), the divided plane was the same, i.e., it contained the axis of missing piezoelectricity along which he pressed the crystal. As Röntgen remarked, this behavior was already observed in the existence of the transverse effect.[107]

Next, Röntgen exercised pressure in various directions in the plane of the great circle perpendicular to the principal axis (the *xy* plane). He found that the angle between the direction of pressure and the division plane is smaller when the direction of pressure is closer to an axis of "missing piezoelectricity." The direction of the maximum effect is also changed with the direction of pressure. In particular, he found that pressure directed 45° away from an axis of missing piezoelectricity produced a maximal electric effect in that axis. This is an electric polarization in a missing piezoelectric axis due to a direct effect. For him, this effect clarified the surprising optical observation of the converse effect. Clearly, an axis of missing piezoelectricity was not indifferent to piezoelectricity. According to Lippmann's argument and to this experimental result, Röntgen explained, an electric field in an axis of missing piezoelectricity should cause a deformation 45° away from that axis, a deformation that causes changes in the refraction of light through the piezooptic effect in the original experiment. Thus, Röntgen explained the surprising results of the optical effect by the existence of a corresponding direct effect.[108]

Applying pressures on the sphere in various directions not perpendicular to the principal axis, Röntgen found that it is always divided by a great circle that contains the principal axis' end. The orientation of this circle is independent of the angle between the direction of pressure and the principal axis. Applying pressure directly in the direction of the principal axis he observed a minute electric effect in a perpendicular direction, which he attributed to an imperfection of the crystal. Thus, he concluded that pressure in the direction of the principal axis does not yield an electric effect. With these experiments, Röntgen completed his examination of the electric effect of unidirectional pressure in any direction on quartz.

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[106] An electroscope yields only qualitative results. Röntgen, however, chose its use due to its low capacity, which does not disturb the system, *ibid.*, p. p. 538.

[107] *Ibid.*, pp. pp. 538–42. Interestingly, although Röntgen mentioned Hankel's paper in his first publication, he did not refer to his observation of the transverse effect, but to that of the Curie brothers.

[108] *Ibid.*, pp., pp. 542–3, 548.

Röntgen finished the systematic study of the spatial properties of piezoelectricity in quartz, in examining the effect of an electric field directed to the center of a quartz cylinder. He took a small quartz cylinder, whose height was parallel to its principal axis. At the center of the cylinder parallel to the principal axis he drilled a hole, filled it with mercury and connected it to an electric source (Holtz's machine), using it as an electrode. The outer surface of the crystal was enclosed by another metal, which was grounded. Thus, the Holtz's machine produced a voltage difference between the cylinder's center and its circumference. In this arrangement the electric field in the entire specimen was oriented toward the center (or the circumference). Sending a beam of convergent light along the optical axis, he found that under electric tension, the regular light circle seen by a Steeg's microscope was no longer a circle but gained a flower shape. Only the circle's six points of intersection with the axes of missing piezoelectricity (which he had marked beforehand) remained in their place; the others were displaced, while the larger displacement was of the points in the polar axes. An alternation of the potential alternated the direction of the displacement. In this way Röntgen managed to observe the six piezoelectric zones at once, in a piezoelectric experiment. Earlier, they were seen together only in pyroelectric experiments.[109]

The study of electrical distribution in piezo- and pyroelectricity was enriched by a new experimental method invented by Kundt in 1883 that displayed the electric effect clearly. Kundt spread a mixture of sulphur and minium that was sifted through a cotton sieve, a process that electrified the sulphur with negative and the minium with positive electric charges. Dusting an electrified object like an excited crystal with this powder provides a picture of its surface electric tension in red and yellow—the red minium colors the areas of negative voltage and the yellow sulphur colors the positive parts. This method was based on a known device invented by G.C. Lichtenberg in 1777. Kundt had already designed another variation based on Lichtenberg's device in 1869 to study conductors, because the original could be used only for dielectrics. Since his new method was very similar to Lichtenberg's original idea, he wondered why no one had suggested this method for crystals before.[110] I cannot answer why no one thought of the method before, but the fresh interest in crystals' electricity following the discovery of piezoelectricity can easily explain why Kundt conceived this method in 1883. Kundt had an old interest in methods for displaying natural phenomena and in dust figures in particular. His first famous work from 1866 was already on dust figures of sound waves.[111] This background probably contributed to his invention. Powdering a few

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[109] *Ibid.*, pp., pp. 550–551.

[110] A. Kundt, "Ueber eine einfache Methode zur Untersuchung der Thermo-, Actino-, und Piëzoelectricität der Krystalle," *Ann. Phy.*, 20 (1883): 592–601. On his earlier invention: "Ueber eine noch nicht beobachtete elektrische Staubfigur," *Ann. Phy.* 136 (1869):612–618.

Georg Christoph Lichtenberg used the electrophore that kept electric charge for a long time, which was invented by Volta in 1775. He discovered that dust on the charged part of the electrophore is situated in lines following the electric field, in similar to iron particles in a magnetic field. See J.L. Heilbron, *Electricity in the 17th and 18th Centuries: A Study of Early Modern Physics*, second edition, Mineola NY: Dover Publications, Inc., 1999, p. 424.

[111] David Cahan, "From Dust Figures to the Kinetic Theory of Gases: August Kundt and the Changing Nature of Experimental Physics in the 1860s and 1870s,"*Annals of Science* 47 (1990): 151–172.

crystal specimens, Kundt examined the division of electricity on them due to pressure, heating, and cooling. His observations displayed clearly the division of quartz into two electric parts under pressure. In heating quartz the experiments showed the known pyroelectric division into six electric zones. Kundt offered clear and vivid colorful pictures that exhibited the division of electricity on crystals. His results agreed with Röntgen's and thus corroborated the latter's conclusion on piezoelectricity.

Kundt's method attracted attention and was soon reported by the leading British and French journals. It was used, however, only in Germany and in its sphere of influence, mostly in Kundt's own institute in Strasbourg. The method was employed mainly in pyroelectric experiments on various species. Such experiments occupied at least eight researchers in the 1880s. Kundt himself, however, was satisfied with his first research and with remarks and supervision of the continuing work in his 'school'.[112]

HYPOTHESES ON THE SOURCE OF PIEZOELECTRICITY

In the first three years after its discovery, Kundt, Röntgen, Hankel and the Curies collected considerable information about piezoelectricity and its relation to pyroelectricity. This body of knowledge included information about the generation of electric charge, and its distribution in relation to crystallographic axes in several crystal species. While rules were formulated for the former, no systematic account was suggested for the data on the relations between the directions of pressure and the electric effect. Such a theory for the special case of quartz was suggested in 1887, a general theory for all crystals was formulated three years later. Early theoretical considerations, on the other hand, focused on the source and cause of piezoelectricity and its relation to pyroelectricity. As mentioned, in 1880, Jacques and Pierre Curie had already suggested a common explanation for both phenomena. According to their model, both originated from changes in the distances between layers of polarized molecules due to changes of pressure and thermal deformation.

Gustav Wiedemann agreed that piezo- and pyroelectricity have a common source, but rejected the Curies' view and Thomson's hypothesis. In his comprehensive two-volume book on electricity *Die Lehere von der Elektricität*, published in 1883, he claimed that when pyroelectric crystals break into two parts they do not display electric polarization. Thus, he denied the existence of permanent polarization or polar molecules. Instead, he thought that the molecules become polar only by and during the physical process. While the Curies saw the basic effect to be mechanical in

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[112] The *Philosophical magazine* published a description of Kundt's original paper in April 1884, (Vol. 17, p. 328). The *Journal de Physique* mentioned Kundt's paper only a year later (4 (1885): 240). Interestingly, papers that used Kundt's method were reported little before in the same issue. On Kundt's "Strasbourg school," see Stefan L. Wolff, "August Kundt (1839–1894) die Karriere eines Experimental-physikers," *Physis*, 29 (1992): 403–446, on "die Strassburger 'Schule' " pp. 436–440. Experiments using Kundt's method in his institute were done by K. Mack (*Ann. Phy.* 21 (1883):410–421, 28 (1886): 153–167), B. Von Kolenko. *Ibid.,* 29 (1886): 416–419), Kalkowsky (*Zeitsch. f. Kryst.* 9 (1885): 1), E. Blasius (with Kundt *Ann. Phy.* 28 (1886):145–153.), Schedtler, (*Neue Jahrb.* 1886, Beilagebd. 4: 519), Bauer and Brauns (*ibid.,* 1889, 1:1). Wulff in Warsaw also used Kundt's method, *Beibl.*, 8 (1884):597.

nature (displacement of molecules), Wiedemann took it to be a thermal effect, due to nonuniform temperature in the crystal. Pressure, he suggested, resulted in nonuniform tension that excites heat, which is the cause of the crystal's electrification. He did not explain why the pressure should cause nonuniform tension.[113]

In contrast, since his entrance to the new field, Röntgen adopted Thomson's hypothesis of inner polarization and assumed polarized molecules as its source, though he preferred not to pronounce his support of the molecular hypothesis.[114] In March 1883, two months after submitting the second paper on the experiments about the geometry of the phenomena mentioned above, he suggested that piezo- and pyroelectricity in quartz have a common origin in changes of tension due to thermal expansion or pressure. Since mechanical tension is the underlying phenomenon of the effects, he named them all under the common name of piezoelectricity. Despite his belief in the molecular hypothesis, his assumption did not presume polarized molecules.

According to Röntgen's own testimony, his earlier piezoelectric experiments, in particular that in which he applied an electric field from a cylinder's center to its circumference, led him to his hypothesis.[115] Yet those experiments did not provide convincing evidence for his opinion. In order to support his assumption that pyroelectricity is an effect of change in the crystal's inner tension, he designed and performed a series of experiments on quartz. In the first experiment he symmetrically cooled a hot quartz sphere. By an unspecified method, he observed an initial increase and then a decrease in the sphere's "electricity." When he connected the sphere to a conductor during the process, he found at the end a charge of an inverse sign to that initially generated.[116] Hankel had observed this behavior before, regarding it as a central evidence for the existence of the two separate and inverse effects of actino and thermoelectricity. In his interpretation, in the first part the dominant electric effect was of cooling by radiation (actino-electricity), while in the second part the regular cooling (thermoelectricity) was dominant. Each induces an opposite electrical effect. Hankel supplied supporting evidence for a direct effect of radiation. He showed that the intensity of the electric effect of heating by flame decreases when high intensity waves were prevented from reaching the crystal. Covering a flame with red and green stained glass he found that the latter glass reduced the electric effect more than the former (which permits the passing of more intense light). He concluded that radiation of high frequency causes the effect. In another experiment he showed that the electric

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[113] Gustav Heinrich Wiedemann, *Die Lehere von der Elektricität*, Braunschweig: Friedrich Vieweg und Sohn 1883, Vol. 2: 336–7. The volume went to press at the end of 1882, before the appearance of Röntgen's and Kundt's papers. Still Wiedemann maintained his explanation in the second edition a decade later (second edition, 1894, Vol. 2427–9).

[114] He reported on his molecular assumption eight years later. The reliability of the claim seems high since it was stated when he concluded that the hypothesis is insufficient. Röntgen, "Electrische Eigenschaften des Quarzes," p. 23. Röntgen referred to Thomson's hypothesis in his first publication, Röntgen, "Aenderung der Doppelbrechung," p. 213.

[115] He hinted at this hypothesis in connection with this experiment on a quartz cylinder at the end of his previous paper, "Aenderung des Quarzes," p. 551. In elaborating his assumption on the next paper he referred to his previous experiments in general, W. Röntgen, "Ueber die thermo-, actino- und piëzoelectrischen Eigenschaften des Quarzes," *Ann. Phy.*, 19 (1883), pp. 513–518, on p. 513.

[116] *Ibid.*, pp. 513–514.

effect of a flame is proportional to the inverse square of the distance as expected for an effect of radiation.[117] That radiation should have a distinct electric effect had also theoretical grounds in Hankel's 1865 vibrating ether theory of electric phenomena. Following Charles Briot's 1864 explanation of double refraction in quartz by circular vibrations in the ether, Hankel concluded that heat waves, which are a kind of vibration in the ether, should produce an electric polarity along the crystal's secondary (polar) axes. The latter phenomenon, according to this view, is totally different from that of regular heating, which is not an ethereal phenomenon.[118]

Röntgen, however, shared neither Hankel's electric theory nor his conclusion about the separate effects. For the cooling experiment, he proposed an alternative interpretation based only on piezoelectricity, i.e., the effect of inner contraction. Röntgen did not address Hankel's supporting empirical evidence, which was far from compelling in the latter's interpretation. According to his explanation, when the cooling begins, the outer layers of the crystal become cooler. Consequently, they contract and therefore press radially the inner layers causing a piezoelectric effect. Later, when the decrease in the temperature of the outer layers stops, they cease their contraction and, because of the contraction of the inner layers, the stress diminishes and results in piezoelectricity of the inverse sign. Hence the total electric effect diminishes until it disappears. If charge were permitted to leak by conduction, the whole sphere would become charged with a charge opposite to that it initially acquired, due to the change in the direction of pressure in the second phase of the cooling. In another experiment Röntgen locally warmed and cooled a quartz specimen by wind directed at a small portion of its surface. He found a strong electric effect at the areas of heating or cooling unless it coincided with a plane of missing piezoelectricity. Heating and cooling developed opposite charges. Like the Curies before him, he found that the effect of cooling is like that of compression in the same direction. The cooled outer layers, he explained, press the inner layers, and cause the electrification.[119]

Röntgen concluded with an examination of the influence of heating and cooling from the center of a circular quartz disc to its circumference and from the circumference to the center. This experiment "seems to me," he wrote, "to be especially suitable to support my theory." It resembled the one he performed on voltage differences between a cylinder's center and its circumference. He drilled a hole at the center of the disc, achieving a wide ring, which he could warm or cool either from its center or from its circumference. He surrounded the ring with silver foil divided into six parts along the axes of missing piezoelectricity, which were connected alternately to an electrometer and to the ground (the electrometer's other sector was also grounded). Heating from the center created the same electric effect of cooling from the circumference (which is the same as that of external pressure) and cooling from the center the same of heating from the circumference. These results agreed with

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[117] Hankel, "actino- und piezoelectrischen Eigenschaften," pp.–530, 527–29, 546 (on the inverse square relation done only with three measurements.)

[118] *Ibid.*, pp., pp. 459–463, Hankel, "Neue Theorie der elektrischen Erscheinungen," *Leipzig Abhandlungen*, 1865, 7–30.

[119] Röntgen, "theremo, actino- und piezoelektrischen," pp. 514–15; About the Curies see above p. 15.

his hypothesis that both cooling from the circumference and heating from the center cause radial tension toward the center, which induce the same electric effect—the source of the observed behavior. Röntgen's experiment showed that the electric effect of a temperature change depends on the direction of the temperature differences inside the crystal, i.e., on the existence and direction of a temperature gradient, rather than on the average change of temperature. Following this result, Röntgen suggested that uniform heating of quartz would not create an electric effect. In other words, he implied that quartz is not pyroelectric in a strict sense.[120]

That was a novel claim, which had not been suggested previously in the study of pyroelectricity. Röntgen established a third, new category between pyroelectric and nonpyroelectric materials—that of those electrified only by nonuniform heating. Logically, this conclusion was independent of any knowledge of piezoelectricity. Röntgen's experiment does not assume knowledge of piezoelectricity. His conclusion could have been deduced from general theoretical considerations of symmetry along the lines of the principle of symmetry that states that the symmetry of the effect cannot be lower than that of the causes. However, this example indicates that this principle was not widely used at the time.[121] However, in practice Röntgen was led to the experiment and to its conclusion by the laws and hypotheses on piezoelectricity and its mechanical origins, rather than by abstract reasoning on the established field of pyroelectricity. Thus, soon after its discovery, the study of piezoelectricity started influencing the older field of pyroelectricity, which physicists like Röntgen considered a secondary phenomenon of piezoelectricity.

Simultaneously with Röntgen, Jacques Curie and Charles Friedel concluded that the effects called by Hankel thermo, actino and piezoelectricity are all manifestations of one mechanical cause. Publishing their conclusions shortly after Röntgen, they summarized: "For Mr. Röntgen the common cause is a change in the internal tension of the crystal. For us, it is more simply a change in the molecular distances."[122] Thus, they maintained Jacques and Pierre Curie's original explanation, suggested two years earlier. In this model, the molecules are permanently polar, so changes in their distances change the inner electric tension. Perhaps, since elastic tension was not the basic phenomenon in their model, J Curie and Friedel preferred the old term pyroelectricity over the new term piezoelectricity, which implies the role of pressure. Ironically, the term piezoelectricity named and accepted by foreign scientists, who thus emphasized its importance, was not adopted by one of the phenomenon's discoverers.[123] The attitudes of Friedel and Curie, on one hand, and of Röntgen, on the

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[120] If pyroelectricity in quartz was a genuine phenomenon of temperature change, the effect would have been independent of the direction of heating and cooling. Heating from the centre would have approximately the same consequences as heating from the circumference, and unlike to those of cooling from the circumference. *Ibid.*, pp., 515–517, quote on p. 515.

[121] On the application of considerations of symmetry see below p. 79.

[122] Curie and Friedel, "Sur la pyro-électricité du quartz." One can doubt whether their hypothesis is simpler than that of Röntgen. Curie and Friedel referred to Röntgen's experiment on heating and cooling from a centre of a plate to support their common claim.

[123] The term piezoelectricity was suggested by Hankel in a paper in which he rejected Friedel's conclusions. Since Friedel and Curie's paper argued against Hankel's, they, and especially Friedel, were not inclined

other, toward the origin of piezoelectricity do not agree with general expectations about national differences. In this case the French physicists presented a more mechanistic and atomistic thought based on a molecular model, than the German's, which was based on a general concept of elastic tension.[124]

Like Röntgen, Curie and Friedel argued against Hankel's distinction between the electric effects of heating by conduction and by radiation, and asserted that the effect of cooling is like that of pressure. The former issue was at the core of the disagreement between Hankel and Friedel regarding the latter's 1879 results. To support their claims and to refute Hankel's contradictory claims, they reexamined Hankel's observation of a change in the sign of the electric tension of the crystal surface during a process of cooling.[125] Röntgen had already supplied an alternative interpretation to that experiment. Friedel and Curie went further by reconstructing Hankel's experiment. They heated a quartz crystal to 200°, cooled it in room temperature and observed the changes of electric tension near its surface, repeating Hankel's result.[126] However, they suggested another explanation based on the effect of inner temperature differences in the crystal. To verify their assumption that the temperature of the crystal was not homogeneous, they measured its surface temperature after the termination of the electric measurement. Then they completed its cooling inside a calorimeter, determining the amount of heat it released in the process. The amount of heat released showed that the crystal's average temperature at the end of the electric measurement was about 10° higher than that on its surface. Thus, the temperature at its center was even higher. They therefore concluded that inner temperature difference, rather than two genuine and different effects of cooling, caused the electrification of the crystal also in Hankel's experiment. Cooling a quartz bar uniformly enough, they verified theirs and Röntgen's conjecture and found no electric effect.[127] The difference between theirs and Hankel's results were not rooted in the experimental methods, which were similar, but in the variant views of the phenomena. Unlike Hankel, Curie and Friedel designed their experiments to detect an effect of temperature gradient. So they added the simple procedure of heat measurement to this kind of experiment.

On the hypothesis that expansion and contraction along quartz's electric axes generate the pyroelectric effect, Friedel and Curie demonstrated mathematically that uniform heating should not produce any electric effect. For this demonstration they

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to adopt his term. Because Friedel was the senior participant in this paper, he probably had the last word on terminology. In 1889 Jacques Curie called the phenomena piezoelectricity, but since others used that term in the past six years, one cannot learn from this about his attitude in 1883, J. Curie, "Quartz piézo-électrique."

[124] Duhem was not the last to attribute abstract reasoning and opposition to molecular notions to French scientists. Modern historians continue to do so. These characteristics are attributed to French experimental physicists, for example, in Garber's recent book (Elizabeth Garber, *The Language of Physics*, pp. 312–16). A more interesting example in our context is Marjorie Malley's paper on the radioactive research of Pierre Curie, who blames his abstract thought in impeding his research ("The Discovery of Atomic Transmutation: Scientific styles and philosophies in France and Britain," *Isis* 70 (1979): 213–223.).

[125] Hankel, "Eigenschaften des Bergkrystalles," pp. 519–523, 530.

[126] Differences in theoretical views did not pose any problem in regaining the same results.

[127] Curie and Friedel, "la pyro-électricité du quartz," p. 1390–91, 1393–94.

assumed that the three hemihedral (polar) axes of quartz expand in the same manner and produce the same electric effect *independently* of each other. The independency of the electric effect in the three axes can be viewed as a consequence of Jacques and Pierre Curie's molecular model for the phenomena, in which the total effect is due to contraction and expansion along electric axes. Yet the Curies' original model was not suggested for a multiaxial crystal like quartz, but for the uniaxial tourmaline. It supposed parallel layers of molecules perpendicular to the polar axis; how it can conform with the three axes of quartz that lie in the same plane is not clear. Friedel and Curie did not refer to the molecular structure of quartz and so did not reconcile the uniaxial model with the crystallography of quartz. Still, they assumed that the total effect is due to independent effects of expansion and contraction along polar axes. Thus, they were able to calculate the sum of the electric effects in these axes in any direction:

> Actually, if we consider a quartz plate with parallel faces, cut parallel to the crystal's principal axis, the surface perpendicular to the plane of the secondary axes [the polar axes], crosses them with angles that will be α for one axis, $60^\circ + \alpha$ for a second one and $60^\circ - \alpha$ for the third one. If we consider an expansion δ of the strip, the quantity of electricity developed by expansion relative to the first axis will be $\delta \cos \alpha$, relative to the second axis $\delta \cos(60 + \alpha)$ and to the third $\delta \cos(60 - \alpha)$, and the two last ones will have signs inverse to that of the first one. The sum will be:
>
> $$\delta[\cos\alpha - \cos(60^\circ + \alpha) - \cos(60^\circ - \alpha)] = \delta(\cos\alpha - 2\cos\alpha\cos 60^\circ),$$
>
> [this] value equals zero, since cos 60 = 1/2.[128]

Thus, a truly uniform heating of quartz does not electrify the crystal. This argument is not limited to quartz. Clearly, other crystals in its class (i.e., crystals that have the same kind of symmetry) are also electrified only by a nonuniform change of temperature. Moreover, parallel arguments hold for other crystal classes. Two months later Friedel and Curie demonstrated that cubic crystals should also have no electric effect due to uniform heating. They confirmed this claim experimentally on a few crystal species.[129]

Friedel and Curie's main results were confirmed in 1884 by B. von Kolenko, who studied pyroelectricity in quartz. Von Kolenko worked at the Institute of Mineralogy

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[128] *Ibid.*, p. 1393. Though Curie and Friedel's conclusion is valid, their argument is highly problematic, since they assumed that the electricity developed in each polar axis is independent of that in the other axes. The consequences of this assumption agree with the experimental findings on the electric division of quartz in heating, and under radial pressure. However, any attempt to apply such a reasoning to cases of unidirectional pressure, would have led to a contradiction with the experimental results. This was later the case with a theory of Paul Czermak.

[129] They used two different methods, both based on Friedel's 1879 apparatus. In one they uniformly heated a blend crystal in an oven, and found no traces of electric activity. In another they heated plate specimens of blend and sodium chlorate with a hemisphere larger than the plates and found no electric effect. However, heating these specimens with a small hot hemisphere, which caused a non-uniform heating, they observed a clear electric effect. Curie and Friedel, "Sur la pyro-éléctricité dans la blend, le chlorate de sodium et la boracite."

in Strasbourg, using Kundt's method of dusting in examining the electrification of the quartz. Hankel, however, was convinced neither by the experiments of the three independent studies nor by Röntgen's or Friedel and Curie's arguments. He continued defending his distinction between the effects of regular heating (thermoelectricity) and heating by radiation (actino-electricity) and the validity of his 1866 and 1881 experimental conclusions. Until his retirement in 1887, he performed experiments supporting his interpretation and published arguments against other experimentalists' results, first against the finding of Friedel and Curie and later against those of von Kolenko. Hankel continued to maintain his views and the dispute between him and other experimentalists was not resolved officially, but the consensus among the experimentalists made Hankel's claims irrelevant.[130]

MALLARD AND THE SYSTEMATIC PRESENTATION OF PIEZOELECTRICITY

Röntgen, J. Curie and Friedel's notion of pyroelectricity gained a clear definition from Ernest Mallard in 1884. Mallard was professor of mineralogy at the prestigious *École des Mines* and a leading crystallographer.[131] According to his definition, pyroelectricity is electrification by uniform heating or cooling. Only crystals electrified in this way are pyroelectric. Therefore, following the findings of Curie, Friedel and Röntgen (which Mallard adopted), quartz is not pyroelectric. This was a novel definition of pyroelectricity, connected to his recognition that the electric effect of nonuniform heating is a secondary effect of piezoelectricity. Mallard, however, did not follow Friedel and Curie in concluding which crystals are not piezoelectric. Instead of calculating the contributions of the effects on each axis, he relied directly on properties of symmetry. Haüy had already recognized that a pyroelectric crystal should lack a center (below p. 26). Yet, Mallard claimed that this is not enough. To be pyroelectric a crystal should have no more than one axis of symmetry. From this

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[130] This interesting episode of controversy over the interpretation of experiments that ceased without admission of the claims from either side deserves an extended discussion in another context. I found only one work that supported Hankel's claims after 1883, in Georg Wulff (Yuri Viktorovich) work from 1884 (Wulff, *Beibl.* 8(1884)597) when he was still a student. For the main participants in the controversy see for example: B. von Kolenko, "Erwiderung, betreffend die Pyroelectricität des Quarzes," *Ann. Phy.*, 29 (1886): 416–419; W. Hankel, "Berichtigung einer Angabe des Hrn. v. Kolenko in Betreff der thermoelectrischen Vertheilung an Bergkrystallen," *ibid.*, 26 (1885): 150–156; *id.* "Endgültige Feststellung der auf den Bergkrystallen an den Enden der Nebenaxen bei steigender und sinkender Temperatur auftretenden electrischen Polaritäten," *ibid.*, 32 (1887):91–108. Hankel repeated his claim on the cooling of quartz in 1892; W.G. Hankel und H. Lindenberg. "Elektrische Untersuchungen 19. Ueber die thermo- und piëzoelektrischen Eigenschaften der Krystalle des chlorsauren Natrons, des unterschwefelsauren Kalis, des Seignettesalzes, des Resorcins, des Milchzuckers und des dichromsauren Kalis," *Leipzig. Abh.* 18 (1892): 363–405, on p. 372.

[131] A. De Lapparent, "François-Ernest Mallard (1833–1894)," *Livre du centenaire* (Ecole Polytechnique), Paris: Gauthier-Villars, 1897, tome I, p. 398 et suiv (electronic version www.annales.org/archives/x/mallard.html).

condition of symmetry he deduced immediately which crystal classes are pyroelectric and which are not.[132]

Although Mallard avoided molecular considerations in the determination of crystal electric behavior, he agreed with Friedel and the Curies on the source of piezo- and pyroelectricity. He accepted their view that in both phenomena "the development of electricity is done in the same manner as if it was simply linked to the variation of the distance that separates the molecules."[133] Both the centrality of symmetry and the inclination toward the molecular view are grounded in Mallard's crystallography. In several studies he resolved apparent contradictions to the rules of symmetry. In others he supported the assumption of polyhedral (asymmetric) molecules.[134] In the second volume of his celebrated treatise on crystallography dedicated to "physical crystallography," Mallard decided clearly for the mechanical source of piezoelectricity. Despite the short time in which Mallard had to compile the findings in the new field, piezoelectricity is systematically accounted for in his treatise. He dedicated more room to piezoelectricity than to pyroelectricity, viewing the former as more fundamental.

Mallard did not carry out research on piezoelectricity, but in writing the first coherent and comprehensive chapter on the phenomena he contributed his suggestions and clarifications for unexplained issues.[135] Such was the mechanical explanation of the transverse effect in quartz. The Curies explained only longitudinal effects with their molecular model. "For explaining the opposition of signs in cases of pressure directed along binary [polar] axis and in that of pressure directed perpendicularly to that axis, one can remark that when one compresses perpendicularly to mn (i.e., along a polar axis Figure 1.5), the molecules are brought closer along the direction of the binary axis, while they are moved away along the same direction, when one compress perpendicularly to mn' [i.e., perpendicularly to a polar axis]".[136] Thus, Mallard was able to embrace the transverse effect into molecular explanation. Yet, he acknowledged that this explanation is not general since the transverse effect is not always opposite in sign to the longitudinal; in tourmaline, for example, they are of the same sign.

The mechanical clarification of the phenomena was known and accepted enough to be applied to explain other phenomena. In 1883 Karl Mack from Kundt's institute in Strasbourg suggested that thermal contraction and expansion that generate piezo- and pyroelectricity cause also a change in the optical behavior of boracite at a certain temperature. According to Mack, one can assume that inner tensions, originated in thermal expansion, alter the crystal's system of planes (*Ebenensystemen*) from one kind to another at the temperature in which it changes its behavior.[137]

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[132] Ernest Mallard, *Traité de Cristallographie géométrique et physique*, Tome 2 "cristallographie physique", Paris: Dunod 1884, pp. 571–573.

[133] *Ibid.*, p. p. 571.

[134] Lapparent, "Mallard."

[135] Wiedemann had published a chapter on piezoelectricity already early in 1883 in his *Die Lehre von der Elektricität*. However he did not refer to the important findings of 1883, and did not suggest a coherent interpretation of the various experimental findings as Mallard did.

[136] Mallard, *Traité de cristallographie*, pp. 559–60.

[137] K. Mack, "Ueber das pyroelectrische Verhalten des Boracite," *Ann. Phy.*, 21 (1883):410–421, on p. 421.

Mallard thought that piezoelectricity originated in changes of distances between molecules and that exact knowledge of these displacements and of "the electric coefficient by which it is needed to multiply this deformation," is probably sufficient to predict the electric behavior of all crystals. However, these, he thought, were "very far from being known." Thus, though ultimately the theory of piezo- and pyroelectricity would be formulated in molecular-mechanical terms, in his discussion he limited these considerations to particular cases and used symmetrical reasoning for the general treatment of the phenomena. This approach was similar to that of the Curies, Friedel and Röntgen, except in making explicit the inability to formulate a general molecular theory and in an attempt to suggest general rules. Mallard generalized the Curies' quantitative findings of longitudinal and transverse effect in quartz to a general rule for the development of charge (q):

$$q = ks\frac{P}{s'} \tag{9}$$

where P is the weight, s the surface area that releases the electricity, s' that of the surface that receives the pressure. However [Mallard continued] in the same crystal, k varies at the same time with the direction of pressure and with the direction of the surface on which one exercised the pressure." The coefficient k is set by the molecular structure of the crystal, but its theoretical determination, as already said, was view by Mallard as unattainable in the foreseeable future. While the value of the coefficient cannot be determined from general considerations, one can learn about the directions of the electric activity from the crystal's symmetry. Mallard thus discussed the symmetry of the phenomena. His conclusion agrees with the rules suggested two years earlier by the Curies: piezoelectricity is developed only along asymmetric crystallographic axes, regardless the crystal inner structure.[138]

The detailed account that Mallard dedicated to piezoelectricity shows the early recognition of its significance. He himself thought that "the study of the electric phenomena in crystals leads to very important consequences, either from the physics of crystals' point of view, or also from the point of view of the general theories of electric phenomena."[139] This assessment, and particularly its second part, was probably considered an exaggeration by many physicists. The subject did not become central in the study of electricity, though it was also treated in some detail in books on that subject, like Wiedemann's *Die Lehere von der Elektricität* mentioned above. Unlike Wiedemann's book, Mallard's volume on "physical crystallography" appeared at an appropriate time in the history of piezoelectricity. He was able to embrace all the important findings on the geometry of the phenomena and its relations with pyroelectricity made during 1883. These enabled him to offer the reader a coherent and

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[138] Mallard, *Traité de Cristallographie*, p. 560–1, quotations from p. 560. On the Curies' suggestion see above p. 18. Indeed theoretical determination of the value of the piezoelectric coefficients was found to be very difficult; for most species it has not been accomplished even until now. However, meaningful knowledge on the variation of the coefficient in the same crystal was gained already in 1890 by Voigt based on the body of knowledge available to Mallard. Voigt's theory is discussed in details in the following chapter.

[139] *Ibid.*, p. , 80.

comprehensive picture of the subject, based on molecular assumptions and symmetric considerations. Moreover, on the findings and conclusions of Jacques Curie, Friedel and Röntgen, Mallard drew boundaries for the new subfield of piezoelectricity, embracing the study of pyroelectricity. Very few studies of piezoelectricity were carried out in the remaining part of the decade. The phenomena did not seem to raise urgent questions. The general properties of the new effect seemed to be known. A systematic theory of the phenomena, on the other hand, appeared to be distant. The molecular notion of the Curies, or a more general concept of mechanical tension, suggested by Röntgen, gave a sound interpretation of the appearances, though they did not provide a rigorous explanation for all the observed phenomena. Apparently, the scientific community was satisfied with the more or less coherent information about the electrification of crystals by pressure. A major change in the study of the phenomena would follow only unexpected experimental results, which the molecular-mechanical model could not explain.

CHAPTER 2

THE ROAD TO THE DESCRIPTIVE THEORY

Early theoretical considerations of piezoelectricity were mostly qualitative. Indeed, Jacques and Pierre Curie mathematically showed the plausibility of their model of permanent polar molecules. Yet, they did this only for an effect along a polar axis in a model of tourmaline. A mathematical account of the observed phenomena was limited to the development of charge in one axis. No mathematical account was suggested for the variation of the phenomenon with the directions of pressure and the measured surface (the value of Mallard's constant k as a function of the directions). The hypotheses on the connection between piezoelectricity and pyroelectricity were qualitative in character. From all the observations on the behavior of quartz under pressure and heating, only the case of uniform heating was illustrated mathematically. A lack of quantitative data on the magnitude of the electric phenomena was an obstacle to the formulation of a mathematical theory. Still, for a few crystal species enough experimental data was accumulated to enable the formulation of a mathematical theory that accounts for some aspects of the phenomena, like the directions of maximal and null effects for any direction of pressure.

CZERMAK'S RESEARCH ON QUARTZ

Paul Czermak attempted to fill the lack of both quantitative data and mathematical description. In 1887, he suggested a mathematical theory for quartz, which describes the electric effect due to pressure in any direction on any other direction.[1] He worked on this problem when he was a guest researcher at Kundt's institute in Strasbourg, completing his unofficial studies after receiving his doctorate under Ludwig Boltzmann in Graz two years earlier. Unlike other contributors to piezoelectricity, Czermak apparently, was not driven to this study through research in a connected area. His former work does not show a direct connection to his study of piezoelectricity. Rather, his move to this field can be explained by his invitation to Kundt's institute. As head of

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[1] Paul Czermak, "Über der elektrische Verhalten des Quarzes," *Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Classe der Kaiserlichen Akademie der Wissenschaften, Wien*, 96 (1887), pp. 1217–1244, 97 (1888), pp. 301–324. Page numbers in parentheses in this section refer to these papers.

the institute, Kundt directed the work of its researchers. As Max Weber observed, "the assistant [in Germany] is just as dependent upon the head of the institute as is the employee in a factory upon the management." This view was accepted by later historians, who pointed out that "foreign physicists sometimes admired the disciplined research army of the German professor." Kundt's management of the research in his institute, and its productivity, were surely exemplary. In Strasbourg, Kundt created a research school, in which the research was more coordinated than in other institutes at the time. It attracted young physicists from Germany and abroad, like Czermak, for its facilities, resources, and the scientific work done under its roof. Piezoelectricity was not Kundt's primary concern in 1887, but he had been engaged in its study since 1883 through his own experiments. Related experiments on pyroelectricity using Kundt's powdering method continued to take place in the institute.[2] Thus, Czermak's choice of research seems to be directed by Kundt.

Though his former work was not directly connected to piezoelectricity, Czermak did gain experience, qualifications, and concerns that shaped his research. His "extraordinary" dissertation on molecular paths in Maxwell's kinetic theory of gases revealed, according to Boltzmann, rare theoretical talent. Still, like most theoretically inclined physicists of his generation, before arriving in Strasbourg Czermak had also carried out research in the laboratory.[3] Theoretical, or mathematical, physicists in the German sphere were characterized by their combination of quantitative physical rules with mathematically analyzed experimental results, and by their interest in exact measurement and determination of constants. Czermak's piezoelectric research displayed these concerns. Compared with previous research on piezoelectricity, Czermak's work is characterized by its emphasis on exact quantitative data and theory and their comparison.

Czermak's theory

Previous experiments, notably those of Röntgen, showed that the electric effect of pressure varies with the direction in which it is applied. Czermak offered a first quantitative theoretical account for the changes in the effect with the direction of pressure and the direction in which the electric effect is measured. Following the empirical findings and the known symmetry of quartz, he, like his predecessors, assumed that quartz has three axes of piezoelectric activity (polar axes), which are the three hemihedral axes (x in Figure 1.4). He adopted the Curies' conclusion that

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[2] The quotations are from Paul Forman, John L. Heilbron and Spencer Weart, "Physics *Circa* 1900: Personal, Funding, and Productivity of the Academic Establishments," *HSPS* 5(1975), on p. 53. See also Max Weber, "Science as Vocation," in *Essays in Sociology* translated by H.H. Gerth and C.W. Mills, New York: Oxford University Press, 1946, pp. 129–156 (the quotation is taken from p. 131). On Kundt's School see Wolff, "Kundt die Karriere eines Experimentalphysikers," on pp. 436–440. For references about experiments on pyroelectricity in Kundt's institute see chapter I note 112.

[3] Christa Jungnickel and Russell McCormmach, *Intellectual Mastery of Nature: Theoretical Physics from Ohm to Einstein*, Volume 2, Chicago, The university of Chicago Press, 1986, p. 68; J. W. Poggendorff, *Biographisch-literatisches Handwörterbuch zur Geschichte der exacten Wissenschaften*, Bd. IV, Ann Arbor, Mich.: J.W. Edwards, 1945, pp. 289–90.

the electric charge in each polar axis is linearly proportional to the pressure. So for a nonvariant electric circuit, as was the arrangement in his experiment, the electric tension measured is proportional to the pressure. He further tacitly adopted Jacques Curie and Friedel's assumption that the effects in the three axes are independent of each other, and the effect in any direction (in the plane perpendicular to the principal axis) is the sum of the influences of the electricity in these three axes on the examined direction.

Czermak presented the Curie's molecular hypothesis, and referred to polar molecules along his published account. Nevertheless, he claimed that his account "is not based on any particular hypothesis" on the source of piezoelectricity.[4] Indeed, the assumption of a linear effect and the existence of three polar axes, were universally accepted and were independent of any particular hypothesis. Yet, this is not true of Czermak's tacit assumption that the effects in the three axes, which form angles of 60° between each other, are independent. Generally, effects in nonorthogonal axes are not independent. However, if one thinks about these axes in terms of the Curies' molecular assumption, a change in pressure along an axis should bring a change in the distances between polar molecules. This, in turn, should induce an electric effect, independently from that induced in another direction. Hence, Czermak's assumption follows from such a molecular hypothesis. Like Jacques Curie and Friedel, he apparently generalized the Curies' original claim stated for the uniaxial tourmaline to the multiaxial quartz. Thus, a close look at Czermak's basic assumptions suggests that they were conceived on a basis of molecular or, at least, mechanical thinking. As a former student of Boltzmann, arguably the dean of the atomists, whose own major work was on the kinetic theory of gases, Czermak's inclination toward a molecular assumption is not surprising. Perhaps Czermak thought that these assumptions were independent of a molecular hypothesis, since they do not necessitate a molecular hypothesis; the logical derivation stems only from the molecular hypothesis to his assumptions and not the other way around. Any mechanical assumption that assumes that the electric effect is due to tension along and *only along* polar axes would lead to the same result. Nonetheless, historically such an assumption was suggested only with a molecular hypothesis. Röntgen, who suggested that the effect be due to inner elastic tension, did not relate it to the polar axes.

To calculate the electric effect of pressure in any direction, Czermak used the assumptions of linear effect and of the independency of the effects in the three polar axes. Where φ in Figure 2.1 is the angle between the direction of pressure (Q) and the near axis of missing piezoelectricity, the component of pressure in the first polar axis p_1 is: $p_1 = a\cos(30 - \varphi)$, where a is the magnitude of the original pressure. This effective pressure induces voltage in that direction. According to the assumption, its projection in the direction of the pressure is added to the total voltage at that direction. By simple trigonometry the voltage v_1 induced by the first polar axis is: $v_1 = bp_1\cos(30 - \varphi) = A\cos^2(30 - \varphi)$, where b is a coefficient and A the multiplication of the pressure (a) and the coefficient b. Similarly, the two other polar

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[4] Czermak "elektrische Verhalten," p. 1227. For a reference to the polarity of the molecules see. p. 303.

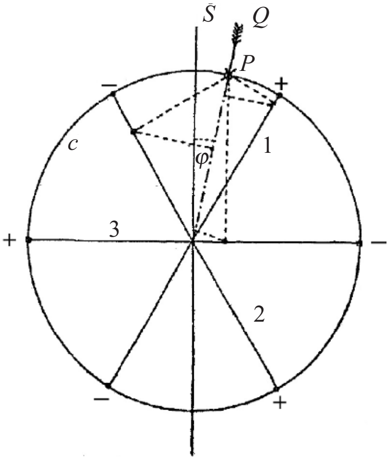

Figure 2.1: Czermak's figure for the voltage in the direction P due to pressure in the same direction. 1, 2 and 3 are quartz's polar axes (from Czermak, "elektrische Verhalten").

axes induced tensions: $v_2 = -A\cos^2(30+\varphi)$, $v_3 = -A\cos^2(90-\varphi)$. Their sum V is the total electric tension:[5]

$$V = v_1 + v_2 + v_3 = A\left[\sqrt{3/4}\,\sin 2\varphi - \sin^2\varphi\right] \tag{1}$$

Next, Czermak developed an expression for the electric tension in any direction due to pressure in another, while both are in the xy plane (perpendicular to the principal axis).[6] ψ is the angle between the direction under question (P) and the axis of missing piezoelectricity, while φ remained the angle between the pressure (Q) and that axis (Figure 2.2). Then the electric tension induced by the first polar axis in the sought direction is: $v_1 = A\cos(30-\varphi)\cos(\psi-30)$, and the total voltage in the ψ direction is (p. 1234):

$$v = A\left[\sqrt{3/4}\,\sin(\psi+\varphi) - \sin\varphi\,\sin\psi\right] \tag{2}$$

Thus, Czermak formulated an expression for the relative electric tension in quartz due to unidirectional pressure in any direction.

Experimental examination

Czermak used this theoretical elaboration in the experimental work, which occupied most of his time. Unlike his host Kundt or Röntgen, he designed the experiment with the mathematical theory in mind, comparing his results with the theoretical

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[5] Ibid., pp. 1228–29. This equation is valid when $0 \le \varphi \le 60°$.

[6] Pressure in any other direction can be resolved to one component in the xy plane and another in the direction of the principal axis. The latter was known to have no electric effect.

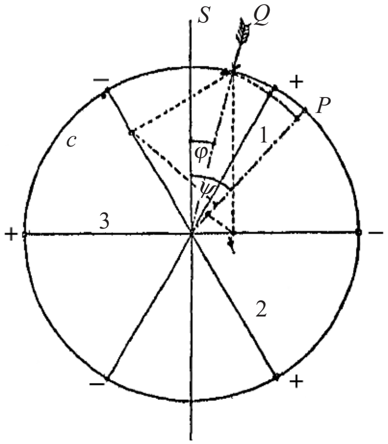

Figure 2.2: Czermak's figure for the voltage in the *Q* direction due to pressure in the *P* direction. 1, 2, 3 are the polar axes (from Czermak, "elektrische Verhalten").

predictions and even employing the theory to interpret the experiment. This approach characterizes theoretical physicists of the time. These physicists also performed experiments but focused their research on quantitative relations accounted for by theory. In his first series of experiments, he measured the electric voltage due to pressure in the direction of measurement. He took two quartz cylinders, whose lengths coincided with the principal axis, and encompassed their circular circumference with 24 steel strips. With a press he compressed the cylinder in 48 different directions through its center, i.e., each 7.5°, and measured the electric voltage in the direction of pressure. The electric voltage was read with an electrometer's dial whose deviation he compared both before and after each measurement with its deviation due to a known "Daniell cell." He carried out these measurements with three different weights for each of the two cylinders. Generally, his results presented the known division of quartz into six electric zones. The distributions of the induced electric in these zones are symmetric (in absolute values) in theory and also approximately so in practice. Thus, he calculated for pressure in each direction relative to a missing piezoelectric axis the average voltage induced in absolute values in the six zones, reducing the 288 measurements to 48 values. Comparing the experimental results with his theory, he found deviations of 2.52° and 2.96° from the directions that he had initially taken to be of "missing piezoelectricity" by optical determination (pp. 1218–30).

Adjusting the data accordingly, he compared the observed values with theoretical calculations. He calculated in an unspecified manner the average value of the coefficient *A* for each weight from experimental data and the theoretical expression (equation (1)). Thereby, he deduced that the phenomenon is linear (in relation to weight) in all directions. Previously, this linearity was examined only for charge in polar axis. Inserting the average values of *A*, he compared the theoretical prediction for the variation of the voltage with direction of pressure with the experimental findings. He did not offer any systematic comparison between the calculated and observed

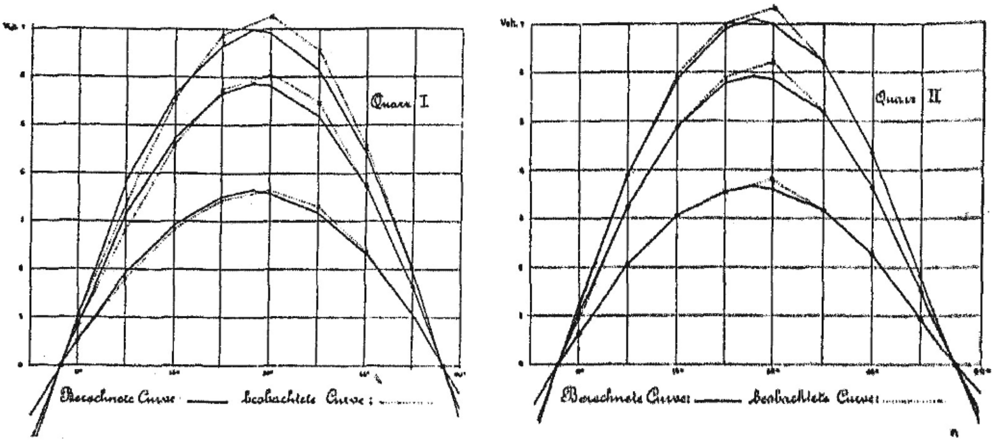

Figure 2.3: Czermak's comparison between curves computed by theory (thick lines) and those drawn between observed values (dotted lines) for two specimens (from Czermak, "elektrische Verhalten").

values but juxtaposed their numeric values in a table and charted lines that connected both values on the same graph (Figure 2.3). The reader was left to assess the confirmation of the expression. Justly, Czermak regarded his results only as an initial rough confirmation of his predictions. Since the main sources of error in this experiment, like the exact direction of the prism's surfaces and irregularities in the quartz crystals, were very difficult to quantify, one cannot calculate the experimental error. Thus, one could not be sure whether the deviations are smaller or larger than the experimental error.[7]

While his own results gave only a rough confirmation of his theory, Czermak found further approval in Röntgen's results. The division of a quartz sphere into two zones by the axis of missing piezoelectricity, when the pressure is either in that axis, or in a polar axis perpendicular to it, derives from equation (2). This equation shows also the locations of the maximal effects, where Röntgen found them. Yet, while Röntgen found that a pressure 45° from an axis of missing piezoelectricity results in a maximal effect in the latter axis and no electric effect in the axis 45° to the other direction, which is a polar axis, Czermak's theory predicted that the direction of no electricity would be only 36.3° from the axis of pressure. Czermak, however, explained away this contradiction by a theoretical analysis of Röntgen's experiment. Using his theoretical expression he showed that a deviation of 3° in the direction in which the pressure was applied yields an electric effect like the one observed by Röntgen. In Röntgen's experiment such a deviation was equal to merely 0.8 mm, which, Czermak claimed, could hardly be noticeable by the experimentalist. Thus, he implied that Röntgen did

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[7] Ibid., pp. 1230–32. Czermak's theory varied from the prediction of modern theory suggested three years later. The modern equation is $V = A' \sin 3\varphi$, where $A' = A/2$, is close to Czermak's equation. One cannot use his experimental results to decide which of them is correct.

not press exactly in the direction that he had intended to and concluded that "Röntgen's research is accounted for very well by this [Czermak's] formulation."[8]

Czermak did not perform his own experiments on the electric effect in directions different from that of pressure. Röntgen, who carried out such experiments, did not measure the magnitudes of the electric tensions. Thus, Czermak did not have quantitative values to examine his equation for the electric voltage in various directions (equation (2)), as he examined his equation for the tension in the direction of pressure (equation (1)). Measuring the voltage in various directions would have required him to construct a new and more complicated experimental apparatus. Apparently, the quantitative agreement between the theoretical and the observed voltage in the direction of pressure and its qualitative agreement with the effect due to pressure in other directions satisfied Czermak's as a confirmation of his theoretical reasoning.

Yet, quantitative measurements of the electric effect in one direction due to pressure along another had been made for one important case, that of the transverse effect. However, Czermak neglected this data. In 1882, Jacques and Pierre Curie published a quantitative law empirically deduced for the transverse effect according to which in a cylinder it is equal in magnitude to the longitudinal.[9] Clearly, this result contradicts Czermak's equation for the transverse effect. In his theory the voltage due to pressure exercised along an axis of missing piezoelectricity (i.e., a transverse effect) is: $V = \sqrt{3/4}A \sin\psi$ where ψ is the direction in which one measures the voltage. Hence, for the polar axis ψ is 90° $V = \sqrt{3/4}A$. However, from equation (1) it follows that the voltage in the polar axis due to pressure along that axis equals only $1/2A$ (pp. 1229–34). These values deviate by more than 40%.

The paper in which the Curies reported on this property is the only one they published in the *Comptes rendus* that was not mentioned by Czermak. Since no reference to this paper was given in the other papers that he cited, one can kindly assume that Czermak did not know about the Curies' quantitative finding.[10] Whatever the reason for his neglect of the Curies' finding, had he regarded it he would have had either to find a good explanation for the deviation, or to change his theory. Other physicists were likely to notice the failure of the theory at this point. Like the present writer they probably saw the origin of this failure in Czermak's dubious assumption that the effects in the three axes are independent. This assumption, however, follows from a molecular model like the Curies'. A discerning observer at the time could have concluded that the current molecular assumption is insufficient to account for piezoelectricity. Yet, I do not know of anyone who actually reached that conclusion from the silent failure of Czermak's theory.

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[8] Ibid., pp.1232–1237, quotation on p. 1237. On Röntgen's experiments see above chapter I p. 53.

[9] The Curie brothers referred to the transverse effect in a qualitative way in the paper "phénomènes électriques des cristaux" which appeared in *Journal de Physique* (pp. 246–7). They announced the quantitative rules of the effect only in a paper that discussed experimental detection of the converse effect. J. et P. Curie "Déformations électriques du quartz," p. 31.

[10] Röntgen mentioned the Curies **qualitative** result about the existence of the transverse effect referring neither to the quantitative result nor to the location of the paper; Röntgen, "Aenderung der Doppelbrechung des Quarzes," p. 541.

Absolute measurement of the piezoelectric coefficient

After establishing the validity of the theoretical expression (equation (1)), Czermak employed it to redetermine quartz's piezoelectric coefficient in absolute units, i.e., in a standard system of units independent of any peculiarity of a specific experiment. He designed a new experiment in which he shaped two square parallelepipeds from the same quartz specimen. Two parallel surfaces of one bar were cut perpendicular to a polar axis, and parallel surfaces of the other were cut at an inclination of 15° from the perpendicular. Applying pressure along these directions, he measured the voltage between the two pressed surfaces with an electrometer dial whose deviation was compared before and after each measurement with that due to a known "Daniell cell." He examined the effects caused by three different weights. To eliminate accidental errors, he repeated his experiment on four different days. These precautions illustrate his concern with experimental accuracy. While his measurements of the first prism (cut perpendicularly to a polar axis) showed the linearity of the phenomenon, those of the second prism (cut at an inclined angle) did not, and thus failed to yield a constant. He explained this apparent contradiction as due to a deviation in the prism's shape (the faces were not exactly parallel). Comparing the results with the theoretical expressions, he determined the presumed actual directions of these surfaces and used them in later calculations. Czermak, thus, used mathematical analysis to eliminate a systematic error.

Because he compared each reading of the voltage to that of a "Daniell cell," Czermak could rely directly on the electrometer's voltage measurement. Yet, the piezoelectric coefficient related charge, rather than voltage, to weight, so, like the Curies, Czermak had to determine capacity. Unlike them, he measured the capacity of the whole system. He used a cylindrical condenser (similar to the one used by the Curies) whose capacity could be altered at will and was calculable in the various states from its dimensions by an equation derived by Kirchhoff. Connecting the condenser to the electrometer (in two states) instead of the apparatus, he obtained a relationship between their capacities and calculated from that the capacity of the apparatus.[11] In this method, he neglected the small capacity of the electrometer. Instead, he made sure that it would be small. From the capacity, he determined a value of 0.06142 statcoulomb/kg (6.27×10^{-8} statcoulomb/dyne) for the piezoelectric coefficient.[12]

As Czermak noted, his result agreed well with the value announced by the Curies six years earlier. They differed by less than 1% (pp. 1237–44). His method, however, was different from theirs. While Czermak's determination was based on measurements not only of the target but also of the apparatus, the Curies based their determination only on two measurements of the target (replicated to reduce errors). The Curies bypassed complicated measurements and calculations by making a "null experiment."

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[11] Czermak did not report his measurement of the relative capacities. Perhaps he compared the deviation of the electrometer after it was charged by a constant voltage charged it, with the condenser and with the apparatus.

[12] As was quite common at the time, Czermak wrote more digits than the significant digits in his experiment, which could hardly yield three significant digits, let alone four.

They did not have to measure the capacity of the system or to translate deviations of the electrometer needle to units of voltage. Thus, the analysis of their experiment was much simpler. Broadly speaking their method reflects a French style of experimentation, while Czermak's reflects a German-theoretical style.[13] Czermak's theory of the experimental instrument was no more complicated than the Curies', but he relied more than the Curies on a theory of the piezoelectric phenomena itself, since he compared the effects of applying pressure along two different directions by his (roughly confirmed) theoretical expression (equation (1)). Moreover, he reinterpreted the data (the direction of pressure) according to the same expression. Thus, the assumption that one constant piezoelectric coefficient exists (in equation (1)) was used to obtain a unique constant and to find its value. This made his experiment less reliable. Its reliability was further diminished by a contradiction between his expression for the electric effect in one direction due to pressure in another and the empirical data, and later by the rejection of Czermak's theoretical explanation in favor of Voigt's more sophisticated theory. Probably, because Czermak's results were so embedded in his (incorrect) theoretical calculations, they were no longer used.[14]

Czermak also applied his mathematical-theoretical approach to the converse piezoelectric effect. Similar to the case of the direct effect, he based his expressions on independent effects along the polar axes induced by electricity in those directions. Thus, the total compression in the direction of a polar (x) axis and in perpendicular to it (y axis) is a sum of three independent contributions of the polar axes. Their ratio gave the tangent of the direction of the resultant pressure. Following Röntgen and Kundt, Czermak did not examine the effect of electricity on pressure or contraction directly, but its indirect optical influence. His experimental apparatus was based on Kundt's electro-optic method. He sent a circularly polarized light along the optical axis (the principal axis z) in the two prisms used before, and examined changes in the radius of the light circle due to double refraction in the direction of an electric field.[15] He applied strong electric fields in three intensities in 0°, 15°, and 30° from a polar axis, and showed that the compound effect in each direction is linear, thus confirming indirectly the assumed linearity of the converse effect. After adjustment to the corrected directions of the prisms (as found in the experiments on the direct effect), Czermak reached a good agreement between theory and experiment concerning the directions of maximal effect. The agreement between the experimental and theoretical magnitudes of the effect in different directions was, however, only qualitative. Regarding the delicacy of the experiment, he considered it "quite good correspondence."[16]

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[13] I discuss this question in chapter 5.

[14] That his results agreed with the Curies' should not surprise us since his theoretical equation agrees with theirs (and with later theory) for the effect in the direction of a polar axis, and deviates in only about 3.5% for the pressure applied in the inclined direction. On Voigt's theory see below p. 77.

[15] On Kundt see above chapter I p. 46.

[16] Lastly, Czermak compared the effects on polarized light of electric tension and of mechanical pressure. From the found average changes in the radius of the polarized light circle for a unit of weight (known from experiments by others) and for electric tension (from his experiment) and his expressions for the change in that radius due to pressure induced by electric field, he deduced the pressure generated by an

In a postscript Czermak expressed his intention to carry out a similar study of tourmaline. Yet, he did not leave a record of such a study. Since tourmaline has more polar axes, it poses a more complex theoretical problem than quartz. Had Czermak tried to deal with this problem he might have found the limits of his theoretical approach, and its tacit molecular assumption. Consequently, he or others might have formulated a new theory. But this apparently was not the case. Czermak left no published record of a further piezoelectric study.[17] In 1888 he returned to Graz as an assistant and then *privatdocent*, and was led to other areas of research. Consequently, the formation of a satisfactory theoretical account of piezoelectricity did not follow a theoretical treatment of tourmaline. Instead, it followed surprising developments in the experimental study of quartz.

THE DISCOVERY OF THE ELECTRIC EFFECT OF TORSION IN QUARTZ

In 1889, Röntgen resumed his piezoelectric research. In his earlier experiments he had examined the electric effect of pressure and the mechanical effect of electric fields in quartz in various directions. Now, he turned to the examination of the electricity induced under torsion. Piezoelectricity dealt with the mutual influences of elasticity and electricity in crystals. Since shearing stress is an integral part of elasticity, the empirical examination of its electric influence was a continuation of the earlier research. Because one kind of stress, namely pressure, produces an electric effect, one had to consider the possibility that the other kind of stress, namely shearing stress, also produces an electric effect. Yet, this assumption did not follow any theoretical expectation concerning the kind of effect one might observe, not even as a refutation of a theoretical prediction. The examined effect was beyond the realm of the original theoretical frame, or proto-theories, in which Röntgen and others conceived previous experiments. Thus, Röntgen's study of torsion seems to be a product of an experimental practice in which one examines the various possibilities without theoretical expectation of their results.[18]

The study of the electric effect of torsion was Röntgen's first research at Würzburg, where he was appointed the professor for experimental physics at 1889. Apparently, this study was not connected to the various experimental studies he made in the six years that elapsed since his previous study of piezoelectricity. Neither these studies nor piezoelectric research done at the time could teach him any new idea or

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electric tension of one esu on a polar axis. He found for the specimen used a value of 0.126 kg per esu. One cannot compare this value, however, with the value of the piezoelectric coefficient since Lippmann's equation connects electric tension with a change of length rather than with pressure. Czermak, pp. 301–307, 320–324.

[17] One cannot rule out the possibility that Czermak did take the study of tourmaline but encountered difficulties, which he could not solve and consequently abandoned it.

[18] Röntgen might have carried out this experiment since he suspected that the principal axis is polar (see below) and that he would be able to observe this by torsion. Whatever is the plausibility of such assumption (which I find unlikely) he did not have any theoretical reason to suspect this polarity.

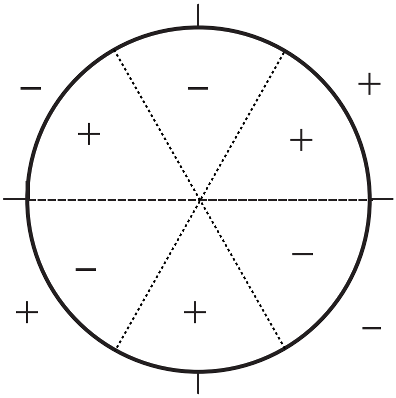

Figure 2.4: Distribution of electricity by pressure (shown inside the circle) and by torsion (shown outside the circle).

experimental procedure that he used for studying torsion in quartz.[19] His move from Giessen to Würzburg was a good opportunity to return to former subjects like that of piezoelectricity.[20] Whatever caused Röntgen to carry out this research in autumn 1889, he had no scientific reason not to perform it six years earlier.

For the torsion experiment he ordered a relatively long quartz cylinder bar (9 cm), whose height coincided with the principal axis. Pressing the bar he found and marked the points of missing piezoelectricity at various heights verifying the uniformity of the crystal. The bar was placed in a "torsion's apparatus," one end of it was fixed and the other connected to a screw. Turning the screw, Röntgen applied shear stress in tangential direction to the circle of the cylinder, i.e., perpendicular to the principal axis. He examined the resultant electric distribution by a metal wire located parallel to the cylinder's principal axis, near its surface but not touching it. This measurement showed qualitatively the distribution of electricity on the circular surface. In particular, Röntgen pointed the directions in which the torsion had no electric effect (he called it "missing torsion-electricity") and compared these points with the marked lines of missing piezoelectricity.[21]

To Röntgen's surprise these directions did not coincide. Moreover, the cylinder was divided into four electric zones of alternate positive and negative charge, in contrast to the six zones one gets by pressure (Figure 2.4). Thus, the phenomena showed a symmetry only of the second order, rather than the known third order symmetry of quartz. Surprised by these results, Röntgen examined a second bar, this time of a left

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[19] On these studies see Glasser, *Röntgen*, pp. 77–79.

[20] One might assume that the richer university of Würzburg supplied him with better means to perform the experiments. However, his laboratory at Giessen was satisfactorily equipped to carry out such experiment. So he could have carried it out in Giessen.

[21] Röntgen, "Eigenschaften des Quarzes," pp. 16–18. Page numbers in parentheses in this section refer to this paper.

quartz (the first was from a right quartz specimen), and found the same effect.[22] To verify these results, Röntgen constructed an experiment on the converse effect of this phenomenon. He placed the bars under an influence of electric distribution like the one generated by torsion, i.e., under positive potential at the middle of two diagonal zones and negative at the middle of the two others. He observed a resulted torsion directly with a telescope and indirectly by optical, electric, and acoustic methods (pp. 19–23). [23]

Apparently, the most surprising property of the electrification by torsion was the division of quartz into four electric zones, which did not coincide with the known polar axes. While the piezoelectric effect of pressure agreed with the crystallographic symmetry of quartz, the electric effect of torsion apparently did not. Seemingly, Röntgen tried to find some clues to this behavior in the difference between the effects in a right and a left quartz. The right and left specimens exhibit mirror images of the distribution of electricity by both torsion and pressure. From this observation Röntgen inferred that the principal axis should also be polar, though it did not show polarization by the application of direct pressure. He probably thought that the asymmetry of the effects in left and right crystals shows that the principal axis (which has the same role in both) is asymmetric, and that it should be polar. Yet, his "initial cherished hope, that a torsion of the bars would make its axis electrically polarized, has not come true" (pp. 21–2). Röntgen's hope to find an axis that would explain the new findings agrees both with the connection assumed between crystal symmetry and physical properties and with the assumption that piezoelectric phenomena are caused by strain along the direction of polar axes. This assumption was first suggested by the Curies and was later used and restated by others including Czermak who made it the basis of his theoretical account. However, Röntgen's experiments suggested that this assumption should be abandoned (pp. 21–2).

Torsion includes effects neither of pressure nor of contraction (or expansion), but only of shearing stress and deformation. Moreover, an effect of deformation along polar axes should have a symmetry of the third order rather than of the second. Thus, one could not explain the discovered phenomenon of torsion by the effect of tension or contraction along the polar axes. The effect could still be connected to deformation but could not be limited to expansion and contraction, as was the hypothesis of polarized molecules. "From the kind and manner in which torsion-electricity and torsion by electrifying come into being [*zu Stande kommt*], I [Röntgen] still have not been able to form a right picture; the assumption of polarized molecules, from which I initially came to my electro-optic and piezoelectric researches, does not lead to the goal" (p. 23). Unable to suggest an alternative explanation, Röntgen left the challenge to others.

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[22] The arcs between the lines of no electric effect varied slightly from 90°, a deviation that he explained by impurities in the specimens.

[23] To observe the effect directly he connected the two bars, making sure that their zones coincide. One end was stuck to hard rubber, the other connected to a mirror. An observer with a telescope directed at the mirror detected the small changes from the circular shape of the bar. Röntgen reported that he repeated this experiment with variations, often using different observers, and found always the same results.

VOIGT'S GENERAL THEORY: MOTIVES AND BASIC ASSUMPTIONS

The challenge Röntgen's findings posed was met by Woldemar Voigt in August 1890, seven months after their publication. Voigt suggested the first theory that accounted for the piezoelectric and pyroelectric behavior of all crystals. He offered a comprehensive and detailed memoir of about a hundred pages entitled "*General Theory of the piezo- and pyroelectric Phenomena in Crystals*."[24] This theory accounted for all phenomena of electrifying by stress and change of temperature, including the effect of torsion on quartz. The "elucidation [*Aufklärung* of torsion's phenomenon] is one of the most interesting tasks of the general theory," Voigt wrote 20 years later.[25] Though this elucidation was an immediate cause for the construction of a piezoelectric theory, Voigt's aim was much broader. He offered a general mathematical theory, based on a few sound assumptions that embraced all phenomena of piezo- and pyroelectricity. Clearly, piezoelectricity lacked such a theory. The few theoretical suggestions were not comprehensive, lacked rigor and did not account for the observed phenomena. Czermak's, which was the only mathematical theory suggested, suffered not only from lack of rigor but also from contradictions with the experiments.

Voigt, the 40-year old professor of theoretical physics at Göttingen, suited the task well. He had begun his work on crystals already as a student in Franz Neumann's seminar in Königsberg in the early 1870s, writing his dissertation on the elastic constant of rock salt (1874). He continued working on the physics of crystals during his entire career.[26] From Neumann he learnt about the relations between the physical properties and the symmetry of the crystals. Following his teacher, he made that a central theme of his research.[27] Voigt's interests in the physics of crystals, elasticity, and electricity made piezoelectricity a natural candidate for his study. His full command of the theoretical and technical methods and assumptions of those fields, uncommon among physicists, made him competent to formulate a theory for the field. Immediate stimuli to study the electricity of crystals came probably from the current pyroelectric research of Voigt's close colleague Eduard Riecke, Göttingen's professor for experimental physics,[28] and from Röntgen's published results.

Only rigorous (i.e., mathematical) theory, Voigt claimed, can establish the validity of certain assumptions, generally accepted, about piezoelectricity.

> The long series of observed analogies between the electric excitation of crystals by external forces, on the one hand, and by change of temperature on the other, has already

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[24] W. Voigt, "Allgemeine Theorie der piëzo- und pyroelectrischen Erscheinungen an Krystallen," *Göttingen Abhandlungen*, 36 (1890), pp. 1–99. Page numbers in parentheses to the end of this chapter refer to this paper.

[25] Woldemar Voigt, *Lehrbuch der Kristallphysik*, Leipzig und Berlin: Teubner, 1910, p. 813.

[26] Kathryn M. Olesko, *Physics as a Calling: Discipline and Practice in the Königsberg Seminar for Physics*, Ithaca: Cornell University Press, 1991, pp. 288–296.

[27] The interest that Voigt exhibited in symmetrical consideration resembles that of Pierre Curie. Their thought about symmetry made the study of piezoelectricity attractive for both, and helped them in this study. According to Marie Curie, Pierre Curie continued working on the theory of crystals and piezoelectricity in particular, using symmetrical considerations long after 1883; Marie Curie, "Préface," p. xiv. I elaborate on the relation of Voigt's work to the teaching of Neumann below.

[28] On Riecke's research on pyroelectricity in tourmaline see below chapter 3 p. 118.

> led several researchers to the opinion that in both processes the deformation of the volume element, no matter whether it is caused by pressure or heating, forms the direct precondition for the electric phenomena. A universal and satisfactory proof of this view could not be possible as long as it was not made the basis of a rigorous theory—a theory that reduces all related phenomena to the least number of constants possible and that after their experimental determination enables physicists to calculate the resultant excitation both qualitatively and quantitatively. (p. 1)

Thus, Voigt adopted the hypothesis of former researchers that piezoelectricity and pyroelectricity are due to inner elastic changes in the crystal. His version is a synthesis of the Curies' and Friedel's assumption that the effect is due to a change of inner distances and Röntgen's view that it is due to an inner tension. Still it is closer to Röntgen, since Voigt considered an effect for any kind of deformation, and did not limit the theory to contraction and expansion along special axes. As in both versions, he also assumed a mechanical source for pyroelectricity.

Accordingly, Voigt's theory of piezo- and pyroelectricity rests on two hypotheses: that the induced electric moment (a Helmholtzian term for the electric polarization of modern terminology) is proportional to the deformation (or strain), and that the phenomena are subject to the symmetrical properties of the crystal, i.e., that "the symmetry of the crystal's structure [is] always lower or equal but never higher than the symmetry of the physical behavior" (p. 8). In other words, the symmetry of the piezoelectric interaction is not lower than the crystallographical symmetry. The linear ratio for a few crystals had been confirmed by the Curie brothers and later by Hankel and Czermak. It further had the advantage of being the simplest assumption. Voigt admitted that the few examined cases did not prove the universal validity of these rules, and therefore left the possibility of adding corrections of higher orders if that were needed. On the other hand, the rule of symmetry did not originate in empirical study of piezoelectricity but was generalized from many observations on various phenomena of crystals, especially of elasticity, optics, and heat. Yet, such a rule was seldom expressed at the time. Nor was employment of explicit and clear rules of symmetry in deriving laws of a physical phenomenon common at the time. The earlier history of pyro- and piezoelectricity supplies a good example for a neglect of formal considerations of symmetry. Indeed, since Haüy the phenomena were linked to rules of symmetry. The Curies and Mallard formulated explicit rules about the appearance of the phenomena depending on symmetry (above p. 18, 61). Nevertheless, no one pointed out that the laws of symmetry rule out the induction of electricity by uniform heating in crystals like quartz. Voigt was the first to point out those consequences (p. 3). Application of rules of symmetry was a novel approach practiced by a few physicists almost only in elasticity. That Voigt took this novel approach was not accidental.

Voigt's piezo- and pyroelectric theory disregards the ultimate source of the phenomena. It assumes that both are effects of crystal's deformations but refrains from any further assumption on how these deformations induce electric effects. In particular, it refrains from any molecular assumption. Voigt made two objections to the assumption, basic to the molecular explanations, that all the phenomena originate in contraction and expansion along specific polarized axes. The first could have been raised already in 1881, and with supporting experimental evidence in 1883. Some crystal species, including quartz, cannot be electrically polarized under uniform pressure, but only under nonuniform pressure. The fact, which has been known since 1883, showed that these crystals cannot be permanently polarized as required by the molecular hypothesis. On the other hand, this fact follows from considerations of the crystals' symmetry.[29] The second objection concerned Röntgen's latest experiment, which showed that a deformation, like torsion, which does not cause contraction or expansion generated electricity in quartz. Thus, the hypothesis that the phenomena can be reduced to contraction and expansion is invalid, and so (though Voigt does not mention them) are the molecular suggestions based on this hypothesis (pp. 5–6). Voigt suggested that any deformation can induce polarization.

THE ROOTS OF VOIGT'S EMPLOYMENT OF SYMMETRY[30]

In a theory of the crystal's elasticity propounded three years earlier, Voigt had already formulated the rule of symmetry, which he later called a principle. Although the theory was molecular, he applied the macroscopic rule of symmetry to derive the elastic coefficients of the different crystal systems, and stated clearly the universal applicability of the rule:

> Observations have shown that in all known physical properties (e.g., with respect to light and heat) crystals possess at least the symmetry of their form, and in most cases still higher symmetries. Therefore, it seems appropriate to deduce from the crystalline form the most general law of symmetry of the crystalline substance, and to assume that the crystal displays the law including the symmetries in all physical properties.[31]

Earlier, Voigt had applied this law of symmetry without reference to a general rule. In 1882, he derived the elastic coefficients of crystals from it assuming linear relation between stress and strain. These premises are very similar to those he adopted eight years later in the study of piezoelectricity. Voigt based his derivation on a method similar to one that Neumann had applied, probably for the first time, in an 1873–1874 course.[32]

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[29] Voigt did not refer to Friedel and J. Curie's demonstration that uniform pressure does not generate electric effect in crystals like quartz, which they based on the assumption that the effect **does** originate from changes of distance along permanently polar axes. Their argument is discussed in chapter 1 above on p. 60. Voigt probably considered their argument as invalid since it assumes an independency of three non-orthogonal axes and it divides the one electric effect into three, due to influences along these axes. Furthermore, the same kind of assumption led to Czermak's incorrect results. Lastly they did not show that such argument is valid for all relevant classes of crystals. I assume that Voigt concluded that their argument is invalid, but decided not to start a debate. Since no one repeated their claim later, and Voigt's position was accepted, he was apparently right in this policy.

[30] For boarder scope on the history of symmetry rules in nineteenth century physics see Katzir, "emergence of symmetry in physics."

[31] W. Voigt, "Theoretische Studien über die Elasticitätverhältnisse der Krystalle," *Göttingen Abhandlungen* 34 (1887), 52 pp., on p. 30.

[32] W. Voigt, "Allgemeine Formeln für die Bestimmung der Elasticitätsconstanten von Krystallen durch die Beobachtung der Biegung und Drillung," *Ann. Phy.*, 16 (1882): 273–321, 398–416, on pp. 275–280. Franz Neumann, *Vorlesungen über die Theorie der Elasticität der festen Körper und des Lichtäthers - gehalten an der Universität Königsberg*, Oskar Emil Meyer ed., Leipzig: Teubner, 1885, pp. 164–202.

Neumann on symmetry

In the course Neumann relied on an older assumption that physical magnitudes in symmetric positions are equal, but employed a new mathematical method based on rotation of the system of coordinates according to the known symmetry. For symmetric positions, the physical magnitudes in the rotated system should be equal to those in the original system; for antisymmetric positions they should have opposite values. He based his derivation on planes of symmetry (planes that divide the crystal into two parts seen as reflections of each other), assuming that the elastic stresses induced by equal distortion on both sides of such a plane should be equal (in absolute values). From these identities he derived the elastic coefficients that equal zero and those that are functions of others for cases of one, two, and three planes of symmetry and for symmetry of the fourth and sixth order with respect to an axis (although he did not refer to the term). In this way he reduced the number of elastic constants, e.g., to 20 for one plane of symmetry and 12 for two. He applied this abstract knowledge to the particular crystal systems, according to their characteristic planes and axes of symmetry and found the constant of each crystal system. In his mathematical approach he directly manipulated properties of symmetry without the mediation of particular crystalline structures, or any hypothesis beyond the linear relation between stress and strain. Voigt would employ a similar method in his studies of elasticity and piezoelectricity; it will be displayed in more detail in the discussion of the piezoelectric theory (below p. 89). Neumann's discussion was limited to holohedral crystals, i.e., crystals that do not have a polar axis, which characterize the seven systems in which crystals are divided. In 1882, Voigt extended the method to hemihedral crystals and by that to all the 32 classes by which crystals are subdivided.

Neumann's interest in the symmetry of physical phenomena in crystals was not new. He had been engaged with the question of the symmetries of crystal forms and mathematical ways to express them since the 1820s. Discussion of symmetry characterized the German school of crystallography of Weiß, Mohs, Graßmann and Hessel. At the beginning of the century, they rejected Haüy's molecular view of crystals according to which crystals are built of small polyhedral solid bodies. Rather than adhering to a solid material structure they advanced a dynamic approach, according to which matter is a manifestation of forces applied by point-like centers or atoms. While Haüy classified the crystals according to their geometric forms (which are also those of their molecules) Christian Samuel Weiß classified crystals according to characteristic systems of axes. These soon became a common and useful device in the dynamic school, enabling a discussion of crystals without relating to material molecules and opening an easier way to direct considerations of symmetry than Haüy's molecular approach. Still, Haüy himself emphasized that symmetry

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Voigt's notes on the elasticity of crystals, in which the consideration of symmetry appeared, were included in the published version of this book. The other parts of the book were based on earlier lecture notes of Oskar Meyer and his brother Lothar, taken in the semesters of 1857–58 and 1859–60. Notes from later courses taken by Baumgartten from 1869–70 and 1870 and those of Voigt from 1873–74 were added. This suggests that Neumann did not teach the subject before 1873.

is a central characteristic of the crystal's structure. Yet only in 1815 did he clearly define symmetry in the modern sense as a repetition of the same pattern, rather than by the old definition of elegant or harmonic relations. With his view of crystals he conceived symmetry as congruence of different faces and edges. The system of axes, on the other hand, suggested consideration of symmetry as a rotation of the system of coordinates around an axis that reproduces the initial picture, for example, a rotation of 90° in a cube around any axis perpendicular to a face. This would later be called an axis of symmetry. In 1826, Moritz Ludwig Frankenheim, who was appointed a year later as professor of physics in Breslau, employed symmetry by rotations of different angles, which correspond to variant orders of symmetry. In 1830, Johann Friedrich Hessel formulated a theory of crystal structure based on classification by the number of symmetric turns possible around each axis. Hessel presented the possible kinds of symmetry in crystals, including that of plane symmetry.[33]

In 1832, Neumann made the first application of mathematical considerations of symmetry to a question of physical behavior—double refraction in crystals. Previously, symmetry was employed mathematically only in discussing the structure of crystals. Following Fresnel, he assumed that refraction in solid bodies depends on small displacements inside the medium, which are known by its elastic constants. Navier suggested an elastic theory in 1824, but it addressed only isotropic matter. According to that theory, the effect of two small parts of matter on each other depends only on the distance between them. However, in crystals, Neumann explained, the effect depends also on the direction of the line that connects them. He introduced a new function, F, that expresses dependence on direction. The elastic constants (on which the optical depend) are integral functions of F. Here the symmetry of the crystal was a help, as Neumann assumed that F has the same value in symmetric positions. From this assumption, he found relations between the constants of elasticity for the main systems to which crystals were classified, reducing the number of independent constants and simplifying the elastic equations.[34]

Two years later, Neumann raised the issue of symmetry at the outset of an extended study of crystal elasticity. He suggested that considerations of symmetry can be employed to study the elastic behavior of crystals just as it was used in the investigation of their crystalline form. The discussion of elasticity was more elaborated than that in 1832, but for the crux of the derivation Neumann directed the reader to his former paper.[35] By making the symmetry of crystal's shape a model of its elasticity, Neumann implicitly assumed that they are equal. Thereby, he made an initial step to the rule of symmetry as was later formulated and employed by Voigt. Later still,

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[33] Erhard Scholz, *Symmetrie, Gruppe, Dualität: zur Beziehung zwischen theoretischer Mathematik und Anwendungen in Kristallographie und Baustatik des 19. Jahrhunderts*, Basel - Boston - Berlin: Birkhäuser Verlag, 1989, pp. 24–62. Scholz discusses thoroughly the emergence and employment of concepts of symmetry in the mathematical study of crystal structure.

[34] Franz Neumann, "Theorie der doppelten Strahlenbrechung, abgeleitet aus den Gleichungen der Mechanik," *Ann. Phy.*, 25 (1832): 418–454, on pp. 423–425.

[35] Franz E. Neumann, "Ueber das Elasticitätsmaass krystallinscher Substanzen der homoëdrischen Abtheilung," *Ann. Phy.*, 31 (1834): 177–192. Neumann classified the crystals by the symmetry around their axes, calling them by the order of symmetry (i.e. the number of identical parts around the axis).

Voigt attributed the rule to Neumann.[36] However, in the 1830s and even in his course 40 years later, Neumann did not formulate this rule, not even implicitly. At most one can attribute to him the implicit view that the symmetry of physical phenomena in general is equal to that of the crystal. Moreover, the connection between the structure of crystals and their physical behavior had already been acknowledged. From the end of the eighteenth century Haüy, the founder of the modern field of crystallography, connected physical phenomena in crystals (e.g., pyroelectricity) to the crystal form (below p. 26). The form, in turn, was linked to the symmetry of the crystal in a law of symmetry, so an implicit connection between symmetry and physical behavior already existed. Neumann's important innovation was the replacement of the crystalline form by symmetry as the organizing principle of the physical study of crystals.

Neumann's introduction of symmetry instead of material structure suggests an influence of the German dynamic school. Neumann was also deeply influenced by the French schools of mathematical physics of Fourier and Poisson and by Bessel and their emphasis on the comparison of quantitative theoretical predictions and observations. "Fourier's method supplied Neumann with a particular model for mathematization, one that deemphasized underlying physical causes."[37] This instrumental style avoided hypotheses about the structure of matter and the nature of forces. Neumann adopted symmetry as a mathematical weapon in the inquiry of nature, free of hypotheses about the nature of crystals. Symmetry turned out to meet the aims of adherents of dynamic ontology and of agnostic French mathematical physics. By advancing arguments based on symmetry, Neumann drew back from any claim about the dynamic or molecular structure of crystals and the nature of elasticity. Symmetry would continue to be employed phenomenologically.

Similar views on the link between symmetry, structure, and physical behavior were also expressed by other scientists. In 1835 Moritz Frankenheim, physics professor in Breslau, related the physical behavior of crystals (e.g., pyroelectricity) to their structure. Symmetry was central in Frankenheim's view of crystals as a common element of the dynamic (German) and the atomistic (Haüy's) approaches. He claimed that symmetry determines the form of the crystals and indirectly influences their physical behavior. Yet, he did not explicitly relate the symmetry to physical properties. In that he was still very close to Haüy. Unlike Neumann, he did not exploit symmetry properties to gather information about physical phenomena. The elementary mathematics that he employed in the study of physics was not suitable for considerations of symmetry like Neumann's.[38]

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[36] W. Voigt, "l'état actuel de nos connaissances sur l'élasticité des cristaux," *Rapports présentés au congrès international de physique*, eds. Ch. Éd. Guillaume and L. Poincaré (ed.) Vol. 1, Paris, Gauthier-Villars, 1900, pp. 277–318, on pp. 308–309.

[37] Olesko, *Physics as a Calling*, quotation on 63, also 33–36, 61–64, 81–82. Jungnickel and McCormmach, *Intellectual Mastery of Nature*, vol. 1, p. 84.

[38] Moritz L. Frankenheim, *Die Lehre von der Cohäsion, umfassend die Elasticität der Gase, die Elasticität und Coharenz der flüssigen und festen Körper und die Krystallkunde*, Breslau: Augus Schulz und Comp., 1835, pp. 285–296, and Scholz, *Symmetrie*, p. 67. I disagree with Scholz's claim "that [for Frankenheim] the symmetry determines the outer form as well as the optic and the electric properties of the crystal."

The French molecular school

Scientists across the Rheine did not adopt the dynamic crystallographic approach. They, however, did not ignore its accomplishments and the challenge it posed to the molecular theory. In 1840 Gabriel Delafosse, Haüy's disciple, adopted the law of symmetry,[39] of his German colleagues, while maintaining the molecular view. According to Delafosse, both the structure and physical properties of crystals should conform to the same symmetry. Haüy's crystallography should be modified accordingly. Delafosse aimed to resolve apparent anomalies to the law of symmetry exhibited by electric and optic effects in certain crystals. These anomalies, he suggested, followed from a mistaken application of the law, deducing the symmetry from the external shape alone. Instead, he claimed that the symmetry of the physical phenomena revealed the true inner structure and symmetry of crystals. Often this structure is more complex than had been previously gathered from the external form. Crystalline molecules, in these cases, are of lower symmetry than the lattice. This substructure explained the behavior of hemihedral crystals, which were not described adequately by Haüy.[40] Delafosse agreed with Neumann and Frankenheim (without mentioning them) that physical effects display the same symmetry as the structure of the crystal. Yet, he was committed to the molecular structure of crystals and the priority of the structure.[41] The underlying notion that symmetry governs the physical behavior of crystals became common at the time, as a report on Delafosse's paper shows.[42]

That the structure dominates all crystal properties was accepted, at least in French crystallography, from the time of Haüy's studies in the late eighteenth century. This rule was supported by metaphysical prepositions and by experimental evidence regarding cleavage, elasticity, optics, and electricity. These experiments were also needed to support Delafosse's derivative claim that symmetry determines physical properties. However, no experiment had been carried out to test directly the dependence of phenomena on symmetry until the experiments of Hureau de Senarmont. At the time of his

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Indeed according to Frankenheim the form is known from the symmetry (p. 287). However in discussing the physical properties symmetry is not mentioned, but only the crystal's structure (pp. 293–4).

[39] According to Delafosse, this is the law "that determines the number and general inclination of the planes that compose the form of a crystalline system." Gabriel Delafosse,"Recherches sur la cristallisation considérée sous les rapports physiques et mathématiques," *Mémoires présentés par divers savants à l'Académie royale des sciences*, 8 (1843): 641–690, on 644.

[40] Delafosse's ideas about the molecular structure were elaborated a decade later in an influential crystallographic theory of Auguste Bravais. Auguste Bravais, "Etudes cristallographiques," *Journal de l'école polytechnique*, *20* (1851), 101–278.

[41] Gabriel Delafosse, "Recherches relatives à la cristallisation, considérée sous les rapports physiques et mathématiques, 1re partie. Sur la structure des cristaux, et sur les phénomènes physiques qui en dépendent," *Comptes rendus*, 11 (1840): 394–400, and the 1843 longer paper submitted with it to the *étrange memoires* of the Academy, especially pp. 644–47, 665–70, 674–76. The delay in publication was common in this journal.

[42] (François Sulpice) Beudant, "Rapport sur Mémoire cristallographique de M. Delafosse," *Comptes rendus* 12 (1841): 205–210 (the committee included in addition Brongniart and Cordier). They reported that the critique and notions of Delafosse had already been expressed. Yet the systematic treatment was his novel contribution (p. 210).

appointment as professor of mineralogy at the *Ecole des Mines* in Paris in 1847, he was examining the applicability of symmetry to heat and electric conductivity in crystals.

Senarmont passed an electric wire through a hole drilled at the middle of a crystal. He heated the wire by an electric current and observed isothermal lines on the crystal by melting wax making circular and elliptical lines following the symmetry of the crystal. In a systematic examination of more than 30 species of crystals, he found that in symmetric crystals "the axes of conductivity always coincide with the axes of optical elasticity and with the crystallographic axes." Two years later he carried out a similar experiment on superficial electric conductivity of crystals, observing associated circles or ellipses, similar to the isothermal lines previously observed. Thus, he concluded, "one finds in these phenomena [of electricity] the same influence of the axes of either equal or unequal symmetry" that was found in optics and in heat conductivity. Senarmont's research showed that different phenomena are subject to the symmetry of the crystal form. He suggested that this common subordination originated in the molecular constitution of matter that governs its behavior under different influences. Senarmont regarded symmetry as a phenomenological means to future knowledge of the true (molecular) causes. For him it was an effective tool for revealing relations but not the last word.[43] This research, in addition to the earlier studies of optical, elastic, and pyroelectric behaviors of crystals, gave the empirical basis for Voigt's later 'rule of symmetry.' Others, however, did not employ symmetry as an organizing principle and doubted its heuristic value.[44]

Considerations of symmetry played an important role in the thought of another member of the French mineralogical school—Louis Pasteur. In 1848, he discovered optical isomerism: the existence of crystals constituted molecules of the same chemical structure except for being mirror images of one another.[45] After the discovery

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[43] Hureau Senarmont, "Sur la conductibilité des substances cristallisées pour la chaleur," *Annales de chimie et de physique*, 21 (1847): 457–470, 22 (1847): 179–211, especially pp. 208–211; "Mémoire sur la conductibilité superficielle des corps cristallisés pour l'électricité de tension," *Annales de chimie et de physique*, 28 (1850): 257–278, quotation pp. 277–78. Albert-Auguste De Lapparent, "Henri Hureau de Senarmont (1808–1862)," *Livre du centenaire* (Ecole Polytechnique), Paris: Gauthier-Villars, 1897, tome I, p. 320 et suiv (electronic version www.annales.org). Walter Fischer, "Sénarmont, Henri Hureau de," *DSB*, Vol. 12: 303–306, on 305.

[44] Gustav Wiedemann related electric conductivity to crystal structure through axes not symmetry, like Senarmont he pointed out the agreement among optic, electric and thermal properties of crystals and their origin in "the form and constitution of bodies. Gustav Wiedemann, "Mémoire sur les propriétés électriques des corps cristallisés," *Annales de chimie et de physique*, 29 (1850): 229–236. (Originally appeared in *Ann. Phy.* 76 (1849): 404). Ångström concluded in 1850 that the systems of axes of different physical phenomena (e.g. the axes of optical or isothermal ellipsoides) do not always coincide with each other and with the crystallographic axes. He did not refer to symmetry in that context. Anders Jonas Ångström, "Ueber die Molecular-Constanten der monoklinoëdrischen Krystalle," *Ann. Phy.,* 86 (1852): 206–237.

[45] For more details on Pasteur's work in this subject see Katzir, "emergence of symmetry," 43–45. Contrary to Pasteur's later claim Gerald. L. Geison and James A. Secord, (in "Pasteur and the process of discovery: The case of optical isomerism," *Isis*, 79 (1988), 7–36) have tried to show that neither hemihedral structure nor symmetry was central in his road to the discovery. To my view, Geison and Secord underestimates the influence of Delafosse on Pasteur's research. Like Pasteur after him Delafosse dealt with the relations between structure, symmetry and properties and in particular with optical behaviour.

Pasteur linked this crystalline property to the symmetry, or, more precisely, the asymmetry of their molecules. Yet he emphasized the connection between the (hemihedral) material structure of the molecules and the physical properties of the crystal. Like his former teacher Delafosse, he deduced the structure and symmetry of crystals from their physical behavior. Pasteur generalized a rule in structural rather than in symmetrical terms: the optical activity of substances originated in their hemihedral molecules.[46] This law guided his work until 1856. Then he found that amyl alcohol displays an exception. Although the alcohol is optically active, it can be crystallized only in holohedral form. This and similar exceptions to the rule made him shift his emphasis from the hemihedral structure to the asymmetry of the molecules.[47]

For Pasteur, the optical activity of amyl alcohol demonstrated the asymmetry of its molecules. This activity, he believed, must originate in asymmetry of a primitive molecular group in the reactants that was preserved during chemical reaction. Since no reactant of the alcohol was a possible candidate, Pasteur conjectured that the alcohol is a product a living agent that produces the asymmetry. That was the key for his celebrated experimental identification in 1857 of a new living agent of fermentation, responsible for the production of amyl alcohol. His view that any fermentation is caused by organic germs originated in that study. For him asymmetry was tightly connected to optical activity, which was more prominent in his thought during that time.[48] Pasteur's reasoning reveals two hypotheses, first that asymmetry must originate in asymmetry and second that living organisms are the only agents that can produce asymmetry. Considerations of symmetry, thus, played an essential role in the discovery of the organic agents of fermentation. Pasteur's first hypothesis was common in Haüy's tradition[49]; his second was more original. In the following years he elaborated and promoted it, making asymmetry a central discriminator between "living matter" and "dead matter."[50]

Pasteur did not apply mathematical considerations of symmetry. Qualitative arguments were enough to show that the rotation of polarized light is asymmetric and thereby requires asymmetric structure to affect it. Other scientists at the time used considerations of symmetry in mathematical derivations. In 1851 George Gabriel Stokes, the new Lucasian professor of mathematics at Cambridge, suggested a theory of thermal conductivity that deduces relations in accordance with Senarmont's finding. Following the latter, he acknowledged the connection between the phenomena

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[46] Louis Pasteur, "Mémoire sur la relation qui peut exister entre la forme cristalline et la composition chimique, et sur la cause de la polarisation rotatoire," *OLP*, 1, pp. 61–64.

[47] Louis Pasteur, "Isomorphisme entre les corps isomères, les uns actifs, les autres inactifs sur la lumière polarisée," *OLP*, *1*, 284–288, Gerald. L. Geison, *The private science of Louis Pasteur* (Princeton, NJ, 1995), 90–109.

[48] Louis Pasteur, "Mémoire sur la fermentation appelée lactique," *OLP*, *2*, 3–13, 3–4, Geison, *Pasteur's science*, 90–109. Geison suggests that Pasteur had already been committed to the connection between optical activity and life (to which symmetry was appended) from the early 1850s.

[49] Although Delafosse referred to symmetry rather than asymmetry in his works, he deduced the symmetry from its lack. So in practice he, like Pasteur, applied an undefined version of Curie's that the asymmetry of the effects must be found in the causes.

[50] Louis Pasteur, "Recherches sur la dissymétrie moléculaire des produits organiques naturels," *OLP*, *1*, pp. 314–344, especially 329–33, 341–342.

and the symmetry of the crystal, and employed it in his derivations but only in a specific case of two planes of symmetry. In that case he showed that the number of constants of heat conductivity reduces from nine to six. However, to reduce the number of constants in other cases (e.g., for the hexagonal system), he employed the crystalline form rather than its symmetry. In both cases the arguments were verbal.[51] A decade later Gabriel Lamé, another mathematical physicist, referred to symmetry on a par with other structural properties, like orthogonality in analytical theory of the same subject. He used both to posit equalities between theoretical entities that characterize the conduction. For example, in "a prism obliquely symmetric" the two symmetric axes of the ellipsoid that characterizes heat conduction are equal. Lamé assumed symmetry of the equations (or their constants) not of the matter. He did not compare physical magnitudes in symmetrical positions.[52] Stokes went the other way around: he assumed a symmetry in the crystal to deduce symmetry in the equations.

In 1854, Stokes's friend William Thomson linked symmetry to physical properties in a similar manner, assuming that "the thermo-electric powers" in the directions parallel and perpendicular to the axis of symmetry are different. As common in French tradition and in Britain, he viewed the structure as more basic than the symmetry.[53] Further, Thomson implied that external forces may cause asymmetry. Inequality in the "thermo electric powers," like the directionality that characterizes crystals, may also be induced to "substances not naturally crystalline . . . by the action of some directional agency, such as mechanical strain or magnetization, and may be said to be inductively crystalline."[54] Stokes, Thomson, and Lamé made good use of symmetry in their mathematical studies. Yet, they employed it sporadically and unsystematically and did not connect it methodically to the physical phenomena.[55]

Delafosse, Senarmont, and Pasteur pointed out a connection between symmetry and various physical effects, acknowledging that the relation should hold for all phenomena in all matter. However, only Neumann and his school developed formal devices to consider the theoretical application of symmetry in a general and systematic manner. In his teaching, Neumann had emphasized the combination of complex mathematics with a thorough knowledge of physical phenomena, and the need for mathematical theory to account exactly for precise experimental results. This approach placed Neumann and the school that followed him in a different position from the French school of physical-mineralogy, which employed only basic mathematics in the study of physical behavior, or the students of geometrical crystallography, who

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[51] G. G. Stokes, "On the Conduction of Heat in Crystals," *Cambridge and Dublin mathematical Journal*, 6 (1851): 213–238 especially pp. 221, 237–38.

[52] Gabriel Lamé, *Leçons sur la théorie analytique de la chaleur*, Paris, 1861, for example p. 50.

[53] William Thomson, "On the Dynamical Theory of Heat," *TMPP 1*, 174–332, on 266–268. The part on pp. 232–291 was first published in 1854.

[54] *Ibid.*, p. 266.

[55] The same was true for William John Macquorn Rankine's employment of symmetry in a study of elasticity in crystals five years earlier. Although he linked symmetry to mathematical equalities, he did not refer to Neumann's method of the equality of magnitudes in symmetric positions. William John Macquorn Rankine, "On axes of elasticity and crystalline forms," *Philosophical transactions of the Royal society of London,* 146 (1856): 261–285.

did not pay much attention to physics, or mathematical physicists like Lamé whose theoretical studies were not so intimately related to experiment.[56] They were also in a better position than most physicists to study the physical consequences of symmetry, since, unlike most, they were familiar with crystals and their structure. The relevance and fertility of symmetry was clearer in these fields than in others.[57]

Neumann's students

While in his lectures at Königsberg in 1873–1874, Neumann derived the elastic constants of crystals from considerations of symmetry, his former student Gustav Kirchhoff developed similar methods in his own lectures in Berlin, published in 1876. The two have similar approaches, both based on rotations of axes; yet they were probably elaborated independently.[58] Both surpassed Neumann's primary study of the 1830s in formulating clearer considerations of symmetry and in the elastic theory employed. Viewed from the 1870s, the elastic theory of crystals on which Neumann had relied 40 years earlier was inadequate. The current theory of elasticity was the starting point of Neumann's and Kirchhoff's discussion of elasticity in crystals in the 1870s. Kirchhoff, who had made important contributions to the study of elasticity, employed a potential function of elasticity (an expression of its energy) and required its symmetry in respect to planes, rather than symmetry of the components of stress. In 1882, Voigt extended the treatment of Neumann and Kirchhoff to hemihedral crystals, i.e., to all crystal species. He referred to axes of symmetry, which Neumann and Kirchhoff had employed in fewer cases and without using the term. A year later Herman Aron, a former student of Kirchhoff and then a professor in Berlin, an inventor and a founder of an electric firm, elaborated his teacher's derivation. Like Voigt, he extended the discussion to all crystals. Unlike him, he did not employ axes of symmetry but only planes of symmetry that meet at angles of 45°, 60°, and 90°. Other scientists considered only perpendicular planes. Still, Aron's derivation was more elaborate and explicit than the earlier ones.[59]

In 1884 another former student of Neumann, Bernhard Minnigerode, Professor of Mathematics in Greifswald, published a general systematic derivation of the elastic

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[56] Although Stocks did carry out experimental research, at least until 1853 it was secondary to his mathematical work, E. M. Parkinson, "Stokes, George Gabriel," *DSB*, *13*, 74–79.

[57] On Neumann his seminar and his school see Olesko, *Physics as a calling*.

[58] Gustav Kirchhoff, *Vorlesungen über Mathematische Physik- Mechanik*, Leipzig: B.G. Teubner, 1876, pp. 389–392. Kirchhoff has taken Neumann's courses between 1843 and 1847. It is unlikely that Neumann offered an explicit discussion of elastic properties based on planes of symmetry then, since that part of his published lectures was taken from the 1873/74 course. Oskar Emil Meyer, who edited the lectures, took the course on elasticity in 1857/58 and again in different form in 1859/60 and did not hear this part (Neumann, *Vorlesungen über Elasticität*, p. vii). Kirchhoff probably delivered his own lectures in the summer of 1875, when he started teaching theoretical physics in Berlin. His lectures there were more advanced than his earlier ones in Heidelberg. Jungnickel and McCormmach, *Intellectual Mastery of Nature*, vol. II, p. 31.

[59] Hermann Aron, "Ueber die Herleitung der Krystallsysteme aus der Theorie der Elasticität," *Ann. Phy.*, 20 (1883): 272–279. "Aron, Herman" in *Deutsche Biographische Enzyklopädie*, ed. Walther Killy, Darmstadt: Wissenschaftliche Buchgesellschaft, 1995, vol. 1, pp. 194–95.

constants. Minnigerode introduced novel mathematical methods (group theory) and an elaborated geometric theory of crystal structure. Voigt regarded his complex mathematical approach as disproportional to the simplicity of the problem. Yet, Minnigerode also showed sensibility to the physical premises of the theory. He offered a clear formulation of the relation between physical phenomena and symmetry, which had not appeared in previous studies of elasticity in crystals. "Physically speaking, crystals have all the symmetrical properties of their form; some of the physical properties, however, have still higher symmetry."[60] However, he claimed, the outer form of the crystal does not always reveal its true symmetry. In such cases he advocated the application of symmetric relations found in optics directly to elasticity. Minnigerode should be credited with formulating the rule of symmetry for all physical phenomena, not just for elasticity. In 1886 he extended the method to derive the constants of heat conductivity in crystals. Heat conductivity had already been connected to symmetry in the experiments of Senarmont and in the theories of Stokes and Lamé. Minnigerode had studied the subject in the early 1860s; that was the subject of his dissertation. Two decades later he returned to the issue with a new interest in symmetry, and with a method to exploit its consequences in all crystal classes. He derived the equation for "all cases" from explicit and systematic considerations of symmetry that reduced the number of constants by showing either relations among them or their equivalence to zero. In common with other members of Neumann's school, Minnigerode based his mathematics on revolving coordinates and the equivalence of physical magnitudes in symmetric positions. This was the earliest application of a rigorous argument of symmetry in physics beyond elasticity.[61]

The small number of physicists, mineralogists, and crystallographers who studied physical properties of crystals acknowledged the dependence of these properties on the symmetry of the crystals. Such a notion can be detected in the thought of contributors to the study of pyro- and piezoelectricity in the 1880s, like the Curies, Friedel, and Mallard. These notions were spelled out as laws for the possible appearance of the phenomena. Yet they did not make symmetry a generative principle of a pyro- and piezoelectric theory. This was similar to the case in other fields. The rigorous mathematical exploitation of the relation between symmetry and physical properties was carried out exclusively by Neumann's school. Voigt, who had already contributed to the rigorous study of crystal elasticity, employed the methods used in that study to piezoelectricity. This required some extensions as the phenomena are more complex and the classes are more varied in their piezoelectric than in their elastic behavior. The physical principle, the general method, and the relation between physical properties and symmetry, however, were ready and well known for Voigt in 1890.

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[60] Bernhard Minnigerode, "Untersuchungen über die Symmetrieverhältnisse und die Elasticität der Krystalle," *Göttingen Nachrichten*, 1884: 195–226, on p. 218. Voigt, "l'état actuel de nos connaissances sur l'élasticité des cristaux," p. 309. Minnigerode emphasized that his study is based on axes rather than planes of symmetry. Axes had been used in this context before (e. g. by Voigt in 1882) but were more central in subsequent works.

[61] B. Minnigerode, "Ueber Wärmeleitung in Krystallen,"*Neues Jahrbuch für Mineralogie, Geologie und Plaeontologie*, 1 (1886): 1–13. Olesko, *Physics as a Calling*, p. 271.

THE GENERAL THEORY: SCOPE AND RESULTS

Voigt formulated a mathematical theory of piezoelectricity, which expressed its two basic assumptions in algebraic form and equations, an outcome of mathematic-physical tradition. The basic and general equation (*allgemeinen Ansatz*) of piezoelectricity, which relates the three components of electric moments a, b, and c to the six components of deformation (or strain) x_x in a differential volume element, expressed the assumption that the effect depends linearly on the strain:

$$\begin{aligned} a &= \varepsilon_{11}x_x + \varepsilon_{12}y_y + \varepsilon_{13}z_z + \varepsilon_{14}y_z + \varepsilon_{15}z_x + \varepsilon_{16}x_y \\ b &= \varepsilon_{21}x_x + \varepsilon_{22}y_y + \varepsilon_{23}z_z + \varepsilon_{24}y_z + \varepsilon_{25}z_x + \varepsilon_{26}x_y \\ c &= \varepsilon_{31}x_x + \varepsilon_{32}y_y + \varepsilon_{33}z_z + \varepsilon_{34}y_z + \varepsilon_{35}z_x + \varepsilon_{36}x_y \end{aligned} \tag{3}$$

where "the 18 piezoelectric constants ε_{hk} are dependent on the character of the crystals and the location of the coordinate system x, y, z."[62] Written for a small volume element, the basic equation enabled Voigt to avoid any assumption about the fundamental structure of crystals. The equation agrees with a continuous picture of matter, but since the volume element can still be finite, the equation can be consistent with any molecular or other structure. This general equation states the relations between the primary variables of the theory: local electric moments and deformations. Thus, Voigt claimed, it is more general than relations between integral magnitudes. He showed how to calculate such observable integral magnitudes like the total voltage and the surface density of charge, from the electric moments and thus from this equation (pp. 6–7).

The basic piezoelectric laws of all crystals

The basic equation of the theory (equation (3)) states general relations without reference to any specific crystal class. In order to find the special relations of each class of crystals, Voigt employed the second assumption of the theory according to which the symmetry of the crystal determines the symmetry of the phenomena. He found for each crystal class which coefficients are identically zero, which are functions of other coefficients and which have independent values. To this end he first found for each order of axial symmetry, plane symmetry, and central symmetry the coefficients that are equal to each other and those that are equal to zero. Of the 32 classes, he found that 20 are piezoelectric—they have at least one nonzero coefficient.

Voigt's mathematical method was based on rotational linear coordinate transformations of the strains (x_x, y_y, etc.) and the electric moments (a, b, c) to a new coordinate system and on equating their values in symmetric positions. It was in the tradition of the earlier derivations from symmetry in Neumann's school discussed above. Comparing the basic equation (3) in the original system of coordinates and in a symmetric rotated system (assuming that the z axis is fixed), he wrote 17 expressions for the piezoelectric coefficients in the original system in terms of other coefficients and the

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[62] Voigt, "Allgemeine Theorie," pp. 3–4. Since the crystal strain tensor is symmetrical ($y_x = x_y$) one needs only six (rather than nine) components of strain in the equation.

cosines of rotation (determined by the degree of symmetry). Inserting these values in the expressions for the piezoelectric coefficients, he attained the piezoelectric equations (i.e., the relevant coefficients) for each degree of axial symmetry in respect to the *z* axis. The equation for axial symmetry in respect to the other axes followed easily. In a similar way, he attained the equations for plane and central symmetry. Then he applied these results to each crystal class according to its characteristic symmetrical axes and planes and drew its piezoelectric equations.[63] Unlike Czermak and previous researchers, Voigt did not study a particular crystal but all crystals in general. Moreover, his derivation was not based on the crystal's polar axes, but directly on its symmetry as stated in orthogonal Cartesian coordinates.

The two classes most discussed at the time, those of tourmaline and quartz, are of interest also for this history. For tourmaline, Voigt found:

$$a = \varepsilon_{15} z_x - \varepsilon_{22} x_y, \quad b = -\varepsilon_{22}(x_x - y_y) + \varepsilon_{15} z_z, \quad c = \varepsilon_{31}(x_x - y_y) + \varepsilon_{33} z_z \tag{4}$$

For quartz he found:

$$a = \varepsilon_{11}(x_x - y_y) + \varepsilon_{13} y_x, \quad b = -\varepsilon_{14} z_x - \varepsilon_{11} x_y, \quad c = 0 \tag{5}$$

In the laboratory, however, one usually applies stress rather than strain on crystals. Thus, Voigt also developed parallel equations for the electric moments in terms of stress, using the same method. For example, for quartz he found:

$$-a = \delta_{11} X_x - \delta_{11} + Y_y \delta_{14} Y_z, \quad b = +\delta_{14} X_z + 2\delta_{11} X_y, \quad c = 0 \tag{6}$$

where X_x are the components of stress, and δ_{ij} were called by Voigt piezoelectric moduli. The moduli relate to the constants ε_{ij} through the crystal's elastic coefficients (pp. 22–35). In previous theoretical and experimental work, physicists employed and measured coefficients parallel to Voigt's moduli rather than to his constants.[64]

The effects due to various stresses

Voigt dedicated most of the memoir to an account of the electric behavior of all piezoelectric crystals under different changes of stress and temperature, describing a few prominent cases in detail. Among these cases, a few will interest us here.[65] Examining the case of uniform pressure, he found that an effect is induced only in crystals that have a unique symmetrical axis. This confirmed his claim that crystals, like quartz, are not polarized under normal conditions (pp. 35–7). Studying the effect of unidirectional pressure, he showed how the known characteristics of the transverse

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[63] *Ibid.*, 8–17. He pointed out that his results were apparently contradicted by Hankel's observations of electric polarity due to non-uniform heating in crystals with central symmetry, crystals which according to the theory should not be electrified. Voigt, however, explained that a break in the central symmetry in Hankel's experiments enabled the appearance of an electric effect, *ibid.*, pp. 18–19.

[64] Voigt further used the same method to derive the already known elastic coefficients and compliances and the coefficients of thermal pressure and thermal deformation for each system of crystals.

[65] For an elaborated description see Shaul Katzir, *A History of Piezoelectricity: The first two decades*, PhD dissertation, Tel Aviv University, Tel Aviv, 2001.

and longitudinal effects in quartz follow from his theory. He showed how the theoretical equations for unidirectional pressure in tourmaline and quartz account for the experiments of the Curie brothers.[66] With further mathematical elaboration he derived the equations of the polarization in one direction due to pressure in another for quartz in the *xy* plane:

$$b' = -p'_x C \sin^3 \varphi, \quad c' = -p'_x C \sin^3 \varphi \tag{7}$$

where, c' and b' are, respectively, the electric moments (polarizations) in the direction of pressure and 90° from it, p'_z the pressure, φ the angle between the pressure and the x axis and C a constant equal to a function of piezoelectric coefficients and elastic compliances. These results, Voigt remarked, clearly display the known symmetry of quartz and the maximal effect at the directions of the polar axes. Czermak had derived a different relation (equation (2)), but Voigt did not refer to it. Neither did he refer to Czermak's explicit experimental examination of this relation, though its results are also accounted for by Voigt's equations. This approach probably reflects Voigt's dissatisfaction with Czermak theoretical work and the dependence of his experimental result on that theory. Voigt compared equation (7) with other observations of Czermak. Regarding experimental errors, he concluded that their agreement seemed "very satisfactory" (pp. 43–6).[67]

Voigt found that one equation expresses the electric effect of torsion in an infinite cylinder for all piezoelectric crystal classes regardless of their piezoelectric coefficients. Practically, the equation is valid for any cylinder whose length is significantly longer than its radius. Torsion in such case generates four electric zones on the crystal's surface. This, Voigt remarked, is exactly what Röntgen had observed in his experiments on torsion in quartz. Röntgen's experimental results were a puzzle, since they apparently disagreed with the symmetry of quartz. Voigt's theory answered that puzzle in a general way, by showing that this behavior is independent of the specific structure of quartz (pp. 49–63).[68] Voigt's theory showed that common and simple basic assumptions, as the linearity of piezoelectric phenomena and its subjection to the symmetrical properties of crystals, can account for various phenomena and yield unexpected results.

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[66] Voigt, *ibid.*, pp. 37–43. Voigt did not refer to the failure of Czermak's theoretical description to account for the later effect, though he referred later to the latter's experimental results, but not to his theory. Voigt preferred showing the correctness of his own results on arguing the fallacy of Czermak's theory.

[67] Voigt referred only to Czermak's experiment in which the latter measured the voltage due to pressures in 15° from a polar axis. As mentioned above, Czermak found that the actual direction of pressure was slightly different, and calculated corrected directions using his own equations. Voigt made an independent correction based on his equations, and compared the observations in these directions with the theoretical prediction for the corrected direction. Practically Voigt's equation gave the same correction as Czermak's: an angle of 11°43' instead of 11°40'. Czermak however, did not show the agreement to his theory after the correction. See above and Czermak, "Verhalten des Quarzes," pp. 1237–1242.

[68] The complicated derivation of the behaviour of torsion and the general character of Voigt's assumptions make the conjecture - that he constructed his theory on this explanation, choosing assumptions that would fit it - highly improbable.

Pyroelectricity

As mentioned, Voigt assumed that like piezoelectricity, pyroelectricity is due to inner deformations in the crystals caused by thermal expansion. The Curies, Röntgen, and Friedel had already advanced the hypothesis that pyroelectricity originates in an electro-mechanic effect. Röntgen's hypothesis is closer to Voigt's since he referred to changes of tension or strain as the cause of the phenomena. Röntgen, however, stated this hypothesis concerning only quartz, which is electrified neither by uniform pressure nor by uniform heating. Moreover, Röntgen, Friedel, Jacques Curie and von Kolenko showed the validity of this assumption only to crystals of this kind. Yet, neither experiment nor argument denied the possibility of a direct effect in crystals electrified by uniform change of temperature. Voigt was probably led to deny such an effect in all crystals by the centrality of quartz, the lack of evidence for the opposite hypothesis, and his wish to reduce the number of assumptions. Indeed, Voigt succeeded on accounting for all known experimental results with this mechanistic assumption. Nevertheless, it remained hypothetical, since its denial would not change the relations predicted by the theory. Thus, Voigt's theory of pyroelectricity was not truly phenomenological. Later he would abandon the hypothesis, first on theoretical and then also on empirical grounds.

Voigt developed expressions for the electric polarizations due to uniform heating in all classes in terms of the coefficients of piezoelectricity and thermal deformation. The expressions completely agree with those of the effects of uniform pressure, showing that both develop electric effect in the same crystals and in the same directions. As had been already stated through direct considerations of symmetry by Mallard, Voigt's equations showed that only crystals with a unique polar axis generate electricity by uniform heating. Thus, he argued with Mallard and Röntgen that many piezoelectric crystals are not pyroelectric under a uniform heating (pp. 67–72). He showed that nonuniform heating excites these crystals. Later, he would call the latter phenomena "false pyroelectricity;" today "tertiary pyroelectricity" is the preferred term.

In the study of nonuniform heating, Voigt derived the relations between pressure and temperature change that had been stated and empirically found at the beginning of the 1880s by Jacques and Pierre Curie, and later also by Friedel, and Röntgen (above p. 56). Voigt studied the special case of heating or cooling from the center and from the circumference of a circular quartz plate, examined in the laboratory by Röntgen. Unlike Röntgen, he was not satisfied with qualitative argument but derived a mathematical expression for the charge density that accounted quantitatively for the division of the circumference to six electric zones observed by Röntgen (pp. 84–5). Voigt claimed that Röntgen's pyroelectric experiments in quartz "contain an important confirmation of the theory, while this, in turn, provides the first complete explanation of the observations" (p. 94). Voigt, we have seen, showed how the results of the previous piezoelectric experiments of Jacques and Pierre Curie, Czermak, and Röntgen derive from the general theory. Yet, he claimed that further experimental work was needed to prove it. He called for experiments on the various effects that the theory describes in different classes of crystals, including those that were not examined before (pp. 7–8). He himself would later be responsible for quantitative examinations of the theory. However, no such experiment would be carried out to test its prediction relating various effects and classes.

CONCLUDING REMARKS TO PART I

Voigt's call for new experiments marked the beginning of a new phase in the history of piezo- and pyroelectricity. His theory organized the field of piezoelectricity on a few theoretical assumptions and mathematical expressions. Before the introduction of the theory, experiments exploring unknown territory determined the development of the field. These experiments originated in some cases in theoretical considerations, assumptions or speculations, and in others in experimental procedures. From now on, the theory took the lead in the development of the field. Further experiments would be performed in view of the theory, trying to examine its predictions and consequences, attempting to measure absolute values for these predictions, or examining its assumptions. Voigt's new theoretical entities—the piezoelectric coefficients—would be measured in the following years. These coefficients became a subject for what was called in Germany "measuring physics," that is, the laboratory study of the exact values of constants. Most previous piezoelectric experiments were done in the tradition of what was called "experimental physics," that is, the exploration of new phenomena and unknown relations between physical magnitudes. Quantitative mathematical relations were not prominent in that tradition. Röntgen and Kundt were important figures in this subdiscipline.[69] Their contributions to piezoelectricity characterize their work: an experimental exploration of properties of the phenomena and their connections to related effects. As these contributions show, theoretical assumptions and considerations, but neither mathematical equations nor systematic theories had an important role in shaping this of kind research, which was sometimes designed to demonstrate the validity of an assumption, like the elastic source of pyroelectricity in quartz. Their researches, especially Röntgen's, were crucial to the development of piezoelectricity including the formation of Voigt's general theory. This theory, however, transformed the field of piezoelectricity from a field dominated by experimental physics to a field dominated by a general rigorous theory and measuring physics. As such, the theory denotes the end of the first phase—the pretheoretical phase—in the history of piezoelectricity.

The general theory suggested by Voigt in 1890 quickly became the reference point for further research. It is still at the basis of current piezoelectric theory. Most later studies of piezoelectricity, whether experimental or theoretical, used or at least referred to the theory. Handbooks described it in detail.[70] Yet, it did not account for a considerable share of the experimental data—that of the converse effect. A theory that

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[69] For a discussion of the two kinds of laboratory activities see Jungnickel and McCormmach, *Intellectual Mastery* Vol. 2, pp. 120–121.

[70] The works discussed in the next three chapters show the centrality of Voigt's theory. The first handbooks that included piezoelectricity to appear after the publication of Voigt's theory described it in details: Wiedemann, *Die Lehre von der Elektricität*, 2nd edition (1894), on pp. 431–439, and F. Pockels, "Pyro- und Piezoelektrizität," in A. Winkelmann (ed.) *Handbuch der Physik*, 1st edition, vol. 3 part 2, Breslau: Eduard Trewendt, 1895: 527–550.

accounts for this effect was formulated in 1890 on the basis of the general theory by Voigt's former student Pockels.[71] This was only the first elaboration of the piezoelectric theory. In the following years, physicists suggested modifications to Voigt's theory, others suggested alternative theoretical structures. Another effort was made in an attempt to reconcile Voigt's phenomenological theory with a molecular hypothesis. Nevertheless, almost all these related to Voigt's work and thereby acknowledged its acceptance as the basic theory of the field.

Voigt's theory succeeded in accounting for the electric behavior of all crystals under changes of stress and temperature and in describing a few prominent cases in detail. This was a notable feat in comparison with previous attempts to account for the phenomena, which well explains the acceptance of the theory. Although Mallard thought that the theoretical determination of the variations in the magnitudes of the piezoelectric constants with the directions of pressure and examined surface (the determination of k in equation (9), Chapter 1) would be unattainable in the foreseeable future, Voigt's general theory reveals much about its variations in various crystals. It shows the constants that are equal to each other and those involved in each kind of change of stress or temperature.

Notwithstanding this achievement, it does not give any clue about the magnitudes of any of the independent coefficients assumed by the theory. Their determination is beyond the realm of the theory. This was still far from an ultimate theory of piezoelectricity, like the one Mallard expected to have one day.[72] We still do not have such a general theory, although the piezoelectric coefficients are calculable today for some crystal species.[73] Piezoelectricity, however, was not unique. The inability to theoretically determine the magnitude of physical constants characterizes most established theories at the time. Voigt's new theory of piezoelectricity did not differ in that from the established theories of elasticity and dielectrics.

The success of the general theory was a triumph for the analytical-phenomenological approach. The theory demonstrated the power of a general analytical method in the tradition of rational mechanics, to account for complicated phenomena and to reveal relations between phenomena. While the success of the kinetic theory of gasses marked a triumph for the molecular hypothesis, it failed to account for many other phenomena, such as piezoelectricity. Czermak's failed attempt to account for the behavior of quartz with a tacit molecular hypothesis against his success in the molecular theory of heat demonstrates well the difference. Where

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[71] F. Pockels, "Aenderung die optische Verhaltens & elastische Deformationen dielektrische Krystalle im elektrische Felde," *Neues Jahrbuch für Mineralogie, Geologie und Plaeontologie.*, 7 (1891) (supplementary volume.), pp. 201–231, see chapter 4 below.

[72] On Mallard see above chapter 1 p. 61.

[73] Apparently, since the late 1990s such a theory became approachable and partial and specific models for crystals and ceramics an active line of research. New methods of calculating properties of solid from "first principles" of their atomic structure enabled determining the values of piezoelectric coefficients and understanding thereby reasons for their divergence. These calculations are still based on different models and approximations rather than on a general theory. For a review see Laurent Bellaiche, "Piezoelectricity of ferroelectric perovskites from first principles," *Current Opinion in Solid State and Materials Science* 6 (2002): 19–25.

molecular theory failed to explain the known phenomena, the phenomenological theory successfully accounted for them and correctly predicted more.

The molecular hypothesis stimulated the discovery of piezoelectricity by the Curies and further experiments in the field, like those about the relations between piezo- and pyroelectricity. Nonetheless, once experimental examination began, it was not dependent any longer on the molecular hypothesis. The further experiments of the Curies, of Kundt and most experiments of Röntgen were not motivated by molecular reasoning. Lippmann's thermodynamic reasoning led to a few experiments on the converse effect. Moreover, experiments revealed the limitations of the original hypothesis of bipolar molecules in accounting for what was found to be complex behavior. That molecular theory failed to explain the phenomena, while the phenomenological succeeded in embracing them on two basic assumptions.

The abandonment of the Curies' molecular hypothesis originated in the failure to construct an explanatory theory on such a premise; it did not originate in resistance to molecular explanations as such.[74] Indeed, "Voigt is regarded in general as a representative of the phenomenological approach [*Betrachtungsweise*] in physics."[75] Olesko, who studied Neuman's seminar, claims further that he, like most students of Neumann, "preferred a 'phenomenological physics' which did not make 'use of hypotheses concerning the mechanism of the process' and, more importantly, which did 'not look for proof other than the agreement of the results of theory with the results of experiment.'"[76] Although by taste and training Voigt was not inclined to employ any hypotheses concerning the ontological structure of matter, he did not reject the molecular explanation of piezoelectricity for being speculative, but for being inadequate. Supporters of the molecular theory like Röntgen took the same position. Pierre Curie, who had originally suggested the molecular model, was satisfied with Voigt's theory.[77] The support a phenomenological theory was independent of a belief in the molecular constitution of matter.[78]

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[74] Previously, in 1886, Pierre Duhem offered an alternative model to the molecular one, according to which piezoelectricity originated in pyroelectricity, which he considered a static phenomenon of thermoelectricity. Regarding Duhem's famous opposition to molecular theory and inner difficulties in his model, his theory can be seen as originating from his resistance to molecular models. Since Duhem's theory made no influence on Voigt's theory, its relevance to the turn to continuum theory is negligible. Duhem's theory is discussed in the next chapter. Pierre Duhem, "Applications de la Thermodynamique aux phénomènes thermo-électriques et pyro-électriques" *Annales de l'Ecole Normale supérieure*, 2 (1885): 405–424, 3 (1886): 263–302.

[75] K. Försterling, "Woldemar Voigt zum hundertsten Geburtstage." *Die Naturwissenschaften, 38* (1951), 217–221, on 217.

[76] Olesko, *Physics as a calling*, 387–388; the inner quotations in single quotation marks are from Voigt. Olesko's claim that "the problem with this way of thinking was that it inhibited the kinds of thinking needed to achieve theoretical results," does not seem to fit Voigt's theoretical achievement in piezoelectricity.

[77] According to Marie Curie following the publication of Voigt's theory Pierre Curie suspended his plan to publish an analogous theory. This shows his acceptance of Voigt's theory. Marie Curie, "Préface," p. xiv.

[78] British physicists continued to think about molecules and probably also to believe in their existence, while preferring phenomenological theories that assumed continuous matter in hydrodynamics in mid-nineteenth century. This is another example that the support of analytical theory did not mean a denial

Voigt himself had developed a molecular theory of elasticity; to resolve the contradiction between the molecular hypothesis and the experiment, he modified the previous molecular hypotheses in an attempt toward a "general and consequential theory of matter." And he came to propose a molecular explanation for the general phenomenological theory of piezoelectricity.[79] Whether or not Voigt preferred a phenomenological to a molecular theory depended on the specific situation in the field and his particular goal.

That Voigt developed molecular theories for macroscopic phenomena suggests that he accepted the molecular structure of matter. From this point of view his general theory of 1890 was an intermediate, temporary step on the road to a molecular theory of piezoelectricity. Yet, in practice it was more than a temporary step. In 1915, after the accumulation of compelling evidence for the atomic constitution of matter,[80] Voigt wrote:

> Once the molecular constitution of matter and electricity is regarded as proven, physicists will be inclined to regard the molecular view as the only proper one and a phenomenological approach as something at best temporarily tolerable. In principle there is certainly no objection to this point of view. However, at least for the present and perhaps for some time, it does not do justice to actual circumstances. Things are not so simple. There is not a free choice between phenomenological and molecular views; in many areas there are very great, even insuperable, difficulties in following the latter way.[81]

According to Voigt, these difficulties originated in the lack of direct knowledge of the molecular and inner molecular behavior and in the failure of most molecular accounts to provide more than a crude picture of reality. Only in a few extraordinary cases could they overcome the difficulties. It follows that molecular explanations could be constructed only by assuming laws, principles, and considerations of symmetry justified from the phenomenological rather than the molecular point of view; a direct deduction from the molecular hypotheses without their help fails to describe the phenomena. Since the molecular assumption itself cannot guide research toward the laws of nature, phenomenological theory remains essential. Moreover, based directly on experimental claims it is more certain than the molecular. Thus, phenomenological theory is not only a temporary scaffold, but also an engine for further work even after

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of the molecular constitution of matter. Maria Yamalidou, "Molecular Ideas in Hydrodynamics," *Annals of Science*, 55 (1998): 369–400. In a similar vain the adoption of continuum approach in elasticity at the same period was not "the tout court refusal of the molecular model in favour of the continuum hypothesis but, more simply, a 'suspension of judgement' on the modality of action between the last elements of matter." Fedrico Foce, "The Theory of Elasticity between Molecular and Continuum approach in the XIX Century," in *Entre mécanique et architecture*, Patricia Radelet-de Grave and Edoardo Benvenuto (eds.), Basel: Birkhäuser, 1995: 301–314, on 305.

[79] Voigt, "Über die Elasticitätverhältnisse der Krystalle," id., "L'état actuel de nos connaissances sur l'élasticité" on 289. On his piezoelectric theory see chapter 3 below.

[80] Voigt mentioned the Brownian motion, the atomistic structure of solid as revealed by x-rays and Millikan's experiment on the discrete character of electric charge, as evidences for their atomic structure.

[81] W. Voigt, "Phänomenologische und atomistische Betrachtungsweise," in *Die Kultur der Gegenwart*, dritter Teil, dritte Abteilung erster band - *Physik,* E. Warburg, ed., Berlin: Teubner, 1915: 714–731; on pp. 722–723.

construction of an edifice of molecular theory. Piezoelectricity was one of the areas in which these immense difficulties were insuperable for a molecular account of the phenomena.[82] Due to these physical and mathematical difficulties Voigt constructed and others adopted a phenomenological theory for piezoelectricity.

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[82] *Ibid.*, pp. 723, 728. Voigt's argument against the reduction of the physical theory to atoms is very close to the argument of solid state physicists against the ability to construct their theories from the behaviour of elementary particles. Apparently, the controversy between 'fundamental' physics and the physics of more complex phenomena did not begin with P. W. Anderson's famous article "More is Different, Broken symmetry and the nature of hierarchical structure of science" (*Science*, 177 (1972): 393–396).

CHAPTER 3

THEORIES AND MODELS ABOUT THE CAUSES OF THE PIEZOELECTRIC PHENOMENA

In its account of the piezoelectric phenomena, Voigt's general theory demonstrated the vigor of the analytical-phenomenological method, yet, as such a theory, it did not explain their source. In this theory Voigt refrained from any hypotheses on how and why strain generates electric polarization. Nevertheless, physicists also attempted to understand the source of piezo- and pyroelectricity. They suggested explanation of the phenomena according to their views of matter, electricity, and heat and to current approaches to physics, each according to his own. These explanations were also formulated to sustain one's own approach by eliminating potential refutations and extending the circle of phenomena it describes. The suggestions present different styles and methods of late-nineteenth century physicists. This chapter shows the significance and influence of these approaches in the theoretical study of a particular phenomenon.

Molecular reasoning was prevalent among these approaches. Matter, most physicists agreed, consisted of molecules and its behavior is determined by their unknown state. Thus, they studied various phenomena from molecular perspectives.[1] Piezoelectricity was no exception. Arguably, molecular interpretations of piezo- and pyroelectricity were proposed even before the discovery of the former. As claimed in Chapter 1, such an interpretation led to the discovery of the phenomena. Yet, Röntgen's 1889 experiment and Voigt's theory and criticism showed the limitations of the current molecular assumptions. Later, molecular explanations would need to overcome the objections to Curies' model. In practice, they would have to agree with the results of Voigt's theory as an accepted description of the phenomena. Moreover, acceptance of a molecular structure of matter entailed neither an agreement concerning the characteristics of these molecules and their connections nor a consensus about the attitude toward molecules and the explanation of physical phenomena in general. Alternative approaches to the molecular, like thermodynamic, which was historically linked to the field through pyroelectricity, were also employed in the effort to explain piezoelectricity. Physicists also differed in their approach to satisfactory explanation in general: Whether it should be based on a mechanical model? Could it involve

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[1] For Germany see Jungnickel and McCormmach, *Intellectual Mastery of Nature*, vol. 2, pp. 100–103.

action at a distance? Which phenomenon is more basic so that it can be taken as the assumption for explaining another? These are a few questions to which different answers were given in diverse theories of piezoelectricity.

This chapter concerns hypotheses, theories, and models suggested to interpret and explain piezo- and pyroelectricity and their sources. It shows the variety of approaches toward the cause of the phenomena and the ways to understand them. It examines whether these approaches succeeded in offering a possible interpretation, i.e., whether they were compatible with the experimental data, and whether they were also plausible. The plausibility of a theory depended on the credibility of its assumptions and the soundness of the structure or mechanism it supposed. The former, however, did not originate from the piezoelectric research, but from general notions of contemporary science. In particular, they were dependent on theories of dielectrics, elasticity, and the material structure of crystals. The central views in the first two are summarized in the first section of this chapter and different assumptions about the structure of crystals are discussed throughout the chapter. Theoretical and experimental constraints did not determine the approaches taken by protagonists and the suggestions they offered. In order to understand the origins of the variant suggestions, this chapter looks at the motivation and at the general attitude of the protagonists toward physical theory. The examination of the explanatory theories reveals the strength and the limitations of the approaches taken; it answers why none of them succeeded in yielding an acceptable explanation for the phenomena. It also displays the divergence in the concepts used and their physical meaning as they were incorporated in concrete theoretical arguments. Physical concepts are not static entities. Changes in the understanding of atoms and molecules are apparent even for the short period described here. Even the novel view of independent "electrons" associated with J.J. Thomson's 1897–1899 experiments stimulated a hypothesis on the source of piezoelectricity.

The suggestions vary. Some were based on thermo-electric processes, some on mechanical motions; the latter were usually connected to a molecular-atomistic approach. Some were only suggestions toward a future detailed theory; others included an argument that articulated the physical relations for particular or general cases. Table 3.1 summarizes major properties of the explanatory theories along these lines. The table can serve the reader for orientation in the following detailed discussion of the theories. Obviously, it cannot encompass their entire complexity and diversity, or even show all the important differences between theories.

In Chapter 1, I discussed a few suggestions to explain piezo- and pyroelectricity before 1890. This chapter discusses mostly later attempts but also former attempts that were not examined in the previous chapters since they did not influence the development of the field. The later theories were generally more elaborated and detailed than the earlier models, since they had to bear on the success of Voigt's theory. The discussion generally follows a chronological order, however, it also describes in successive order three approaches to the problem of explaining piezoelectricity: the thermodynamic (a theory of Duhem), the continental-molecular approach (theories of Riecke and Voigt), and the mechanistic British approaches (theories of Kelvin). The British approach also opens the discussion of the explanations with a hypothesis suggested a few years before the discovery of piezoelectricity. It was, obviously,

Table 3.1: Explanatory models, theories and suggestions of Piezoelectricity

Theory/model	Compatibility with Voigt's theory	Mechanical[a]	Molecular/ Atomistic	Thermo-electric	Elaborated explicitly[b]
Lodge's 1st	−	+	−	−	−
Lodge's 2nd	−	−	−	+	−
The Curies'	−	+	+	−	+
Wiedemann's	−	−	+	+	−
Duhem's (1886)	−	−	−	+	+
Riecke's 1886	−	+	+	−	+
Theories suggested after the introduction of Voigt's theory:					
Riecke's 1891–2	+	+	+	−	+
Voigt's elaboration of Riecke's	+	+	+	−	+
Voigt's own	+	+	+	−	−
Kelvin's for quartz	partial	+	+	−	+
Kelvin's general	+	+	+	−	−
Kelvin's atomistic	+	+	+	−	−

[a] A theory/model in which the electric effect is due to a mechanical process of pressure and/or a variation of temperature, such as a change of distance between charged corpuscles.

[b] A theory/model explicitly elaborated mathematically or by other reasoning to attain relations with physical significance, i.e., results that could be tested in the laboratory.

suggested to explain only pyroelectricity. As mentioned, the first sections review the relevant elasticity and electricity theories.

APPROACHES TOWARD ELASTICITY AND ELECTRICITY

Piezoelectricity intermingles the electric and elastic effects. Thus, any theory of the phenomenon, whether explanatory or phenomenological, concerned notions from the study of both elasticity and electricity (or, to be more specific, of dielectrics). Theories of piezoelectricity assumed certain laws and relations about elasticity and dielectrics. As is common, these relations were borrowed from corresponding theories of both fields. A review of current ideas about dielectrics and elasticity would, therefore, display options open to physicists who suggested explanations of piezoelectricity. Of the two fields, dielectrics attracted more attention. This was, at least, partly due to disagreement between the two major schools of electromagnetism on the meaning of fundamental concepts, like charge and polarization. By virtue of this controversy, the theory of dielectrics, though peripheral in itself, was linked to a central debate of the late-nineteenth century on the nature of electromagnetism and its actions. Moreover, the disagreement led to dispute about the principal phenomenon of dielectrics, namely polarization, known also as electric polarity and electric moment. On the other hand, the principal phenomenon of elasticity gained a common interpretation as a displacement of matter due to stress (i.e., force per area). Thus, it is not surprising that the issues of dielectrics were more central than those of elasticity in the formulation of the variant piezoelectric theories.

Notwithstanding the agreement about the fundamental phenomenon of elasticity, the relation between its theoretical description and the molecular structure of matter was under dispute. So was the relation between electromagnetic theory and the molecular structure. In studying solid matter and crystals in particular the problem became even more complex, since no agreement existed about their molecular–atomistic structure and its relation to the non-controversial descriptive crystallography.[2] Still, as mentioned, the vast majority of physicists and mineralogists assumed that matter ultimately comprises atoms and molecules. However, how these atoms are arranged and how they relate to the observed phenomena of elasticity and dielectrics was an open question. Explanatory theories of piezoelectricity tried to answer how mechanical displacements of these molecules, whose structure is unknown, cause electric effect.

Theories of elasticity

Elasticity was characterized by two approaches: molecular and continuous. The former "rests on the hypothesis that the action between two molecules is in the line joining them and is a function of their distance. In other words, it proceeds on the assumption that the behaviour of solid bodies is the same as it would be if they were composed of an immense number of *material points*, between which are forces of attraction or repulsion, following a certain law."[3] The latter does not limit itself to central forces between molecules, and is associated with an assumption of continuous matter. Commonly, it is based on the analytical differential function of the stress and strain associated with the name of George Green. By the end of the nineteenth century this function was viewed as an expression of elastic energy. The two approaches lead to a different number of elastic constants. The continuum approach leads in a non-isotropic case to 21 constants and to two for isotropic solid, while the molecular approach leads to 15 and one constants, respectively. Thus, Karl Pearson, the nineteenth century historian of elasticity, called the former the multiconstant and the latter the rari-constant theories. Both theories were first formulated in an advanced form in 1823. Both involved complex mathematics, which many physical-mathematicians during the century continuously expanded and studied. The controversy between the two approaches concerned both physical-mathematical deductions (which are valid derivations from each assumption) and experimental evidence and its interpretation.[4]

From the middle of the century experiments carried out by Guillaume Wertheim, Gustav Kirchhoff and others confirmed the multiconstant theory. Still, a few other experiments supported the rari-constant theory. Moreover, adherents of the rari-constant theory claimed that the examined solids were not isotropic as the experimentalists assumed but non-isotropic, and thus cannot testify to the number of constants in isotropic

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[2] See below footnote.

[3] A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity*, Cambridge: Cambridge University Press, 1892, p. 15.

[4] The part on elasticity is based on *ibid.*, pp. 14–18 and Fedrico Foce, "The Theory of Elasticity between Molecular and Continuum approach in the XIX Century," in *Entre mécanique et architecture*, Patricia Radelet-de Grave and Edoardo Benvenuto (eds.), Basel: Birkhäuser, 1995.

bodies. According to their view, the experiments only revealed that more solids than had previously known are non-isotropic. They had no bearing on the elastic theory. In a series of experiments in 1887–1889, Voigt had circumvented this objection by examining non-isotropic crystals whose symmetry was known from other properties, with compelling findings against the rari-constant theory. In 1892 A. E. H. Love suggested "that a single result of this kind, once firmly established, is sufficient to discredit the molecular or rather *point-atom* hypothesis as a basis for elastic theory."[5] However, Love had additional reasons to prefer the continuum approach, which leads to the multiconstant theory:

> Modern physics [he wrote] is perfectly capable of deducing a theory of elasticity from the known laws of energy, without the aid of a subsidiary hypothesis about intermolecular force, and, being in that position, *it is bound to discard the hypothesis*. Such a device is merely a phase in the development of scientific thought, and, having served its turn as a means of introducing generality into the subject, *it must give place again to a still more general method*.[6]

Love's criterion of rejecting unnecessary hypotheses was not shared by many of his colleagues. Perhaps for them he raised another theoretical objection to the molecular theory. He claimed that "modern speculations in molecular dynamics" point to "the intervention of a continuous medium" in the mutual action between molecules. In the current ignorance about "the nature of the medium and the nature of the atoms, we can only invoke the known laws of energy . . . but we are not thereby in a position to prove that the molecular hypothesis in question is not an adequate mathematical representation of the facts."[7]

The status of the point-atom hypothesis in elastic theory was very similar to that of the Curies' molecular hypothesis in piezoelectricity. Both contradicted the experiment. Love's rejection of such a theory was more sweeping than Voigt's rejection of the Curies' theory, but both revealed the same inclination toward general nonhypothetic theories. Still, both acknowledged a molecular structure of matter. In both fields the rejection of a specific theory did not entail rejection of molecular theory as such. Love called the molecular theory the point-atom hypothesis to indicate that current knowledge contradicts this specific hypothesis but not any molecular assumption. Indeed, (although not mentioned by Love) a few molecular theories that were based on hypotheses different from that of point-atom had already been suggested. This is parallel to the post-1890 molecular theories of piezoelectricity, which abandoned the Curies' simple assumption for more complex molecular strictures and actions. Prominent among the theories in elasticity was Voigt's molecular theory of 1887, which assumed polar molecules, instead of point-like atoms. Voigt's assumptions led to the results of the multiconstant theory, which he championed experimentally during the same years.[8] Since both continuum and molecular views of elasticity were possible, piezoelectric theories could be built on either. As we will see below, because the

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[5] *Ibid.*, p. 19 (italics in the original) and *ibid.*, pp. 304–313.

[6] *Ibid.*, pp. 19–20, my emphasis.

[7] *Ibid.*, p. 16.

[8] Voigt, "Elasticitätsverhältnisse der Krystalle."

description of its basic phenomenon was not sanative to the question discussed here, the latter had little relevance to the ways in which piezoelectricity was explained.

Theories of dielectrics

Controversies in the theory of dielectrics had more consequences on the attempts to explain piezoelectricity. Two questions were under dispute concerning the theory of dielectrics: the relation between charge and polarization (and the place if any of a field), and the acceptance or rejection of action at a distance. It was part of a general debate on electromagnetism, which can be seen as a deep disagreement between the schools of British and Continental physicists. The British approach is traced backed to Faraday and that of the continental to Ampère, Coulomb, and the French mathematical physics of the turn of the century. The former is usually associated with the names of William Thomson and Maxwell, the latter with those of Franz Neumann, Weber, and Helmholtz. Both were not homogenous schools with a fixed dogma, but two general approaches with many inner and sometimes even bitter disagreements. So, Thomson fought Maxwell's theory, and Helmholtz harshly criticized Weber's force law, to mention only two examples. During the last two decades of the nineteenth century, the British and continental schools approached each other, and a third "synthetic" school associated with the name of Lorentz emerged. Yet, the different attitudes still struck out.

The issue of action at a distance was the simpler of the two mentioned. Continental physicists admitted action at a distance without the need for an intermediate medium. That was true both of Weber's formulation of the theory on the basis of electromagnetic force and of the formulation by potential function of Neumann and Helmholtz. Maxwellians denied such a possibility. They thought that any action should be transmitted by fields through the intermediate medium—the ether. Lorentz's theory and the other electron theories agreed with the Maxwellian by denying action at a distance and instantaneous forces. The issue of action at a distance did not have much practical consequence for dielectrics since Maxwell also used potential function, which allow calculations and examinations based on distance charged bodies. It has little relevance to piezoelectricity. Effects due to the finite speed of propagation of the electric action do not arise in this field, which involve practically static phenomena in very small crystals.

The concept of electric polarization of nonconducting matter, which was dubbed dielectric, originated in Michael Faraday's work in the middle of the 1830s. Based on Poisson's 1824 memoir on magnetism, in 1838 Faraday suggested a comparison between dielectric and magnetized iron. "The particles of an insulating dielectric," he wrote, "whilst under induction may be compared to a series of small magnetic needles, or, more correctly still, to a series of small insulated conductors."[9] Under the influence of an external charged conductor these "small conductors" are polarized. For Faraday, the polarized bodies did not involve any free charge, as he denied its existence. He claimed that "it is impossible to charge a portion of matter with one electric force

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[9] Quoted from Edmund Whittaker, *A History of the Theories of Aether and Electricity*, New York: Humanities Press, 1973, Vol. 1: pp. 187–188.

independently of the other." By that he "meant that the charge would be the starting point of an induction that would end somewhere (possibly very far) as an opposite charge." Both charges reside at the dielectric upon the surface of conductors.[10]

A decade later, Ottaviano Mossotti suggested a theory based on central forces in the Laplacian tradition of dielectric polarization. Mossotti adopted Faraday's assumption that the small parts of the dielectrics were polarized under electrical influence. Yet, he ignored Faraday's rejection of electric fluid or free charge. Moreover, he identified the small bodies with molecules, which, according to his view, were polar due to "ether" in them. The properties of this "ether" are like those of electric fluid or charge, and in this way later physicists understood it. In his view, "ether" (charge) was the source of electric forces. Polarization was a state of "ether" distribution in the molecules of the dielectric. Although "Mossotti's work was not very influential theoretically," as the ideas of electric fluid and ether were increasingly distrusted, later continental electricians shared his main approach to polarization.[11] They considered dielectrics as comprising many smaller "polar molecules," while polarization is a local displacement of electricity under electromotive forces. Despite differences between the theories of Weber and Helmholtz, they coincide on this issue. Both assumed the existence of free charge independent of opposite charge. They supposed that molecules are polarized by inner charge distribution, itself caused by external charge. Continental physicists adopted charged particles (atoms, ions, etc.) which are not bound to any corpuscle with opposite charge, and even considered (especially in Weber's school) the existence of pure atoms of electric charge. In that approach the carriers of the electric charge (whether pure electric or not) were the source of all electromagnetic phenomena.[12]

Maxwellians, on the other hand, conceived charge as discontinuity in an electric field. It was the outcome rather than the cause of electric polarization, induction or displacement. "According to this theory, all charge is the residual effect of the polarization of the dielectric," Maxwell wrote.[13] Thus polarization, rather than charge, is the primary property of dielectrics. This is a continuous picture of matter and polarization that views the dielectric as a whole. As such, it contradicts the continental view of discrete polarized molecules. Still, Maxwell's theory did not deny the polarization of small dielectrics, as long as it is not regarded as a result of charge distribution. Yet this approach made any attempt at a molecular theory of electricity problematic. Olivier Darrigol has observed that "the macroscopic character of his [Maxwell's] unification of electrodynamics, electrostatic, and optics, conflicted with the empirical need to introduce the molecular structure of matter. Maxwell did not know to what extent his electromagnetic concepts applied at the molecular scale. He avoided microphysical considerations whenever the macroscopic approach proved sufficient."[14]

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[10] Olivier Darrigol, *Electrodynamics from Ampère to Einstein*, Oxford: Oxford University Press, 2000, p. 94, (first quotation of Faraday the second of Darrigol) and the discussion pp. 85–96.

[11] Jed Z. Buchwald, "Mossotti, Ottaviano Fabrizio" *DSB* 9: 547–549, quotation on p. 549.

[12] Darrigol *Electrodynamics, passim*, and pp. 61–64, 164, 227–228, 265–270.

[13] James Clark Maxwell, *A Treatise on Electricity & Magnetism,* 3rd edition, New York: Dover Publications, Inc., 1954, p. 167.

[14] Darrigol, *Electrodynamics*, p. 172. By "the empirical need" Darrigol has referred to experimental results that were not explained by macrophysics theory. On these limits of Maxwell's theory see Jed Z.

Nevertheless, Maxwell did not deny the possibility of particles with discrete charge. Following Clausius (and unlike Faraday), he assumed that in an electrolyte the molecules are decomposed to ions and cations (i.e., charged atoms). In discussing electrolysis he was led to admit "the fact of the constant value of the molecular charge, and that we call this constant molecular charge, for convenience in description, *one molecule of electricity*. This phrase, gross as it is, and out of harmony with the rest of this treatise [i.e., with Maxwell's theory], will enable us at least to state clearly what is known about electrolysis, and to appreciate the outstanding difficulties." He thought that "[i]t is extremely improbable however that when we come to understand the true nature of electrolysis we shall retain in any form the theory of molecular charge."[15]

Darrigol has observed that "Maxwell's British and German followers . . . expected the atomic structure of matter to play a role in electric conduction, in the magnetic properties of matter, and in a number of optical phenomena." Still, their approach differed from that of Weber's or Helmholtz's schools. "According to natural Maxwellian tendency, the molecules of matter acted on the ether by modifying its *mechanical* properties. This modification was itself to be described mechanically."[16] In this vein, British Maxwellians started to admit electrified particles in the study of conduction in electrolytes and gases. In 1887, J.J. Thomson employed a view of a molecule as "a pair of charged atoms." These "were the seeds of a new, Maxwellian microphysics, in which ions contributed to the basic field processes from which charge and current derived." In the following decade Thomson suggested an explanation for free charged bodies based on mechanic tubes of force, following a suggestion of Faraday. Thus, J.J. Thomson, like other Maxwellians, maintained the view of charge as a derivative of a continuous field. Yet, he simultaneously admitted its use as a basic component in the study of electrical phenomena. In 1890, Arthur Schuster reconciled bodily electrifications (i.e., charged corpuscles) with the Maxwellian view by reference to the assumed discontinuous structure of matter. Due to that structure "we may take them [the bodily electrifications] to be really only surface electrifications between atoms and the medium." Other Maxwellians, like Oliver Lodge, did not acknowledge the appearance of independent charges. In 1885 he suggested an alternative explanation for phenomena of electrolysis that others explained by ions.[17]

In Lorentz's theory, charge became an independent entity. In this theory pure charge "electrons" are seated in electrically indifferent neutral matter and determine its electric properties and behavior. Lorentz developed a synthesis between the Maxwellian and the Continental approaches. This theory, which was first labeled "ion theory" and later "electron theory," admitted both electromagnetic fields and free independent charges. As in the continental approach, polarization was conceived as a product of charge distribution inside the dielectric. Yet it was not necessarily proportional to either the free charge on the conductors that surround the dielectric (as in the continental

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Buchwald, *From Maxwell to Microphysics: Aspects of Electromagnetic Theory in the Last Quarter of the Nineteenth Century*, Chicago: The University of Chicago Press, 1985.

[15] Maxwell, *Treatise*, §260, pp. 380–1.

[16] Darrigol, *Electrodynamics*, p. 265.

[17] *Ibid.*, pp. 265–300, quotations on pp. 265, 293–94, 291, the last one from Schuster.

approach) or the displacement (as in Maxwell's theory). The electron theory had an additional independent variable of polarization to that of the earlier theories. One of the rare applications of the additional variable was in piezoelectricity. This was implied in Voigt's elaboration of the phenomenological theory in 1894, but without reference to Lorentz's theory. The issue was not relevant to the explanatory theories. Overall, Lorentz's theory and Larmor's similar electron theory did not influence piezoelectric research before 1901. This is not surprising as the electron theories were not established in the early 1890s. Although Lorentz had introduced his ideas in 1875, they did not get much attention until he returned to the subject in 1892. Larmor started to develop his ideas in the early 1890s.[18]

Hertz's celebrated experiment on electric waves in 1888 demonstrated for many continental physicists the advantage of Maxwell's theory. Consequently, many of them studied Maxwell's theory and adopted the famous Maxwell's equations. Yet only a small minority adopted his approach. Initially, the majority accepted the equations through the prism of earlier theories, especially that of Helmholtz. As mentioned, a compromise between the two approaches was also made by the British with the admission of free charge. Yet, until the turn of the century, Maxwellians, both British and continental, tried to avoid the assumption of atoms of electricity.[19] Probably, it is not an accident that none of them suggested an explanatory theory for piezoelectricity. However, Oliver Lodge suggested an explanation for pyroelectricity.

LODGE AND THOMPSON'S HYPOTHESIS OF UNILATERAL CONDUCTIVITY

A hypothesis for the origin of pyroelectricity "suggested itself independently" to Silvanus P. Thompson and Oliver Lodge following the latter's 1876 mechanical model of electric current. In 1878, they suggested "that the internal polarization of each particle of the crystal, which had been assumed by Sir William Thomson as a sufficient cause of the phenomena of pyroelectricity, might become explicable if it could be shown that such bodies as possessed pyroelectric properties possessed also a unilateral conductivity for electricity." Unilateral conductivity is the state in which the conductivity (of heat or electricity) from point A to point B is different from the conductivity in the opposite direction (i.e., from B to A). Such behavior was observed by Schuster in 1874. The hypothesis of unilateral conductivity was already implicit in Lodge's model of electric current in 1876.[20]

Lodge designed a model of the electric current to illustrate phenomena like electric conduction and dielectric polarization as conceived in Maxwell's theory. This model of the young graduate student was but the first of his suggested models for clarifying Maxwell's ideas and it followed his first thorough study of the latter's *Treatise*. For

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[18] On the electron theories see *ibid.*, pp. 322–350.

[19] *Ibid.*, pp. 252–264.

[20] S. P. Thompson and O. J. Lodge, "On Unilateral Conductivity in tourmaline Crystals," *Philosophical Magazine* 8(1879): 18–25, quotation on p. 18. Page numbers in parentheses in this section refer to this publication.

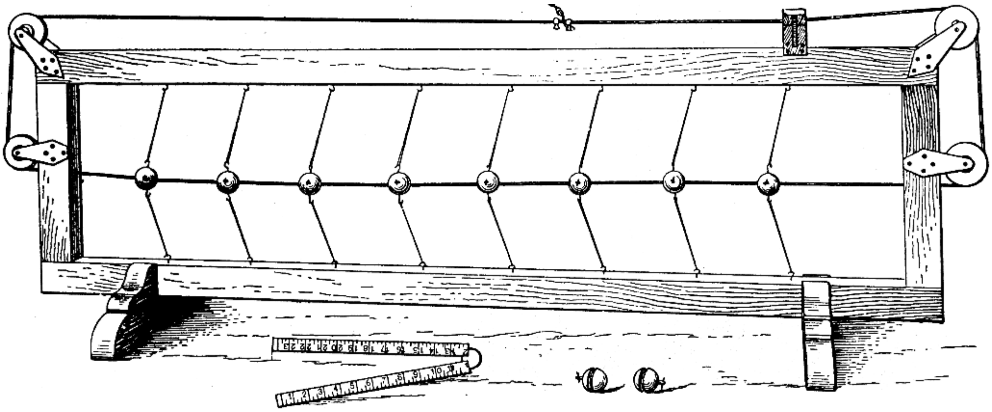

Figure 3.1: Lodge's cords, strings and buttons model of electric current (Reprinted from *The Maxwellians*, by Bruce J. Hunt. Copyright ©1991 by Cornell University. Used by permission of the publisher, Cornell University Press).

Lodge, as for other British physicists, mechanical models were a way to understand and explain physics. Throughout his career, Lodge sought the true mechanical model of ether that would account for all of electromagnetism. Yet, before that would be found, he was content with models that illustrated electromagnetic phenomena, like his model of electric current.[21]

Lodge compared the electric current to a cord threaded through buttons which are connected by springs to a fixed frame (see Figure 3.1). When the cord is free to move with low friction through the buttons, the model is analogous to a conductor, when it is fixed to a dielectric then the tension of the cord simulates the displacement. The buttons are analogous to the particles of the ponderable matter and therefore should develop "heat motion" of oscillation (taken for simplification to be harmonic). To explain Thomson's hypothesis of permanent polarization, Lodge suggested that the friction between the buttons and the cord might not be symmetric in pyroelectric crystals. In that case "the simple to-and-fro oscillations of the buttons would confer a progressive motion on the cord," i.e., an electric current. "The cord will be displaced by the unequal friction only so far as the dielectric will permit it, and the result will be a state of [electric] strain inside the crystal." Additional heating would cause stronger oscillations and, therefore, a larger electric displacement. Cooling would cause "advantage of elasticity" and the cord would return to his position. Lodge's view of permanent polarity as an elastic strain fits Maxwellian thought well.[22]

Were this explanation correct, tourmaline would have unilateral conductivity, since the motion of the cord, i.e., the current, was assumed to be asymmetric. Thompson and

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[21] On Lodge and his mechanical models see Bruce J. Hunt, *The Maxwellians*, Ithaca: Cornell University Press, 1991, pp. 25–28, 87–104.

[22] Oliver Lodge, "On a Model illustrating mechanically the Passage of Electricity through Metals, Electrolytes, and Dielectrics, according to Maxwell's Theory," *Philosophical Magazine* 2 (1876): 353–374; *id.*, "On a Mechanical Illustration of Thermo-electric Phenomena," *ibid.*,: 524–545 especially pp. 525 and 531–32; the quotations are from p. 525.

Lodge examined this consequence empirically. First, they examined heat conductivity, since "if the development of opposite electrical states at the two ends, and the establishment of a difference of potential between them, were a result of unilateral conductivity, all the analogies of the conduction of heat and electricity pointed to the probability that the tourmaline would be found to possess a unilateral conductivity of heat also" (p. 19). Observing isothermal lines they found "that *in a crystal which was getting warmer* the heat flowed more easily *toward* the analogous pole than away from it" (p. 20). Lodge continued the research alone with an experiment on electric conductivity, discharging a condenser through the crystal. He found that

> when the temperature of the tourmaline was *rising*, a distinct difference was perceived between the to-and-fro discharge. Also, when it was *falling* there was a difference, in the other direction. (These effects are, of course, due to that which is ordinarily termed electromotive force in the warming or cooling crystal.) But with a perfectly steady temperature, which was only attained after some hours, not the slightest difference could be perceived (p. 23).

Lodge had to admit that "our original hypothesis with regard to the cause of the internal polarity of the particles of pyroelectric crystals, . . . has not been confirmed by experiment." Yet, he was "unable to give it quite up even now." He still believed that in hemihedral crystals "there should in fact be something analogous to *barbs*, or *valves*, so that when a nondirectional disturbance (like a uniform rise of temperature) was imparted to the crystal the electricity should be urged from α to β more strongly than in the reverse sense"(p. 24). Nevertheless, he pointed to an alternative explanation that emerged from Thompson's findings that "heat flows more easily with electricity (i.e., from the antilogous toward the analogous pole) than it does against the electricity." This "convention of heat by electricity has an apparent analogy with the effect . . . in unequally heated metals [thermoelectricity—see below p. 111]." (p. 24) However, in 1884 Franz Stenger showed that differences in the heat conductivity of tourmaline in opposite directions are "very unlikely."[23] Whether he knew about it or not, this finding did not change Lodge's opinion. Even after the discovery of piezoelectricity (which he did not mention) and the introduction of a molecular explanation to the phenomena, he continued suggesting the latter hypothesis.[24]

The theory of thermoelectricity, to which Lodge referred, was founded on thermodynamics. Thus, he turned from a mechanical to a thermodynamical hypothesis. Yet, Lodge's mechanical and thermodynamic hypotheses were not so alien to each other as one might assume. Both explained the internal polarity by a continuous process involving the current. Moreover, in both the electricity (i.e., the electric charge) was a product, a derivative rather than an elementary entity. This last feature was very important for Maxwellians since they conceived charge as a derivative magnitude. Molecular explanations based on a view of a molecule as a system of electric charges did not fit well this view of charge. Maxwellians were more reluctant to build an explanation on a notion of discrete electric charges than on thermodynamics, which

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[23] B. Minnigerode, "Ueber Wärmeleitung in Krystallen," *Neues Jahrbuch für Mineralogie, Geologie und Plaeontologie*, **1** (1886): 1– 13, on 2.

[24] Oliver Lodge, *Modern Views of Electricity*, London: McMillan and Co., 1883: pp. 121–3. The same description was published in the second edition (1892: pp. 133–5) and in the third (1907: pp. 121–3.).

does not contradict Maxwell's theory. Lodge would find an unexpected partner in his preference of thermoelectric and rejection of molecular explanation of pyroelectricity in Duhem, a famous opponent of Maxwell's theory.

DUHEM'S THERMOELECTRIC THEORY

In 1885–1886, Pierre Duhem explained piezoelectricity as an epiphenomena of thermoelectricity. As a famous antagonist of atomism Duhem did not base his theory on any molecular assumption. According to him, piezoelectricity is a secondary phenomenon of pyroelectricity, which itself is a specific case of thermoelectricity originated in inhomogeneity in structure and temperature. Piezoelectricity was conceived in this manner as a thermal phenomenon and its analysis a part of a thermodynamic theory of thermo- and pyroelectricity.[25]

Like other early researchers of piezoelectricity (Jacques and Pierre Curie, Czermak) Duhem was a young physicist, a fourth year student at the *École Normale* in Paris. Though a beginner, he had already published four papers the year before. In October 1884, while still a third year student, he submitted a doctorate dissertation in physics, although students of the *grandes écoles* did not usually present themselves for a doctoral degree, let alone in the middle of their studies. However, his dissertation on "The thermodynamic potential and its application to mechanical chemistry and to the study of electric phenomena," was rejected by a committee chaired by Gabriel Lippmann. Although Duhem recalled that he had entered the *École Normale* in 1882 as a "convinced mechanist," he had soon converted to a thermodynamic view, rejecting mechanistic and molecular explanations. His new belief is manifested in his dissertation and early published work from the end of 1884. Following Gibbs and Helmholtz he employed thermodynamic functions (today commonly known as free energy), which he dubbed thermodynamic potentials to areas like physical chemistry, electricity, and capillarity. For him, this method suggested an alternative to mechanical assumptions of molecules, forces, etc., that is, to the reduction of physical effects to local motion. Thus, regarding capillarity he stated that thermodynamics "emancipates that part of physics from the hypothesis of molecular attraction." In 1884–1885 Duhem was already engaged in embracing physical theories in thermodynamics and avoiding mechanical assumptions.[26] His theory of thermo, pyro- and piezoelectricity

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[25] Pierre Duhem, "Applications de la thermodynamique aux phénomènes thermo-électriques et pyro-électriques," *Annales Scientifiques de l'école normale supérieure*, 2(1885): 405–424, 3(1886): 263–302. Page numbers in parentheses in this section refer to this publication.

[26] Stanley L. Jaki, *Uneasy Genius the Life and Work of Pierre Duhem*, The Hague: Martinus Nijhoff Publishers, 1984, 37–53, quotation on pp. 47–48. Duhem published his dissertation in 1886, probably after some changes. Unfortunately the original manuscript was lost and the kind of changes Duhem made are unknown. The rejection of Duhem's thesis is an interesting historical episode. Current accounts find the reason for the rejection mostly in academic politics. Brouzeng focuses on the power of the French chemist Berthelot, whose theory of "maximal work" was rejected by Duhem (Paul Brouzeng, *Duhem: Science et providence*, Paris: Belin, 1987, pp. 31–40). Jaki focuses on Lippmann's personal opposition to the young physicist, who earlier rejected results of the former. The personal-political considerations surely played a role in this story, but Lippmann probably had the physical reasons to reject the work. These could illuminate the approaches towards thermodynamics at the time. I suspect that Lippmann

was part of this program. According to him, he carried the theory in his dissertation and generalized it to systems in nonuniform temperature (p. 405). Still, as I show below, his use of thermodynamics did not mean that he refrained from hypothetical assumptions about the phenomena and their causes. His theory of pyro- and piezoelectricity suggested that he did not reject hypothetical explanations as such, but attempted to replace molecular and mechanical causes by thermal ones.

Thermoelectricity is the generation of electric current by temperature differences in inhomogeneous circuits. In 1821, Thomas. J. Seebeck found that heating either junction of copper and bismuth in a circuit made of these metals induces what he viewed as magnetic polarization, which others immediately conceived as having originated in an electric current. In 1834 Jean C. A. Peltier discovered that current in such circuits heats one junction and cools the other. Unlike the regular heating that was described by Joules's equation, this "Peltier effect" is reversible. As an unexplained reversible phenomenon of heat, thermoelectricity was one of the first subjects to receive a thermodynamic theory. In 1851 William Thomson formulated this theory that embraced the two effects and predicted a third effect: current in a homogenous conductor under differences of temperature would cause one end to be cooler and the other hotter. In the following few years he carried out a few sensitive experiments, by which he eventually succeeded in verifying his theoretical prediction. Thermodynamics continued to guide him and Rudolph Clausius in their studies of the phenomenon in the 1850s.[27] Yet, Duhem thought that these theories suffered from shortcomings, which attracted him to study the phenomenon.[28]

Thus, thermoelectricity was a natural candidate for an elaborated thermodynamic theory. Pyroelectricity and piezoelectricity, on the other hand, did not seem natural candidates. Early theories of these phenomena did not relate to thermodynamics; piezoelectricity was not even associated with heat. Yet, Duhem claimed that the accumulated and diverse experimental data on pyro- and piezoelectricity could be encompassed by such a theory. He mentioned two approaches for viewing the phenomena. Gaugain had suggested a thermoelectric model for pyroelectricity, but his ideas were abandoned.[29] Thomson, on the other hand, had assumed inner permanent electric polarity compensated by superficial electric charge.[30] Though Thomson's

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disapproved Duhem's abstract mathematical style and his use of thermodynamic potential. Recall that Lippmann himself employed thermodynamic reasoning (unlike Berthelot who did not use the second law), but through analogies and not general abstract formulation (see above p. 36, on thermodynamic potentials see below chapter 4 p. 157).

[27] Bernard S. Finn, "Thermoelectricity," *Advances in electronics and electron physics*, 50 (1980): 175–239; Caneva, Kenneth L., " 'Discovery' as a site for the collective construction of scientific Knowledge," *HSPS* 35 (2005): 175–291, on pp. 190–96, 206–9; Crosbie Smith and M. Norton Wise, *Energy and Empire: A Biographical Study of Lord Kelvin*, Cambridge: Cambridge University Press, 1989, pp. 332–33, 403–4. Duhem, *ibid,* p. 420–21.

[28] As he recalled in 1913: Pierre Duhem, *Notice sur les Titres at Travaux Scientifiques de Pierre Duhem*, Bordeaux: Imprimeries Gounouilhou, 1913, p. 88.

[29] Duhem did not mention objections to Gaugain's assumptions, like those of the Curies (see chapter 1 note 45).

[30] Thomson's hypothesis was connected by readers (like the Curies and Voigt) and later by himself with molecular assumptions. That surely did not make the hypothesis attractive to Duhem, but he did not refer to the question of molecularism here.

suggestion was widely accepted (if not by all), Duhem rejected it. He claimed that such a compensating charge is unknown in any other part of physics, and is, therefore, implausible. Instead, he adopted Gaugain's thermoelectric analogy (pp. 268–9). Undoubtedly, Duhem's decision was influenced by the suitability of Gaugain's analogy to his thermodynamic research program. Thus, the analogy with thermoelectricity and the need for a theory of the phenomena made piezo- and pyroelectricity appropriate candidates for a thermodynamic theory. Thermoelectricity was not only an analogy for Duhem; he conceived piezo- and pyroelectricity as a thermoelectric process.

As piezoelectricity had not been discovered by then, Gaugain and Thomson suggested their hypotheses to explain only pyroelectricity. Like others, Duhem assumed that pyro- and piezoelectricity have a common explanation, so these hypotheses were also relevant for the latter. The Curies, Friedel, and Röntgen had shown similarities between the phenomena. Yet, Duhem rejected their suggestion of a common mechanical explanation based on Thomson's hypothesis (be it a change in inner tension or in the distance between molecules). Such mechanistic reduction was alien to Duhem. Engaging in a thermodynamic research program and having the thermoelectric analogy in mind, he preferred regarding piezoelectricity as a secondary phenomenon of pyroelectricity.

Since Duhem regarded pyroelectricity as a kind of thermoelectricity, he employed results derived for the latter phenomenon in elaborating a theory of the former. Thermoelectricity concerns closed electric circuits and practically permanent currents. Thus, he needed to assume permanent currents in pyroelectricity. That was a problematic assumption because: (a.) pyroelectric materials are poor conductors, and more importantly, (b.) the phenomenon also appears without observable current. It was also observed in crystals that were not connected to an electric circuit (e.g., by Kundt's dusting method) and in other cases was considered to induce a static effect only. Duhem bypassed the latter problem by considering a specific and atypical experimental setting in which a pyroelectric crystal **is** a part of a closed circuit. Such was the situation in an experiment of Emil du Bois-Reymond in which two edges of a tourmaline bar were connected by a conductor to each other, while the crystal was heated. Du Bois-Reymond observed an electric current in this circuit by a magnetic needle.[31] Yet Duhem did not show that current flows in other pyroelectric experiments. Instead of facing the question of the conduction properties of the pyroelectric crystals, usually regarded as dielectrics, he simply treated them as conductors (pp. 405–20, 269–70). As will be discussed below, this peculiar assumption did not fail to attract criticism.

Duhem's theory assumes thermodynamic equilibrium where the temperature is steady in time but nonuniform in space. This equilibrium is analyzed in terms of heat, work, and entropy. The work done by the electric charge is divided into two parts: the "noncompensated work" (*travial non compensé*) that is converted to heat in a nonreversible process according to Joule's law, and the "compensated work" that

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[31] Duhem referred only to a short notice on the usually neglected experiment of du Bois-Reymond that appeared in Peter Theophil Riess, *Die Lehre von der Reibungselektricität*, Berlin: August Hirschwald, 1853, p. 475.

represents the work done by the reversible thermoelectric process.[32] Thus, the heat dQ released by current I at a volume element is:

$$dQ = AI^2 dR\,dt - AI\mu(T)dT\,dt \tag{1}$$

where the first member represents the Joule heat and the second the thermoelectric, dR is the resistance of the element, dT the temperature difference between its edges, $\mu(T)$ a function that characterizes the matter, which depends on its temperature and A the mechanical equivalent of heat. Differently from the Joule heat, the heat gain (or loss) by the second term is proportional to the current and not to its square. This "compensated work" appears in pyroelectricity as well as in thermoelectricity.[33]

Duhem showed that a necessary and sufficient condition for the generation of thermoelectric motive force is that both the function $\mu(T)$ and the temperature would vary along the circuit, i.e., its material should be heterogeneous and its temperature is not uniform. This, accordingly, should also be the case for pyroelectricity, as a particular case of thermoelectricity. So Duhem attributed pyroelectricity to **inner differences** of temperature while other researchers (Gaugain, Friedel, Thomson, Riecke, Voigt) attributed it to **changes** in the temperature of the whole crystal. On the other hand, his conclusion that pyroelectric materials are not homogeneous agrees with Bravais's finding on the reticular structure of crystals. Yet, to prevent confusion, Duhem twice clarified that this conclusion is independent of the true nature of matter. "We will have no restriction on the manner in which the constitution of the material at the interior of one of the net's stitches [of the crystal's lattice] varies; this constitution will be able to vary from a continuous or discontinuous manner." (p. 271, see also p. 277).

Duhem developed an equation for the electromotive force as an integral over a continuous function of the temperature that depends in addition on the orientation of the isothermal planes inside the crystal. The existence of these planes follows from his assumption of nonuniform temperature. To facilitate the derivation he treated only the case of parallel isothermal planes.[34] From this equation Duhem concluded that "natural" pyroelectric crystals have no center of symmetry and no more than one symmetrical axis. As he wrote, this conclusion had already been stated earlier by Mallard in 1884,[35] and it agrees with the observations of Friedel and Jacques Curie. Other crystals have only "accidental pyroelectricity" caused by deformations in the crystal's structure (pp. 283–5). Accidental pyroelectricity stood at the basis of his explanation of piezoelectricity.

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[32] Duhem relied on his dissertation in claiming that the work done by charge is equal to its multiplication by the potential difference between the points it passed through and a constant.

[33] In the pyroelectric part Duhem preferred to formulate the work in terms of charge density instead of current, in accordance with the usual accounts of pyroelectricity, which did not refer to currents. *Ibid.*, 405–417. Compare eq. (15) p. 416 in the thermoelectric part with eq. (2) p. 275 in the pyroelectric part.

[34] *Ibid.* 271–279. For a discussion of Duhem's derivation see Katzir, *History of Piezoelectricity*, pp. 101–103.

[35] Ernst Mallard, *Traité de Cristallographie géométrique et physique* Tome 2 "cristallographie physique", Paris: Dunod 1884, on pp. 571–2. See chapter 1.

Duhem concluded the discussion of pyroelectricity by showing that his theory accounts for Gaugain's laws for the development of charge (above Chapter 1, p. 19). In particular, he showed that the effect is independent of the width of the crystal plate. However, Duhem admitted that "the conditions in his [Gaugain's] experiments were much more complex than the assumed conditions that we have carried out." Therefore his own theory does not provide "the theoretical explanation" of these experiments (pp. 292–3). In his discussion Duhem assumed a thin crystal plate (not used by Gaugain) with parallel isothermal surfaces in a closed electric circuit through which current flows. However, many experiments did not use a closed electric circuit. He justified the approximation of a bar by a thin plate by Lamé's equation for heat diffusion, originally formulated for homogeneous material, though he used it for the nonhomogeneous crystals. Since the theory dealt with thermostatic equilibrium, Duhem admitted an approximation of an infinitely slow cooling process (pp. 285–93). Due to the mathematical complications of nonuniform heating, Duhem did not try to elucidate such experiments which he took as showing only "accidental pyroelectricity."

Piezoelectricity had only a secondary place in Duhem's theoretical picture, as a complicated manifestation of pyroelectricity. According to the theory in "natural" pyroelectric crystals, like tourmaline, pressure generates heat, which induces temperature differences, responsible for the appearance of "regular" pyroelectricity. In nonpyroelectric crystals, i.e., crystals that do not become electric due to uniform heating, pressure has an additional effect of deforming the material and thus reducing their structural symmetry. The reduction of symmetry enables the induction of pyroelectricity in that crystal as in "natural" pyroelectrics.[36] With this explanation of diminishing symmetry he accounted for the effect of pressure on quartz in a hemihedral (polar) axis and for the inverse sign induced by pressure in a perpendicular direction. This reasoning also explains why compression in the principal axis has no effect, since it does not change the symmetry of any of the three hemihedral axes. Yet, he admitted that Röntgen's early experiments from 1882–1883 are too complex for a full explanation along these lines. Overall, the discussion of piezoelectricity is even more qualitative than that of pyroelectricity.[37] Although Duhem cited the equation for the heat released by pressure in order to indicate the possibility of regarding piezoelectricity as a thermal effect, he did not support his hypothesis by any quantitative comparison between the magnitudes of the alleged pyroelectric effect of pressure and the piezoelectric effect despite his access to relevant data (pp. 293–9).[38]

In 1887 Duhem published a short account of his theory in the more widely distributed *Journal de physique théorique et appliquée*. Probably in response to

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[36] Duhem referred explicitly to symmetry as expected from an opponent of the molecular view. The idea that pressure diminishes the symmetry was probably inspired by Thomson's remarks in that direction in his 1854 paper on thermoelectricity (see above p. 86).

[37] Only briefly did Duhem discuss the converse piezoelectric effect for the case of the "natural" pyroelectric tourmaline, writing the pyroelectric equations that underlie the effect.

[38] Duhem referred to Riecke's paper in which the latter published absolute measurements of the pyroelectric effect in tourmaline (E. Riecke "Ueber die Pyroelectricität des Turmalins," *Ann. Phy.*, 28 (1886): 43–80). As mentioned in chapter 1 Measurements of tourmaline's piezoelectric coefficient were made already by the Curies.

objections, he added a mechanism that maintains the equilibrium, i.e., maintains perpetual temperature differences inside the crystal. He assumed that a small deviation from equilibrium induces a very weak electric current. The heat that the current produces according to the regular (Joule's) work is negligible, since it depends on its second order. However, the heat produced by thermoelectricity, which depends on the first order of the current, is significant. The thermoelectric work releases heat in the already warmer parts and absorbs heat from the colder ones. Therefore, it works against the heat transfer in keeping the temperature of the crystal constant with time.[39]

The mechanism that Duhem added was quite objectionable in itself and did not, of course, answer other objections. These were raised at the French society of physics in 1887. Pierre Curie, the co-discoverer of piezoelectricity, and a champion of a molecular-mechanistic model of the phenomena was among the critics. Curie objected that Duhem attributed a conductivity to the crystal, which does not exist in nature. He added that the electric phenomena produced by pyroelectricity in a connected circuit are fundamentally different from those of an electromotive force as assumed by Duhem. Duhem answered that Gaugain's and du Bois-Reymond's experiments showed that pyroelectricity produces phenomena like those of a battery with high electromotive force and high resistance. The two scientists did not agree on the meaning of the experimental data. For Curie, apparently, an electric source with high resistance (much higher than that of the circuit) was not a battery. Curie raised two more objections. First, the thermal effect of compression, suggested as an explanation by Duhem, is too small to explain the observed electric effect. Second, the electric effect of pressure is instantaneous, but that could not have been so according to Duhem's mechanism. Duhem did not answer the latter objections.[40] As mentioned, he himself did not examine the magnitudes of the assumed effects.

The discussion was not limited to active researchers in the field of piezo- and pyroelectricity. Aimé Vaschy, a young telegraph engineer, a lecturer at the *École supérieure de télégraphie* who discussed piezoelectricity,[41] raised another objection. He referred to the experimental finding that the electric effect is proportional to the difference between the crystal's initial temperature and its final temperature. This was accepted knowledge articulated by Gaugain, and repeated in an authoritative general book like that of Mallard,[42] two sources on which Duhem relied. Moreover, Vaschy added, after the crystal reaches a new uniform temperature it maintains its charge. Hence, he denied Duhem's claim that the effect depends on inner temperature difference. In his answer Duhem claimed that the charge is maintained only in crystals that are poor conductors. Yet, he did not answer the objection's first part, which reveals

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[39] P. Duhem, "sur une théorie des phénomènes pyro-électriques," *Journal de Physique Théorique et appliquée*, 6 (1887): 366–373. on p. 373.

[40] "Sur les phénomènes piézo-électriques" in *OPC*, pp. 33–34.

[41] Three years later he published a textbook on electricity and magnetism based on his lectures that discusses also piezoelectricity, Aimé Vaschy, *Traité d'électricité et de magnétisme*, 2 Volumes, Paris: Baudry et Cie, 1890.

[42] Mallard, *Traite de Cristallographie*, Vol. 2 p. 570.

a disagreement between the theory and the experimental data.[43] Obviously, Duhem's theory was not accepted by his colleagues.

Notwithstanding, Duhem himself did not see the strength of his theory in its agreement with the observations despite his attempt to show at least general accordance. His aim was to construct a unified thermodynamic scheme for three physical phenomena rather than to construct a theory that would give a detailed theoretical account for possible experiments, as Voigt's theory would do a few years later. In his 1887 paper, he summarized what he considered to be the merit of his theory:

> One sees that, according to this theory the piezoelectric phenomena are not other than pyroelectric phenomena in which the crystal plate is heated by compression; that the pyroelectric phenomena themselves are only thermoelectric phenomena produced in conductors in which the lack of homogeneity is due to their reticular structure; consequently, that if this theory is accurate, these three chapters of physics: thermoelectricity, pyroelectricity, and piezoelectricity are united in one [*se trouvent réunis en un seul*], which thermodynamics makes possible to discuss [*triter*] in a totally rational manner.[44]

Duhem was engaged in a program of embracing separate physical phenomena in a thermodynamic account. In this case this goal was attained by reducing piezoelectricity and pyroelectricity to thermoelectricity. Pierre Curie shared Duhem's reductionist notion that piezoelectricity and pyroelectricity should have a common origin, but found it in mechanical deformation.[45] Since Duhem explained both piezo- and pyroelectricity on a third phenomenon (thermoelectricity) and Curie on one (pressure) that is almost tantamount to stress in crystal, one can even regard Duhem as more reductionist than Curie. The different reductions of piezoelectricity that the physicists sought reveal opposing views of physics: thermodynamic of Duhem versus corpuscular-mechanistic of Curie. The debate between the two young physicists demonstrates the gap between these approaches. Yet, the discussion in the physical society was not on the proper way to explain physical theory in general, but on the explanation of piezo- and pyroelectricity. So it focused on the disagreement between Duhem's theory and the experiment. Curie's concern with the exact experimental results stands in contrast with Duhem's concern with general principles and "a totally rational manner." Apparently, at this stage Duhem was not willing to give up a nice theory only because of ugly experimental facts. Almost 15 years later Curie had similar objections to a disagreement between a theory of Duhem and the experiment, this time concerning the theory of magnetism, which was a main interest of Curie. Duhem's physics was no longer thermal reductionist, but a similar difference between him and Curie concerning the experiment still existed.[46] This difference might have been connected to the fact that Duhem was one of the first theoreticians who did not carry out

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[43] "Sur les phénomènes piézo-électriques" pp. 33–34.

[44] Duhem, "théorie des phénomènes pyro-électriques," p. 373.

[45] "Sur les phénomènes piézo-électriques" p. 33.

[46] On the disagreement concerning magnetism see Paul Brouzeng, "Magnétisme et énergétique. La méthode de Duhem. A propos d'une lettre inédite de Pierre Curie," *Revue d'historie des sciences* 36(1978): 333–344. Brouzeng claims that the letter mentioned in the title reveals "more than the opposition between two men, that between two approaches of scientific reality (sic): the one [Curie's] heir to the experimental and rational tradition of French science, the other more intent on submitting reality to the great principles of general thermodynamics (or energetics)" (from the abstract p. 333). I found

any experimental research, while Curie was always connected to the laboratory. Whatever its source, the difference in their concern for the experimental results put their theoretical approaches apart, perhaps more than their disagreement on molecularism. On the one hand, Duhem's ease with apparent experiential contradictions to his theories agrees with his skeptical philosophical view of the experiment and the dependence of its results on theoretical interpretation (although it clearly does not follow from that). On the other hand, Duhem who saw the aim of scientific theory in saving the phenomena, ironically, was less committed to these phenomena than a realist like Curie.

Stanley Jaki, Duhem's biographer, claimed that by the early 1890s his subject had "a clear notion of thermodynamics as distinct from its mechanical interpretation and also from its definition as a strictly separate branch of physics. Such a notion of thermodynamics did not have its foundation, and not even for its starting point, hypotheses about the structure of matter, but abstract and formalistic axioms analogous to the ones on which Lagrange based his purely analytical mechanics."[47] In his 1886 theory of pyro- and piezoelectric Duhem refrained from any assumption on the nature of matter. Yet, the theory was not free from hypothetical assumptions on the phenomena and their causes, as it explained the phenomena as **thermal** effects (i.e., based on heat). Then Duhem already had "a notion of thermodynamics as distinct from its mechanical interpretation," yet this theory suggests that he did not have a clear notion of it "as distinct from its definition as a strictly separate branch of physics." His attempt at a causal nonmechanical mechanism shows that at an early stage Duhem tried to replace mechanical reduction by thermal reduction, substituting one speculation by another.

This conclusion contradicts Jaki's claim that by 1885 "long before Duhem articulated at length in a classic monograph the features of an ideal physical theory, based on thermodynamics and free of any speculation about the "nature" of things and their interaction, he was most consciously committed to the ideal."[48] This suggests that at that period Duhem had not developed his later philosophical position according to which physical theory should not aim at explaining nature but only at describing the observed phenomena. Clearly, he did not follow such a rule. From an early date Duhem was antiatomist, but like other supporters of that stand, that did not entail antirealism or positivism.[49] The first stand is independent of the latter.

By 1892, however, Duhem had changed his view on pyro- and piezoelectricity and his philosophical position. In a series of articles written between 1892 and 1894 he expressed his "mature" epistemological theses, on which he based his position on the aim of theory.[50] In the same year he published a new theory of pyro- and piezoelectricity after he had realized that the older "theory, as Lorberg remarked to us, is completely

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Brouzeng's picture too dichotomous, but I agree that one can see here two different approaches, even if they do not completely contradict each other.

[47] Jaki, *Uneasy Genius*, p. 269.

[48] *Ibid.*, pp. 47–48. As much as I found this claim has not been contested by others, e.g. Maiocchi, who studied the development of Duhem's thought, Roberto Maiocchi, "Pierre Duhem's The aim and structure of physical theory: a book against conventionalism," *Synthese, 83* (1990), 385–400.

[49] Ostwald is a good example for a scientist who rejected atomism but admitted other theoretical assumption.

[50] Maiocchi, *ibid.*

erroneous."[51] His new theory did not include such hypotheses. As before, the theory was based on a thermodynamic potential, but this time on general thermodynamics without any reductive hypotheses. Apparently, he no longer identified himself with the thermal reduction suggested in his earlier theory. General thermodynamics was an appropriate method for his later physics, which avoids hypotheses about real causes and unobserved processes. The theory based on it fitted the empirical findings better.[52] As a descriptive theory Duhem's 1892 account will be treated in the following chapter. Interestingly, in the same years Georg Helm, another prominent representative of the energetic school, followed a similar path from a mechanical view through a flirt with thermal/energetic reductionism to champion a physics based on the energy concept and free of speculation.[53]

Duhem had clear and specific physical reasons to abandon his earlier theory. Its failure was also a failure of his attempt to reduce static and nonthermal effects to the dynamic process of heat transfer. I suggest that this failure contributed to his rejection of a causal explanation in favor of a nonhypothetical energetic view that looks for formal, rather than reductive, unification of science. If that were so, it could not have failed to stimulate his philosophical reflection on physics. The temporal coincidence of the change in the piezoelectric theory and the writing on philosophy supports the assumption of such an influence.

MOLECULAR THEORIES

Riecke's molecular theory of pyroelectricity

If pyroelectricity was, as Duhem claimed, a phenomenon of inner temperature differences, the electric polarity of the crystal would not last long after

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[51] Duhem, *Leçons sur l'électricité et le magnétisme*, Vol. 2. p. 391. Hermann Lorberg (1831–1906) was at the 1880s a high school teacher in Strasbourg, which was annexed by Germany in 1871 (J. C. Poggendorff *biographisch-literarisches Handwörterbuch*, Volume IV, Ann Arbor, Mich. : J. W. Edwards, 1945). In 1888 he published an examination of thermoelectric theories, which showed high esteem for Duhem's theory, with a kin interest in the general thermodynamic approach (H. Lorberg "Zur Theorie die Thermoströme," *Ann. Phy.*, 34 (1888): 662–672, 736). Lorberg probably communicated his objections to Duhem privately. Apparently, Duhem found it easier to accept the criticism when it arrived from a physicist who shared his general approach to physics, like Lorberg, than from supporters of molecularism, regardless that the former was a German that worked at occupied Strasbourg (In 1889 Lorberg moved to Bonn where he received a professorship) and the latter his compatriots. Thus even for a very patriotic (arguably a chauvinist) physicist like Duhem the approach a scientist took toward his study was more important than his national identity.

[52] In a later report on his physics Duhem wrote about his 1885 thermodynamic theory of thermoelectricity with no mention of the problematic theory of pyro- and piezoelectricity developed with it, Duhem, *Notice sur travaux scientifiques* p. 88.

[53] In 1881 Helm clearly held a mechanical view. In his 1887 book he once wrote that "energy is the true substance of the world," but was in general ambiguous about its real existence and meaning. In 1898 he explicitly rejected reduction to either matter or energy. Robert J. Deltete, "Die Lehre von der Energie: Georg Helm's Energetic Manifesto," *Centaurus* 47(2005): 140–162. I thank Robert Deltete for turning my attention to Helm's case.

heating/cooling ceased, since heat conductivity would lead to uniform temperature (Duhem's mechanism for the maintenance of inner temperature differences is unlikely to compensate the whole effect for a long time). However, examining six different tourmaline species from various places, Eduard Riecke, the Göttingen professor for experimental physics, showed in 1887 that the crystal maintains permanent electricity up to 24 hours after it was cooled.[54] Regarding the various ways in which charge could leak from the tourmaline's surface, the results indicated that the phenomena involved permanent electric polarization, as suggested by Thomson's hypothesis.

In order to minimize the electric leakage from the tourmaline, Riecke had to construct a delicate experimental apparatus. After heating the specimens, he cooled them by dry air inside a receiver of an air-pump. The crystal was hung by silk threads that kept it electrically isolated. Inside the receiver a gold electroscope, placed in such a way that it would not influence the tourmaline, deviated due to the electric charge of the specimen. Through a special glass window, Riecke observed the electroscope's pointer with a telescope. Air was pumped out of the receiver after the first observation, assuring low conductivity of the surroundings. The results showed a very slow decrease in the electric tension (pp. 890–902).

Clearly, this experiment was designed to demonstrate that "tourmaline is a permanent electric body, whose principal electric moment falls in the direction of its axis" (pp. 889–90). Riecke used the demonstration of permanent electric polarization to support an explanation of pyroelectricity, based on Thomson's hypothesis of inner polarization. Like the Curies and Friedel, Riecke explained the permanent polarization on a molecular assumption. Already in 1885 in his first paper on pyroelectricity, he assumed that "the molecules of tourmaline have a permanent polarity in the direction of their axes," responsible for the bulk electric activity of the crystal (p. 889). Since 1874, two years after earning his doctoral degree, Riecke had employed hypotheses of charged molecules in explaining electric phenomena of bulk matter. A treatment of pyroelectricity from molecular perspective seems a natural continuation to his previous molecular studies of electricity in dielectrics and of electrification by friction.[55]

Riecke differentiated between two kinds of pyroelectric researches. One kind explores the connection between the crystallographical structure and the distribution of charge on the crystal's surface; another examines the development of electricity with the crystal's temperature. Recent research focused on the former, while the latter was neglected, Riecke claimed. The interest of the 1880s in the connections between pyroelectricity and piezoelectricity only reinforced the emphasis on the former. Yet this interest put pyroelectricity on the scientific agenda, and also encouraged research on the development of electricity in crystals. Riecke stated three aims to his experimental research in 1885: (a) examining the development of charge over time during heating, (b) verifying Gaugain's law that the development of charge depends only on the temperature difference, and (c) determining the absolute magnitude of the charge

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[54] E. Riecke, "Zwei Fundamentalversuche zur Lehre von der Pyroëlectricität," *Ann. Phy.*, 31 (1887): 889–912. Page numbers in parentheses in this section refer to this paper.

[55] E. Wiechert, "Eduard Riecke," *Göttingen Nachrichten*, 1916: 45–56, on p. 48.

created. The first examination combined experiment and theoretical reasoning in a way that illuminates the explanation of the phenomenon, and will therefore be dealt with here.[56]

Riecke assumed that polar molecules arranged along tourmaline's axis are responsible for the external electric moment of the crystal. Each element volume of the crystal possesses an electric moment. The change of temperature varies the value of the electric moment directly and by change of the material density (the number of molecules in the element) due to thermal expansion. The change of temperature is a process that takes finite time. While Duhem assumed that the temperature of tourmaline is steady but nonuniform, Riecke assumed that it is uniform but variable over time. Both assumptions are problematic. Riecke admitted that the temperature was not strictly uniform but he assumed that the results of cooling with small temperature differences (as done in his experiments) are approximately the same as that of the uniform temperature assumed by the theory. Expressing his assumptions mathematically, Riecke derived an expression for the free electric charge density η in terms of the maximal free charge density H:[57]

$$\eta = H\frac{qe^{-az} - ae^{-qz}}{q - a} \tag{2}$$

where z is the time, a the Newtonian cooling coefficient and q the electric conductivity. When he compared this equation with the experimental results, he found good agreement for two of the three examined tourmaline specimens. The results for the third specimen from Brazil did not coincide with the equation. Riecke explained the disagreement by variations in the crystal's electric conductivity with the temperature, which are not accounted for by his theory. He, therefore, regarded the experiments as a support to his molecular hypothesis.[58]

A way out of the problem raised by the changing electrical conductivity was to minimize its effect. This was the motivation for a second experimental design, reported in the aforementioned 1887 paper. A simple way to eliminate the effect of conductivity was to discharge the tourmaline bar. Without, or with a small, free charge the effect of conductivity is negligible. Yet, the implementation of this simple idea in a meaningful experiment required skill and ingenuity. Riecke performed this experiment by cooling tourmaline to room temperature. He connected the negative electric end (that which is known to become negative in cooling) of a tourmaline to an electroscope's aluminum leaf and the positive end to the earth. The aluminum leaf was put between a positive and a negative electrode. Once its charge reached a certain amount (about 5% of the maximal charge) it struck the electrode with the opposite charge, and was neutralized.

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[56] E. Riecke "Ueber die Pyroelectricität des Turmalins," first read before the Göttingen society for science in 1885 (in either August or December).

[57] *Ibid.*, 70–73. The symbols in the equation follow Riecke's later symbols from 1887. For more details see Katzir, *History of Piezoelectricity*, pp. 110.

[58] *Ibid.*, 74–78. Riecke discussed the conductivity of the various species of tourmaline in detail, referring also to experimental findings on their behaviour in different surroundings (*Ibid.*, 46–48). This discussion is an example of the way in which he considered various difficulties in his experimental devices, and the limitations of his results.

In the experiments it struck only the positive electrode, showing, in accordance with the theory, that the same kind of charge is continually developed. The number of strikes was proportional to the total charge density developed by the pyroelectric effect. Riecke recorded the exact time of each strike, obtaining thus the time it took the charge to develop. He compared these results with a simpler version of equation (2) for the development of electricity: $\eta = H(1 - e^{az})$, which neglects electric conductivity. Now he found agreement with the experimental results for all tourmaline species including those from Brazil (pp. 902–10).

Since Riecke derived his equation for the development of electricity from a molecular assumption, he saw in its confirmation a corroboration of his hypothesis of polar molecules. Thus, his interest in the development of the charge in time was at least partly due to his concern regarding the nature of pyroelectricity. This series of experiments as well as the demonstration of the persistence of the electric charge, he claimed, "shows that tourmaline seems like a solid body whose molecules have a permanent polarization in the direction of the axis." He added that "one is inclined to apply, therefore to accept" the same general picture also for the other pyroelectric crystals, although the picture might be more complicated, involving multipoles. This molecular polarization, he claimed, influences other physical properties of the crystals like their elastic coefficients (pp. 911–2).

An adherent of molecularism, Riecke himself was inclined to accept a corpuscular picture of physics and electromagnetism in general, and of pyroelectricity in particular. He was a student of Wilhelm Weber, and succeeded him at his prestigious post in Göttingen in 1881. Weber, a leading adherent of corpuscular charges in electromagnetic theories, was the major influence on Riecke's physics. Though Riecke adopted newer treatments of electrodynamics, he remained an active supporter of the hypothesis of a corpuscular carrier of discrete charge.[59] However, a closer look at Riecke's evidence reveals that his claim for the molecular assumption was far from compelling.

Riecke's demonstration of the persistence of electric charge on tourmaline clearly supported the assumption that the crystal has permanent polarization. However, the assumption was first suggested by Thomson independently of a molecular hypothesis. Permanent polarization in pyroelectric crystal is also a result of Voigt's 1890 macroscopical theory. So this result cannot be regarded as an evidence for the molecular structure. Riecke's second evidence is no more compelling. The derivation of equation (2) for the development of charge is actually independent of the molecular hypothesis. He used the hypothesis only to justify the assumption that every element of volume has a permanent electric polarization that depends on the temperature directly and indirectly through the change of material density.[60] However, these assumptions do not entail a molecular structure. An assumption of an inhomogeneous matter is enough. Such an assumption agrees, for example, with the Maxwellian approach. Thus, Riecke showed only the possibility of a molecular theory of pyroelectricity.

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[59] Stanley Goldberg, "Riecke, Eduard" *DSB* Vol. 11: 445–447. Voigt, "Eduard Riecke als Physiker," *Physikalische Zeitschrift,* 16 (1915): 219–221.

[60] Riecke, "Ueber die Pyroelectricität," p. 70.

Riecke's elaborated molecular explanation for piezoelectricity

After 1890, Riecke's model was insufficient. The field of pyro- and piezoelectricity had been profoundly changed since 1885. Röntgen's 1889 experiment showed the limitations of the early molecular explanations of piezoelectricity. Still, the theoretical development was more significant. Voigt's general theory gave the first comprehensive account of the phenomena. Now a molecular theory was expected to account not only for the experimental facts, but also for the equations of the phenomenological theory. As a close colleague of Voigt in Göttingen, surely Riecke could not ignore his theory. He accepted Voigt's account but searched for a more fundamental level that would explain the continuum theory. "It is not without interest," he wrote, "to ask further, how a simple elastic or thermal displacement of the molecules can give rise to the creation of electric moments, or electric displacements."[61] His theory would thus demonstrate the possibility of a mechanical-molecular explanation, but not the truth of his particular suggestion. In 1885 he had already assumed that part of the pyroelectric effect is due to a mechanical process (through changes in the density of the ponderable matter), in the new theory he assumed that the whole effect is due to local motions. Like Voigt, he assumed that pyroelectricity was a secondary phenomenon of piezoelectricity.

Riecke sought a model that would account for the known phenomena. He thought that by a model "any relation taking place between the real bodies [has] a particular mechanical connection, each change in the world of bodies corresponds to a particular alteration in the model." The model should be a copy of the world of phenomena; it is not "only a means of representation, [but] a main connecting thread [*Leitfaden*] to new experiments, to the discovery of new phenomena." Thus, the model is an essential tool for physics. A model can be correct when it represents the phenomena accurately. By leading to novel discoveries it can also show the truth of its basic hypotheses, in this case the molecular one.[62]

The theory that he presented in 1891, and in more detail a year later, aimed at deriving the piezoelectric equations of Voigt's theory from molecular displacements inside the crystal. By molecule Riecke understood not the elementary building blocks of nature, but rather combinations of atoms that determined their behavior. He did not think that phenomena should always be reduced to the most fundamental level. A reduction to a simpler level or even to simpler assumptions was for him the common, irreproachable practice of physics.[63]

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[61] Eduard Riecke, "Zur Moleculartheorie der piëzoëlectrischen und pyroëlectrischen Erscheinungen," *Göttingen Nachrichten*, 1891: 191–202, the quotation from p. 193. *id.*, "Molekulartheorie der piëzoelektrischen und pyroelektrischen Erscheinungen," *Göttingen Abhandlungen*, 28 (1892) 1–52. The later presentation is a detailed explication of the former with few elaborations and generalizations and with minor alternations (like those between the titles). The differences do not reveal almost any interesting development in Riecke's thinking. Therefore, I will refer below to the later more elaborated presentation. References in parentheses in this section refer to this later publication.

[62] Eduard Riecke, *Lehrbuch der Physik*, dritte Auflage, Leipzig: Veit & Comp., 1905, p. 4.

[63] Riecke, "Thermodynamik des Turmalins" p. 32.

In order that a simple displacement of molecules could elucidate the phenomena described in the phenomenological theory, the distribution of electricity in the molecules had to be more complex than previously assumed. Riecke assumed molecules following a general crystallographic structure. Yet the structure he suggested for them did not coincide with any particular crystallographic theory. He supposed that the central points of the molecules form a lattice (*Raumgitter*). Each crystal system is characterized by its own polyhedral lattice of the system's symmetry (the symmetry of individual classes could be lower). Riecke further assumed that "each molecule is surrounded by a system of electric poles; its arrangement has the symmetric relation of the specific class, to which the crystal under consideration belongs. The system is connected to the molecule in such a way that its planes and axes of symmetry coincide with the corresponding elements of symmetry of the lattice." (see Figures 3.2 and 3.3). His discussion in the following shows that the center of the polar system always coincides with the center of the molecules. Moreover, while the distances between the molecules vary, the distances within the polar systems are fixed. Consequently, the molecule has a fixed polarity.

Changes in the polarity of the crystal arose only through changes in the relative position of the molecules. This is consistent with the question he posed: how can molecular displacement cause the creation of an electric moment? Thus, he implicitly identified the polar system with the molecule and the poles as atoms or groups of atoms.[64] These molecules are not necessarily identical to the chemical molecules. By assuming that only the inter-molecular distances are changed, Riecke's theory presumed a different binding inside the molecules (or the polar systems) from that between them. This is a model of crystals based on separate distinctive molecules. These molecules possess specific polarity in accordance with the symmetry of the crystal. In contrast to his early pyroelectric theory, this theory assumed a **specific** molecular structure of crystals.

In 1915, Voigt would observe that the latest X-ray observations on the structure of crystals indicated that a molecular explanation of piezoelectricity should be sought in another direction.[65] However, in 1892 Riecke justly stated that his picture of crystals agrees with accepted crystallographic and physical theories of crystalline structure. In particular, he mentioned Arthur Schoenflies, who published his comprehensive and innovative mathematical theory of crystallographical point-groups (the vertices of the lattice) in 1891 (p. 5). Riecke had a chance to learn Schoenflies's theory directly from its author, who was a lecturer at the mathematical department in Göttingen. Schoenflies himself refrained from any hypothesis on what occupies the vertices of the lattice. In this sense Riecke's picture resembles more Bravais's theory of 1866 that locates the vertices of the lattice at the centers of gravity of molecular polyhedra. Yet Riecke assumed a simpler model in which the polar systems are two dimensional or rest in two parallel planes, while Bravais assumed three-dimensional molecules.

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[64] Riecke, "Molekulartheorie," *passim*. See for example his discussion in pp. 11–12 of the axial and the trigonal systems of poles and his reference to "molecules **with** uniaxial/trigonal etc. system of poles" pp. 33, 37, 39, 41. See also the description of his theory below.

[65] W. Voigt, "Eduard Riecke," p. 220.

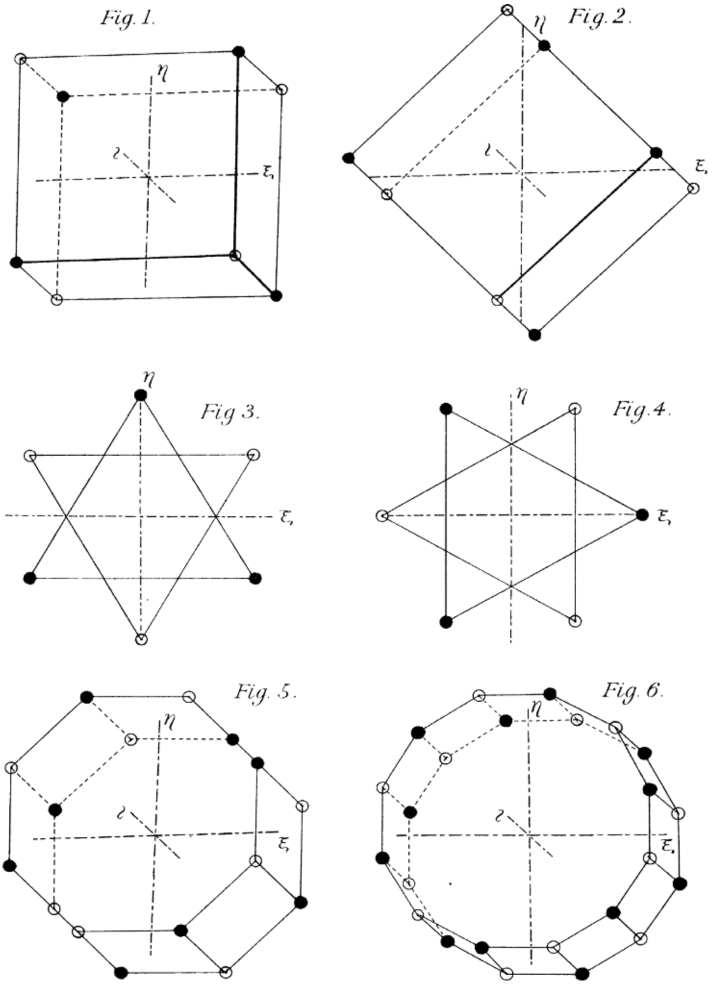

Figure 3.2: Individual molecules (poles-systems) according to Riecke's theory. Small, full and empty circles represent positive and negative poles. Figures 1, 2, 5, 6 are projections of three-dimensional molecules; the poles in 3 and 4 lay in the plane of the paper. Figures 1 and 2 show two cases of tetrahedral poles-system, figures 3 and 4 two of trigonal (the first of them is of tourmaline) and figures 5 and 6 two cases of dihexagonal (from Riecke, "Molekulartheorie").

Unlike the situation in 1915, in the 1890s the arrangement of "the chemical atoms or molecules . . . within the unit cells formed by the space lattice remained a matter of speculation."[66] Riecke could thus suggest a model for crystals of separate molecules.

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[66] John G. Burke, *Origins of the Science of Crystals*, University of California Press: Berkeley and Los Angeles, 1966, p. 171. On Crystallography in the second half of the nineteenth century see also Auguste Bravais, "Etudes cristallographiques," *Journal de l'école Polytechnique,* 20 (1851): 101–278; Arthur Birembaut, "Bravias, Auguste," *DSB* Vol. 2: 430–432; Marjorie Senechal, "Brief History of Geometrical

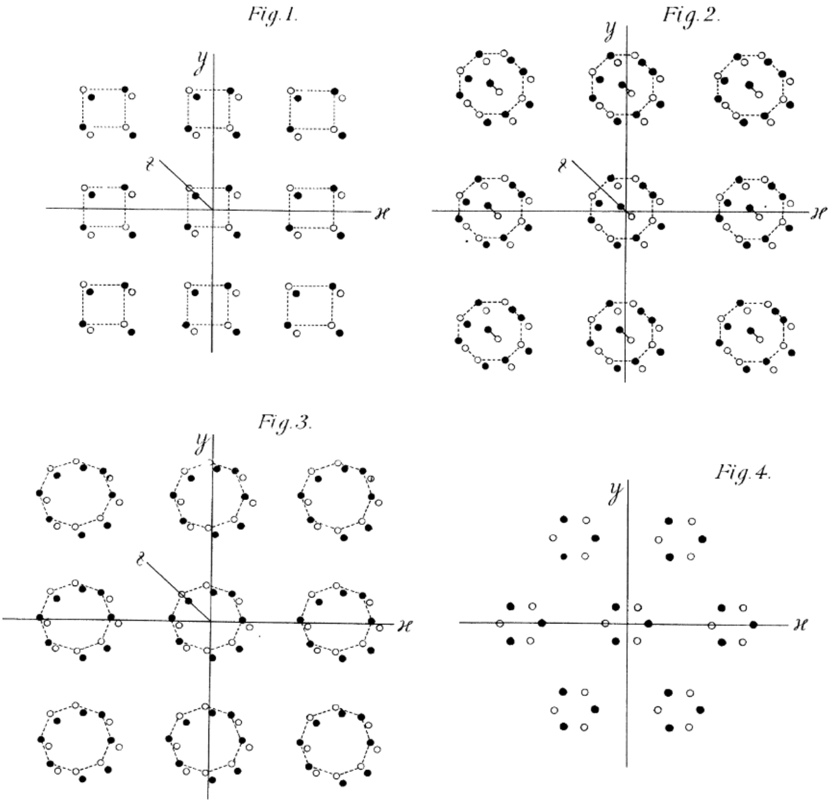

Figure 3.3: Systems of molecules according to Riecke's theory. Figures 1, 2, 3 are projections of two layers on the plane of the paper. They show different classes of the quadratic system each based on another poles-system (molecule). In figure 4, which shows a class of hexagonal system, all poles are in the plane of the paper (from Riecke, "Molekulartheorie").

Although crystals were known to possess strong connections between their molecules, one could only speculate whether these connections were stronger or weaker than those within the molecules. Riecke's model enabled him to attain his aim of finding a way in which "a simple elastic or thermal displacement of the molecules cause the creation of electric moments." He claimed neither that his is the only possible model nor that it is based on the true hidden inner structure of crystals. Indeed, as will be shown below, another basis for molecular theory of piezoelectricity was suggested a little later.

First let me describe Riecke's theory in more detail. Since according to the theory all molecules are polarized, they constantly exert electric force on one another. A

Crystallography," in *Historical Atlas of Crystallography*, edited by J. Lima-de-Faria, Kluwer Academic Publisher: Dordrecht, 1990, pp. 43–59; Paul Forman, "The Discovery of the diffraction of X-Rays by Crystals; A critique of Myths," *AHES* 6 (1969): 38–71; P.P. Ewald, "The Myth of Myths; Comments on P. Forman's paper on 'The Discovery of the diffraction of X-Rays by Crystals," *Ibid.*:72–83, which discusses also Schoenflies's attitude towards molecular explanation.

permanent electric field and polarization, the resultants of all these forces, exist in all piezoelectric crystals and not only in pyroelectrics. As assumed by Thomson, superficial charge balances this polarization. According to Riecke's theory, the piezoelectric effect derives from the sum of all the changes in the fields of the molecules, caused by relative displacements between them. To find this magnitude, Riecke studied the electric field exercised by each kind of polar molecule, the field due to a system of all these molecules, the changes in the electric field due to translation and rotation of the molecules in general, and for the particular polar system assumed. From these expressions he obtained equations for the electric effect of pressure in the five polar systems that he assumed as functions of the locations of the molecules, a constant (whose value varies from crystal to crystal), and strains. For example, for the "total electric force" due to strain in the x direction Ξ in the second principal case of the trigonal polar systems he obtained:

$$\Xi = 2E \sum \left[6\frac{x_1^2}{r_1^7} - 28\frac{x_1^4}{r_1^9} + 63\frac{x_1^6 - 3x_1^4 y_1^2}{r_1^{11}} \right] a_{12} \tag{3}$$

where the sum is on all the molecules 1 to n, E is a constant of the particular molecule (multipole), r the distance and a_{12} the component of strain. In this analysis Riecke employed mathematical considerations of symmetry according to the structure of the lattice. Thus, he applied macroscopical considerations in a discussion of hidden microscopical fields. He justified their application on the basis of the negligible number of molecules at the surfaces of the crystal and on the short range that characterizes the electric fields inside the crystals.[67]

Since each class is characterized by its symmetry, for each he had only to apply the equations of the relevant polar system or to combine the equations for the relevant polar systems to gain the equations for electric polarization due to elastic strain. Since the piezoelectric coefficients of Voigt's general theory are, by definition, the coefficients of the strains in these equations, Riecke could identify them with the expressions that multiply the strains.[68] Thus, he found which coefficients differed from zero and which have the same value for each crystal class. His findings agreed with Voigt's. Hence, he deduced the equations of the general theory for all classes from molecular assumptions. Yet, in applying considerations of symmetry, his derivation followed Voigt.

Although the expressions for the coefficients in the molecular theory contained many unknowns (through the constant that depends on the magnitude of the electric poles, the size of the molecules, their density and distances), in one case they supplied a basis for quantitative comparison between different coefficients of the same crystal. The phenomenological theory provided no guidance in this question. For the class

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[67] Riecke, "Molekulartheorie," pp. 6–43. For a more detailed discussion of the theory see Katzir, *A History of Piezoelectricity*, pp. 116–118.

[68] Since the polarization **P** is proportional to the electric field **E** (neglecting possible variations due to possible changes in the electric susceptibility with the direction) and since Riecke has a constant in his equations that can contain also the dielectric susceptibility, the same equations hold for the electric field and for the polarization (with another value for the coefficient).

of tourmaline, which combines "trigonal polar system of the second situation" with "uniaxial polar system," Riecke obtained the value of the coefficient ε_{22} from the term that multiplies a_{12} in equation (3). The equations for the uniaxial polar system supplied expressions for three other coefficients ε_{15}, ε_{31}, and ε_{33}. Thus, he found expressions for the piezoelectric coefficients based on apparently more fundamental variables. Moreover, Riecke pointed out an agreement between the order of magnitude of the coefficients of tourmaline and their dependence on the power of the distance r. He explained that "the constant ε_{22} is relatively small [0.49, in comparison with –3, –7.28 and –9.35 of the three others, all in units of 10^{-4}] because of its dependence on a polar system of a higher order, whose potential is given by a spherical function of the -4^{th} order. Against that the constants ε_{15}, ε_{31}, and ε_{33} depend on a uniaxial system whose potential is of the -2^{nd} order." (p. 50). While the former coefficient depends on the seventh order of r, the last depends on the fifth (pp. 43–52).

It appears that by explaining relative magnitudes of piezoelectric coefficients in the same crystal, Riecke's theory succeeded in accounting for phenomena beyond those assumed in its formulation, in a manner similar to the prediction of an unobserved phenomenon.[69] Elsewhere, Riecke claimed that "[t]he discovery of new phenomena on the basis of such a forecast [by a theoretical model] forms the true touchstone for the correctness of the underlying hypotheses, [and] for the usefulness of the models constructed with their help."[70] Riecke did not elaborate on the significance of the explanation of the relative magnitudes of the piezoelectric coefficients. He did not refer to any species but tourmaline in this context, despite the availability of relevant data for quartz, through Riecke's own experiment in collaboration with Voigt.[71] In fact, the theoretical argument that works for tourmaline fails for quartz. No relation exists between the order of the spherical function and the magnitudes of quartz coefficients.[72] This failure does not refute the argument. Since the magnitudes of the coefficients depend not only on the spherical function of the potential, and also on unknown characteristics of the polar system. The expressions for the coefficients of tourmaline involve similar complications. Riecke's success with tourmaline was coincidental and not a demonstration of the theory's general explanatory power beyond the reach of the phenomenological account.

Riecke's alleged explanation of the coefficients' relative magnitudes was not even mentioned, let alone discussed or criticized, in publications of his contemporaries, nor did he mention it in later publications. Describing his theory again in 1905 and 1912, he

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[69] In both cases the theory predicts unintended results that are found (by new or old experiment) to be true. In both cases the theory is formulated before the particular prediction, and is not modified in accordance with the observation.

[70] Riecke, *Lehrbuch der Physik*, p. 4.

[71] On these experiment see chapter 5.

[72] According to Riecke, quartz combines a trigonal polar system with a dihexagonal polar system. The coefficient (ε_{11}), due to the trigonal polar system, is given by a spherical function of the order of −4, while the other coefficient (ε_{14}), due to the dihexagonal system, is given by a function of the order of –8. Yet the former is only about five times larger than the latter. About the coefficients of quartz see p. 51 (17. Trapezoëdrische Gruppe), for their expressions p. 49 (Gruppe 12, 13), for the expression of the parameters used there pp. 15, 19, and for the development of the potential functions for both polar systems pp. 12–21.

did not refer to his previous argument even when discussing the exact expressions for the piezoelectric coefficients of tourmaline.[73] In 1910 Voigt claimed that no molecular theory had yet predicted "specific results, such as numeric relations between the parameters" of the basic piezoelectric equations.[74] Since Voigt knew Riecke's theory well, he apparently did not accept Riecke's argument. The daily working connections between the two and the fact that Riecke did not repeat his claim suggest that Voigt may have expressed the objections to him privately.[75]

The comparison between the piezoelectric coefficients of the same crystal also raises a conceptual difficulty in Riecke's theory: How does the same crystal have two different systems of poles? Riecke does not refer to this question. Since the poles' systems are flat or almost flat (a compound of two parallel planes), it seems that Riecke thought of different systems in perpendicular planes. However, this invites more questions, like how do they match together? Clearly, more conceptual work could be done on that. Apparently, Riecke was not too concerned about the issue; he was satisfied in showing that such a molecular arrangement could account for the known equations. In doing that, he relied at the end on the same tools used by Voigt—the symmetrical properties of the crystal (though he used them in a less general and abstract manner). His combination of various symmetrical properties of each class in finding its coefficient is close to the method used by Voigt in deriving the same results in the continuum theory.[76] It is not surprising that the molecular structure started to blur when Riecke combined different symmetrical properties that had separate structural manifestations in the molecular structure he had suggested. Yet Riecke himself was content with the theory; he continued to present it and regarded it as a certain conclusion for his work on the subject.[77]

Voigt's elaboration

Perhaps the conceptual gaps in Riecke's polar systems motivated Woldemar Voigt to suggest a generalization of the theory in 1893. He adopted the premises of

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[73] Riecke, *Lehrbuch der Physik*, pp. 145–155; *id.*, "Zur Molekularen Theorie der Piezoelektrizität des Turmalins," *Physikalische Zeitschrift*, 13 (1912): 409–415, the expressions on p. 411. *id.,* "Pyroelektrizität und Piezoelektrizität," in L. Graetz (editor) *Handbuch der Elektrizität und des Magnetismus*, Leipzig: Johann Ambrosius Barth, 1912, Vol. 1 pp. 342–420. In this detailed paper Riecke describes his molecular theory at length (pp. 375–398).

[74] Voigt, *Lehrbuch der Kristallphysik*, p. 846–7.

[75] In the first shorter communication on his molecular theory, Riecke did not mention the argument on the relative magnitudes of the coefficients (he did not write the expressions for tourmaline coefficients there). He probably thought about it only later after writing explicitly the expressions for the coefficients. This supports the assumption that Voigt corrected him privately, only after the publication of the argument in 1892. Since he had a general objection to the way Riecke built the polar systems, Voigt was probably satisfied in elaborating publically on this aspect (as he did in 1893) without mentioning problems with the consequences Riecke drew from his theory.

[76] Riecke's treatment of the molecule as a dielectric body with specific polarization is another example of applying macrophysical concept to the microphysical domain (Riecke, "Molekulartheorie," p. 6). These examples illustrate the mixture of macro- and microphysical considerations in Riecke's thinking, but also in that of other physicists at the time.

[77] Riecke, "Thermodynamik des Turmalins," p. 19. And the publications mentioned in footnote 73.

unchangeable molecules whose centers coincide with centers of multipoles that occupy the lattice points. But he went beyond Riecke in allowing the symmetry of the pole system to be higher than that of the crystal. Whereas Riecke considered only five particular and relatively simple systems of poles, which have the same order of symmetry as the crystal, Voigt studied an arbitrary system of 2^n poles. Therefore, his strategy differed considerably from Riecke's. Rather than studying the electric potential and fields of each system of poles, Voigt examined the consequences of various symmetrical conditions on the general equation of the induced electric fields of arbitrary multipole due to translation and rotation of the molecules in a crystal. From these general considerations he found the relevant piezoelectric coefficients according to the symmetry of the crystal. Only then did he show which polar system fits which class of crystals. Thus, instead of deriving the behavior of the crystal from its hypothetical structure, as Riecke tried to, he derived a possible structure of the crystal from its behavior.[78]

Voigt expressed the electric field induced by translation and rotation of the molecules in terms of strains and spatial derivations of the original electric potential similarly to Riecke. In addition to those contributions that were treated by Riecke, he considered the contribution of the molecule's own electric field on the induced field at its center. Yet this contribution does not change the number of nonvanishing piezoelectric coefficients. Next, he applied symmetrical conditions directly to the potential's spatial derivations, finding the equations for the induced field in each case of symmetry. His method was similar to the one he used in elaborating the general theory three years earlier. The electric moment (or polarization) is the sum of the induced fields from translation, rotation, and self-rotation, multiplied by a tensorial dielectric constant, whose number of independent variables can be reduced by considerations of symmetry. The expressions for the electric moments show the strains that induce electric field. Voigt compared these to the piezoelectric relations of the same orders of symmetry, showing that each piezoelectric constant can be expressed by a potential function, dielectric coefficients, and coefficients that depend on molecular rotation (pp. 651–8).

Next, Voigt turned to match a potential function to each class of crystals according to its symmetry. From the potential function he deduced the number of poles in each class. He assumed a general form of a potential function of a binary multipole (having 2^n poles):

$$P = \chi \frac{\partial^{\nu}(1/r)}{\partial a^{\alpha} \partial b^{\beta} \partial c^{\gamma} \dots} \tag{4}$$

where $\nu = \alpha + \beta + \gamma$, ν is the order of the pole, P is the potential, χ a coefficient, a, b, c etc. are directions of the dipoles, r is the distance, where $1/r$ is the potential of a free charge. Voigt's restriction to potentials of binary multipole is convenient mathematically. One does not have a general expression for multipoles of other terms. Yet, it excluded likely polar systems including three out of the five that Riecke had suggested (pp. 658–9). The multipoles that Voigt found for the various crystal classes

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[78] W. Voigt, "Beiträge zur molekularen Theorie der Piëzoelectricität," *Göttingen Nachrichten*, 1893: 649–671, especially pp. 649–651. Page numbers in parentheses in this section refer to this paper.

were physically less plausible than those that he rejected. Moreover, both he and Riecke assumed that the charge on all the poles is equal. Yet, if one identifies the poles with the atoms, chemical considerations suggested that in some cases, especially when dealing with complicated molecules, the charges on different atoms should not be equal.

In Voigt's hands the general mathematical expression for the potential became a powerful tool for finding the polar system of each class of crystals. He studied the relations between the order of the potential and its differential form, and the symmetric properties of the potential function. The potential function of each crystal class should be of the same symmetry as the crystal in the same axes. The polar system, however, can have higher symmetry. For example even crystals without any symmetry have potential function from the third order (i.e., one differential in each direction), so they have a polar system with $2^3 = 8$ poles. In general each of his polar systems has 2^{3+n} poles, where n is the crystal's order of symmetry. The number of poles in these systems can be smaller in some cases,[79] but in most cases it reaches this limit. Voigt's polar systems ran from 8 to 8192 poles. These numbers are too high for geometrical visualization. They made any identification of the poles with the chemical atoms implausible (pp. 659–68). Although too complex for a geometrical picture and unlikely for physical, Voigt's theory was mathematically simpler than Riecke's, and it had the advantages of ascribing only one polar system to every crystal.

Voigt's alternative

Voigt himself did not regard this model as physically plausible.

> Another way of interpreting the piezoelectric phenomena seems to me to have the advantage of greater simplicity over Riecke's in many respects. Mr. Riecke represented molecules as dielectric polarized bodies, around which an invariable system of electric poles forms a group; on the other hand, I consider molecules that cannot be dielectrically polarized, but which contain poles, attached to individual atoms, that are *movable in respect to each other*. The phenomena in electric fields, like [those] effected by deformations, are then only a result and an expression of inner molecular rearrangements (p. 669, emphasis in the original).

In contrast to Riecke's theory, Voigt's sketchy suggestion assumes no permanent electric polarization in crystals that are not electrified by uniform pressure (like quartz). A change in the locations of atoms in the molecule can create an electric field where it did not exist before. The dismissal of permanent polarization left the molecular hypothesis in better agreement with the experimentally verified phenomenological theory. Moreover, Riecke's theory required the assumption of strong internal polarization (much stronger than that observed for piezo- and pyroelectricity), while no such assumption is needed in Voigt's model. A few years later Voigt remarked that this assumption of "exorbitant large permanent specific moments [polarization]" adds theoretical complications that have no justification in the observations, and it is

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[79] This enabled the existence of systems of unique non-binary multipoles - those that have a potential as that of a binary multipole.

"unpleasant."[80] Furthermore, Voigt noted that his hypothesis would allow construction of a theory that would account for the symmetry of the crystal from the geometry of the atoms, without a need to use the potential function. The symmetry of the atoms in the molecules would be similar to that of the crystal as a whole and not much higher, as in his elaboration on Riecke's model (pp. 669–71).

Unlike Riecke, Voigt did not regard the binding of the atoms in the molecules as totally rigid in comparison with the binding between the molecules. He did not elaborate upon his ideas, but his neglect of the interaction between atoms located in neighboring molecules reveals a tacit assumption that the diameters of the molecules are significantly smaller than the distances between them. With this assumption, he maintained Riecke's concept of separate molecules. Voigt seems to embody more surely than Riecke a new microphysical thinking, ascribing different properties to microscopic than to macroscopic objects, e.g., the molecule is no longer a dielectric like the crystal (it cannot possess polarization). Moreover, his idea agreed well with the chemical concept of atoms inside the molecule and the physical consideration of internal molecular degrees of freedom, as attributed to atoms in the kinetic theory of gases.[81] Yet, crystals are very different from simple gases. A stereometric structure of a tourmaline molecule (chemical formula $NaMg_3Al_6(OH)_4(BO_3)_3Si_6O_{18}$) has many more possible configurations and degrees of freedom than a diatomic gas molecule. The problem becomes even more complicated when the relative positions of atoms in several such molecules in a crystal are considered. One can understand why Riecke preferred to deal with separate molecules with constant polarity. Voigt himself did not pursue his own hypothesis; he did not suggest any geometrical structure for any crystal.

In elaborating Riecke's theory, Voigt displayed clearly the particularity of its assumptions. Riecke's choice of polar systems was at least partially arbitrary. Its merits were its agreement with the piezoelectric theory and with the concepts of crystal structure. However, it also had disadvantages. Voigt's contributions indicated three central problems in Riecke's theory: it was not general mathematically, it assumed high unobservable electric moment, and lastly, it did not agree with Voigt's own view and with recent findings about molecules and their relations with atoms. In suggesting an alternative explanation based on inner molecular changes, Voigt revealed the significance of the last two problems to his view of physics. The first mathematical objection was answered by his elaboration of Riecke's theory rather than by his alternative. Notice that while the former of these originated from piezoelectricity the latter originated from other fields of physics. The choice between these alternative explanations of piezoelectricity was based on plausibility of hypotheses estimated by considerations external to the field. That Voigt did not formulate a new theory suggests, however,

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[80] Voigt, "Electrisches Moment eines Turmalins," p. 370.

[81] Interestingly this piezoelectric model does not agree so well with Voigt's own molecular theory of elasticity, suggested six years earlier. The latter assumed discrete molecules with a fixed polarity of their intermolecular forces (whose nature remained open). The two are not contradictory since the internal motion of the atoms in the molecules could be assumed to have only a negligible influence on the inter-molecular forces, while it has significant influence on the hitherto non-electric molecules. Voigt, "Theoretische Studien über, Elasticitätverhältnisse."

that he considered the current knowledge on the structure of crystals insufficient for an elaboration of a plausible molecular explanation of the phenomena.

LORD KELVIN'S MECHANICAL MODELS

First molecular model

Simultaneously with Voigt William Thomson, now Lord Kelvin, suggested a model of piezoelectricity based on displacements of atoms inside the molecules.[82] Thomson had an important influence on the discovery of piezoelectricity, and the early understanding of the phenomena, through his explanation of pyroelectricity from 1860. However, he did not contribute directly to the study of piezoelectricity until 1893. That summer, as in the preceding winter, "Lord Kelvin [was] busy with the molecular tactics of cleavage planes and faces of crystal."[83] In October, at the end of a trip to France, Kelvin read a paper on piezoelectricity to the Parisian Academy of Science. Another paper on the piezoelectricity of quartz, read at the meeting of the British Association for the Advancement of Science about a month before, was published the same month in the *Philosophical Magazine*. Then he became better acquainted with the experimental instruments of Jacques and Pierre Curie and with their previous publications.[84] To the paper on quartz he appended an extract from a 1890 French pamphlet that describes the piezoelectric part of an electrometer constructed by the Curies in 1885. This electrometer was based on the transverse piezoelectric effect in quartz (the effect of pressure in an axis perpendicular to a polar axis in the plane of the polar axes). Recall that traverse pressure creates an electric effect in an inverse sign to that of longitudinal effect and with the same magnitude multiplied by the division of the length of the crystal by its width. Its dependence on the ratio between the length and width facilitates its use in an electrometer. Thomson was impressed by the instrument and acquired one that was made for him "under Mr. Curie's [probably Pierre] direction."[85]

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[82] William Thomson, "On the Piezo-electric Property of Quartz," *TMPP*, 5: 311–322. The paper appeared originally in *Philosophical Magazine* of October 1893. Voigt's paper, in which he suggested his molecular theory, was signed in August, and published in November. It was first represented before Göttingen's Academy of Science on July 29th. It is highly unlikely that Thomson attended or heard about Voigt's talk.

[83] From a letter of Lady Kelvin (neé Frances Anna Blandy) to George Darwin from July 1893, quoted in Silvanus P. Thompson, *The Life of William Thomson Baron Kelvin of Largs*, MacMillan and Co.: London, 1910, p. 932.

[84] In the autumn Lord and Lady Kelvin were in the French Alps (*ibid.*). Lord Kelvin probably stopped in Paris in his way to the Alps.

[85] Thomson, "Piezo-electric of Quartz," p. 311–12. On the Curie's electrometer see the appendix to the paper on pp. 320–22. It is an extract from J. and P. Curie's pamphlet, published by the *Société Centrale de Produits Chimiques* in 1890. This society also built the electrometer that is described in the pamphlet, but an earlier version of it was built by Bourboze, a Parisian instrument builder, already in 1885. The guiding principles of the instruments are described by Jacques Curie, "Quartz piezo-électrique," in *OPC*. See also the editors' note at the end of this article.

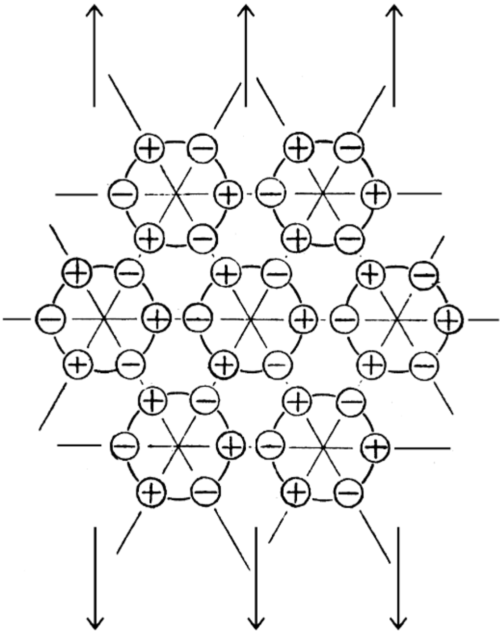

Figure 3.4: Quartz crystal in normal state according to Kelvin's model. Plusses represent silicon atoms, minuses couples of oxygen atoms (from Kelvin, "Piezo-electric of Quartz").

Unlike Voigt, Kelvin was not interested in introducing general principles for a future theory, but in finding a specific illustration for the particular phenomena of the transverse and longitudinal pressures in quartz. "Electric eolotropy [his term for anisotropy] of the molecule, and nothing but electric eolotropy of the molecule, can produce the observed phenomena," he claimed. He assumed the simplest kind of such "eolotropy" that he could imagine. Each crystalline molecule of quartz was assumed to consist of three chemical molecules of SiO_2 clustered together. The three atoms of silicon and the three couples of oxygen atoms are "at equal distances of 60° in alternate order, silicon and oxygen, on the circumference of a circle."[86] He further supposed that the crystalline molecules are arranged in such a way that a (positive) silicon atom of one molecule is close to a (negative) oxygen atom in the neighboring molecule (Figure 3.4). This structure implies that in a regular case the electric effects of the atoms neutralize each other. Yet once a pressure is applied, it deforms both the molecules and their relative positions, and moves atoms of silicon and oxygen closer or apart (Figure 3.5). This leads to an accumulated electric effect, and the creation of what Kelvin called an electric moment (in parallel to the magnetic moment).[87] With

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[86] *Ibid.*, p. 312.

[87] Curiously Kelvin claimed he did not know previous uses of such a term, though even he himself used the term electric moment for the polarization of a dielectric, and it was in frequent use in the German literature.

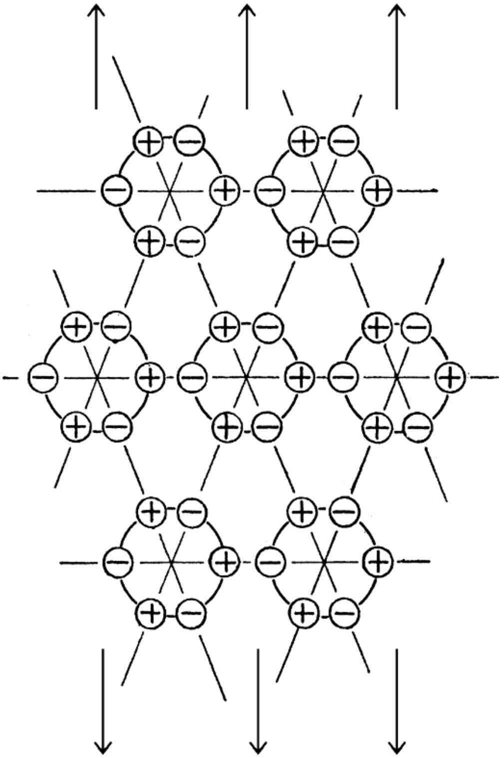

Figure 3.5: Quartz stretched by external force according to Kelvin's model (from Kelvin, "Piezo-electric of Quartz").

simple geometry, he found an expression for the electric moment (μ) as a function of the charge of each atom or couple of atoms (q), the radius of the molecules (b), their number (N) and the change in the direction of the diameters of the molecules due to strain (θ):[88]

$$\mu = Nq4b\theta \cos 30^\circ \tag{5}$$

Kelvin designed a model of his quartz molecules. He represented the silicon atoms by small balls of zinc and the double oxygen atoms by small balls of oxidized copper.[89] In Kelvin's model the six atoms of the same "molecule" are connected by metal to each other, and by isolator to other molecules. This is parallel to the assumption that the forces inside the molecule are qualitatively different from those between the molecules. He had referred also to the possibility that the forces are of a similar kind. Since zinc and oxidized copper have electrochemical properties very close to that of silicon and oxygen, he employed measurements on these metals in the model

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[88] *Ibid.*, 314–16.

[89] William Thomson, "on the theory of Pyro-electricity and Piezo-electricity of Crystals," *TMPP*, pp. 325–332.

to estimate the charge of the crystal's atoms (considering the different radii). This estimation, combined with figures for the number of molecules per cubic centimeter and the radii of the molecules, enabled him to find a quasi-theoretical electric moment due to a change in the direction of the axes in quartz. Comparing this result with the Curies' measurements for real quartz, he showed that the model predicts for a pressure of 5 kg per centimeter a change of 1/2598 radian in the direction of the diameters through the atoms (θ in equation (5)). This is a plausible figure in agreement with the empirical knowledge of the elastic deformation of quartz. Kelvin also actually made "a rough mechanical illustration of the theory of electric atoms to account for the piezoelectric properties of crystals, [which] is presented in an electrically working model of a piezoelectric pile."[90] As Kelvin himself acknowledged, following his visit to Paris in October 1893, in 1881 Jacques and Pierre Curie had already described such a pile, using the same materials. The paper of the Curies suggests that they were content with a virtual model. Kelvin, however, physically built such a pile and observed its behavior.[91]

Kelvin's model can explain why pressure in a perpendicular direction induces an effect of an inverse sign. Pairs of atoms that move closer by strain in one direction would move apart by strain in the perpendicular direction. This explanation seemed so obvious that Kelvin did not even bother to mention it. A similar explanation based on hypothetical polar molecules, like those assumed by the Curies, was suggested by Ernest Mallard nine years before. According to Mallard, a pressure in a polar axis moves the molecules closer together in this axis, while a pressure in the perpendicular axis moves them farther apart in the same ratio, and thus raises an inverse electric effect. However, he noted that this cannot be considered a general rule, since other crystals, like tourmaline, do not have such reverse effects.[92] Since Kelvin explained the behavior on inner molecular motion, his model did not have this problem. One should devise a different model for tourmaline.

Yet Kelvin was not satisfied with this kind of molecular explanation but sought to "prove, without any hypothetical assumption," the inverse behavior of strains in perpendicular directions. His proof was based on the indifference of quartz to uniform pressure, which was an empirical finding. Assuming a quartz specimen strained in a longitudinal direction, he added a uniform strain (or "elongation" in his terms) equal in its magnitude and opposite in its direction. The resultant is a transverse strain of an inverse sign. Since the uniform strain did not change the electric effect, the electric effect of the inverse transverse strain is equal to that of the original longitudinal strain.[93] This elegant proof explains immediately why tourmaline and other crystals that react electrically to uniform pressure do not show this relation between the transverse and the longitudinal effects. According to the same argument,

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[90] Thomson, "Piezo-electric of Quartz," pp. 316–7.

[91] Thomson, "theory of Pyro-electricity and Piezo-electricity," pp. 325–6. J. et P. Curie, "phénomènes électriques de la tourmaline," – and the discussion in chapter 1.

[92] Ernest Mallard, *Traité de Cristallographie*," Vol.2: pp. 559–560. See chapter I.

[93] Thomson, "Piezo-electric of Quartz," pp. 317–8.

pressure in any direction (in the polar plane) causes electric effect.[94] Thus, Kelvin recognized the fragility of arguments based on plausible but hypothetical explanatory models. When available, he preferred macroscopic, nonhypothetical arguments. Still the effect of torsion is unaccounted by this argument and Kelvin did not mention it, although a previous reference by him to Voigt's general theory shows that he was familiar with it.[95]

The method of models

Kelvin applied to the study of piezoelectricity his methodology of models, based on a tacit molecular structure. "I never satisfy myself until I can get a mechanical model of a thing," he stated a decade earlier in his "Baltimore Lectures." The model had a fundamental place in the processes of comprehension and scientific discovery. This methodology, based on models and exemplar calculations, "saves brain" by supplying a sensory perception to the hands and the eyes.[96] The electro-mechanical model of quartz suggested a way to visualize and thereby to understand piezoelectricity in this crystal. He thought that concrete mechanical models are especially useful for crystallography. "I advise any of you who wish to study crystallography [he told a young audience in Oxford in May 1893] to contract with a wood-turner, or a maker of beads for furniture tassels or for rosaries, for a thousand wooden balls of about half an inch diameter each."[97] He himself used models made of such balls in his studies of crystals. Yet, as Smith and Wise emphasize, Kelvin did not see in the model a justification for a theory or a demonstration of any truth about nature. It was more a way to explain and understand phenomena than a claim about nature. This is seen also in this episode. In order to sustain his claim about the relations between the transverse and the longitudinal effect, he abandoned the model for a nonhypothetical argument based on the experiment.

Mechanical models were suggested in the study of piezoelectricity almost from its beginning in the aforementioned model of the Curies. This model, which was stimulated from an early suggestion by Thomson, probably helped them discover the phenomenon. More sophisticated models that accounted for the whole range of the accumulated experimental data were suggested by Riecke and by Voigt.

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[94] Kelvin thought that this contradicts Röntgen's claim on the existence of axes of missing piezoelectricity in quartz. However, Röntgen defined them as axes in which no longitudinal effect exists. He knew Curie's result concerning the transverse effect and he himself observed electric effects due to pressure in the axes of missing piezoelectricity, in a paper to which Kelvin referred. Indeed, Röntgen chose an ill terminology, perhaps because he first thought that no electric effect exists in these axes. Yet Kelvin's objection is unjustified

[95] He referred to it in a general lecture in May 1893, "On the Molecular Tactics of Crystal," Appendix H in *Baltimore Lectures on Molecular Dynamics and the Wave Theory of Light*, London, C. J. Clay and sons, 1904, pp. 602–642, on p. 639.

[96] See Smith and Wise's discussion of Thomson's methodology of 'look and see,' in *Energy and Empire*, pp. 463–471, the quotation is from p. 470.

[97] Thomson, *Ibid.*, p. 605. Notice the practical instructions he gave, to which he added that "holes through [the balls] will do no harm, and may even be useful; but make sure that the balls are as nearly equal to one another, and each as nearly spherical as possible."

Riecke suggested a concrete molecular structure that was even illustrated in figures (Figures 3.3 and 3.4). Still, he did not suggest constructing any actual physical model; he had only a geometrical model. While Kelvin, even when he did not construct one, suggested how, in principle, such a model should be constructed—which materials to use and how to connect them. In this case he also built a simple model. Riecke was interested in reconciling the molecular hypothesis, in which he believed, with the new piezoelectric theory that was supported by experiments. His model was not suggested as a means for a better comprehension of piezoelectricity. Voigt's molecular theory hardly suggests a geometric model—he did not specify the locations of the atoms in the molecules. The high number of poles in these molecules made any attempt to picture the structure of the molecules to be unpractical (how would one place 8192 poles in a sphere?). His abstract approach to physical theory differs clearly from that of his colleague Riecke. The differences in style between him and Kelvin are conspicuous. While Voigt relied on general mathematical reasoning even in his development of a hypothetical molecular theory, Kelvin applied concrete geometrical thinking even in his nonhypothetical argument to deduce the behavior of pressures in different directions.

Pierre Duhem, who himself attempted at an explanation of piezoelectricity, was one of the early observers and sharpest critics of Kelvin's methodology—the Lord was then still Sir William Thomson. For Duhem, though Scottish, Thomson represented, what he called, the English School. "Understanding a physical phenomenon, he wrote, is therefore, for the physicist of the English school, the same thing as designing a model imitating a phenomenon; whence the nature of material things is to be understood by imagining a mechanism whose performance will represent and simulate the properties of bodies. The English school is completely committed to the purely mechanical explanations of physical phenomena."[98] Apart from the last sentence these words describe well Thomson's work on the piezoelectricity of quartz in particular, and his physics in general. However, Kelvin did not suggest a purely mechanical explanation, but used a mechanism that contains electrochemical forces.[99] According to Duhem, the methodology of the English school is the creation of "the ample but shallow mind (*esprit de finesse*)". This mind "consists essentially in the aptitude to see clearly a very large number of concrete notions, and to grasp simultaneously the whole and the details." In contrast to it stands the abstract-mathematical mind (*esprit géometrique*), which is "strong enough to be unafraid of abstraction and generalization but too narrow to imagine anything complex before it is classified in a perfect order." The ample mind characterizes the English physicists, the abstract mind their French and German colleagues. Yet Duhem himself clarified, that in every nation one can find

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[98] Pierre Duhem, "Abstract Theories and Mechanical Models," Chapter 4 in *The Aim and Structure of Physical Theory*, tran. Philip P. Wiener, Princeton: Princeton University Press, 1954, pp. 55–104, on p. 72.

[99] Indeed, ultimately electric action should be explained by mechanical forces and Thomson made several attempts in this direction. Yet, not only was he aware of their problems, but he did not attempt to explain the different electric potentials of different chemical materials on mechanics. Thus, in the present situation of the physical knowledge a non mechanical model was good enough. See also the discussion in Smith and Wise, *Energy and Empire*, pp. 463–471.

both minds. He referred to Voigt's physics as a good example for the abstract mind that follows logical mathematical reasoning.[100] However, it is difficult to regard Riecke's theory as the product of such a mind. The early model suggested by the Curies seems to better fit Duhem's characteristic of the English ample mind, than that of the French mathematical mind.

Second molecular model

No single characteristic of the "English school" irritated Duhem more than the fact that "to a physicist of the school of Thomson or Maxwell, there is no contradiction in the fact that the same law can be represented by two different models." This contradicted Duhem's basic search for theoretical unity. He called to preserve "the right to impose on physical theories unity and logical coordination."[101] If the models suggest a way to understand physics, multiplications of models suggest a few parallel ways to understand the same phenomenon. Precisely because Kelvin agreed with Duhem that the models are not pictures of the inner physical realities, he felt free to use contradictory models for different ends. So while his model for piezoelectricity in quartz appeared on the pages of London's *Philosophical Magazine*, Kelvin presented to the Parisian Academy of Science an incompatible model for all piezoelectric crystals, based on unchangeable molecules.[102]

Kelvin based his theory on Jacques and Pierre Curie's aforementioned electrochemical model of piezoelectricity in tourmaline. He wrote:

> The doctrine of bodily electro-polarization masked by an induced superficial electrification [which he had suggested in 1860] . . . wanted a physical explanation of the assumed molecular polarization to render it a satisfying physical theory of pyro-electricity; a short but very important paper by MM. Jacques and Pierre Curie . . . supplies that want in a manner which suggests what seems to me the true matter-of-fact electro-chemical theory of a crystalline molecule, and at the same time makes easy the extension of my primitive doctrine, to remedy its defect in respect to multipolarity, and to render it available for explaining not only the old-known pyro-electricity of crystals, but also the piezo-electricity discovered by the brothers Curie themselves (p. 325).

Kelvin offered an extension of the Curies' suggestion to multipolarity. "The true matter-of-fact" for Kelvin was the view of the molecules as microscopic electrochemical cells: compounds of material with different electrochemical potentials. In the model the molecule was taken to be "a rigid body of any shape, bounded by a surface made up of pieces of different metals, soldered together so as to constitute one

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[100] Duhem, "Abstract Theories," quotations on p. 60–61, 64. In 1915, in the spirit of the Great War, Duhem elaborated on the German mind (Pierre Duhem, *German Science*, Tran. Jon Lyon, Open Court: La Salle IL, 1991). He referred explicitly to Voigt, taking the arrangement of his textbook on Crystal's physics as an example where "[t]he exclusive pursuit of algebraic precision [*rigueur*] often leads mathematicians [*géométrés*] on the other side of the Rhine into the most complete disdain for the order which, in the subject treated, would be imposed by natural affinities" (p. 59).

[101] *Ibid.,* p. 81, p. 100.

[102] Thomson, "Theory of Pyro-electricity and Piezo-electricity," – page numbers in parentheses in this section refer to this paper.

metallic conductor." These molecules are arranged "as a Bravais homogenous assemblage" of a crystal. Each molecule is connected to its 12 closer neighbors "by springs of nonconducting material," but can also be electrically connected to them by fine wires. Variations in pressure change the distances between the molecules and thus the electric polarization of the assemblage. This model accounts also for pyroelectricity when one assumes that variation in temperature changes either the "contact-electricity" in the molecules or "the configuration of the assemblage, whether by changing the shape of each molecule or by changing the forces of the springs" (p. 326). Kelvin, thus, assumed the possible existence of a direct nonmechanical effect of temperature.

This model of a piezoelectric crystal supposed the general characteristics of "the molecular tacit of crystal" that Kelvin presented in May 1893. Crystallographic considerations, and physical properties of crystals led to this general molecular structure.[103] Like most of his contemporaries he defined "every crystal [as] a homogeneous assemblage of small bodies or molecules." These molecules can have any shape, but they have to be identical, oriented in the same way, and arranged homogeneously in a lattice surrounded by 12 close neighboring molecules. Mathematically one can draw infinite cells that repeat themselves in a crystal and arbitrarily call any of these a molecule. However, such a mathematical definition did not satisfy Kelvin. He presumed the existence of a nonarbitrary physical boundary of a molecule—an entity that was assumed to be an individual unit.[104] The solid metal molecule of the piezoelectric model is such a "physical" molecule. With a few simplifications Kelvin derived a solvable but very complex mathematical problem from the model and sketched its solution. Yet he preferred an experimental solution to the mathematical problem. Such an experiment had already been performed by the Curies without Kelvin's model (pp. 326–30).[105] Yet, one can doubt the fertility of a model that helps to predict results only by measuring the phenomena that it was to elucidate.

Kelvin concluded the paper with instructions for constructing a concrete model based on the same principles that would enable finding the piezoelectric coefficients. This model is designed to yield 21 piezo- and pyroelectric coefficients: Voigt's 18 and 3 independent pyroelectric coefficients.

> The inclusion, he wrote, of this [latter] case is important to guard against a tendency which I find in the writing of both MM. Curie and of Voigt—a tendency to a hypothetical assumption unduly limiting the pyro-electric property to identify with the piezo-electric effect produced by force causing the same change of shape or bulk as that which is produced by the change of temperature (p. 329).

Kelvin's model accounts for pyroelectricity but does not suggest an explanation for its source.[106] Like his earlier models, this model is based on metallic molecules, each "spherical or not wildly different from spherical" made of 22 parts, one of

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[103] Kelvin did not refer to the recent development in mathematical crystallography that had little to offer for his needs.

[104] Thomson, "On the Molecular Tacit of a Crystal," p. 602, 607–611 and *passim*.

[105] For more details see Katzir, *A History of Piezoelectricity*, p. 133.

[106] Of interest is to note that in this case Kelvin was more cautious of hypothetical assumptions on the source of phenomena than Voigt.

zinc and 21 of copper. These molecules should be connected with a nonconducting material to form a homogenous lattice in which all are oriented to the same direction, in accordance with Kelvin's description of the structure of the crystal. One should then subject the assemblage to six different strains and to one change of temperature successively. Measuring each time the electric moment in the three directions, one would obtain 21 multipliers. Next, one should change the place of the zinc in all the molecules in the same way and repeat the measurements. The procedure should be repeated 21 times, each time changing the location of the zinc in the molecules to provide 21^2 multipliers. These appear in 21 equations for the 21 piezoelectric coefficients, the first of which being:

$$[x, e, 1]v_1 + [x, e, 2]v_2 + \cdots [x, e, 21]v_{21} = (x, e) \tag{6}$$

where $[x, e, 1]$, is the electric moment measured in the x direction due to a strain e (x_x in Voigt's notation) "$v_1, v_2, \ldots v_{21}$ denote the volta-electric differences from copper which must be given to" any of the 21 parts in the molecule, and (x, e) is the piezoelectric coefficient (parallel to ε_{ij} in Voigt's notation). Thus, Kelvin concluded, "we have, in idea, constructed a model for the piezoelectric and pyroelectric quality of a crystal in which each one of the 21 piezoelectric and pyroelectric coefficients has an arbitrary given value" (p. 331–2). This is an electrochemical-mechanical analogy to a piezoelectric crystal. Its use resembles analog calculating machines. Kelvin was highly impressed by such a machine designed to adjust the compass according to the influence of the metals in ships built by Archibald Smith. He himself constructed a "kinematic machine" for calculating and predicting tides, including the height of water.[107] Yet the measurements Kelvin suggested here can yield only the coefficients of the model assemblage, not that of a real crystal. The coefficients of the model depend on the way one constructs the metal "molecules," and have no clear connection to the properties of a natural crystal. That the model had a limited practical value did not seem to bother Kelvin. Its role was to supply a visualization of piezoelectric phenomena and thereby a way to understand them. The complicated construction that Kelvin suggested and the limited knowledge obtainable from it perhaps explain why no one tried to actually build such a model. Similar concrete models that can yield an analogue phenomenon to the natural one, were not suggested later in Kelvin's spirit. Thus, in a sense Smith and Wise's general conclusion that "Kelvin's methodology died with him" is also true for piezoelectricity.[108] However, the use of models which does not reflect the true structure of matter as an illustration continued. In the 1940s, Kelvin's model for quartz was extended to torsion for pedagogical ends.[109]

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[107] Smith and Wise, *Energy and Empire*, pp. 369–371.

[108] *Ibid.*, p. 491.

[109] The model was elaborate by Warren P. Mason for introducing Bell's engineers to the field. Mason knew well its limits: "since Kelvin's model of the quartz molecule does not agree with that found by X-rays, his explanation can be regarded as qualitative and descriptive. His model does illustrate some of the symmetry of quartz, however." Warren P. Mason, "Quartz Crystal Applications," in in *Quartz crystals for electrical circuits, their design and manufacture,* Raymond Alphonsus Heising ed., New York: D. Van Nostrand Company, 1946, pp. 11–56, quote on p. 18.

An atomistic model

In 1901 Kelvin advanced yet a new explanation for piezoelectricity. Although this theory is beyond the period discussed in this book, it is worth a detailed description due to Kelvin's prior work and the interesting characteristics of his new ideas. Unlike his former creations, this explanation was based on atomic rather than molecular considerations. It appeared in a paper introducing a new model for the atom. It originated from the development in the atomic theory, rather than from internal developments in piezoelectricity as was the case in the 1890s. However, Kelvin showed a unique interest in the consequences of novel theories of atomic structure to complex phenomena, like the explanation of electrification by friction, the polarization of dielectrics, the permeability or susceptibility of gases and solids, conductivity of solids and lastly, in more detail pyro- and piezoelectricity. While Kelvin connected his theory to macroscopic phenomena, other physicists were interested in effects that were agreed to originate from the atomic structure like spectroscopy. The questions that Kelvin treated would be later connected more to solid state physics than to atomic and particle physics, and would not be dealt by "atom builders." His interest in them reveals old-fashioned concerns that characterize the physics of the nineteenth century. This is not surprising; Kelvin was a prominent representative of Victorian science. For him the new atomic theory, among others, suggested a novel view of the source of pyro- and piezoelectricity.[110]

Following the experimental findings in the late 1890s by Kaufmann, Wiechert, and prominently J.J. Thomson, physicists believed that the atom was a compound object. The newly discovered negative corpuscles were suggested to be universal subatomic particles. Kelvin's model of the atom probably originated from the view of the electron that J.J. Thomson suggested in 1899, after establishing the negative charge of the particle and its role on processes of ionization.[111] Thomson wrote:

> I regard the atom as containing a large number of smaller bodies which I will call corpuscles; these corpuscles are equal to each other . . . In the normal atom, this assemblage of corpuscles forms a system which is electrically neutral. Though the individual corpuscles behave like negative ions, yet when they are assembled in a neutral atom their negative effect is balanced by something which causes the sphere through which the corpuscles are spread to act as if it had charge of positive electricity equal in amount to the sum of the negative charges on the corpuscles.[112]

J.J. Thomson's view that the atom contains "a large number" of corpuscles was shared by many, since it could explain the mass of the atom which is from about a

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[110] Lord Kelvin, "Aepinus atomized," *Baltimore Lectures*, appendix E pp. 541–568, "from the Jubilee Volume presented to Prof. Boscha in November 1901," reprinted in *Philosophical Magazine* 3(1902): 257–283.

[111] On J.J. Thomson work see George E. Smith, "J.J. Thomson and the Electrons, 1897–1899," in *Histories of the Electron: the Birth of Microphysics*, Jed Z. Buchwald and Andrew Warwick (eds.), Cambridge Mass.: The MIT Press, 2001.

[112] Quoted from Heilbron, *Atomic Structure*, p. 111.

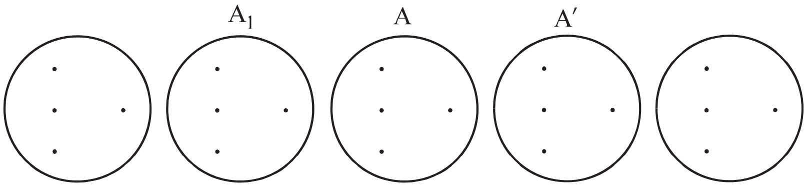

Figure 3.6: “A row of equal tetra-electrionic atoms,” according to Kelvin. The dots represent the electrons; the middle electrion in the left column “is alternately on the far side and the near side of the plane of the paper” (from Kelvin, “Aepinus atomized. *Baltimore Lectures*, pp. 541–568).

thousand times bigger than that of the electron, and the “the great number of spectral lines emitted by even the lightest atom.”[113]

Kelvin returned to Aepinus’s old theory of one electric fluid. He suggested “that the Aepinus’ fluid consists of exceedingly minute equal and similar atoms, which I call electrions” (p. 541). These electrions are the corpuscles of J.J. Thomson since they “act as extremely minute particles of *resinously* [negative] electrified matter.” They repel each other and attract ponderable matter, which comprises the bulk of the atoms. The atoms of ponderable matter are assumed to repel each other. The electrions were assumed to be very small relative to the atoms and able to move freely in the atoms and from them.

> [Kelvin] assume[d] for simplicity that the attraction experienced by an electrion approaching an atom varies exactly according to the inverse square of the distance from the center, as long as the electrion is outside; has no abrupt change when the electrion enters the atoms; but decreases to zero simply as the distance from the center when the electrion, approaching the center, is within the spherical boundary of the atom. This is just as it would be if the electric virtue of the atom were due to uniform distribution through the atom of an ideal electric substance” (p. 542).

Unlike J.J. Thomson, Kelvin supposed that the number of electrions in an atom could be small. The electrions inside the atom are in static equilibrium. He studied their distribution for a few simple cases.

The distribution of the electrions in the atom is the key to Kelvin’s explanation of piezo- and pyroelectricity. Though the distribution of the electrions in the individual atoms must be symmetric, their order might create an electric effect. This, he suggested, might be the case of pyroelectric crystals. As a model of such a crystal he considered a “row of tetra-electrionic atoms,” whose electrions are at the corners of a tetrahedron which has the same orientation relative to the row in all the atoms (Figure 3.6). “An easy calculation shows that the quartet of electrions within [atom] A, regarded for the moment as a group of four material points rigidly connected, is attracted to the left with less force by A_1 [the ponderable matter] than to the right by A'. There are corresponding smaller differences between the opposite attractions of the more and more remote atoms at the two sides of A” (p. 560). The net forces originate

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[113] *Ibid.*, p. 114.

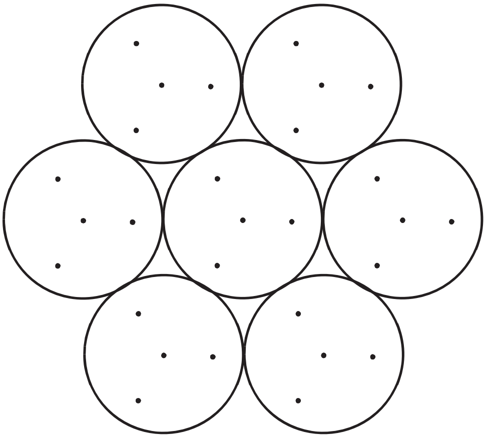

Figure 3.7: Kelvin's second model for octo-polarity, based on equal "tetra-electrionic atoms." The four electrion form a tetrahedron. The outer electrions are in a plane parallel to the plane of paper. The middle one is in the other side (from Kelvin, "Aepinus atomized. *Baltimore Lectures*, pp. 541–568.).

from the geometrical distribution of the electrions in the atoms and the orientation of the atoms in space. Despite variations due to mutual actions between the rows, Kelvin claimed that "the general character of the result will be the same," when one considers many such rows together in a crystal. This can explain pyroelectricity in bipolar materials, in accordance with his 1860 hypothesis of permanent polarization (p. 560).

A model for piezoelectric crystals that have more polar axes and that does not possess permanent polarization is more complicated. Kelvin suggested two incompatible models for an octo-polarity in the cubic class. In the first he supposed a combination of two assemblages of four atoms of two kinds (both tera-electrionic). Set properly, this structure, he claimed, entailed "the kind of aeolotropy which constitutes octo-polar quality" (pp. 561–4). A later, simpler model, assumed only one kind of tera-electrionic atoms. Each atom is surrounded by six atoms in the plane (Figure 3.7).

"The quartets of electrions are supposed to have their edges parallel to the six lines of symmetry of the assemblage." The electrions are not in the plane of the paper. One is a distance *r* on the near side and the other three in a distance 1/3 *r* on the other. Examining the mutual electric forces between the electrions in this case, he concluded: "we have thus found that an equilateral homogeneous assemblage of atoms each having four electrions within it, arranges these electrions in equilateral quartets all oriented in one or other of two ways. The assemblage of atoms and electrions thus produced is essentially octo-polar" (pp. 565–6). These assumed to be stable states, which do not have permanent polarization.

Piezoelectricity is induced by a stretch (or contraction) perpendicularly to the plane of the paper. "The contrary inward movements of the single atoms on one side of the plane, and of the triplets on the other side, cannot in general be in proportion of three to one. Hence, the geometrical centers of gravity of the quartets [of electrions] are now displaced perpendicularly to the plane of the paper to far side or near side; I cannot tell which without calculation," which Kelvin did not make since it "is easy but essentially requires much labor" (p. 567). Next, he examined the effect of the variations of the distances between the atoms due to such an elastic force. Uniform stretch in all directions does not displace the center of gravity of the electrions. However, a stretch in any direction in the plane of the paper "leaves all the atoms out of this plane predominate, and cause[s] a definite calculable displacement of the centers of gravity of all quartets" perpendicular to the plane and therefore induces electric effect (p. 567). Furthermore, the cubic class, which this structure models, behaves, according to Voigt's theory, like quartz. Comparing the qualitative effects predicted by the model with those observed by the Curies in quartz, Kelvin found complete agreement.

As in Kelvin's earlier models of piezoelectricity, his aim here was to illustrate a way of understanding the phenomena rather than to propose its true mechanism. He also wanted to demonstrate the explanatory power of atomic theory. Indeed, the model should be based on principles that might be those that actually produce the phenomena, but not necessarily on the real structure of matter. The mono-atomic model is truly simple, but it seems to be an inferior representation of real crystals, most of which are composed of poly-atomic molecules. Indeed, Kelvin supposed that in chemical bounds the centers of two atoms might coincide; then the two atoms can be considered as one. Yet, it seems dubious that the molecules of all crystals are such "compound" atoms. Moreover, the four electrions assumed in the "hypothetical atoms" put a limit to the number of atoms in a molecule, which is much smaller than the number of atoms in chemical molecules of many crystals. Kelvin had no solid knowledge about the atomic structure of crystals. In suggesting specific models he preferred the simplicity of the explanation on the plausibility of its specific hypotheses.

CONCLUDING REMARKS

In all the molecular theories suggested for piezoelectricity the molecules of the crystal were considered to be independent physical entities. This is clear in Riecke's model and in Kelvin's second model, which are based on non-deformable molecules. But it is also true for Kelvin's model of quartz and for Voigt's suggestion, which are based on inner changes in the molecules. Still, the connections and the distances between the submolecular particles in the molecule are different from those between the molecules.[114] Thus at least from this example, it seems that during the first half of the 1890s, the molecules in solids in general, and in crystal in particular were usually thought to be individual entities separate from each other, like balls in one of

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[114] Even Kelvin's atomistic theory (in the model for pyroelectrics and the second model for piezoelectrics) implicitly regards the molecules as independent entities, if one identifies its atoms with the molecules, as it is possible in that theory.

Kelvin's models.[115] These molecules were not necessarily identified with the chemical molecules. Among the physicists discussed here only Kelvin stated connections between the crystal and the chemical molecules, assuming that three chemical molecules of SiO_2 combine to form a quartz molecule. Voigt preferred to refer directly to the atoms that constitute the chemical molecules. Riecke refrained from identifying the submolecular particles with the atoms, but evidently shared the assumption of submolecular particles. This seemed to be a tacit assumption shared by most physicists in thinking about the structure of matter. Duhem, of course, rejected any assumption about the structure of matter. However, a physicist with clear phenomenological orientation like Voigt shared the assumption of a molecular and atomic structure of solid matter.

The theories suggested to explain piezoelectricity were all based on Coulomb's law. The molecular theories used the expression for the electric potential due to electric charge derived from this law; Duhem used the expression for the work done by charge, which was based on Coulomb's and Ohm's laws. Since piezoelectricity is an electrostatic phenomenon, considerations of electrodynamics were unnecessary in its interpretations. The different electromagnetic theories and schools agreed on Coulomb's law and its manifestations in the electrostatic potential and in Gauss's law. Yet, they viewed dielectrics in different ways. Accounting for dielectric phenomena on particles, electric force and potential fitted better the concepts and practices of Weber's electrodynamics than that of others. Indeed Riecke, an adherent of Weber's school, introduced it to the field of piezoelectricity. Though Maxwell mentioned the electric potential in his famous *Treatise*, Maxwellians were not inclined to base a theory of a phenomenon on the potential due to discrete charges or dipoles. Indeed in the only attempt at an explanation of the phenomena by Maxwellians, Lodge suggested a mechanical illustration of pyroelectricity based on strain, friction, and current in a continuum. Yet no Maxwellian model for piezoelectricity was suggested. No Maxwellian exhibited any interest in the phenomena of piezoelectricity.

Voigt and Riecke represent two major schools in German physics of the nineteenth century, those of Franz Neumann and Wilhelm Weber, respectively. Their different attitudes toward hypothetical theories of piezoelectricity demonstrate well the differences between the two schools. Riecke thought that such ideas can lead to correct physical laws. By models, he thought, one can learn the truth of hypotheses.[116] In suggesting and elaborating molecular assumptions he displayed his belief in the usefulness of hypothetical models. On the other hand, Voigt's reluctance toward hypothetical theories is shown by his view of Riecke's theory. His focus on analytical

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[115] These theories corroborate Forman's claim in his controversy with Ewald that physicists in the 19th century universally assumed a lattice structure of crystal. Even Duhem assumed a lattice structure. Furthermore, a molecular basis of such a lattice was generally assumed (here Duhem is an exception). Yet Ewald's claim in his answer that the findings of x-ray diffraction in crystals were accepted with surprise, since molecules and not atoms were considered to occupy the points of the lattice, can also be supported by the piezoelectric example. However, the twenty years that separate these theories from the experimental findings make any conclusion problematic. See Forman, "The Discovery of the diffraction of x-rays" and Ewald, "Comments on P. Forman's paper."

[116] Riecke, *Lehrbuch der Physik*, pp. 2–5.

and experimental research of piezoelectricity (most of it will be discussed in the following chapters) shows his preference for the phenomenological approach. Yet, he did not refrain from working on a molecular assumption of piezoelectricity. He even suggested his own hypotheses. Perhaps the difference between him and a physicist like Riecke is that Voigt did not pursue his own speculations. Thus, the two schools show only general tendencies, not strict rules of how one ought to do physics.

Elaborating the phenomenological theory in 1894, Voigt did not even mention the molecular suggestion, which he himself had treated and advanced a year earlier.[117] Although handbook articles described one or more explanatory theories, Voigt's influential textbook of 1910, discussed them only briefly. Experimental accounts also gave them scant attention; only two experiments were related to these theories.[118] Thus, most involved in the research usually expressed indifference to the molecular theories of piezoelectricity. Yet at least Riecke's theory and its modification, suggested by Voigt himself, were in agreement with experiment and with physical knowledge. Apparently, this was not enough. Their shaky and controversial basis and their inability to predict further relations did not recommend them.

Kelvin's atomic explanation depended on his atomic model. The rejection of the model entailed the rejection of the explanation. No reference to the latter occurs in the literature on piezoelectricity.[119] The binding of the fate of explanatory theories with ideas of the structure of matter is most conspicuous in this example, but characterizes all mechanisms suggested for the source of piezoelectricity. All the mechanisms contained arbitrary elements constantly under threat of incompatibility with new views and findings on the physical structure of crystals. That was true for Riecke's theory—the most elaborate explanatory suggestion—as well as for Kelvin's atomic theory. Until the former was found incompatible with current views on the structure of crystals,[120] a quarter of century after it had been suggested, it rested on shaky and criticized foundations.

The molecular theories of piezoelectricity well illustrate Voigt's claim that successful ones could only be constructed with reference to the phenomenological theory.[121] Examples are the principles of symmetry used by Riecke and Voigt. Kelvin, too, relied on Voigt's phenomenological theory to determine the number of parts in his model molecule and the number of measurements to obtain them. This property of the molecular theories made them appear ad hoc and arbitrary. Change in the phenomenological theory and the molecular theory can be adjusted to the new theory. Probably,

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[117] W. Voigt, "Piezo- und Pyroelectricität, diëlectrische Influenz und Electrostriction bei Krystallen ohne symmetriecentrum, *Göttingen Nachrichten,* 1894, 343–372. The paper is discussed in the following chapter.

[118] These were the measurement of tourmaline's permanent electric polarization and the experimental detection of direct pyroelectricity both by Voigt in 1896 and 1898. See chapter 5.

[119] For example E. Riecke, "Pyroelektrizität und Piezoelektrizität;" F. Pockels, "Pyro- and Piezoelectrizität," in Winkelmann, A., *Handbuch der Physik*, Leipzig, vol. 4 part 1, 1905: pp. 766–791.

[120] In 1910 Voigt commented that "our modern views [*Anschauungen*]" of the electrons agree better with the assumption of inner molecular changes than with Riecke's assumption of solid molecules. Voigt, *Lehrbuch der Kristallphysik*, p. 847.

[121] Voigt, "Phänomenologische und atomistische," p. 723.

it is for this reason that physicists felt dissatisfied with these theories. Moreover, the molecular theories were shown to be only, at best, plausible but not unique. Their failure to provide any unknown or unexplained relation made them also unfruitful. Riecke observed that "the true touchstone for the truth of the underlying hypotheses" is "the discovery of new phenomena."[122] Where molecular theories managed to reveal new relations, they were generally accepted.

In explaining the success of the corpuscular-hypothetical theory of electrons in approximately the same years, H. A. Lorentz wrote:

> [T]he theory of electrons is to be regarded as an extension to the domain of electricity of the molecular and atomistic theories that have proved of so much use in many branches of physics and chemistry. Like these, it is apt to be viewed unfavorably by some physicists, who prefer to push their way into new and unexplored regions by following those great highways of science which we possess in the laws of thermodynamics, or who arrive at important and beautiful results, simply by describing the phenomena and their mutual relations by means of a system of suitable equations. No one can deny that these methods have a charm of their own, and that, in following them, we have the feeling of treading on firm ground, whereas in the molecular theories the too adventurous physicist often runs the risk of losing his way and of being deluded by some false prospect of success. We must not forget, however, that *these molecular hypotheses can boast of some results that could never have been attained by pure thermodynamics, or by means of the equations of the electromagnetic field in their most general form*, results that are well known to all who have studied the kinetic theory of gases, the theories of dilute solutions, of electrolysis and of the genesis of electric currents by the motion of ions.[123]

The situation in the field of piezoelectricity was very different. Its explanatory theory failed to attain results unaccounted for by the phenomenological theory. As discussed, their premises were controversial. Hence, they remained highly hypothetical.

Thus, the theories on the source of the piezoelectricity were almost impractical for further physical research. One could neither gain more knowledge on the phenomena from their study, nor construct experiments to examine their predictions. At most one could construct an experiment to examine an element of such theories, which was shared also by phenomenological theories, like the permanent polarization of pyroelectric crystals. Other influences of these theories, if they existed, were by inspiration or association. Hence they had negligible influence on the development of piezoelectric research. The knowledge on the phenomena expanded "following the firm ground" of analytical theoretical research and through experiments. I will discuss them in the two following chapters, first the theoretical developments and then the experimental work.

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[122] Riecke, *Lehrbuch der Physik*, p. 4.

[123] H. A. Lorentz, *The Theory of Electrons*, pp. 10–11, text of 1909, italics in the original.

CHAPTER 4

THEORETICAL ELABORATION OF VOIGT'S THEORY

Voigt's general theory reawakened an interest in piezoelectricity. The number of publications on the subject increased from three papers in 1890, to five in 1891 and seven in each of the following two years. More papers on piezoelectricity were published at the beginning of the 1890s than at the beginning of the 1880s, when the phenomena was discovered by the Curies.[1] Still, this was a small field. While the contributions to the study of piezoelectricity during the 1880s were mainly experimental, only a small share of the contributions following Voigt's theory included experimental work. Accordingly, the subject attracted either theoreticians or theoretically inclined professors of experimental physics, like Thomson and Riecke.[2] The experimental work on piezoelectricity focused on the confirmation of the theory, the determination of its coefficients and its relationship to the kin phenomena of pyroelectricity and electro-optics. This work will be the subject of the next chapter. In the theoretical study, I differentiate between the theoretical speculations about the source of piezoelectricity, and elaborations of the phenomenological accounts. The former were the subject of the previous chapter; the latter are the subject of this one.

Even before the publication of Voigt's general theory, Friedrich Pockels, Voigt's former student, was extending it to the converse piezoelectric effect.[3] Theoretical interest was immediate, but brief; it ended in 1894. At that time the general theory of piezoelectricity included the major features that continued to be used in the

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[1] Twenty papers on piezoelectricity were published between 1880 and 1884. Nine of them were written by the Curies, and another one by Jacques Curie and Friedel. Twenty-four papers were written between 1890 and 1894. The length of these papers much exceeded the average length of the early papers, many of them published as notes in the *Comptes rendus*.

[2] The sole exception is Hankel, who continued his long experimental research apparently disregarding the new theory. Experimentalists like Kundt and Röntgen, who played an important role in the first phase of the history of piezoelectricity, did not contribute to its study in the 1890s. Röntgen returned to the subject in the 1910s.

[3] Pockels's paper was published in 1891 but was sent on July 17, 1890, while Voigt presented his general theory on August 2nd. F. Pockels "Ueber die Aenderungen des optischen Verhaltens und die elastischen Deformationen dielektrischer Krystalle im elektrischen Felde," *Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie - Beilage-band*, 7 (1891): 201–231, on p. 231.

twentieth century. The main effort during that short period was directed at studying the foundations of the theory.

The elaboration and elucidation of piezoelectric theory can be divided into four general themes. Of these, two were linked to the study of its foundations and were historically closely connected to each other. These were the elaboration and extension of the theory to encompass all phenomena of piezoelectricity including those that involved the converse effect and secondary phenomena and its formulation in thermodynamic terms. A third theme was the relation between the new theory and others, especially that of electric fields. One can also view the thermodynamic formulation and the attempts to explain the appearances on a molecular basis, which were discussed in the previous chapter as part of this theme. Otherwise, little was written about it, but I assume that it attracted more interest than its share of words in publications indicates. A fourth theme was the study of the relationship between piezoelectricity and other effects like pyroelectricity and electro-optics in view of the new theory. Determining whether these effects are only secondary phenomena of piezoelectricity could be decided only by accurate measurements in the laboratory, which will be discussed in the next chapter. This chapter treats the theoretical study of these relations. In addition to these themes, Voigt's theory promoted mathematical study of specific problems that derived from it. These works are discussed in Appendix 2.

Like the narrative in previous chapters, the story of the theoretical elaborations during the first half of the 1890s generally follows the chronological order rather than the thematic order suggested above. Yet, the four themes (elaboration of the theory, its thermodynamic formulation, its relations with other theories, and with other effects) are encountered implicitly more than once in this narrative, and are discussed explicitly in a few appropriate places. However, special attention is given to the thermodynamic formulation and its historical roots. Piezoelectricity was one of the first physical fields that gained a general thermodynamic formulation. The interest in thermodynamics, however, originated more from general interests of the contributors to the field than from intrinsic piezoelectric reasons. Thus, in tracing the origins of piezoelectric theories, developments in the application of thermodynamics (these deserve more attention from historians) are also discussed here.

POCKELS'S THEORY OF THE CONVERSE EFFECT

Voigt's treatment of the direct piezoelectric effect displayed the need to account also for the converse effect. Voigt himself did not mention this effect in his long memoir, perhaps because his former student Friedrich Pockels was already working on it.[4] Before studying piezoelectricity, Pockels worked on piezo-optics (the effect of stress and strain on optical properties of crystals). He developed a theory of piezo-optics in his dissertation under the instruction of Voigt and submitted it in 1888. In 1890 he constructed a theory of electro-optics (the effect of electric fields on optic properties of crystals). In the study of this theory he examined the converse piezoelectric effect.

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[4] Pockels, "Aenderungen des optischen Verhaltens." Page numbers in parentheses in this section refer to this publication.

Pockels continued elaborating optic theory in crystals and became a (arguably, the) leading expert in crystal optics, a subject on which he published a textbook in 1906. Voigt saw in Pockels one of the best students he had ever had (the other was Drude). Pockels's research resembles his teacher's both in his interest in crystals and their symmetrical properties and in his preference for mathematical phenomenological theories. The highly mathematical character of Pockels's works during the 1890s caused Boltzmann to consider him one of the more promising young theoretical physicists in Germany but "more of a pure mathematician."[5] In 1890 he was still a young doctor, an assistant at the Göttingen Institute of Mineralogy. As his work on piezoelectricity shows, he continued a working connection with Voigt at the Physical Institute to which he returned a year later. The Physical Institute in Göttingen was the center of the work on piezoelectricity in the 1890s; most of the work on the subject was done there.

Electro-optic theory

In 1883 Röntgen and Kundt had already connected electro-optics to the converse piezoelectric effect. They showed that the electric field alters the double refraction of light in quartz in agreement with the change that converse piezoelectricity would induce. Both independently assumed that they observed a combined effect of piezoelectricity and piezo-optics: the electric field deforms the crystal (converse piezoelectricity), thereby inducing a change in its optical properties (piezo-optics) that resulted in a change in its birefringence.[6] Pockels did not adopt their supposition that the effect of electricity on optic properties is a secondary phenomenon of piezoelectricity. Instead, he accounted for the interaction "without any hypothesis," i.e., without assuming any intermediate mechanism in a way similar to his theory of piezo-optics and Voigt's theory of piezoelectricity. His basic equations directly show the dependence of the optic coefficients of double refraction on the electric moment (p. 201). He left open the question of whether the indirect effect of elastic deformation can explain this effect completely (p. 222). However, Röntgen, Kundt, and Czermak, who assumed that the effect is a secondary phenomenon, did not support their assumption with quantitative evidence. Apparently, the possibility of a direct effect did not occur to them. Since they were interested in the existence of an indirect effect through piezoelectricity and not in its magnitude, their neglect of the possibility of an **additional** direct effect is not surprising. Pockels's "nonhypothetical" theory allowed quantitative examination of the question, as he himself did in 1894. His finding of a clear direct electro-optic effect gave further justification to his cautious approach.[7]

Crystals are double refractive when the velocity of light in them varies with the direction. In that case a ray at an acute angle with the crystal axes is split into two. The mathematical study of the refractivity was often based on the refractive indices

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[5] Jungnickel and McCormmach, *Intellectual Mastery of Nature*, p. 122, On Boltzmann's opinion p. 289.

[6] See Chapter 1 pages 44–48.

[7] Pockels, "Ueber den Einfluss des elektrostatischen Feldes auf das optische Verhalten piëzoelektrischer Krystalle," *Abh. d. Gött. Ges.* 39 (1894). A summary by the author appeared in *Fortschritte der Physik* 50 (1894): part 2: 121–126. On this work see chapter 5.

of light (reciprocal to the light velocity) in the various directions. These indices, called optic polarization constants, determine the path of any beam of light through the crystal. In the tradition of Fresnel and Neumann in which Pockels worked it was common to study double refraction through the "Fresnel ellipsoid," or the index ellipsoid, which connected the optical constants. This ellipsoid called by Fresnel an ovaloid of elasticity, was written in general by him as:

$$\rho^2 = B_{11}x^2 + B_{22}y^2 + B_{33}z^2 + 2B_{23}yz + 2B_{31}zx + 2B_{12}xy \tag{1}$$

where ρ is the constant radius vector of the ellipsoid, x, y, z the coordinates and B_{ij} are "determining pieces [*Bestimmungsstücke*] of the ovaloid," which are called optical polarization constants in other publications. In media that do not show double refraction, the constants B_{11}, B_{22} and B_{33} are equal to each other. The constants B_{23}, B_{31} and B_{12} are zero in any crystal free from external elastic or electric stress.[8]

Pockels assumed that the change in the optic polarization constant is linearly proportional to the electric moment (a, b, and c). This leads to six fundamental equations of the theory. Each equation connects the optical polarization constants with the components of the electric moment and the principal velocities of light in a free crystal (ω_x, ω_y, ω_z):

$$\begin{aligned}
B_{11} - \omega_x^2 &= e_{11}a + e_{12}b + e_{13}c \\
B_{22} - \omega_y^2 &= e_{21}a + e_{21}b + e_{23}c \\
B_{33} - \omega_z^2 &= e_{31}a + e_{32}b + e_{33}c \\
B_{23} &= e_{41}a + e_{42}b + e_{43}c \\
B_{31} &= e_{51}a + e_{52}b + e_{53}c \\
B_{12} &= e_{61}a + e_{62}b + e_{63}c
\end{aligned} \tag{2}$$

where e_{ij} are 18 constants of the crystal. Pockels distinguished between this effect and Kerr's effect, which appears in all dielectrics. The latter depends on quadratic expressions of the electric moment, and is negligible in comparison to the linear electro-optic effect (p. 202–4). The physicists who had worked on the phenomena before, like Röntgen and Kundt, had already differentiated between the two effects.

From the basic equations (equation (2)) Pockels derived the specific equations for all the classes of crystals, i.e., he found the independent coefficients, those that were identical to zero and those equal to each other, in a method similar to Voigt's in the general theory. Like his teacher, Pockels based his derivation on considerations of symmetry.[9] He found that the same crystals show both piezoelectric and electro-optic properties in the same directions (pp. 206–11). Thus, he claimed that piezoelectricity

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[8] Following the common assumption in electricity, Pockels assumed that the tensor B is symmetrical so $B_{ij} = B_{ji}$, which fixes the number of constant at six.

[9] Like Voigt Pockels transformed all the variables to a different coordinates system with rotated axes and compared the new expressions with those of the original system, bearing in mind the symmetry under consideration. The mathematical problem here is a little simpler since one has only three components on the right side of the equations instead of six as in Voigt's theory of the direct piezoelectric effect. On Voigt's method, see chapter 2, p. 89.

might be the sole source for electro-optics (p. 222). This result is not surprising since both the theories are based on similar physical assumptions, translated mathematically into an equation that lays out (in modern terms) a linear correlation between a symmetric tensor of second degree (of the strain or optic constant) and the vector of electric polarization.

A comparison of the theory with experiment was quite problematic since only quartz was examined in the laboratory. Moreover, the experiments measured neither the optical constants nor the principal velocities (of light in the crystal), but the changes in circular polarization due to alterations in their values. To compare his theory with observation, Pockels employed optical theory of crystals (of Voigt) and plausible assumptions about the velocities in the plane of the secondary axes (*xy*). The details of these should not concern us in this context. He found that the electric moment changed circular polarization into elliptical and that the angle between the principal axis of the ellipse and the x-direction (that of a polar axis) is half the angle between the x-direction and the electric field. As Pockels remarked, these results were observed by Kundt and Röntgen (pp. 211–5). Kundt's figure vividly displayed this relationship between the direction of the electric field and that of the ellipse (see Figures 1.8 and 1.9). Pockels showed that the theory accounts for the details of Röntgen's optical experiments. Czermak's results, on the other hand, contradict Pockels's theory. Pockels claimed that the disagreement originated from undetermined experimental error in Czermak's experiments and in problems in their analysis. He fiercely criticized Czermak's theory, which was indeed mistaken but still deserved more balanced evaluation.[10] Pockels was unable to use the former's experimental finding to determine the value of the electro-optic constant e_{11} (pp. 216–9).

Theory of the converse piezoelectric effect

Since the experiments of Röntgen and Kundt it was clear that converse piezoelectricity contributes to the electro-optic effect. Whether this is the sole source of the phenomenon could be established, Pockels claimed, only by exact measurements, compared through a mathematical theory of both effects. Thereby, in the second part of his paper he studied the "elastic deformation in electric field." In analogy to his equations for the electro-optic effect he proposed equations for the elastic deformation due to an electric moment. Again these are six linear equations; this time for the six strains. He wrote the first of these equations as:

$$x_x = \mu_{11}a + \mu_{12}b + \mu_{13}c \tag{3}$$

with five parallel equations for the other strains, where μ_{ij} are 18 constants, parallel to the 18 electro-optic constants e_{ij}. However, these constants are identified neither

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[10] Pockels pointed out that by using surfaces that were not parallel to each other, Czermak relied on problematic assumptions in determining the correct direction of light relative to the crystal axes. He did not attempt to find the source of Czermak's error (the treating the three secondary axes as independent), but found inner contradictions in the theory, which were not contradicting according to the (problematic) meaning Czermak gave to his variables. On Czermak's experiment and theory see above chapter 2 p. 73.

with the electro-optic constants nor with the piezoelectric constants (ε_{ij}) nor with the moduli (q_{ij}) in Voigt's equations. The combination of the optical effect of strain (piezo-optics studied by Pockels in 1888) and these equations show a secondary effect of piezoelectricity on double refraction (pp. 222–4).

Pockels examined the relationship between the converse effect and the direct effect through the connections between the coefficients of his equations (μ_{ij} in equation (3)) and Voigt's piezoelectric constant (ε_{ij}, equation (3), Chapter 2). This was done by a study of concrete conditions rather than by abstract mathematical manipulation of the equations. Thereby, he offered the first examination of the changes in both electric and elastic variables due to the simultaneous application of electric and elastic forces. Pockels studied a small cylindrical plate cut from a very large, thin crystal whose height is much smaller than its diameter (so surface effects are negligible). The bases of the cylinder are connected for a short time to an electric source with known voltage and are then electrically isolated and put under stress by known weights. His method of analyzing the situation was similar to that employed by Lippmann in 1881. Like him he based his derivation on energy conservation and exact differentials. Pockels's discussion was both more detailed (taking all the constants into consideration) and more general. Following Lippmann he used the fact that the electric density – e should be constant on the plates, so it has an exact differential, which takes the following form:[11]

$$de = C\,dV - \sum \frac{\partial m}{\partial X_i} X_i \tag{4}$$

where C is the capacity, V the voltage, m the magnitude of the electric moment—equal to the surface charge density in an isolated system—and X_i the stress. The strains are also due to both elastic stress and electric moment, and their differential is:

$$dx_j = \sum_{i=1}^{6} \frac{\partial x_j}{\partial X_i} dX_i + \sum_{n=1}^{3} \frac{\partial x_j}{\partial a_n} \frac{\partial a_n}{\partial V} dV \tag{5}$$

where a_n are the electric moments. Tacitly, Pockels assumed that the phenomena are reciprocal. So the change of energy of the system consists of two parts: electric and elastic (assuming no loss to heat), whose differential dE is:

$$dE = Vde - \sum X_i dx_i. \tag{6}$$

Inserting the expressions for de and dx_i (equations (2), (4), and (5)) and the explicit forms of the electric moments in terms of the electric voltage that produce them (the latter relationship holds only with isolated electrodes) he wrote a detailed, though rather cumbersome expression for the energy differential.

$$\begin{aligned} dE = {} & VCdV - \sum_{l} \sum_{k} X_k \frac{\partial x_k}{\partial X_l} \partial X_l + \left(\sum_{i=1}^{3} \cos(nx_i) \chi_i \sum_{k=1}^{6} \frac{\partial x_k}{\partial a_i} X_k \right) dV \\ & - \sum_{k=1}^{6} \left(\sum_{i=1}^{3} \cos(nx_i) \frac{\partial a_i}{\partial X_k} \right) V dX_k \end{aligned} \tag{7}$$

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[11] P. 226. For sake of simplicity I use the modern abbreviated notation, which does not appear in Pockels's. Instead of X_x, Y_y etc. I write X_1, X_2, etc.

where χ_i are the dielectric susceptibilities, (nx_i) is the angle between the electric field and the electric moment in the i direction (pp. 224–7). Note that despite the original separation between electric and elastic parts in the initial differential of the energy (equation (6)) the final expression includes mixed members of electric and elastic origin, originated in the differentials of the charge and strain (equations (2), (4), and (5)). The mix members would become explicit in the expression for free energy.

The first two terms of the energy differential (equation (7)) are of pure electric and elastic energy, which were known to be exact differentials. Therefore, the other two terms, of piezoelectric energy, should also be exact differentials. So he obtained 18 equations:

$$\chi_k \frac{\partial x_l}{\partial x_k} = -\frac{\partial a_k}{\partial X_l} \tag{8}$$

where l varies from 1 to 6 and k from 1 to 3. The derivatives in the equation are the constants of Pockels's and the moduli of Voigt's equations, respectively, written as[12]:

$$\chi_m \mu_{nm} = \delta_{nm}. \tag{9}$$

Using Voigt's relation between the constants of the general theory δ and ε, Pockels expressed his constants in terms of the piezoelectric constants: $\chi_i \mu_{hi} = \sum_1^6 \varepsilon_{ik} s_{hk}$, where s_{hk} are the elastic susceptibilities (called by Pockels elastic moduli). These equations state the relations between the converse and the direct effect. In later formulations of the theories, the equations for the direct and converse effect would be chosen in a way that would enable employing the same piezoelectric constant in both. Since Pockels chose to write the equations of the converse effect with the same variables that Voigt used for the equations of the direct effect (electric moment and strain), he did not find a simple relation between the constants (μ and ε). The relation is more complicated than it seems from the expression, since often the relation between the electric moment and the field is not expressed correctly by the dielectric susceptibility. In such cases, one needs another way to compare the effects. Pockels did not mention these problems here, but they influenced later work on the reciprocity of the phenomena. Yet, the complex relations between the variables had already led Pockels to derive an expression for the influence of the electric field on the elastic susceptibilities (p. 225–9). This was the first expression of secondary piezoelectric effect, which would receive a more systematic treatment by Voigt in 1894.

Pockels showed that Lippmann's law of the relation between the converse and direct effects follows from the theory. He stated Lippmann's claim more clearly than its original author. According to Pockels, "when a face A of a crystal plate becomes electrically positive by *pressure* normal to that face, then a positive charge on the same face A would cause a *dilatation* in a normal direction" (emphasis in the original, p. 229). Pockels easily verified the law by examining the situations stated by Lippmann first with Voigt's equations for the direct effect and then with his equations for the converse effect, comparing them by using the relationship found between the constants (equation (8)).

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[12] Here and in the following Pockels used an abbreviated notation.

However, by formulating the law in terms of the electric moment he showed that the law is more perplexing than Lippmann's formulation suggested. "When *pressure* in a certain direction *n* generates a positive moment *m* in this direction, then a positive moment *m* induced by electric force leads to *contraction* in the direction *n*. In this setting the law appears paradoxical at first glance; because it states that compression produced by pressure is reinforced by the simultaneously resulting dielectric moment." He concluded that "*in general no simple reciprocity exists between the deformations and the dielectric moments*"(p. 230–1, emphasis in the original). Pockels tried to dissolve this paradox by appealing to the effects in other directions than that of the pressure. Since one can choose a crystal in which the sole effect is in the direction of pressure (even quartz pressed at a polar axis is an example of that), this argument could not work. Pockels did not consider objections to his argument, yet he did not refer to it again. The complication of reciprocity continued to occupy the study of piezoelectricity for a while. Further treatments of the relationship between the converse and direct effect were based on thermodynamic formulations of piezoelectricity. Pierre Duhem was the first to treat both piezoelectricity and its reciprocity from this perspective. His thermodynamic theory of piezoelectricity is the subject of the next section.

DUHEM'S THERMODYNAMIC THEORY

After the failure of his 1886 thermoelectric theory of pyro- and piezoelectricity, Duhem returned to the subject in his *Leçons sur l'électricité et le magnétisme*, published in three volumes in 1891–92.[13] This time, however, his approach was very different—abandoning explanatory to descriptive theories. Like other textbooks of the time, it was more than just a didactic summary of existing knowledge. Duhem presented his own version of electromagnetism, based on general mechanics and thermodynamics, which was highly influenced by Helmholtz's. This was part of Duhem's research programme, by which thermodynamics should "embrace all the changes of states of bodies, the changes of location as well as the changes of physical qualities, in common principles."[14] Following the works of Gibbs and Helmholtz, Duhem believed that thermodynamics could supply a rigorous and coherent framework for physics and chemistry. In this spirit he aimed at a new theoretical synthesis of electromagnetism, perhaps as an alternative to Maxwell's *Treatise* (Vol. 1, pp. v–vii). Theoretical innovations like new theories of pyro- and piezoelectricity based on thermodynamics also had a place in such a book. Still, the nature of such a general work limits the space given to these theories and thus, their scope. These theories appear in the second volume, which was published in 1892. Nevertheless, Duhem knew neither of Voigt's general theory, nor of Pockels's theory of the converse effect.[15]

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[13] Pierre Duhem, *Leçons sur l'électricité et le magnétisme*, Paris: Gauthier-Villars, 1891–2. Page numbers in parentheses in this section, unless otherwise stated, refer to the second volume of the work.

[14] Duhem, *Notice sur les Titres at Travaux Scientifiques*, p. 39

[15] According to Duhem's testimony *ibid.*, p. 92–3. As will be shown below this can also be seen from his theory.

The thermodynamic functions

Duhem based his discussions of electromagnetic systems on what he called the internal thermodynamic potential signified by F, commonly called Helmholtz's free energy. John Theodore Merz summarized the origins of this function: "the general use of the conception for free energy must be dated from the remarkably lucid expositions of Helmholtz, though it is now recognized by all who have studied the history of this fertile conception that the physical notion of available energy goes back to Thomson and Maxwell; that the mathematical formulæ were given by Massieu [in 1869 and 1876] and more definitely explained and applied to the physical phenomena of dissociation by Gibbs [in 1875–78]."[16] Gibbs had already laid foundations for the function of free energy in 1871. He elaborated them in a seminal memoir published in parts between 1875 and 1878. In this memoir he employed the new thermodynamic function to the study of various subjects including elasticity, electrochemistry, electromagnetism, electro-capillarity, and thermoelectricity.[17] Chemistry was still the major subject to which the new device was applied.

In 1872, Horstmann, a former student of Helmholtz, had already applied equations similar to those of the free energy to chemistry. His former teacher derived the equations independently for a study of chemical processes a decade later. In his rejected 1885 dissertation Duhem studied the application of Gibbs and Helmholtz's thermodynamic functions to theories of chemical reactions and electricity.[18] At that time the general thermodynamics suggested by Gibbs was uncommon. Gibbs's memoir was neglected by most physicists. Leading scientists like William Thomson and Lord Rayleigh considered it too difficult and unfertile. This might have also been the approach of Lippmann, who chaired the committee that rejected Duhem's work. In the late 1880s and early 1890s, however, an expanding group of scientists employed thermodynamic functions for several problems, especially ones connected with physical chemistry, gases, and solutions.[19] Merz observed "that it is especially owing to the labors of Duhem that the subject has received the attention of chemists."[20] Yet as Dolby remarks, more than one person was involved in the project. "It was not until the emergence of the new speciality of physical chemistry [especially in Germany] in the late 1880s, that appreciation of [Gibbs's] paper was being spread effectively." Physical chemistry attracted much attention due, among other reasons, to a controversy between the supporters of thermodynamic approach and the adherents of the earlier

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[16] John Theodore Merz, *A History of European Thought in the Nineteenth Century*, Edinburgh and London: William Blackwood & Sons LTD, 1927 (reprint), Vol. 2: p. 173 (footnote), references are omitted.

[17] Martin J. Klein, "Gibbs, Josiah Willard," *DSB* 5: 386–93; Wilhelm Ostwald, *Lehrbuch der allgemeinen Chemie*, 2ed edition, Leipzig: Wilhelm Engelmann, 1911, vol. 2, part 2: 141–48.

[18] Helge Kragh, "Between Physics and Chemistry: Helmholtz's route to a theory of chemical thermodynamics" in David Cahan (ed.) *Herman von Helmholtz*, Berkeley: University of California Press, 1993, pp. 403–431; J. R. Partington, *An Advanced Treatise on Physical Chemistry*, London: Longmans, 1949, Vol. 1: p. 184–87; P. Duhem, *Le potentiel thermodynamique et ses applications a la mécanique chimique et l'étude des phénomènes électriques*, Paris: Hermann, 1886.

[19] This group included among others Planck, Ostwald (who translated Gibbs's to German in 1892) and Helm; Klein, "Gibbs"; Smith, *The Science of Energy*, pp. 303–304.

[20] Merz, *European Thought*, p. 173.

thermo-chemistry. Physicists like Helmholtz, Duhem and Planck took a vital part in the emergence of the new speciality.[21] These scientists employed thermodynamics to embrace parts of chemistry in physical theory. In his work on electromagnetism Duhem presented an analogical treatment of that field, which was already part of physics, as part of his plan to embrace all physical science. Overall this project turned out to be less successful than the thermodynamic formulation of chemical questions. Still, as will be seen below, Duhem's work contributed to the subsequent presentation of piezoelectricity, if not all electromagnetism, by thermodynamic functions.

Duhem's application

According to general thermodynamics, a system reaches stability when its thermodynamic potential reaches an extremum. Thus, the condition that the thermal potential will be at an extremum determines the relations between the variables of the system. This condition leads to one or several equations for the phenomenon under consideration, which enable further elaboration of its theory. The particular expression of the thermodynamic potential is, thus, the central premise of a theoretical account of a phenomenon. In Duhem's book the terms of the potential function vary from one case to another, according to the interactions that characterize the phenomena under consideration. Pyroelectricity and piezoelectricity are part of the theory of dielectrics, which is developed after a theory of magnetism. For Duhem, these two are connected subjects, based on the same mathematical principles, since both lack monopoles. Duhem's emphasis on the lack of monopoles, i.e., electric charge, in dielectrics stands in contrast to the approaches taken by Riecke, Kelvin and even Voigt in their molecular theories of piezoelectricity. The latter preferred to view dielectrics as composed of charges of inverse signs that can be (at least in principle) separated from each other, unlike magnetic dipoles that cannot be divided into monopoles. Duhem's choice demonstrates his antagonism toward a corpuscular hypothesis. Nonetheless, Duhem's view of magnetism and dielectrics followed a long tradition that connected the two subjects. At least since Aepinus the electric properties of dielectrics, in particular those of pyroelectrics, had been compared to the behavior of magnets.[22] In the nineteenth century this tradition was influential both in the work of the French mathematical physicists at the beginning of the century and in that of Faraday and therefore, in that of his followers.[23]

Duhem expressed the thermodynamic potentials of both magnetism and dielectrics in the same way and used expressions derived from the treatment of the former in the study of the latter, retaining the symbols of the variables, and changing only their meaning. For example, A, B, and C signify the components of the intensity of magnetism and later the component of the dielectric induction, or polarization (pp. 339–44). This procedure often leaves the reader confused, especially when one

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[21] R. G. A. Dolby, "Thermochemistry versus Thermodynamics: The nineteenth century controversy," *History of Science* 22 (1984): 374–400, quotation on p. 385.

[22] On the bearing of this analogy on the study of pyroelectricity and eventually of piezoelectricity see chapter one, p. 27.

[23] On the theory of dielectrics see above p. 104.

wishes to study only a part of the work, like the theory of piezoelectricity.[24] He used the equations derived for the intensity of magnetism from the thermodynamic potential for the pyro- and piezoelectric polarization; the first of the three equations is

$$A = -\frac{1}{\Phi}\left(\delta_{11}\left[\varepsilon\frac{\partial(V+V')}{\partial x}+\lambda\right]+\delta_{12}\left[\varepsilon\frac{\partial(V+V')}{\partial y}+\mu\right]\right.$$
$$\left.+\delta_{13}\left[\varepsilon\frac{\partial(V+V')}{\partial z}+\nu\right]\right) \tag{10}$$

where x, y, and z are the coordinates, V the potential of the free charge and V' the potential of the polarization (or that of bound charge in other terms), λ, μ, and ν are coefficients that depend on the physical properties of the dielectric but are independent of the polarization, ε is the dielectric coefficient, Φ is a coefficient and δ_{ij} are dielectric coefficients (p. 383).[25] Duhem did not clarify the meaning of the functions and coefficients used. This attitude is probably connected to the highly abstract view that he had of physics and his rejection of hypothetical theoretical entities. Still one can infer, from his use of the magnitudes and their place in the equations, something about their physical significance when applied to dielectrics. The gradient of the potentials is commonly regarded as the electric field, though Duhem did not identify it with the field. So the "coefficients" λ, μ, and ν should be seen as a kind of electric field of nonelectromagnetic origin (they are not associated with electric potential). This is how the contemporaries regarded them without much ado.[26] Thus, Duhem's polarization (A) is inverse to the sum of the "regular"electric field and electric effect due to other interactions. Later, he implied that δ_{ij}/Φ is the "dielectric induction" (p. 401), which is parallel to the dielectric susceptibility (with an opposite sign).

In order to study pyro- and piezoelectricity, Duhem assumed that the crystals are homogeneous conductors so that the sum of the electric potentials ($V + V'$) inside the crystal is constant and its gradient is zero. Notice that the potential itself V can still vary. For Duhem the constancy of the potential meant the nonexistence of free charge inside the crystal. While virtually all workers in the field assumed the nonexistence of free charge in the crystal, they objected to the assumption that the crystals are good conductors. Moreover, some physicists assumed the possible existence of electric displacement inside a piezoelectric crystal in contrast to Duhem's assumption used here. Duhem's supposition of high conductivity in his 1886 theory of pyroelectricity

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[24] This difficulty in reading Duhem's *Leçons sur l'électricité et le magnétisme* was probably one of the causes of the "scarcity of printed reaction to it" (Jaki, *Uneasy Genius,* p. 99). As Hertz, one of the more competent electrodynamicists of the day, wrote to Duhem, "such a work must not be read in haste" (quoted by Jaki, *ibid.*, p. 100).

[25] For Duhem's treatment of these equations in the part on magnetism see *Leçons* pp. –296–299. For a more elaborated discussion of his derivations regarding piezoelectricity see Katzir. *History of Piezoelectricity*, pp. 158–163. For a discussion of his electromagnetic theory see Octave Manville, "La Physique de Pierre Duhem," in [id.] *L'Œuvre scientifique de Pierre Duhem,* Bordeaux: Feret et fils, 1927, pp. 3–467.

[26] Pockels referred to them as the components of the electric force (in modern terms field) without further comment. Pockels, "Ueber die elastischen Deformationen piëzoelektrischer Krystalle im elektrischen Felde" *Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie* 8 Beilage-Band (1893): 407–417, on p. 408.

was shown to him to be in contradiction to experiment. The new theory supposed neither steady currents nor high conductivity, yet the assumption of conductivity was still questionable. With that equation (10) becomes:

$$A = -\frac{1}{\Phi}(\delta_{11}\lambda + \delta_{12}\mu + \delta_{13}\nu). \tag{11}$$

All the variables on the right-hand side maintain a constant value in the whole crystal. Therefore, the polarization is constant. This and the two similar equations for B and C, are the equations for both pyroelectricity and piezoelectricity. They express the polarization due to the inner state of a crystal free from any potential gradient. Duhem assumed that in pyroelectric crystals at least one of the magnitudes λ, μ, and ν has a nonvanishing value that depends only on the nature of the crystal and its temperature. Thus eventually, he adopted Thomson's 1860 hypothesis that pyroelectric crystals have permanent polarization, which he had rejected in 1886. He was one of the last to oppose Thomson's hypothesis that now became accepted knowledge.[27] Duhem did not express the way in which λ, μ, and ν are dependent on the temperature (pp. 383–5).

Piezoelectric crystals are characterized by the dependency of their polarization on the strains. So Duhem assumed that λ, μ, and ν are linear functions of the strains:

$$\lambda = \lambda_0 + l_1x_x + l_2y_y + l_3z_z + l_4y_z + l_5z_x + l_6x_y \tag{12}$$

where l_i are coefficients.[28] μ and ν have parallel expressions with coefficients m_i and n_i. He further assumed that the variation of the crystal's dielectric properties during the process is negligible. In pyroelectric crystals at least one of the coefficients λ_0, μ_0, and ν_0 expresses the field due to temperature and is not null. Still, strain does not change their value. Its electric effect is expressed through the 18 piezoelectric coefficients l_i, m_i, n_i. Unlike Voigt (in 1890), Duhem regarded pyro- and piezoelectricity as independent effects, with different coefficients. This assumption agrees well with his general preference in 1892 for eliminating unnecessary hypotheses, like the piezoelectric origin of pyroelectricity.[29] He restated the known rule that to be piezoelectric a crystal should have a hemihedral axis and no center without demonstration (pp. 395–8).

Inserting equation (12) into (11) one obtains the general equations for polarization due to strain, which, however, do not appear explicitly in Duhem's book. The expressions in these equations are more complicated than those of Voigt since in Duhem's version the influence of the strain on the polarization is not expressed directly, but via the magnitudes λ, μ, and ν. The translation involved the dielectric susceptibility—generally a tensor, but often can be expressed as a vector or a scalar. In the latter case each component of the polarization depends only on the correspondent coefficient (λ, μ, or ν). Duhem employed this property in analysing quartz. In this case, Duhem's

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[27] In the 1894 edition of his comprehensive *Lehere von der Elektricität* (second edition, Braunschweig: Friedrich Vieweg und Sohn, 1894. Vol. 2, p. 429) Gustav Wiedemann continued to reject the assumption of permanent polarization, on the basis of experiments by Hankel. Wiedemann did not mention that his assumption is incompatible with Voigt's theory, which he described in some detail a few pages later.

[28] Duhem expressed the strains explicitly as derivatives of place.

[29] The question of the relations between pyroelectricity and piezoelectricity is dealt with more detail in the next chapter, relating to empirical work of Riecke and Voigt.

$-\frac{\delta_{11}}{\Phi} l_j$ is equivalent to Voigt's piezoelectric constants ε_{1_j}. Yet the equivalent is valid only under constant relations between polarization and the magnitudes λ, μ, and ν, i.e., between polarization and electric field. To this end one has to assume with Duhem that the gradient of the electric potentials inside the crystal is *always* zero. However, the relations between polarization, electric potential and electric field depend on the source of the electrical excitement and the specific experimental arrangement. For example, in an electrically isolated piezoelectric crystal the dielectric susceptibility does not appear in the equations for polarization. Duhem independently obtained similar equations, but not always equivalent to Voigt's. Pyroelectricity and piezoelectricity were the only known phenomena in which the polarization was not due to the electric field, and therefore the only example in which the electric field alone does not determine the polarization. This latter point was not articulated clearly at the time and, as mentioned below, was a source of further confusion.

Duhem did not attempt a general theory that would supply specific equations for all classes of crystals like that of Voigt. Two examples, tourmaline and quartz, were enough for his purpose. His discussion of their particular behavior, i.e., the specific coefficients that do not vanish in their cases, was based on unsystematic, even naive considerations of symmetry, dissimilar to Voigt's. This reasoning led him to piezoelectric coefficients for tourmaline that explain its electric behavior due to pressure applied in the direction of the principal axis as observed by the Curies. However, the result does not agree with the coefficients derived by the general theory, which were confirmed experimentally. Duhem, however, probably did not know about these experimental results that were published only in 1892. The shortcomings of Duhem's treatment are clearer in his account of quartz. From the symmetry of quartz around the principal axis he concluded that when the pressure in the xy plane is uniform ($x_x = y_{y)}$ no electric effect should appear. Therefore, he proposed:

$$\begin{aligned} A &= -\omega l(x_x - y_y) \\ B &= -\omega m(x_x - y_y) \\ C &= 0 \end{aligned} \tag{13}$$

where ω is the coefficient of dielectric induction, B is the polarization in the direction of a polar axis and C in the direction of the principal axis. Duhem's reasoning did not lead to an effect for shearing stress. He relied on the experiment to conclude that l should be either zero or very small.[30] Combining this conclusion with equation (13), he could explain the relative magnitude and sign of the transverse and longitudinal effects. He left more complicated experiments like those of Röntgen in1883 out of the discussion in this noncomprehensive textbook of electromagnetism (pp. 398–404). However, he failed to mention that some results contradicted his equations. In particular, Röntgen also showed the appearance of electric tension associated with polarization perpendicular to a polar axis - A in Duhem's notation. Thus, Duhem's equations were invalid. Had he known Voigt's theory, he would have realized that

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[30] Duhem chose a slightly different coordinate system than the one usually employed. His x is the others' y and vice versa. Compare these equations with Voigt's ch. 2 eq.

quartz has more nonvanishing coefficients, necessary for accounting, for example, for Röntgen's torsion experiments.

The converse effect

Duhem also employed the thermodynamic potential to the study of the converse piezoelectric effect. As in the treatment of the direct effect, the discussion was based on expressions derived first for magnetism, and then modified according to the new problem. The method of derivation was similar for both effects: expressing the appropriate thermodynamic potential and obtaining equations for its minimum. Yet he based the new derivation on a different and more complex expression for the potential. To deal with the complex mathematical expression he used more elaborated mathematical techniques, like integration by parts of dF and the study of the integral equation of the crystal's surface. Assuming that the crystal is in electric equilibrium and that it possesses no free charge, and neglecting second-order effects, Duhem arrived at six equations for the mechanical deformation of crystal due to homogeneous electric polarization. He wrote only the first of these as:

$$a_{11}x_x + \ldots = l_1 A + m_1 B + n_1 C \tag{14}$$

where a_{ij} are the elastic constants, which are also called elastic stiffness coefficients. The equation is valid only for nonpyroelectric crystals, since Duhem had to assume that $\lambda_0 = \mu_0 = \nu_0 = 0$.[31] Duhem's formulation had the advantage over Pockels's of using the same variables and piezoelectric coefficients in the equations for the direct and converse effects. That these are the intensive variables of electric moment and strain increased the usefulness of the formula (p. 467–72). However, the two sets of equations originated from two different expressions of the potential function. Furthermore, in the case of the direct effect, Duhem did not establish a direct relation between strain and polarization; the relation he suggested was not valid for every case. The asymmetry should not be surprising. We have seen that two years earlier, Pockels had concluded (in a paper Duhem did not know) that "in general no simple reciprocity exists between the deformations and the dielectric moments [polarization]."[32] Duhem's failure to derive all his equations from one expression for the potential reflects his unfortunate choice of variables from a thermodynamic perspective.[33] In addition to these questionable features, Duhem made a slip in a sign in the derivation of the equations for the converse effect. An error in a sign appeared in the equations for the converse effect and the complexity of his equations did not help him in recognizing this slip. Had he based his theory on direct derivation from one explicit thermodynamic potential he would probably not have missed such a slip. This mistake, as we

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[31] Duhem's equations are more cumbersome than those of Pockels, since the left side of each includes all the six unknown strains. Yet, recognizing that the left side in each equation equals a component of stress $\sum a_{ij}x_j = -X_i$, this complication can be removed.

[32] Pockels, "Aenderungen des optischen Verhaltens," p. 231.

[33] The transformation between the electric variables in Duhem's expression confused a careful observer like W. Cady about the basis of his theory, which is a polarization theory in Cady's term (like Pockels') and not a kind of "Voigt's theory." (Cady, *Piezoelectricity*, p. 251)

will see below, led to an erroneous interpretation of the relations between the converse and the direct effects. In his 1910 textbook, Voigt acknowledged Duhem's priority in introducing the thermodynamic method, "though" he added, "in a not totally correct manner."[34]

Duhem concluded that piezoelectric crystals are deformed in linear proportion to "the intensity of the electric field in which the crystal is placed" (p. 473). The deformation of nonpiezoelectric bodies, on the other hand, is in an order of magnitude smaller than the polarization and is too small to be observable. The latter conclusion does not follow directly from the equations, which show no effect in this case. Its origin is rather in the physical considerations that led to the equations, namely the negligence of higher orders of strains. This is parallel to the linear assumption made by Voigt. Duhem showed here considerable awareness of the limits of both his theory and current experiments (p. 472–4).

Merits and limitations of Duhem's work

In *Leçons sur l'electricité,* Duhem suggested the first derivation of piezoelectric equations from thermodynamic potential. As early as 1886 he had introduced thermodynamic potentials to the study of pyro- and piezoelectricity, but his 1892 potential reflected the direct and independent interactions of elasticity and electricity and yielded acceptable equations. It is compatible with his mature philosophy, which prohibited hypotheses about real causes and unobserved processes. Duhem did this with a thermodynamic potential, but it could be done by another method. Furthermore, the use of such a potential does not ensure avoidance of hypotheses about causes and hidden precesses, as his earlier theory demonstrates. Still, the way Duhem used the thermodynamic potential in 1892 is especially suitable to this kind of nonhypothetical physics. His mature scientific method—energetics, he explained in 1913 "presents no revelations on the true nature of matter. Energetics claims to explain nothing. Energetics simply gives general rules of which the laws observed by the experimentalists are particular cases."[35] This was true of his 1892 theory of pyro- and piezoelectricity, but not of his 1886 theory.

Duhem insisted on his priority in applying thermodynamics to the study of piezoelectricity, an application that was soon followed by Riecke, Pockels and Voigt (according to Voigt, independently).[36] In this vein, Donald G. Miller, claims that "Duhem was able to treat pyroelectricity and piezoelectricity without needing the special hypotheses of F. Pockels and W. Voigt."[37] The "special hypotheses" Miller had in mind are probably the basic equations of piezoelectricity assumed in both the theories. Their theories have no other "special hypotheses."

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[34] Voigt, *Lehrbuch der Kristallphysik*, p. 815

[35] Pierre Duhem, "Logical Examination of Physical Theory," trans. Roger Ariew and Peter Barker, *Synthese* 83 (1990): 183–88, on 183.

[36] Duhem, *Notice*, pp. 92–3. Asserting his priority Duhem referred to Voigt but failed to mention the latter's critical remark quoted above.

[37] Donald G. Miller, "Duhem, Pierre" *DSB*, Vol. 4, p. 231. Miller seems to echo Duhem's own rhetoric.

Nominally, Miller is right; Duhem was able to deduce the equations that were postulated in Voigt's and Pockels's theories. However, in order to deduce these equations, Duhem had to assume specific expressions for the interaction of matter and polarization in the thermodynamic potential function. While Voigt assumed linear equations for the polarization, Duhem assumed that the magnitudes λ, μ, and ν are linearly dependent on the six components of strain. There is no real difference. In both the theories the assumptions do not become necessary by any intrinsic theoretical reasoning, but depend on external empirical knowledge. For example, one could assume that the piezoelectric effect depends on all the nine strains (i.e., the influence of x_y is not equal to that of y_x) and thus one would have 27 coefficients instead of 18, or one could assume that the effect is not linear. The hypotheses in Duhem's theory are located in different stages but have the same nature as Voigt's and Pockels's. Duhem's procedure has a potential advantage in assuming the nature of dependency only once for the equations of both the direct and the converse effect. However, Duhem did not exploit this possibility since he used two different expressions for the potential. Anyway, I doubt that this advantage justifies Miller's claim.

Thermodynamic potentials are a powerful theoretical tool for the discussion of various equilibrium phenomena, like piezoelectricity. Contemporaries realized its power. Reading Duhem's *Leçons*, Pockels saw in its use of potential an advantage over his and Voigt's formulations. The former is more general in its ability to include nonlinear effects, and thus to account for nonhomogeneous fields (this is not true about the equations Duhem derived from the potential function).[38] Curiously, Duhem, a major adherent of "general thermodynamics," did not exploit central properties of the potential. He used neither Maxwell's relations between partial derivations of different variables, nor the immediate meaning of the potential partial derivations as would be done by Riecke a year later and by Voigt a year after that. Modern expositions utilize the free energy to display the relations between various phenomena and the transformations of energy from one kind to another, like from mechanical to electrical in piezoelectricity. Almost needless to say, this kind of presentation does not appear in Duhem's book; to the best of my knowledge it was not used at the time. Thermodynamics supplied a unified logical theoretical scheme for the various electric phenomena that could be treated by similar procedures. For Duhem, its logical unity was the compelling reason to adopt thermodynamics. Other physicists, however, had different priorities.

Duhem relied on "specific hypotheses" for elaborating theories for specific crystals, like tourmaline and quartz. Unlike Voigt, he had no general treatment of the relations between the crystals' symmetry and their piezoelectric behavior,. Moreover, these specific equations disagreed with the observations. The determination of the piezoelectric equations of each crystal group and the behavior of the crystals under specific physical conditions is the core of Voigt's general theory, not its basic equation as implied in Miller's claim. Voigt provided a theory that accounted for all experimental data and supplied a basis for further experimental work. This was not Duhem's intention. As he wrote in its preface, he did not intend his book for direct use in the laboratory:

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[38] Pockels, "elastischen Deformationen," p. 416.

> Our aim, moreover, is not to write a manual suitable for serving as a guide to the experimentalist and the practitioner, but to indicate plainly the theoretical link [*lien*] that unites the diverse parts of electric science. The clear view of this link will stimulate the discovery of new phenomena, new laws, that, in their turn, will be used for its corroboration and extension. (Vol. 1, p. viii)

Voigt also did not write a manual for the experimentalists. He, however, displayed much more concern with the appearance of the phenomena in the laboratory, and with the experimental examination of the theory. Like most contemporary theoreticians, Voigt performed experiments himself, mainly following his theoretical work. In the laboratory Voigt tested his piezoelectric theory, and Pockels the relations between piezo-optics and piezoelectricity. Duhem, on the other hand, was one of the first of a new kind of theoreticians who did not do any experimental research.[39] His distance from the laboratory is manifested in his theoretical work.

DUHEM AND POCKELS ON THE RECIPROCITY OF THE PHENOMENA

Duhem returned to the theory of piezoelectricity soon after the publication of *Leçons sur l'électricité et le magnétisme*. Now he attempted to generalize Lippmann and Pockels's conclusion about the reciprocity of the phenomenon. Duhem became familiar with Pockels's theory of the converse effect through an offprint, which the latter sent him only after the publication of his textbook. There Duhem found a reference to Voigt's general theory, of which he had not known before. Perhaps these papers, which were not published in central journals of physics (Pockels's in a journal for crystallography and mineralogy, Voigt's long memoir as a separate publication of the *Göttingen Abhandlungen*) were unavailable in Duhem's provincial university at Lille. His ignorance of these publications also suggests that he did not make much effort to locate papers relevant to his theories in the scientific literature. In any case, Pockels's paper motivated Duhem to show the advantage of his method in displaying the general relations between the converse and the direct effects. He was further attracted by Pockels's reference to the paradoxical result, which Duhem believed he could resolve. Pockels's solution, we have seen, was not acceptable. Lippmann's rule, Duhem claimed, is a particular case of "the principle of displacement from

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[39] Few physicists before Duhem were not engaged in experimental study. From the generation before Duhem one can point out Gibbs and Clausius as two early pure theoreticians, though Clausius had experimental experience. Still Planck, who started his scientific career a little before Duhem, was regarded as the only important pure theoretician in Germany. In France Duhem was the only physicist who did not perform experiments. A few mathematicians made important contributions to physics (one can mention for example Poincaré) but they were mathematical physicists rather than theoretical physicists. The status of the mathematical-physicists in Italy was problematic in this respect since they were associated with mathematics rather than with physics. Planck and Duhem on the other hand viewed themselves as physicists and were regarded institutionally as such, although eventually Duhem had to submit a dissertation in mathematics, after his physics dissertation had been rejected by Lippmann. On the rise of theoretical physics in Germany see Jungnickel and McCormmach, *Intellectual Mastery of Nature* vol. 2, On Clausius Vol. 1 pp. 198–9.

equilibrium" (*Principe du déplacement de l'équilibre*). According to this principle, after disturbance from equilibrium, systems tend to return to their original state. In 1888 Ferdinand Braun derived the principle from a general notion of stability. Braun's argument "was purely qualitative."[40] In 1890 Duhem showed that this principle could be derived analytically from the theory of thermodynamic potential.[41]

Although Duhem was familiar with Pockels's discussion of reciprocity, he did not follow the latter's method of comparing the two effects under concrete conditions. Instead, he derived the relations directly from the equations of both effects as they appear in *Leçons sur l'électricité et le magnétisme*. These equations determined the relations between the constants and thereby, the relations between the converse and direct effects. Duhem employed the equations of the direct effect for a crystal subject only to an elastic force (combination of equations (12) and (11)), and the equations for the converse effect for a crystal subjected only to a uniform gradient of the electric potential (equation (14)).[42] By algebraic manipulation he combined them and obtained a general inequality (pp. 168–73) from which he concluded:

> *When one sets certain forces F upon a piezoelectric crystal, removed [*soustrait*] from any electric influence, these develop inside this crystal a certain dielectric polarization. If, by the action of an electric field, one developed the same polarization inside the crystal, the crystal would experience a certain deformation* Δ*. The forces F are those whose action opposed the deformation* Δ.
>
> One recognizes immediately in this statement a consequence of the general law of the displacement from equilibrium. One would be tempted to view this as a generalization of the statement given by M. G. Lippmann; we shall see that it is not so at all, on the contrary, the proposition proven by M. G. Lippmann is *in contradiction* with the former. (p. 173, emphases in the original.)

Duhem proceeded by examining the specific example given by Lippmann and Pockels reaching indeed a contradictory conclusion. According to Duhem, when one positively charges an electrode at the base of a piezoelectric crystal plate that becomes positive by pressure, the crystal would contract rather than dilate as Lippmann and Pockels claimed. Lippmann, Duhem claimed, confused between real and fictive (bond charge) in his demonstration, and thus arrived at the wrong conclusion.[43]

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[40] *Ibid.*, vol. 2, p. 100. The German experimental physicist Ferdinand Braun made his most important contribution in electromagnetism and the theory behind electro technology in general and wireless telegraphy in particular. For this work he received the Nobel prize in physics, which he shared with Marconi in 1909 (a year after Lippmann). Harold I. Sharlin, "Braun, Ferdinand," *DSB*, Vol. 2:427–428.

[41] P. Duhem, "Sur la déformation électrique des cristaux," *Annales scientifiques de l'École normale supérieure*, 9 (1892): 167–176, on p. 168. Page numbers in parentheses in this section refer to this publication.

[42] The text mistakenly refers to magnetic field. Although this slip did not change anything in the following, it sheds light on Duhem's use of the same equations for the magnetic and electric interactions, and his general, abstract use of the symbols in his equations. Of course, Duhem would have corrected it if someone had shown it to him.

[43] Duhem's criticism is unjustified. Lippmann's analysis is valid for the example treated. For more details see above chapter 1, p. 37.

Lippmann's conclusion rather than Duhem's seemed to agree with the principle of displacement from equilibrium. However, Duhem explained, when the electrodes are connected this is no longer the case. In this arrangement, by Lippmann's argument true charge induced from pressure would generate further contraction in contradiction to the equilibrium principle. On the other hand, according to Duhem's results in this case, positively charging the electrode that becomes positive by pressure causes an expansion, as one would expect from the displacement from equilibrium.

Pockels had already pointed out the paradoxical character of Lippmann's rule but still regarded them as valid. Contrary to Pockels's own conclusion, Duhem thought that Pockels's demonstration contradicted Lippmann's conclusion and supported his own. Duhem did not show high esteem to Pockels's qualitative arguments. He ignored Pockels's warning about the lack of a general relation between the reciprocal effects (p. 203). Yet, Pockels's formulation of Lippmann's rule probably helped to convince Duhem that the rule contradicts the general principle of equilibrium and, therefore, is probably wrong. His antagonism toward Lippmann, who as professor at the Sorbonne rejected his first dissertation, could only help convince him that the professor for experimental physics at the Sorbonne was wrong. Since he did not respect Lippmann as a scientist, he probably considered the possibility that Lippmann had made an error and that Pockels had drawn the wrong conclusion by following convention and authority.

Duhem's mathematical derivation is rigorous and general. His arguments against Lippmann's reasoning and about the principle of displacement from equilibrium might seem convincing. According to Duhem, a denial of his conclusion leads to an endless reaction (electric charge causes contraction that generates more electric charge etc.), in other terms, a kind of *perpetuum mobile*. Yet, Duhem's conclusions are erroneous; Lippmann and Pockels were correct. A rigorous mathematical derivation based on erroneous equations usually leads to erroneous results. The mistake in the sign in Duhem's equations led to a mistaken conclusion about the reciprocity of the effect. In this case a change in the sign leads to a contradictory conclusion. Duhem failed to learn from Pockels's paper that the piezoelectric interactions are more complicated than a simple reciprocity between strain and electric moment; they involve also stress and electric field. Thus, he was led astray by his simplistic interpretation of his principle of equilibrium. He also failed to follow Pockels's example in examining the relations between the constants in the equations in concrete physical conditions. This could have been done, and would actually be done later, also in a thermodynamic approach. It was enough to derive the equations for both the direct and the converse effects from the same thermodynamic potential function. Even a repetition of the derivation in his textbook would have led Duhem to discover his trivial algebraic slip.

Perhaps due to the different variables used, Duhem did not notice that his and Pockels's basic equations do not agree, and so their conclusions should not. This probably made him think that Pockels's mathematical argument supports his conclusion. Following the publication of Duhem's argument, Pockels pointed out to him the mistake he had made. Duhem was quick to admit his mistake in public in a related paper on the principle of displacement from equilibrium. "The results that I obtained," he wrote, "must all consequently be *changed in sign*, this will remove the discrepancy that they presented with those of M. Lippmann and M. Pockels. I thank M. F. Pockels for being kind enough [*d'avoir bien voulu*] to point out this inaccuracy to me."[44] Duhem did not refer to his earlier physical arguments for the agreement of his mistaken results with the principle of displacement from equilibrium, and how the danger of *perpetuum mobile* could be avoided.

Pockels, on the other hand, did discuss this principle in light of the valid results of the relations between the converse and direct effects. He discussed Duhem's results and corrected them in a special publication sent in June 1892. In this article he reformulated Duhem's statements in the correct form. The corrected statement made Duhem's reference to the "principle of the displacement from equilibrium" problematic. Pockels stated that in the correct form two cases out of the three considered by Duhem contradict this principle; while the third, which is the one considered by Lippmann, agrees with it. He added that according to Duhem's mistaken conclusion, such a problem still exists, therefore the last case contradicts the principle. He dismissed Duhem's claim that the contradiction disappears when one considers the differences between real and bound charges. He, however, did not try to propose his own reconciliation of the paradoxical results as he had done two years earlier. Instead, he claimed that the principle of displacement, which he called a law, is not always valid. Duhem's own attempt to generalize the law, he added, has only limited validity.[45] Pockels did not try to formulate a more sophisticated law that would also encompass such cases. In this publication he also showed the disparity between Duhem's results and his and Voigt's theory, and showed how to derive the correct result by Duhem's method. By that he adopted Duhem's thermodynamic approach to piezoelectricity. With the correct sign in the equations, Duhem's argument became a true generalization of Lippmann and Pockels's claim, and was considered as such in later publications.[46] The early disagreement between Duhem's results and those of Lippmann and Pockels was not mentioned any more. This seems to be characteristic of many representations by physicists in papers, textbooks, and handbooks, which tend to chart a linear progress of knowledge, omitting past mistakes and controversies.

RIECKE'S THERMODYNAMICS OF TOURMALINE

According to Eduard Riecke the alleged paradoxical character of the reciprocity was based on a misconception. The mathematical results, he wrote in 1893,

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[44] Duhem, "Sur le déplacement de l'équilibre," *Annales scientifiques de l'École normale supérieure*, 9 (1892): 375–379, on p. 379. Duhem's note implies that Pockels corrected him in a private communication. It is not surprising that this came from Pockels and not from Lippmann. In another paper Pockels refuted Duhem's claim for contradictions in Maxwell's theory, F. Pockels, "Ueber die durch dielektrische und magnetische Polarisation hervorgerufenen Volumen- und Formänderung (Elektrostriction und Magnetostriction)," *Archiv der Mathematik und Physik*, 12 (1893): 57–95, on 58.

[45] Pockels, "elastischen Deformationen," pp. 415–6.

[46] A year later Riecke mentioned Duhem's use of free energy, Eduard Riecke, "Thermodynamik des Turmalins und mechanische Theorie der Muskelkontraktion." *Göttingen Nachrichten*, 1893: pp. 19–45, on p. 30. Riecke did not mention the mistake in Duhem's original paper.

> lead to an apparent strange circle (*eigenthümlichen Cirkel*). The dilatation z$_z$ generates a positive moment γ, conversely [*umgekehrt*] the moment γ [generates] a dilatation z_z, so the two themselves appear to present mutually intensified effects. Actually this interpretation is not correct, since the equations in question are based on the application of different independent variables. Moreover, one could reach exactly the same conclusion from the following relations of the equation of gases $\frac{\partial v}{\partial p} = -\frac{RT}{p^2}$, $\frac{\partial p}{\partial v} = -\frac{RT}{v^2}$, [where v is the volume, p the pressure, T the temperature and R a constant].[47]

Thus, according to Riecke the principle of displacement from equilibrium is irrelevant to the equations of the converse and direct piezoelectric effect. These equations are of two different physical situations rather than of the same process. Thus, the question of equilibrium does not arise. These are no secondary effects of each other. By a new derivation of the reciprocal relations based on thermodynamic function, he showed how the equations depend on different independent variables. This was also a first step in the study of secondary phenomena.

Riecke's derivation of the reciprocal relations was part of a thermodynamic treatment of pyro- and piezoelectricity in Riecke's "hobby horse"—tourmaline. All Riecke's theoretical works on the subject, except his molecular theory, treated only tourmaline. Like Duhem, Riecke based his derivation on the free-energy function. Unlike Duhem, he incorporated results of Voigt's theory into the thermodynamic treatment, making it the first thermodynamic formulation compatible with the general theory. Riecke, we have seen, was an adherent of a molecular theory in physics in general, and of piezoelectricity in particular. He utilized many hypotheses about the structure of matter, the kind of forces in nature etc. Thus, he does not seem to be a likely candidate for carrying out the first thermodynamic formulation of Voigt's phenomenological theory. His colleagues in Göttingen, Voigt and Pockels, with their positivistic tendency to refrain from ungrounded hypotheses seem better candidates. However, Riecke's contribution was not exceptional. He had employed thermodynamics in the study of a few phenomena since 1890.[48] His employment of general thermodynamics show that in the early 1890s it was not limited to physicists who either denied atomic structure or postponed its study to the future.

The use of thermodynamic potential was promoted in Germany since 1882 by Helmholtz. Planck joined the plea in his researches five years later. Although Helmholtz derived the function of free energy independently—since 1887 Gibbs's work was known and used by a few German scientists. As mentioned, Duhem had applied Gibbs's formulations a few years earlier in France. With thermodynamic studies of dilute solutions and changing conditions in multi-phase systems in 1890, Riecke joined this small but active and expanding group of physicists, which examined a growing list of subjects.[49] These subjects included also electricity in fields like

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[47] Riecke, "Thermodynamik des Turmalins," p. 30. Page numbers in parentheses in this section refer to this publication.

[48] Wiechert, "Riecke," p. 50.

[49] Contrary to the suggestion of Klein and following him Smith, Riecke's papers indicate that Gibbs's theory was known and used in Germany before its translation by Ostwald in 1892. (Klein, –"Gibbs," Smith, *Science of Energy*, pp. 303–4). Planck mentioned Gibbs's theory in 1887 (Jungnickel and

electrochemistry and thermoelectricity.[50] Piezoelectricity was an appropriate candidate for such a treatment. That Duhem had already suggested a thermodynamic but defective theory made the subject especially appropriate for thermodynamic treatment.

Like many physicists at the end of the nineteenth century, Riecke appreciated the power of thermodynamic tools, and used them for his own purposes. For him, as for many others, this was an additional tool that did not contradict any physical hypothesis about the nature of the interactions. He recognized that molecular theory, like his, is impractical as a basis for elaborations. Here he used thermodynamics to suggest a speculative hypothesis according to which the contraction of the muscles is due to a piezoelectric process.

Two years earlier, in 1891, Georg Elias Müller, a professor of physiology in Göttingen, suggested that muscle contraction is caused by pyroelectric reactions, using Riecke's results on the pyroelectricity of tourmaline. The institutional connection at the University of Göttingen probably improved the communication between the physiologist and the physicist. Riecke, however, disagreed with Müller's hypothesis of **a pyroelectric** source. Still, the latter's theory suggested to him a **piezoelectric** model for the origin of muscle contraction. Being a physicist and not a physiologist, Riecke excused his treatment of the subject by the connection already made by Müller to the electricity of tourmaline. In that he showed awareness of the disciplinary boundaries. Unlike in his other works on tourmaline, in this research he did not perform any experiments himself but relied on empirical data found by physiologists as collected by von Fick in 1882. Disciplinary boundaries did not prevent this type of interdisciplinary work.[51] Riecke further remarked that "the investigation of the electric properties of crystals . . . reached for me a certain conclusion through the determination of the piezoelectric constants of quartz and tourmaline with Voigt and through my treatise about the molecular theory of the electric phenomena." (p. 19) So the new contribution was not part of his original research program, but a consequence of Müller's theory. Müller induced Riecke to suggest the first application of piezoelectricity to another branch of science, and indirectly to develop a thermodynamic formulation of piezoelectricity in tourmaline.

The concept of free energy was still so novel that Riecke opened the paper with a discussion of its properties in mechanical-electric systems that are not subject to

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McCormmach *Intellectual Mastery of Nature*, Vol. 2: 52). Eduard Riecke, "Das thermische Potential für verdünnte Lösungen," *Ann. Phy.* 42 (1891) 483–501 (originally appeared in *Göttingen Nachrichten* of the previous year); "Beiträge zu der von Gibbs entworfenen Theorie der Zustandsänderungen eines aus einer Mehrzahl von Phasen bestehenden Systems," *Zeitschrift für physikalische Chemie*, 6 (1890), 268–280. See also the discussion on the thermodynamic potential below p. 157

[50] Both were treated already by Gibbs. Electrochemistry was elaborated by Planck circa 1890, Jungnickel and McCormmach, *Intellectual Mastery of Nature*, p. 53.

[51] The physical study of physiology was common in the 19th century. It was advocated by a circle of Berliner physiologists, but the application of physics and chemistry to the life sciences began much earlier (at least in the 17th century) and did not require their manifests. Riecke's suggestion was special for the disciplinary belonging of its author, not for its content. Yet, physicists worked on perception, e.g. Ernst Mach. Herman Helmholtz is an interest example of transcending the disciplinary boundaries from physiology to physics, Frederic L. Holmes, "The physical sciences in the life science," in *The Modern Physical and Mathematical Sciences*, M. J. Nye (ed.), Cambridge: Cambridge University Press, 2003: pp. 219–236.

piezoelectricity. The latter was discussed in the special case of tourmaline. He did not write a general expression for piezoelectric free energy, but expressed tourmaline's free energy with the terms relevant to that species according Voigt's theory:

$$\begin{aligned}2F = 2f - r_1\mathrm{A}^2 - r_2\mathrm{B}^2 - r_3\Gamma^2 - \frac{A\varepsilon c\vartheta^2}{\Theta} - 2\mathrm{A}[\varepsilon_{15}z_x - \varepsilon_{22}x_y]\\ - 2\mathrm{B}[\varepsilon_{15}y_z - \varepsilon_{22}(x_y - y_x)] - 2\Gamma[\varepsilon_{31}(x_x + y_y) - \varepsilon_{33}z_z]\\ - 2\vartheta(q_1x_x + q_2y_y + q_3z_z) - 2\vartheta(e_1\mathrm{A} + e_1\mathrm{B} + e_3\Gamma)\end{aligned} \tag{15}$$

where f is the free energy of pure elasticity, A the mechanical equivalent of heat, Θ the temperature, ϑ its change, x_x the strain and A, B, Γ the electric force (field). Riecke did not identify the other coefficients, notice that ε_{ij} are the piezoelectric constants, e_i are the pyroelectric constants, q_i the coefficient of thermal expansion and r_i the dielectric susceptibilities. The partial derivatives of this expression immediately give the piezo- and pyroelectric equations for tourmaline. For example, for the stress and electric moment (γ) in the direction of the principal axis Riecke obtained the expressions:

$$\begin{aligned}Z_z &= -\frac{\partial f}{\partial Z_z} + \varepsilon_{33}\Gamma + q_3\vartheta\\ \gamma &= \gamma_3 + \varepsilon_{31}(x_x + y_y) + \varepsilon_{33}z_z + e_3\vartheta.\end{aligned} \tag{16}$$

These equations and the similar equations for the other directions and for the strains express the dependence of the electric moment on the external electric field, the pressure, and the change in temperature. Previously, Voigt and Pockels had written the contribution of the piezoelectric effect in isolation from the electric effect. The thermodynamic function, on the other hand, immediately yields all the possible influences in one equation (pp. 20–5).[52]

To study the relation between the different coefficients involved in the piezoelectric process, Riecke also examined the equations derived from a free energy function expressed in terms of stress instead of strain. This is parallel to Voigt's second set of equations with the electric moduli δ (as in equation (6) Chapter 2). The equation for the electric moment in the principal axis (z) becomes:

$$\gamma = \rho_3\Gamma - \delta_{31}(X_x + Y_y) - \delta_{33}Z_z + f_3\vartheta \tag{17}$$

where ρ_3 and f_3 are constants of dielectric susceptibility and (secondary) pyroelectric effect, respectively, for constant stress, while the parallels coefficients r_3 and e_3 are for constant strain. Thus, they are constant under different physical conditions. Riecke

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[52] Voigt and Riecke's 1892 experiments on tourmaline indicated that the pyroelectric constant e_3 is smaller than the experimental error. This enabled Riecke to assume that it is exactly zero, and by symmetry that the constant e_1 should also equal zero. Thus he assumed that pyroelectricity (in tourmaline) is wholly a secondary phenomenon of piezoelectricity. The electric moment still depends on the temperature but its coefficient is not an independent pyroelectric constant but a function of thermal expansion and piezoelectric coefficients: $e_3 = 2a_1\varepsilon_{31} + a_3 + \varepsilon_{33}$,where a_i are coefficients of thermal expansion. Interestingly, referring to the same experimental results a year later, Voigt assumed the existence of a direct pyroelectric effect. On the opinions and evidence concerning the existence of direct pyroelectricity see chapter 5.

showed sensitivity to the different physical conditions under which they are constant. Using Voigt's relation between the coefficients ε and δ, and the expressions for the moments (equations (16) and (17)), he derived the relations between the coefficients of dielectric susceptibility under stress and strain. For our example, he found:

$$\rho_3 = r_3 + 2\varepsilon_{31}\delta_{31} + \varepsilon_{33}\delta_{33}. \tag{18}$$

Thus, the relation between Δ_3 and r_3 depends on the piezoelectric properties of the tourmaline. This is an example of a secondary effect of piezoelectricity (pp. 26–7). These effects would be studied in a more general way a year later by Voigt.

From the two sets of equations (in terms of strain and stress) Riecke derived the reciprocal relations in the principal axis by partial derivatives. From equation (17) and a related one for the strain he found an inverse relation between the effect of the electric field and the effect of stress:

$$\frac{\partial y}{\partial z} = -\frac{\partial z_z}{\partial \Gamma} = -\delta_{33}. \tag{19}$$

The sign of the direct effect (the first term) is opposite to that of the converse effect (the second term). This is the relationship that Lippmann had obtained, which Riecke reiterated verbally. He added that the relation holds exactly only when the width of the plate is maintained by external pressure. Neither Lippmann nor Pockels had recognized this condition. This restriction reveals Riecke's awareness that in each the piezoelectric behavior depends on its specific free variables. It also shows an advantage of the careful thermodynamic derivation, which immediately show the values that should be constant during a process. Like Pockels and Duhem before him, Riecke showed that with different free variables the two effects are no longer of an inverse sign. From the equations in terms of strains (like equation (16)) one obtains the same sign for both effects:

$$\frac{\partial y}{\partial z_z} = \frac{\partial Z_z}{\partial \Gamma} = \varepsilon_{33}, \tag{20}$$

Since the piezoelectric coefficient and modulus always have the same sign and Δ is positive the derivatives have the same sign (pp. 29–30). This is the apparent "strange circle," which Riecke discussed in the quotation at the beginning of this section.

Notwithstanding his contribution to the general thermodynamic formulation of piezoelectricity, Riecke's goal here was the application of the theory to a model for muscle contraction. Riecke justified the choice of the crystal on the analogy between its electric properties and muscle contraction. Both are reciprocal phenomena free of heat production that retain their properties after several repeated cycles. He showed that the conditions of muscle contraction are similar to the exertion of external pressure and external electric field in tourmaline. The basic equations for the contraction of muscles contain two additional terms to those in the equations of tourmaline: one for the muscle's "swelling pressure" (*Quellungsdruck*), which has no parallel in crystals, and the other for the quadratic influence of the electric field, which is negligible for tourmaline. Altogether, Riecke considered the influences of four independent variables in his theory: elastic pressure, (electric) tonic force, temperature, and "swelling pressure." Yet, under specific conditions he succeeded in reducing them to two independent variables in accordance with the piezoelectricity of tourmaline.[53]

A piezoelectric explanation of the contraction of muscles involves a reduction of biological phenomena to physical inorganic phenomena and laws. Yet the theory does not hypothesize about the nature of muscles (which, of course, are not made of tourmaline) only about the physical laws that govern them. In order to come closer to reality (*Wirklichkeit*), Riecke explained that the muscle should be considered as "an aggregate of many different bodies." However, this would complicate the theory. The simpler schema is sufficient to display the main phenomena. He defended the neglect of the inner parts of the muscles on the nonreductionist practice in the physics of inorganic matter. Bodies that are aggregates of smaller crystals are treated as continuous; the heat motion of the molecules, which always exists, is considered only in the theory of gases. Moreover, from the atomic perspective ultimately all phenomena must depend on the molecules and their chemical structure (p. 32). Riecke legitimized here the use of theories that are based on composed entities, which might even contradict knowledge about more elemental building blocks of matter. This approach differs from a strong reductionist approach that one might attribute to Riecke for his attempts to explain piezoelectricity on molecules. Riecke rather suggested "gradual reductionism": reduce phenomena to "deeper" processes closer to their deeper cause. Phenomenological theory of piezoelectricity is more fundamental than physiological laws of muscles' contraction. Molecular theory of piezoelectricity is more basic than the phenomenological theory. Whenever possible, Riecke preferred reduction to the apparently basic entities.

Thermodynamics enabled Riecke to derive equations for the elastic and electric effects in respect of all the free physical variables—electric field, elastic pressure and temperature difference—simultaneously, as he needed for his equation for muscle. Yet the discussion of the theory of muscle contraction itself (the stated aim of the paper) made no use of thermodynamics. Moreover, Riecke could have arrived at his equations for the contraction of muscle as well as for tourmaline without thermodynamics.[54] These would have been somewhat less elegant and perhaps even a little vague conceptually, but valid. Clearly, the general discussion of free energy was not necessary for a theory of muscle contraction. It rather reveals an interest of the writer in the subject. His use of thermodynamics was a choice, not a necessity. This

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[53] Riecke's suggestion was not accepted. Muscles do not show strong piezoelectric properties. However, Riecke's work can be seen as the predecessor to extensive, complex and delicate work on the piezoelectricity of organic material during the second half of the twentieth century. Many dry organic materials display piezoelectric properties. Piezoelectric study was also done on wet tissues but failed to yield piezoelectric patterns. The research on piezoelectricity in biological materials is done mainly by biological or medical physicists. See Wendell S. Williams, "Piezoelectric Effects in biological Materials" in George W. Taylor et al. (Editors), *Piezoelectricity,* Gordon and Breach, Science Publishers: New York, 1985, pp: 213–248.

[54] For tourmaline one should add the electric, piezoelectric and pyroelectric equations together. Riecke himself used no thermodynamics in developing the equations for muscle contraction from these equations.

choice reflects a general tendency of Riecke at the time to use thermodynamics in his physics. The specific decision to employ this approach to piezoelectricity was probably influenced by Duhem's theory of the subject and by an independent application of thermodynamics to the same questions by Voigt. Though Voigt did not apply thermodynamics in published work on piezoelectricity until a year later, in 1892 he had already employed it in his lectures.[55] At that time, the question of the thermodynamic formulation of piezoelectricity was probably being discussed in Göttingen also in relation to the controversy between Pockels (who was a *privatdocent* at the university) and Duhem. From a more general perspective, Riecke's use of thermodynamics exhibits the appeal that the approach had at the end of the nineteenth century to many physicists dealing with various questions.

Thermodynamics was not the only source of potential functions in physics. In elasticity such a function has been used since its introduction by George Green in 1839. According to Green, "if all the internal forces exerted be multiplied by the elements of their respective directions, the total sum for any assigned portion of the mass will always be the exact differential of some function." This function has been later named "strain-energy function."[56] It expresses the elastic energy of the system, although it was formulated before the discovery of the general principle of energy conservation. Unlike the thermodynamic potential of Gibbs et al., it does not include any term for the entropy, which is constant in the process. In 1855, William Thomson showed that the two laws of thermodynamics are needed to derive Green's function.

> It might be at first sight regarded as simply a consequence of the general principle of mechanical effect [i.e., conservation of energy, he wrote]; but this would be a mistake, fallen into from forgetting that heat is in general evolved or absorbed when a solid is strained in any way; and the only absurdity to which a denial of the proposition could lead would be the possibility of a self-acting machine going on continually drawing heat from a body surrounded by others at higher temperature, without the assistance of any at a lower temperature, and performing an equivalent of mechanical work.[57]

Thomson thus connected Green's function to the new thermodynamics and the "physics of energy." Neither Gibbs's thermodynamic functions nor Helmholtz's free energy was needed to show the agreement of elasticity to the two laws of thermodynamics. Subsequently, Green's function was adopted and extended, especially in

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[55] Considering the close working relationship between the professors of experimental and theoretical physics in Göttingen in general and their joint laboratory work on piezoelectricity in particular, it is unlikely that Voigt did not inform Riecke about his use of thermodynamics. In 1894 Voigt claimed that he had employed thermodynamic potential "independently of him [Duhem] little later in my lectures." W. Voigt, "Piëzo- und Pyroelectricität, diëlectrische Influenz und Electrostriction bei Krystallen ohne Symmetriecentrum," *Göttingen Nachrichten*,1894: 343–372, p. 344. Unfortunately the collection of his notes for courses in Göttingen includes neither this nor other courses from that period.

[56] Fedrico Foce, "The Theory of Elasticity between Molecular and Continuum approach in the XIX Century," in *Entre mécanique et architecture*, Patricia Radelet-de Grave and Edoardo Benvenuto (eds.), Bassel: Birkhäuser, 1995: 301–314, on p. 305.

[57] W. Thomson, "Elasticity of Solids or Fluids not subjected to Magnetic forces," *TMPP*, **1**: 291–305, (a reprint with marked additions from "on the thermo-elastic and thermo-magnetic properties of matter," *Quarterly Journal of pure and applied mathematics*, 1(1855): 57–77) on p. 295.

Britain by Tait, Stokes, Maxwell, and others.[58] In the 1880s it was common in treatment of elasticity, not least in Neumann's school. Kirchhoff, Voigt, Aron, and Minnigerode all employed it. Voigt used it even in his 1887 molecular theory of the subject.[59] Riecke and Voigt extended the "strain-energy function" of elasticity to include also piezoelectric processes. At least Voigt's application of potential function to piezoelectricity was influenced by his experience with elastic potential functions.

VOIGT'S THEORY OF SECONDARY PHENOMENA

In 1894 Voigt employed free energy for the first time to derive general equations for piezoelectricity that include all the relevant influences of elasticity, electricity, and temperature in the same expression. Riecke had used the same method to derive the particular equations for tourmaline. These equations, which encompass both the electric and elastic conditions, enabled Voigt to develop a theory of secondary piezoelectric phenomena. In his general theory four years earlier, he had accounted only for the direct effects of strain and temperature change. Now, he explained, this is only an approximation, the theory should also account for the indirect phenomena caused by electric and mechanic changes induced by the piezoelectric effect. In 1891, he and Riecke confirmed experimentally relations derived from the 1890 general theory, which disregards secondary effects. Could these results be legitimately regarded as confirmation of the general theory? Voigt asked. In other words, does the theory still lead to the relations that experiments (included those of the 1880s) confirmed when secondary effects are considered?[60] Such a question, Voigt claimed, can be answered only by theoretical examination of secondary influences.[61] As mentioned, Pockels derived an expression for the changes in elastic susceptibilities due to the electric field,[62] and Riecke derived a parallel expression for dielectric susceptibility in tourmaline (equation (18)). Voigt generalized these sporadic treatments into a coherent discussion of secondary phenomena, based on equations valid for all crystal classes in any state. Since mere abstract relations between the equations are insufficient to study secondary effects, the theory concerned concrete physical conditions relating stress, strain, electric field, etc.

Voigt based his thermodynamic formulation of piezoelectricity on the assumption that the "phenomena are completely reversible," so they can be described by

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[58] Foce, "Elasticity between Molecular and Continuum," pp. 304–307.

[59] Kirchhoff, *Vorlesungen über Mathematische Physik- Mechanik* (1876); Voigt, "Allgemeine Formeln für die Bestimmung der Elasticitätsconstanten von Krystallen"(1882); id. "Theoretische Studien über die Elasticitätverhältnisse der Krystalle" (1887); Aron, "Ueber die Herleitung der Krystallsysteme" (1883); Minnigerode, "über die Symmetrieverhältnisse und die Elasticität der Krystalle" (1884). Neumann did not employ the potential in his published lectures, Neumann, *Vorlesungen über die Theorie der Elasticität* (based on lectures between 1857 and 1873).

[60] In order to maintain the theory approximations to these relations could be sufficient.

[61] W. Voigt, "Piëzo- und Pyroelectricität, diëlectrische Influenz und Electrostriction bei Krystallen ohne Symmetriecentrum," *Göttingen Nachrichten*, 1894: 343–372. Page numbers in parentheses in this section refer to this publication.

[62] Pockels, "Aenderung des optischen," p. 229.

thermodynamic potential. This assumption had been implicit in Lippmann's prediction of the existence of the converse effect and later in Duhem's and Riecke's thermodynamic treatments of piezoelectricity. The reciprocal relations follow immediately from this assumption. Yet, Voigt did not elaborate on this aspect, which Riecke had clarified. In 1898, he returned to this question in more detail in a didactic publication. There he explicated the thermodynamic cycle associated with the phenomenon.[63]

Assuming small values for the variables, Voigt expressed the free energy of a piezoelectric crystal ξ in a quadratic form in terms of the strain and electric field:

$$\xi = \varphi + f_d - \frac{1}{2} r\tau^2 - \tau \sum_{i=1}^{6} q_i x_i - \tau \sum_{i=1}^{3} r_i E_i - \sum_{l=1}^{3} \sum_{k=1}^{6} E_l \varepsilon_{lk} x_k \tag{21}$$

where f_d and φ are the pure electric and pure elastic potentials (Green's function), τ is the temperature, E_i the electric field, x_i the strain, q_i "the thermal pressure," r_i the pyroelectric coefficient, and ε_{ij} the piezoelectric coefficients. Physically, the third term in the expression represents heat energy, the fourth the energy associated with heat expansion, the fifth is associated with pyroelectricity and the last with piezoelectricity. Partial derivations of the free energy leads to basic equations for the stress (Ξ_i), and for the electric moment (α_i):

$$\begin{aligned} \Xi_i &= X_i + q_i \tau + \sum_{j=1}^{3} \varepsilon_{ji} E_j \\ \alpha_i &= \alpha_i^d + \sum_{j=1}^{6} \varepsilon_{ji} x_j + r_i \tau. \end{aligned} \tag{22}$$

The stress is a sum of pure elastic stress (X_i) and the piezoelectric and pyroelectric effects; the electric moment is the sum of the moment due to pure electricity (α^d) and the mentioned effects. These are general expressions for all crystal classes, parallel to those derived by Riecke in a similar way for the special case of tourmaline. Voigt's derivation of the general piezoelectric equations can be seen as the conclusion of a short development of thermodynamic formulation from Duhem's work through Riecke's. As in Riecke's theoretical treatment, thermodynamics on its concepts and devices was unnecessary for Voigt's theory of secondary effects. Still, one had to assume the reciprocity of the phenomena and the conservation of energy.[64] These assumptions already amount to a major share of the thermodynamic, or energetic, approach. Still, thermodynamic formulation provided a practical, elegant, and economic method to analyze the theoretical problem. It illuminates the relation between the different interactions. Thermodynamics united the equations for the various physical magnitudes into one expression. In agreement with Duhem's view, all the phenomena

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[63] Voigt, *physikalischen Eigenschaften der Krystalle* , pp. 225–9.

[64] Voigt could have reached the same equations by considering the various influences. For example, one could have assumed that the total stress is the sum of the external stress, the stresses due to thermal expansion and the converse piezoelectric effect. In such a case one would have to show the relations between the coefficients in that equation and in the equation for the electric moment, similarly to the elaboration in Pockels's first publication on the converse effect.

connected with piezoelectricity were embraced by it. The role of thermodynamics, however, ended with the derivation of the basic equations (equation (22)). Voigt exposed the physical meaning of these equations by physical-mathematical elaboration that made no use of thermodynamics.

While previously Voigt had regarded pyroelectricity as a mere secondary phenomenon of piezoelectricity, his new theoretical account considered the direct electric effect of temperature change. Riecke thought that his joint experiment with Voigt justified ignoring such an effect, at least in tourmaline, which was the only pyroelectric crystal quantitatively examined in the laboratory. He assumed only an indirect effect of temperature change (see note 52). Voigt agreed that the experiments legitimized the view of pyroelectricity as only a secondary effect of piezoelectricity, but did not deny the possibility of a direct effect. Retreating from his original position he assumed the possible existence of a direct effect, for the sake of the generality of the theory. By this step Voigt adopted the objection of Kelvin to his prior "tendency to a hypothetical assumption unduly limiting the pyro-electric property to identify with the piezo-electric effect."[65] Voigt's admiration for Kelvin[66] probably helped him accept the objection, which, moreover, agreed well with his own methodology of science. In a general-phenomenological theory, Voigt tried to refrain from any hypothetical assumption. Yet, molecular consideration provided Voigt an additional reason to assume a direct effect of heat. Following Kelvin, he thought that thermal motion of atoms and molecules, which does not cause thermal expansion, could change the electric state of the molecules and generate an electric effect.[67] Voigt, however, did not commit himself to the existence of a direct pyroelectric effect. By retaining special coefficients for pyroelectric effect, he left the question of whether it can be accounted for by the piezoelectric effect open. This is very similar to Pockels's approach regarding the direct electro-optics and its coefficients. In both cases, Pockels and Voigt separately found the existence of direct effects later.[68]

For Voigt, piezoelectricity was an effect of strain. He therefore formulated the free energy and the derivative equations in terms of strain (he did not suggest two alternative formulations for the free energy as Riecke had done). Yet, in many applications stress is more useful than strain. So he next developed the piezoelectric equations for stresses from equation (22). With the substitution of the free with the constant variables between strain to stress, other coefficients like those of dielectric susceptibility change their meaning and value. This change reflects a secondary effect of piezoelectricity, which does not exist in nonpiezoelectric bodies. For example, the dielectric susceptibility under constant stress (γ_{hi}) is expressed in terms of the susceptibility

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[65] Kelvin, "Pyro-electricity and Piezo-electricity," p. 329.

[66] Voigt dedicated his textbook on thermodynamics to Lord Kelvin (William Thomson): Woldemar Voigt, *Thermodynamik*, Leipzig: G. J. Goschensche, 1903.

[67] This view agrees with Voigt's molecular hypothesis, since the latter permits the creation of an electric moment by changes inside the molecule, like those caused by thermal motion. Reconciling this conjecture with a view like that of Riecke of fixed molecules with constant electric field is more difficult. W. Voigt. "Lässt sich die Pyroelectricität der Krystalle vollständig auf piëzoelectrische Wirkungen zurückführen?" *Ann. d. Phy.* 66 (1898): 1030–1060, on p. 1034.

[68] See chapter 5.

under constant strain (β_{hi}) as: $\gamma_{hi} = \beta_{hi} + \sum_{j=1}^{6} \delta_{hj}\varepsilon_{ij}$ Riecke had already derived a particular case of this equation for tourmaline (equation (18)) (pp. 348–50).

Strictly speaking, dielectric susceptibility is not constant for piezoelectric materials. The two different values γ_{ij} and β_{ij} are valid only in special cases. "For each single case" the susceptibility gains a special value according to particular electric and elastic conditions. However, this complication often does not alter the interpretation of experiments, Voigt explained, since in most settings the coefficient has a constant value.[69] Then, it can be identified with the "dielectric constant" (permittivity) k_{lm} through the relations: $4\pi\gamma_{ll} = (k_{ll} - 1)$, $4\pi\gamma_{lm} = k_{lm}$.[70] In particular, this was the situation in the experiments he had performed with Riecke. That was not accidental, since in its design they had attempted to make it as simple as possible and to eliminate complex phenomena like secondary effects. Other experiments reveal similar attempts. This design points out at an awareness of the potential influence of secondary effects. Later theoretical articulation of the conditions in which these effects have a significant influence was not required in order to try avoiding them (pp. 350–3).

As the significance of secondary effects depends on the physical arrangements and cannot be studied by mere abstract manipulations with the equations, Voigt studied them in concrete but still general physical conditions. For example, in a large, thin crystal plate subject only to elastic pressure perpendicular to the plate in the z direction (assuming isothermal process), the electric moment and strain are expressed as:

$$\alpha_i = -\left(\delta_{i3} - \frac{4\pi\delta_{33}\gamma_{i3}}{1 + 4\pi\gamma_{33}}\right)\Pi$$

$$x_j = \left(s_{j3} - \frac{4\pi\delta_{33}\delta_{3j}}{1 + 4\pi\gamma_{33}}\right)\Pi \tag{23}$$

where s_{ij} are the elastic susceptibilities. "The second members in all the parentheses contain the influence of the secondary effects (p. 357)." However, when the plate is placed between two conductors with electric potentials of V_0 and V_1, respectively (so that electric field was only in the z direction), the expression for the electric moment becomes:

$$\alpha_i = \gamma_{i3} = \frac{V_0 - V_1}{H} - \delta_{i3}\Pi \tag{24}$$

where H is the plate's width. Voigt used this equation to derive the surface charge density of the plate.[71]

He next examined the influence of an external capacitor on the coefficients. This setting was important due to its use by Jacques and Pierre Curie in their quantitative experiments. Voigt found that when the capacity of the plates is small in comparison

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[69] Since the value of the susceptibility was determined experimentally, the contribution of a secondary piezoelectric effect could not be distinguished (in this case) from that of the 'original' susceptibility.

[70] Voigt defined the dielectric constant by the equation: $4\pi\alpha_i = (k_{ii} - 1)E_i \sum_{i \neq j} k_{ij}E_j$. To prevent confusion I have not employed his symbol for the dielectric constant.

[71] On the derivation and Voigt's concept of charge see appendix 3.

to that of the capacitor, secondary effects are negligible (pp. 358–61).[72] Thereby, he justified his earlier account for their results, which ignored secondary phenomena. In constructing their apparatus the Curies did not consider piezoelectric secondary phenomena. They used a capacitor in order to measure the charge on the plate, bypassing error-prone conversion of a deviation of an electrometer needle to charge. Yet they displayed efforts to eliminate errors that charge on the plate might cause, even when their specific sources and nature were unknown.[73] Voigt examined additional cases. In most, like in this one, he showed that the secondary effects are insignificant; in some cases they have strictly no influence. This justified the relations of the first order theory in analyzing experimental results.

Secondary effects of piezoelectricity account at least for a large share of pyroelectric phenomena. Voigt developed equations for the electric and elastic effects of temperature change, considering direct and indirect contributions. His derivation was based on a small temperature gradient between two infinite material layers. He claimed that the argument could be generalized to any continuous surface, exhibiting small differences in temperature. The results would be only little more complicated (pp. 366–9).

PIEZOELECTRICITY AND THEORY OF DIELECTRICS

Armed with results of the thermodynamic theory of piezoelectricity, Voigt scrutinized more general issues of electric theory. He referred, in particular, to Hertz's formulation of Maxwell's field theory from 1890. Two years earlier its author's celebrated discovery of electric waves was accepted as a triumph of Maxwell's continuous theory over continental "action at a distance" theories. Hertz thought that "the system [of Maxwell] should be so constructed as to allow its logical foundations to be easily recognized; all unessential ideas should be removed from it, and the relations of the essential ideas should be reduced to their simple form." Since Maxwell himself failed to offer such a formulation, Hertz took the task upon himself.[74] Hertz's reputation, and the lack of expositions of Maxwell's theory on the Continent, made his paper (which was soon reprinted in his collection of papers on electric waves) an almost official version of Maxwell's field theory in Germany.[75]

According to Hertz (and to any formulation of Maxwell's theory), the divergence of the electric displacement is equal to the total charge, or to what Hertz called the true charge. In his work on piezoelectricity, Voigt did not use the concept of displacement

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[72] This result remains valid when one of the plates is connected to the earth and the other to a capacitor, as the Curies did.

[73] See Chapter 1 p. 21.

[74] Hertz, "On the fundamental Equations of Electromagnetics," p. 195. Hertz published two papers: one on bodies at rest to which Voigt referred, and another on moving bodies.

[75] Hertz published the first German presentation of Maxwell's theory, independent of Helmholtz's potential theory. Further presentations of the theory were made in textbooks of Boltzmann in 1891, Drude and Föppl in 1894. Hertz's papers remained the concise formulation of the theory. Olivier Darrigol, "German Expositions of Maxwell's."

but only those of electric force and potential. Both are central in Helmholtz's potential theory, which was based partly on that of Franz Neumann, Voigt's teacher.[76] Following Hertz, however, the displacement can be written as a function of the electric force:

$$D_i = \sum k_{ij} E_j \tag{25}$$

where D is the displacement. However, Voigt's earlier discussion showed that the dielectric susceptibilities (γ_{ij}) are variable and so the dielectric coefficients k_{ij}, which depend on them, are not constants. The applicability of Hertz's equation is limited, since "by considering the mechanical-electrical transformations [*umsetzungen*] the [coefficients] k_{ij} lose in general their meaning as the substance's individual constants" (p. 370). Thus, the equations given by Hertz are inadequate to account for phenomena in piezoelectric crystals.

Hertz's equations, Voigt showed, can lead to paradoxical results. Hertz assumed (and Voigt agreed) that by exciting the dielectric one can get only "free or apparent, but not true [charge] density" (p. 370).[77] Yet, Voigt demonstrated that such a charge appears when one adopts Hertz's equations. In an isolated crystal under pressure in an electric field, according to Helmholtz's electromagnetism (which Voigt adopted here), "the potential function of the free charge" (the electric potential) inside the crystal—V_i satisfies the equation: $\Delta V_i = 4\pi \sum \frac{\partial \alpha_k}{\partial x_k}$. Thus, the electric field is equal and inverse to the electric moment (polarization). This is parallel to the claim in terms of field theory (which Voigt did not use) that the displacement is null.[78] Adding this relation to Maxwell's equation for the displacement, he got:

$$4\pi(\rho + div\ \alpha) = div\ (D - E). \tag{26}$$

From Hertz's equation (25) and the relations between the dielectric constants and susceptibilities, the right-hand side is equal to the divergence of the moment from electric origin, α_d. So he got:

$$-\rho = div\ (\alpha - \alpha_d) \tag{27}$$

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[76] An antagonism towards the introduction of the electric displacement as a new electric entity was shared by Voigt's former student, Paul Drude. Drude avoided the use of the displacement vector in his textbook on Maxwell's theory. Yet the concept of displacement entered his discussion, and was expressed mathematically by the multiplication of the electric field by the dielectric constant. This is not unlike many modern expositions of electromagnetism. *Ibid.*, pp. 264–7.

[77] "Apparent charge" is a Maxwellian term, which was not adopted by Hertz. Voigt revealed here knowledge of Maxwellians terms, beyond Hertz's work.

[78] As pointed out by Buchwald, Helmholtz's original presentation of the equations was perplexing, since he used the same symbol for the potential function associated with the polarization, and that associated with the free charge. Moreover, he claimed that the equation is valid for free charge, as Voigt quoted. Lorentz corrected Helmholtz's error without comment. Voigt here followed Helmholtz in claiming that this is a general equation. However he applied it only in the example of isolated dielectric by which it is valid. In the example of a non-isolated crystal he used equations that contradict this relation. Jed Buchwald, *From Maxwell to Microphysics: Aspects of Electromagnetic Theory in the Last Quarter of the Nineteenth Century*, Chicago: The University of Chicago Press, 1985, pp. 179–181 H. Helmholtz, "Über die Theorie der Elektrodynamik. I. Über die Bewegungsgleichungen der Elektricität für ruhende leitende Körper," *Wissenschaftliche Abhandlungen*, Leipzig, 1882, Vol. I: 545–628, on p. 613.

which states the appearance of true electric surface density on the dielectric, in contradiction to theoretical assertions. The contradiction can be seen also in Hertz's formulation.[79] Voigt blamed the false results on Hertz's "definitions and expressions for the true and the free charges". These, he claimed, were "established on special phenomena that probably have internal kinship [*Verwandschaft*] neither with permanent magnetism nor with the piezo- and pyroelectric excitation." (p. 372). Hertz himself excluded "permanent magnetism" from the realm of his theory.

Apparently, Voigt made too much of Hertz's definitions of charge, and not enough of his own observation that the dielectric constants are not truly constant.[80] Since the electric coefficients are not always constants, equation (25) between the electric field and the displacement does not always hold. Thus, that the application of this relation leads to contradiction should not be surprising.[81] For a modern observer, Voigt showed that in such cases the displacement and the electric field are independent variables. To account for an electric moment that does not originate from an external electric field, modern theory assumes the existence of two independent electric variables, while Hertz used only one. The dielectric coefficients become irrelevant in such cases. In general, one cannot determine the displacement from the electric field alone, but only from the relation between both magnitudes and the polarization ($D = E + 4\pi\alpha$). Voigt understood that the relationship between the displacement and the field is problematic, but did not realize that by rejecting the universality of this relation the contradiction immediately resolves itself. Thus, he failed to suggest this relatively simple solution to the problem. Yet he avoided the use of such fixed relations between the electric magnitudes (in his theory these are only electric moment and field since he did not use displacement). Voigt put his finger on the problem in Hertz's formulation, but was led astray by Hertz's foreign Maxwellian concepts. Suspecting these concepts he thought that their alteration would solve the contradiction.

Hertz himself had already considered the introduction of an additional free variable to his theory, an introduction that would solve the problem raised by Voigt. He admitted that his choice of one free variable could not account for all the phenomena.

> It is an essential and important hypothesis of our present theory, he wrote, that the specification of a single directed magnitude is sufficient to determine completely the change of [the electric and magnetic] state under consideration. Certain phenomena, e.g.,

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[79] According to equation the displacement has non zero value, while the equation was constructed with the assumption that it is zero (only under this condition the electric field is equal and inverse to the polarization).

[80] Two years later Voigt did not point out the contradiction with Hertz's definition of charge but took the results as indicating the existence of true electric charge in such cases. Woldemar Voigt, *Kompendium der theoretischen Physik*, Zweiter Band, Leipzig: Veit & Comp., 1896 pp. 118–19. In this textbook Voigt presented piezoelectric theory from a thermodynamic approach along the lines of his paper on secondary phenomena.

[81] Alternatively one can claim that the source of the divergence was in Voigt's use of Helmholtz's relation $divE = -div\alpha$ (whose validity is limited) in his equation, following Helmholtz's loose use of symbols. Two objections should be raised against this interpretation. 1) In the example here Voigt considered only a dielectric crystal, without mention of external electric field or conductors. 2) When dealing with cases in which the above relation does not hold Voigt did not use it - suggesting he realized its limitations.

> those of permanent magnetism, dispersion, etc., are not intelligible from this standpoint; they require that the electric or magnetic conditions of any point should be represented by more than one variable. For this reason such phenomena are excluded from our consideration in the present state.

Moreover, in a note to the 1891 reprint of the papers, he referred in particular to the relationship between the field and the displacement:

> The 'force' and 'polarisation' [displacement] in this paper are not to be regarded as two variables in this sense; for they are connected by a fixed linear relation. If a general relation is allowed to drop, by regarding it as a special case of a general relation, then 'force' and 'polarisation' may serve as two variables. But it would be more convenient to introduce the polarisation of the ether as one variable, and the polarisation of the ponderable matter as the other.[82]

A Maxwellian could not accept Voigt's suggestion to modify these definitions. Hertz's definition of true charge was essential to his Maxwellian view of electromagnetism. A Maxwellian could not understand true charge but as the divergence of the electric displacement. On the other hand, in his 1892 ion theory, H.H. Lorentz suggested a separation between the two. He supposed more complicated relations between charge and electric displacement that permitted their view as independent variables. The additional independent variable resolves the problem pointed out by Voigt.[83] Yet Voigt did not refer to Lorentz. His treatment of Hertz reveals his own difficulties in understanding and employing the Maxwellian concepts, especially that of displacement. These difficulties were shared by most of his colleagues in Europe. Yet his critique of Hertz's equations should not be seen as only another attack on Maxwell's field theory. Voigt was not hostile to that theory. On the contrary, he adopted a version of Maxwell's theory in his own works. A few months before he presented this paper, he suggested a kind of mechanical model of the ether that yields Maxwell–Hertz's equations. Two years later he introduced Hertz's formulation in his textbook.[84]

At the core of Voigt's criticism was the neglect of the phenomena of crystals and complex matter in the formulation of Hertz's equation. The implication of this claim went beyond this specific theory to the formulation of fundamental theories in general. Permanent magnetism, pyroelectricity, and piezoelectricity, which Voigt mentioned, are three important examples of phenomena that appear only in ordered solid matter.[85] These phenomena, Voigt claimed, should also be described by the fundamental equations of physics. This is far from a reductionist claim. Voigt did not call for an explanation of these phenomena on any deeper level, but for general theories that could

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[82] By polarisation of the ether Hertz referred to the displacement or induction, by that of matter to what is usually called polarization. Hertz, *Electric waves* p. 198, 276. Voigt referred to the original publication of the paper. He probably had not seen this note.

[83] Whittaker, *History of Electricity*, pp.397–9.

[84] W. Voigt, "Ueber Median ohne innere Kräfte und über eine durch sie gelieferte mechanische Deutung der Maxwell-Hertz'schen Gleichungen," *Ann. Phy.* 52 (1894): 665–72, *id., Kompendium*.

[85] Interestingly Pierre Curie turned from the study of piezoelectricity to that of the complex phenomena of magnetism. The similarity between these phenomena had been recognized since Aepinus (obviously only for pyroelectricity).

also embrace these theories. In showing the implication of a theory of macroscopic phenomena (like piezoelectricity) on fundamental theories of physics, Voigt demonstrated the importance and independence of the study of complex phenomena. At a time when microphysical effects were at the focus of the electrodynamic research, Voigt's critique of the electrostatic theory displayed the relevance of the physics of crystals. He showed that a study of complex phenomena can reveal shortcomings and so point out required changes in a general theory of physics. Thus, he implied that this kind of research makes its own independent contribution to physics. The concern Voigt showed is not so much philosophical as methodological. He pointed out the negligence of the study of complex phenomena and implied that physicists should pay more attention to this field, especially in formulating comprehensive theories, like that of electromagnetism.[86]

The rules of the genre did not permit Voigt to elaborate on his concerns for the lack of interest in the physics of crystals in a scientific paper. In later private communications and in addresses he was more explicit. "The physics of crystals is far from the problems that have occupied the larger number of physicists during the thirty odd years of his work on the subject," he told the audience at the opening of the new Physics Institute in Göttingen in 1905. "It is also far from the fields that are cultivated in our university under the support of Göttingen's Association [for the promotion of applied physics and mathematics]." The association was founded in 1898 by Felix Klein—the powerful professor of mathematics at the university. It supported research that had promise for technological applications. Crystal physics, Voigt agreed, has hardly any technological applications.[87] The study of crystal physics, he explained, means a renunciation of the interest of a wide circle of physicists in one's results. So what attracted him and his few fellow researchers to the field? Voigt found the answer in the special aesthetic appeal of the field and in an interest in knowledge for its own sake in the tradition of nineteenth century German humanistic study. He compared the physics of crystals to the harmony of an orchestra. The gases, on the other hand, are like the cacophony of many solo violinists who play each in his own time and tempo.[88] Still "to his colleagues Voigt sometimes spoke plaintively of his work. It was 'hermit's work, in areas that otherwise did not excite interest,' he told Sommerfeld [in 1909]. When he told Kayser [in 1910] that he would send him a copy of his text

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[86] In the same vain Voigt tried to show the relevance of pyroelectricity to the developing quantum mechanics in 1913. He suggested that a quantum effect analog to that that governs specific heat in low temperatures diminishes the value of the pyroelectric constant under similar conditions, (Jagdish Mehra, *The Solvay Conferences on Physics: Aspects of the Development of Physics Since 1911*, Dordrecht: Reidel, 1975, p. 198).

[87] Only a decade later piezoelectricity would find an important application in technology for underwater detection. The physics of crystals, and piezoelectricity in particular, became a major subject for applied research in physics in the twentieth century. Voigt, of course, could not have known that in 1905.

[88] Voigt, "Rede" in *Die Physikalischen Institute der Universität Göttingen*, Leipzig und Berlin, Teubner, 1906, pp. 37–43, quotations on p. 39. Voigt was an enthusiastic music lover and wrote a book on Bach's cantatas. His choice of Bach, rather than the more popular romantic or contemporary expressionist music coincides well with his style of physics. Like Bach's music, his physics with its preference of mathematical structure and secure foundations was less grandiose than assumptions on fundamental forces and entities or the big machinery of application-oriented science.

on crystal physics, he added that it would appear to him 'as a guest from a rather strange world.'"[89] In elaborating the piezoelectric theory of the secondary effect in 1894, Voigt found an opportunity to show the relevance of his work in his cherished field, to questions that occupied the physics of the time. He tried to use this occasion to call for more attention to complex phenomena and for their consideration in the construction of general physical theories.

* * *

In the 15 years since the discovery of piezoelectricity, a small body of knowledge, both empirical and theoretical, concerning the phenomena was established. Voigt's theory of secondary effect combined the thermodynamic approach with the symmetrical considerations of his "general theory." This theory accounted rigorously for the observed piezoelectric phenomena. Concluding the development of Voigt's general theory, his theory of secondary phenomena marks the establishment of a solid body of knowledge of piezoelectricity. It also marks the complete embracement of the field in general thermodynamics. Following the publication of this paper, the average number of annual contributions on piezoelectricity dropped drastically from 4.8 in the first half of the decade to one in the second (three of the five were written by Voigt). The essays on piezoelectricity in the editions of Winkelmann's *Handbuch der Physik* exhibit the stabilization of the field. The first edition of the *Handbuch* appeared in 1895. Pockels contributed a 25-page essay on pyro- and piezoelectricity; most of it dedicated to the latter. He needed to add very little, and to change virtually nothing in the second edition of the *Handbuch*, which appeared 10 years later. The developments in the subject at that period were only marginal.[90] This stands in clear contrast to the developments in the decade before 1895. Wiedemann's account of piezoelectricity in his *Lehere von der Elektricität*, which summarized the empirical and theoretical knowledge in the field, had been changed significantly between the first edition of the book in 1883 and the second in 1894. The space dedicated to piezoelectricity was increased four-fold between the first and the second editions; many paragraphs were rewritten. The differences between Wiedemann's accounts reflect the growth and changes in the knowledge of piezoelectricity.[91] Consider the changes between the 1895 and 1905 editions of the *Handbuch* in the essays on electron theory, electrodynamics of moving bodies and radiation, to name only a few examples. In the piezoelectric field, on the other hand, 1895 marked the consolidation of a paradigm based on experimental research of the 1880s and on Voigt's general theory in its thermodynamic formulation. Molecular theories had only an insignificant role in this process. Their influence on the phenomenological-thermodynamic theory was very

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[89] Jungnickel and McCormmach, *Intellectual Mastery of Nature*, p. 273.

[90] F. Pockels, "Pyro- und Piezoelektrizität," in A. Winkelmann (ed.) *Handbuch der Physik*, 1st edition, vol. 3 part 2, Breslau: Eduard Trewendt, 1895: 527–550; *Ibid*, 2nd edition, vol. 4, part 1, Leipzig, Johann Ambrosius Barth, 1905: 766–793.

[91] Gustav Heinrich Wiedemann, *Die Lehre von der Elektricität*, 1st edition 1883, Vol. 2: 330-346, 2nd edition, 1894, Vol. 2: pp. 390–443.

limited and indirect.[92] Unlike the thermodynamic theory, they did not offer a stabilized or accepted theory, even if only one new model was suggested in the decade after 1895.[93] The field of piezoelectricity would be the subject of more intensive development again only during the First World War. But that is another story.

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[92] It can be traced, as mentioned, in Voigt's consideration of direct pyroelectricity, but only as a possible additional motivation.

[93] Pockels's handbook's article did not elaborate on this model.

CHAPTER 5

EMPIRICAL WORK IN THE 1890s

Experiments played a major role in the development of the piezoelectric research in the pretheoretical phase. The formulation of Voigt's general theory followed empirical findings and it was designed to account for the experimental results. Unlike this theory, however, the *later* theoretical developments during the 1890s, which I described in the previous two chapters, were virtually independent of the experiment. Among the issues they raised, only the theoretical question about the relations between related phenomena like piezoelectricity and electro-optics invited experimental resolution. These relationships were first studied theoretically and later, as will be shown below, examined in the laboratory. Thus, while Voigt's 1890 theory shaped most experiments performed in the 1890s, the theoretical developments after its introduction had little influence on the experiments performed at the time. This is also true of the molecular theories, with the sole exception of Voigt's molecular theory, which motivated the construction of one experiment and was in the background of another.

Following Jacques and Pierre Curie's announcement of the discovery of piezoelectricity, there was much interest in the new phenomenon and experimental work on its properties commenced. The publication of Voigt's theory had a similar influence. However, this time the work was focused on theory; only few experiments were done. This might be surprising for anyone who thinks that the central role of experiments is to confirm or refute theories. Moreover, all the empirical tests of the theory were done at Göttingen, where Voigt had suggested the general theory, and were related to him personally. Still, one should remember that the theory had an empirical basis from its introduction in the experiments performed during the 1880s.

VOIGT AND RIECKE'S DETERMINATION OF PIEZOELECTRIC CONSTANTS

The confirmation of the theory

The only experiment constructed in order to test Voigt's general theory was performed by Voigt himself with his colleague Riecke in 1891. In this work they had taken upon themselves to not only confirm the theory but also determine the piezoelectric coefficients of quartz and tourmaline. Since the coefficients make sense only in the realm of the theory, this step displays a confidence in the validity of the theory. Their confidence in the theory was at least partly based on the agreement between its results and the empirical data collected during the 1880s, i.e., before its formulation. However, Riecke and Voigt wrote, "since the former measurements were conducted with no consideration of a theory and in many cases in only a *qualitative* way, they are not suitable for a completely satisfactory examination of the theory. It, therefore, remained to perform extended (*ausgedehntere*) quantitative determinations of several cases that were accessible (*zugänglichen)* to theoretical treatment and after calculating each substance's individual piezoelectric constants to compare them with the theoretical laws." They did this on tourmaline and quartz.[1]

Probably no one was better suited for this research than Riecke and Voigt. I have mentioned more than once their interest in piezoelectricity. Voigt's interest in his general theory is obvious. Since 1885 Riecke had done a few experiments on pyroelectricity and also exhibited theoretical interest in piezo- and pyroelectricity. The skills needed to confirm Voigt's theory were different from those required in examining unknown physical behavior as in Röntgen's experiments. In the former case one had to carry out exact measurements with crystals, a practice in which Riecke and Voigt had expertise. They exhibited a high degree of precision in their experiments and mastery of physical-mathematical techniques in analyzing their results. Voigt had performed experiments on elasticity of crystals since his student years, while Riecke carried out electromagnetic measurements from his early researches in 1871. Voigt and Riecke belonged to two different schools of German physics (Neumann and Weber), yet exact measurements in absolute units and the elimination of experimental error were regarded essential in both.[2] The friendly relationship between Riecke and Voigt (which was not the usual case with the relationships between the experimental and theoretical physicist in the German universities) facilitated their collaboration.[3]

Indeed Riecke and Voigt made much effort to get precise results and to eliminate experimental errors. For example, they concluded that they could not simply apply weights by a lever on the crystal they wished to press, since repeated readings for the same weights did not yield steady values (they attributed that to uneven distribution of pressure in such an arrangement). Instead, they devised a more complicated arrangement in which weights (W in Figure 5.1) were loaded in a pan of a balance. The pan was connected by a rigid vertical hanger to a small steel block (S), placed above the middle of the pressed surface on a brass plate covered with rubber. In this way they applied unidirectional pressure on rectangular crystal plates. One surface of the plate was connected to a Thomson's electrometer (EM—with its other side grounded)

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[1] E. Riecke und W. Voigt, "Die Piëzoelectrischen Constanten des Quarzes und Turmalines," *Ann. Phy.* 45 (1892):523–552, on p. 524, my italics. Page references in parentheses in this section refer to this paper.

[2] Jungnickel and McCormmach, *Intellectual Mastery of Nature*, vol. 1, *passim* and Olesko, *Physics as a Calling*, *passim*. See there on Voigt's early works pp. 287–297. On Riecke's see Wiechert, "Eduard Riecke," p. 47. For a view of the two traditions similar to the one presented here see Darrigol, *From Ampère to Einstein*, p. 75.

[3] They were heads of two independent institutes, Riecke for experimental and Voigt for theoretical physics. This uncommon administrative arrangement probably contributed to their good working relations.

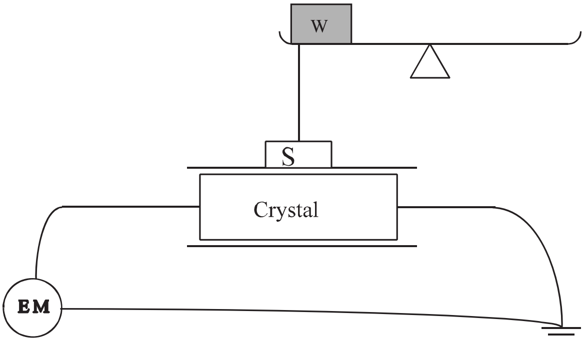

Figure 5.1: A schematic description of Riecke and Voigt's experiment (my reconstruction).

and the other surface to the ground (through a gas pipe).[4] The entire arrangement was set on a stable table in a glass box. A net of brass wire lined the inner part of the box and the surface of the table was covered with silver foil, so that the external electric field would not influence the apparatus (pp. 531–2). Riecke and Voigt measured the deviations of the electrometer needle due to the electrification of the crystals on an arbitrary scale. Like Czermak four years earlier, they compared these readings after each measurement to the deviation caused by a known electric tension. They used a "Clark cell" (1.435 V at 15°C), which was considered steadier and more reliable than a "Daniell cell," which Czermak had employed.

Their apparatus enabled them to load and unload weights and to measure the effects, assumed to be equal, of both increasing and decreasing the pressure. Between measurements, they probably connected both faces to the ground. This setting enabled them to make several measurements with the same pressure, reducing the influence of a single error. However, they noticed a deviation in the position of the electrometer needle between successive measurements. After deciding that the deviation was due to unavoidable damping and diffusion of electricity, they formulated a mathematical expression that corrected the reading of the needle. They confirmed it with 70 measurements of both loading and unloading (pp. 533–6). This sequence demonstrated their meticulous efforts to reach precision by eliminating experimental errors and their use of mathematical techniques to do so.

Previous quantitative experiments measured the effect of pressure in a direction that involved only one piezoelectric modulus. The confirmation of the general theory required the comparison of the effects of various situations in which more than one modulus was involved. For simplicity, Riecke and Voigt chose to apply unidirectional rather than more complicated pressures. Still, they had to apply them in various

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[4] Gas pipes were used for grounding electric instruments since they were connected to the ground to protect them from lightning. Usually, like in this experiment, the gas pipe was also a convenient way to close the electric circuit (as was usually done by grounding), so that the electrometer measured the tension between the edges of the crystal. The arrangement when the examined face was the pressed one was somewhat more complicated.

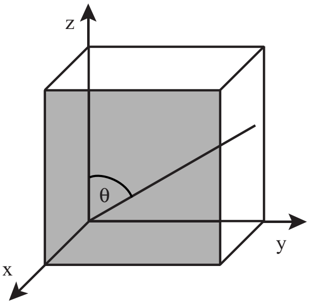

Figure 5.2: Pressure in Riecke and Voigt's experiment was applied along directions that form an angle with the z axis in the yz plane. The electrodes were connected to the yz planes—the shaded plane in the figure and the one parallel to it.

directions corresponding to the crystals' piezoelectric constants. For quartz, which has two moduli, equal pressures in five different directions in the same plane, perpendicular to a polar axis (the yz plane, see Figure 5.2) were sufficient. They applied these pressures on three bars of quartz cut from the same plate. Voigt had already used the same plate to determine quartz's elastic constants in 1887. The bars' long edges (from 11 to 17 mm) were at angles of 22.5°, 45°, 112.5°, and 135° from the principal (z) axis in the yz plane. Pressure of two-kg in weight was applied in the directions of the long edges, perpendicularly to the polar axis $-x$. The electric effect was always measured by connecting the yz face (i.e., perpendicular to the polar axis) to an electrometer. Comparing the reading of an electrometer with the reading of one cell, they calculated "an electric moment in Clark" $-m_x$. From the piezoelectric equation of quartz (Chapter 2. Equation (6)) they derived an equation that expresses the electric moment in terms of the two sought moduli and the geometry of the plate:[5]

$$-\frac{m_x}{p}\frac{q}{q_x} = -\delta_{11}\sin^2\theta + \delta_{14}\sin\theta\cos\theta \tag{1}$$

where q is the area of the pressed face q_x that of the yz face, whose voltage was read, p the weight and y is the angle between the direction of pressure and the principal axis in the yz plane as shown in Figure 5.2.

In each direction of pressure they made three to six measurements and found the average value for the expression on the left side of equation (1). From these averages, they used the least squares method to calculate the values of the moduli in arbitrary "Clark scale" (they did not elaborate on this calculation and the mean deviation found by this procedure). They used these values, in turn, to calculate the theoretical predictions for induced electric tension in their experiment and to compare them with the observed values, concluding that the agreement "is satisfactory" (p. 539).[6] In

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[5] The equation is valid only for the polarization in a polar axis, i.e. it can be applied only in this case when a surface perpendicular to that axis is connected to the electrometer.

[6] Indeed, the maximum deviation is less than 3% (0.191 calculated against 0.186 observed). Unlike the electric moments observed, the values of the moduli taken directly from different observations deviates

showing the agreement of equation (1) derived from Voigt's theory with the observations, they confirmed the general theory for the first time. Since former experiments examined only one piezoelectric coefficient in quartz (δ_{11}), this was the first quantitative examination of the dependence of the electric effect on the direction of the stress.

The measurements of tourmaline were somewhat more complex. Since it has four rather than two piezoelectric coefficients, applying pressure in different directions in one plane would not suffice to find the value of all its coefficients. Riecke and Voigt therefore measured eight different combinations of directions of pressure and the faces on which the effect was observed in four crystal bars.[7] This time, they did not develop a general expression for all the cases but compared each measurement with its specific theoretical expression. In each measurement, they expressed the potential in Clark units and found the average for each combination. These averages led to eight equations with four unknowns. The piezoelectric moduli were derived directly from this system of equations. In such a derivation, they could not use an error analysis method like the method of least squares. Instead, they showed that independent determinations of the coefficients led to similar results. However, they determined the value of one moduli (δ_{15}) only once, though they could have determined it twice. Instead, they determined the value another three times. This choice somewhat weakened the confirmation. Still they concluded that the agreement between their values "can be described as satisfactory."[8] Thus, their observations corroborated the relations deduced from Voigt's general theory and confirmed it. Still, the use of the method of least squares for quartz made the confirmation in that case more satisfactory (also by Riecke and Voigt's own standards) than that of tourmaline (pp. 539–44).

Riecke and Voigt confirmed the theory for only two species, which represent only two classes of crystals out of the 20 that, according to Voigt's theory, should show piezoelectric behavior. Apparently, they and others regarded this as satisfactory. Later, the theory was regarded as confirmed, as shown, for example, in the review articles of Riecke and Pockels. From the various cases studied in Voigt's general theory, Riecke and Voigt discussed only that of unidirectional pressure derived for a cylindrical bar. The prisms they examined were not cylinders but their dimensions enabled the use of the equations that Voigt had found for this case. Evidently, they saw no need for a confirmation of Voigt's predictions for various geometrical circumstances, since they

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significantly from their mean value. For example a calculation of δ_{14} from one observation (either in 45° or 135°) with the found value of δ_{11} (from a direct measurement) deviates by almost 10% from its mean value given by least squares. The deviation has a smaller influence on the value of the expression displayed by the experimentalists since δ_{14} is significantly smaller than δ_{11} (pp. 537–9). They did not comment on the large deviation in the values of δ_{14}. This deviation did not weaken the confirmation of the theory (which accounted for the observations) but did weaken the determination of the coefficients.

[7] As with quartz, they used crystal specimens that Voigt had already used for elastic experiments (this time in experiments that he performed in 1890).

[8] The values of two moduli (δ_{22} and δ_{31}) vary in about 10% between their determinations. Yet since their values are one order of magnitude smaller the other two, an error of 1% in the values of one of the others can lead to an error of 10% in the smaller moduli. Thus, Riecke and Voigt could regard the confirmation as satisfactory. The deviation in the values of the small moduli is parallel to the deviation in δ_{14} of quartz whether the latter is calculated directly and not by the method of least squares (footnote). Riecke and Voigt, however, did not mention this similarity (or the deviation in the quartz's modulus).

were derived mathematically from the basic equations, whose confirmations were the subject of their research. This reveals a known and by then virtually universal confidence in mathematical deductions in physics.

German versus French methods of determination

The measurements in arbitrary units were sufficient for the confirmation of the piezoelectric theory. Determination of its coefficients in absolute units did not add to its confirmation but demonstrated that they are true constants of the crystals by comparing them with previous observations. Nevertheless, Riecke and Voigt regarded this determination as an important task of their piezoelectric experiment, an aim independent of the confirmation of the theory. As mentioned, determination of theoretical coefficients in absolute units was an important theme in the work of both.[9]

However, the determination turned out to be more complicated than they had expected. As in the previous measurements by the Curies and Czermak, voltage was the electric quantity read in the experiment. Voigt's piezoelectric moduli, however, related elastic pressure or stress to polarization. Polarization was known to be equal to the charge surface density, which could be calculated from the voltage (in absolute measurements) and the capacity of the system. Like their predecessors, to this end they used an external condenser, whose capacity was calculated from its dimensions, but in a somewhat different way from both Czermak and the Curies. Voigt and Riecke connected the condenser to the apparatus and compared voltage readings due to the piezoelectric effect with and without the condenser, finding the ratio between the capacity of the system in the two states. From their ratio and the capacity of the condenser, they calculated the capacity of the apparatus (p. 534, 544–5). With its value, they found that $\delta_{11} = 5.31 \times 10^{-8}$ statcoulomb/dyne for quartz and $\delta_{33} = -4.70 \times 10^{-8}$ for tourmaline.[10]

Their experimental method was closer to Czermak's than to the Curies'. In measuring coefficients of quartz and tourmaline, the Curies determined only the electric charge due to an additional weight on a known condenser by a null deviation of an electrometer needle (above p. 21). Their method bypassed the measurement of the capacity of the system and translation of a deviation of an electrometer dial to voltage. Czermak and Riecke and Voigt, on the contrary, measured and accounted for all the magnitudes involved in their experiment. They measured the capacity of the system rather than bypassing it, and they read a deviation in the electrometer dial and compared it with a standard cell rather than perform a "null experiment." Czermak tried to account for all parts of the apparatus, but less rigorously. For example, in measuring the capacity of the system, he neglected the small capacity of the electrometer (p. 98). Moreover, Riecke and Voigt reduced systematic and accidental sources of errors mathematically. They accounted for the divergence from the correct position of their electrometer dial (an error that did not arise in the Curie's setting); they carried

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[9] See the references in note 2.

[10] E. Riecke und W. Voigt, "Die Piëzoelectrischen Constanten des Quarzes und Turmalins," *Göttingen Nachrichten*, 1891 (No. 8; 11 Nov.): 247–255, on p. 254.

out observations under several conditions; and they used the method of least squares for error analysis. Riecke and Voigt's experiment was more meticulous than that of the Curies as they examined every detail of their apparatus.

Yet, whether it was really more accurate was a matter of opinion. They surely agreed with most of the German measuring physicists that their experiment would yield more precise and accurate results. German measuring physicists thought that one should account for external influences on experimental results rather than bypass them. Among the students of Neumann like Voigt, this was even clearer. "Neumann and his seminar students did not believe that redesigning an instrument could reduce all errors. In their view, it would be futile to pursue the material perfection of instruments over the accurate mathematical determination of errors."[11]

A controversy in 1860s about the appropriate way to reach exact and valid results between Carl Pape, another member of Neumann's school, and the influential French experimentalist Henri-Victor Regnault illustrates their attitude. Would accuracy be achieved by noting all errors and accounting for them through mathematical analysis, as Pape claimed, or through elimination of errors by an experimental arrangement that would permit their neglect, as Regnault claimed? Regnault considered mathematical techniques unsuitable for the examination of experiments because they were too far from the realities of the laboratory. "With his so-called *methode directe* Regnault tried to obtain data directly by varying experimental apparatuses and arrangements *a priori* rather than calculating errors of experimental data *a posteriori*." For him, the skill and mastery of the experimentalist produce reliable and accurate results, evident through their consistency. While Pape favored carrying out experiments under various conditions, Regnault preferred comparing results of experiments performed under the same conditions. Errors, except accidental errors, should be reduced in the experiment itself by modifying the setting, the apparatus and the target according to the judgment of the experimentalist, not in its data analysis. In the words of Jean Baptiste Dumas, "A severe critic, he allows no causes of error to escape him; an ingenious spirit, he discovers the art of avoiding all of them."[12] Pape pointed out that Regnault was and would be unable to avoid significant experimental errors. Pape thought that by accounting mathematically for errors, a scientist could reach more accurate and valid results than in an attempt to eliminate them. The scientist could not rely on the personal mastery of the experimentalist but on physical-mathematical analysis. Dörries noted that Regnault's "whole measuring enterprise became artistic to an extent where subjective judgment prevailed at the expense of objectively reproducible measurements."[13]

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[11] Olesko, *Physics as a Calling*, p. 302.

[12] Matthias Dörries, "Vicious Circles, or, The Pitfalls of Experimental Virtuosity," in Heidelberger and Steinle (eds.), *Experimental Essays - Versuche zum Experiment*, Baden-Baden: Nomos, 1998: 123–140, on p.124. Dumas is quoted in Hasok Chang, "Spirit, air, and quicksilver: The search for the "real" scale of temperature," *HSPS* 31 (2001): 251–286, on 274.

[13] Olesko, *Physics as a calling*, pp. 378–382; Matthias Dörries, 'Easy Transit: Crossing Boundaries between Physics and Chemistry in mid-Nineteenth-Century France' in C. Smith and J. Agar (eds.), *Making Space for Science,* Houndmills: Macmillan, 1998, pp. 248–262 on p. 260, quotation from "Vicious Circles," p. 137.

Pape and Regnault present two attitudes toward experimentation: a mathematical versus an artisanal approach. The former used common procedures in locating possible errors and reducing them; the latter employed more particular solutions to specific experimental settings and their modification. They resemble analytic and synthetic geometry. Nothing in the "artisanal" approach was intrinsically more artistic than synthetic geometry. Experimentation in both the approaches involved theoretical considerations and assumptions about the working of the apparatus, even if Regnault attempted to eliminate them. In the "artisanal approach" these were primarily applied in designing the experiment before its performance while in the "mathematical," primarily after it was performed.

Like Pape, Voigt and Riecke displayed a high degree of confidence in their analysis of experimental instruments and their systematic and accidental errors. Like him, they preferred the mathematical analysis of all the experimental components to bypassing measurements. Other German measuring physicists, which included most theoreticians, revealed the same tendency. Data analysis and mathematical theory of measuring instruments and their deviations were central to both Neumann's and Weber's schools. This centrality indicates that German measuring physicists trusted their method of analyzing complicated results more than experimental methods for bypassing complexities.[14] Czermak, who belonged to neither of these schools but was educated as a theoretical physicist in the German sphere, displayed a similar approach in his experiment. He, however, put less emphasis on error analysis. The Curies, on the other hand, proved themselves true and successful followers of Regnault. By appropriate design of their apparatus, they measured the sought magnitude almost directly, without a need for elaborate data analysis and mathematical elimination of error. Jacques Curie continued using this method (reaching excellent results) well after Riecke and Voigt's experiment. Pierre Curie continued to use it in other fields like radioactivity (below p. 214). This example suggests that French physicists were right in acknowledging Regnault's lasting influence.[15] Elisabeth Garber claims that the disciplinary borders between experimental physics and mathematics were more rigid and defined in France than in Germany and Britain. "Experimental physicists in France [she further claims] regarded their work as purely empirical and devoid

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[14] For example, Friedrich Kohlrausch, who was an influential teacher of Riecke (Voigt, *"Riecke als Physiker," Physikalische Zeitschrift* ***16*** (1915), 219–221) considered calculation of the effect of the earth's magnetic moment necessary for exact measurement of electric resistance standards. "The British, aware of the difficulties involved [in the magnetic measurements], tried to develop alternative methods that would bypass it. Kohlrausch did not"). See Kathryn M. Olesko, "Precision, Tolerance, and Consensus: Local Cultures in German and British Resistance Standards," *Archimedes: New Studies in the History and Philosophy of Science and Technology*, 1996:117–156, p. 138. Olesko's work demonstrates the centrality of data analysis for German physicists in both Weber's and Neumann's schools. Olesko reveals differences between German and British attitudes towards practices of exact measurements. The examples of the Curies' experiment and Regnault indicate that the French were closer to the British than to the Germans in their preference for bypassing the complicated mathematical analysis of unnecessary influences.

[15] Chang, "search for 'real' scale," p. 273, Dörries, "Easy Transit," p. 260.

of all hypotheses."[16] The German measurements in piezoelectricity did not involve more hypotheses than the French, but clearly did apply more mathematics. If Garber is right about the status of mathematics in French physics, its consequences should be most conspicuous in quantitative measurements, as suggested by the example of piezoelectricity.

Determining the constants

Riecke and Voigt's results, presented to the Göttingen Society for Science on August 1, 1881, did not agree with those of the Curies. They were lower by 16% (for quartz, 5.31 compared to 6.32) and 13% (for tourmaline, 4.7 compared to 5.4) than the Curies'. In the published version of the communication, dated November 11, these results were given alongside those of the Curies, without any further comment.[17] Yet before they sent a more complete report of their experiment to the *Annalen der Physik*, dated "autumn 1881," they realized that the value calculated for the capacity of the system given earlier "was however surely too small" (p. 545). Therefore, their figures for the moduli were also too small.

The estimation of the capacity was too small, they explained, because shellac on the external condenser increased its capacity while it was not accounted for by the calculation. Moreover, the particular state of the condenser did not permit a theoretical calculation of the capacity. They had to find it experimentally. They used an electromagnetic method of alternating current suggested by Maxwell in his *Treatise of Electricity and Magnetism*.[18] Here, the capacitor was connected by a tuning fork to a battery that charged it and a galvanometer through which it was discharged. This method required a special series of complicated measurements to find the capacity of the external condenser.[19] With the new value for the condenser, Riecke and Voigt recalculated the capacity of the experimental apparatus (pp. 546–9). The long procedure

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[16] Elisabeth Garber, *The Language of Physics,* p. 314.

[17] Riecke and Voigt quoted 6.3 and 5.3 respectively. I presume that they did not attribute to the Curies' experiment higher precision than that (the Curies themselves published a value of 6.32 in 1889). The error in the latter number is probably due to a simple mistake. Riecke and Voigt, "Die Piëzoelectrischen Constanten," *Göttingen Nachrichten*, pp. 254–55.

[18] Maxwell, *Treatise,* (3rd ed.) pp. 420–425.

[19] The tuning fork alternates between the battery and the galvanometer, acting as oscillating switch. At a certain frequency of oscillation (in their experiment, 31.47 times a second) the needle of the galvanometer is steady. To measure this frequency exactly, they used a special apparatus with photographic paper. The capacity is then expressed as a function of the resistance of the galvanometer, the frequency of steady current, and the ratio between the current that discharges the condenser and that in a "branch circuit" in which a resistance of 22,000Ω was connected to the battery. (The measurement of the current in the "branch circuit" actually indirectly gives the voltage of the cell, which is not expressed directly by the formula. In this way they measured the voltage of the pile rather than relying on their "book values" as the Curies did with the same kind of "Daniell cell.") The last two were measured in the experiment. They made about twenty measurements of the two currents with and without the measured condenser. In each case they calculated the capacity of the system. From these measurements, they obtained the mean values of the capacities of the "tuning fork circuit," and of the circuit without the condenser. The difference between those two values gave the capacity of the condenser.

required to determine the capacity is a good example of the effort needed for exact measurements.

Only after this lengthy procedure they could calculate the absolute magnitudes of the piezoelectric moduli of quartz and tourmaline. Their values were now little higher than those Jacques and Pierre Curie had found a decade earlier. For δ_{11} of quartz they found 6.45 versus 6.32; for δ_{33} of tourmaline, they found -5.71 compared to -5.4, all multiplied by 10^{-8}. This time, Riecke and Voigt stated that the smaller discrepancy "might well be especially due to that we took into our account loss of electricity that took place during the observation. In Messrs Curie's not the least remark relating to this is found" (pp. 549–50). In particular, they probably had in mind the corrections they made in the reading of the electrometer. Yet, their critique was not limited to a specific procedure. It also revealed their uneasiness with the brief and general descriptions of the Curies' experiments, in which only the end results, but not the values of the various observations, were given. In this they did not follow Regnault. Riecke and Voigt probably shared Wilhelm Weber's ideal of an experimental account. Weber argued that the "'surety and certainty of the result' was founded in good part on the investigator's thoroughness in reporting the experiment's instruments, how they were used, how the trials were performed and what changes were made, and how the data was taken and reduced."[20] The Curies' reports lacked this thoroughness and thus did not give German physicists the desired certainty.[21]

According to Riecke and Voigt, their earlier determination of the condenser's capacity was "surely too small" because the calculation disregarded the accidental shellac that increased its capacity. Thus, they implied that no external stimulus was required to convince them of the need to reexamine the capacity that was "surely" wrong. However, this was not obvious to them when first analyzing the results of the experiment. Even in a public announcement of its results, and in its later written version, they gave results based on "surely too small" capacity. Only a close reexamination of the apparatus, including the condenser, made it clear that the earlier values were wrong. A new set of measurements to replace those made on a mistaken premise was necessary. Evidently, a surface examination of the condenser was not part of the procedure that they applied in this experiment.

But why did Riecke and Voigt take the trouble to return to the laboratory and start inspecting apparatus that they had already checked, and from which they had even published experimental results? I think the answer lies in the disagreement with the earlier results of the Curies and, to a lesser degree, those of Czermak.[22] In spite of their greater trust in their own method, Riecke and Voigt did not dismiss the Curies' method and results—results confirmed, though unsatisfactorily, by Czermak.[23] The

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[20] Olesko, "Precision, Tolerance, and Consensus," p. 119.

[21] The presentation of the Curie's results also leaves much to be desired by the historian, especially considering the absence of their laboratory notes.

[22] The published sources are silent about the reason for the re-determination. I failed to locate any manuscript that illuminates the question.

[23] Riecke and Voigt did not mention Czermak's determination, but they knew the paper (Voigt quoted results from it as early as 1890, Voigt, "Allgemeine Theorie"). They probably disregarded Czermak's result because they depended on his mistaken theory. Yet, despite the problematic determination of

higher accuracy that they attributed to their own method was not sufficient to account for the large gap of 16% between the results. The errors accounted for by their analysis were much smaller than this gap, which suggested a fault in one of the experiments. Since Riecke and Voigt could not examine the Curies' apparatus, they probably decided to reexamine their own. An error was indeed found in the value ascribed to the capacity. It is common to reexamine experiments and even to perform them again in cases of discrepancy with a theory. This was not the case here, since the piezoelectric theory was indifferent to the magnitude of the moduli. Here the results of an earlier experiment offered grounds for comparison and thus influenced the results of the later experiment.[24] It is unlikely that Riecke and Voigt would have noticed a little shellac on a condenser had their results agreed with those of the Curies or had the Curies not performed any previous measurements.

Pyroelectricity

Correcting the values of the moduli was important not only for the records and agreement with the Curies' results but also for inferring the existence of a genuine direct pyroelectric effect. Following others, Voigt assumed in his general theory that pyroelectricity is an electric effect of strain, due to thermal deformation of the crystals, rather than a direct thermal effect. Thus, the theory expressed the electric effect of temperature change as a function of the coefficient of thermal expansion and the piezoelectric constants in the relevant crystal classes (above p. 92). If pyroelectricity was only a secondary phenomenon of piezoelectricity, the constant calculated from these two coefficients would be equal to the one obtained from direct measurements. Riecke and Voigt compared the calculated constant from this experiment with the one obtained by Riecke from direct measurements on another specimen a year earlier. Since Voigt had already measured the elastic constants for the same tourmaline specimen in 1890, calculating the value of the piezoelectric constants from them and the moduli was straightforward (p. 550). The coefficients for the thermal expansion of tourmaline were determined by Pfaff in 1861, though on another specimen. From this they calculated 1.34 (statcoulomb/cm^2 per degree C) for the electric charge due to piezoelectricity caused by thermal expansion. Riecke's direct measurement led to an average value of only 1.13 for the total effect. Yet the results pointed out an additional second-order term, i.e., a term that was dependent on the square of the temperature. Adjustment of the value from 18°C, at which it was originally determined, to 28°C, in which the piezoelectric measurements were taken, raised the value to 1.23. Considering that a number of constants were involved in the determination of the theoretical value, they concluded that the agreement between the results confirmed the basic assumptions of the theory. In the future thus, they wrote, "one will have no need to distinguish between pyroelectricity and piezoelectricity as two different

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Czermak, one could use the measurements that he did not need to modify (those on the plates with parallel surfaces) to reach results that are close to the Curies'.

[24] It should be clear that the contingent historical way in which the experimental results were attained does not alter the validity of the methods eventually used, or their results.

phenomena. Both have their common origin in deformations that occur inside the crystals." (p. 552)

Interestingly, the correction of the piezoelectric moduli did not change their conclusion that pyroelectricity is a secondary effect of piezoelectricity. They also found reasonable agreement with their earlier mistaken values, though these were lower by 20% than the corrected values. In their earlier report Riecke and Voigt calculated a lower value for the secondary pyroelectric effect of only 1.08. However, they still claimed that it agreed with Riecke's value, which this time they cited, without discussion, as 1.18.[25] In this publication they did not refer to any second-order term. The arrival at the same expected conclusion from two different sets of values revealed flexibility in analyzing a precise qualitative experimental result. Their conclusion is very close to the position that Riecke had taken already in 1885 and that Voigt adopted somewhat more cautiously in 1890. Perhaps the flexibility in interpreting the experimental results contributed to Voigt's retreat from the conclusive statement in his 1894 theoretical work (Chapter 4, p. 177) and his return to empirical examination of the existence of a direct pyroelectric effect in tourmaline in 1898. I will discuss his later experiment below.

HANKEL AND LINDENBERG'S EXPERIMENTS

Piezoelectric and pyroelectric phenomena were also studied empirically by W. G. Hankel. Hankel maintained his view that experiments on heating and pressing crystals involve three independent effects with different characteristics: pyro-, piezo-, and actino-electricity (Chapter 1). After his retirement from teaching at Leipzig University in 1887, Hankel continued his old research program on the pyroelectricity of crystals, publishing treatises 19 to 21 on his "electric researches" in the 1890s. In 1892 and 1895 he published two accounts of electric examinations of 13 different crystals, done in collaboration with a certain H. Lindenberg. Pyroelectricity, which he called thermoelectricity, continued to play the leading role in these experiments. In discussing each crystal they started with its pyroelectric behavior, then discussed its piezoelectric behavior and compared them with each other regarding the directions and kinds of effects. Perhaps the only change in the methods and aims of Hankel's experiments from the 1860s was the introduction of piezoelectric experiments in 1881. As in Hankel's previous experiments, Hankel and Lindenberg did not cut the crystals to plates or bars along polar axes or axes in which they were particularly interested, as others did, but left the crystal in an essentially natural form. In a few cases they cut a crystal to have a plane surface but then the "interesting" part of the mineral was left in its natural form (e.g., they cut strontium sulfate parallel to its hexagonal shape). They were more interested in the various properties of the crystals they examined than in general properties of pyro- and piezoelectricity. Thus, they discussed at length the

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[25] Without their explanation for the cited value I can offer only speculations. The value they quoted might be an adjustment of Riecke's original value to 23°. This was also the value of one of the five specimens that Riecke had measured, so perhaps they decided that it is more reliable then other values. *Nachrichten*, p. 255.

specific forms of the specimens and investigated crystals of special form like twin crystals.[26]

Reading only Hankel and Lindenberg's papers, one cannot even guess that a theory of the examined phenomena was suggested a few years earlier. They made no reference to Voigt's general theory or to any of the theoretical discussions in the field. Examining many different crystals they could have contributed much to the confirmation (or refutation) of the theory by comparing their results with the theoretical expectations, as Riecke and Voigt did for quartz and tourmaline. Hankel and Lindenberg, however, did not make the measurements needed for such examination. Using crystals in their natural form they pressed them in directions dictated by their form and not by theory and did not make sure that the pressure was uniform. They indicated numeric results of the potential of the crystals on an arbitrary scale, which was compared with a known cell. However, this is not enough for an examination of the mathematical theory. To examine whether the coefficients given by the theory are sufficient to account for the phenomena, one needs to have more quantitative, systematic information about the directions of pressure and the measured surfaces and about the capacity in different settings. Clearly, this did not concern Hankel and Lindenberg, who did not relate their finding to the theory even when they could.

Two years later, Pockels indicated that two qualitative observations that they made on Rochelle Salt can be seen as a confirmation of the general theory. Their observations on the appearance of electric charge due to pressure in various directions were in accordance with its predictions.[27] Hankel and Lindenberg themselves indicated that crystals of the same classes show the same electric behavior. This observation supports Voigt's general theory. Yet, this assertion was not particular to Voigt's theory. The connection between the crystallographic and electric properties of crystals has been accepted since the work of Haüy a century earlier. That crystals of the same class should show the same kind of pyroelectric effect had already been assumed when Hankel had started his researches in the subject in 1839. Another of their experimental findings contradicted both Voigt's general theory and the assumption of workers in the field for decades. Hankel and Lindenberg found that pyroelectricity is not limited to hemihedral crystals. They observed a pyroelectric effect in potassium dichlorate, a crystal that has a center of symmetry. However, the observational results were not consistent; the side that became positive in most specimens became negative in others. Such behavior suggests that the phenomenon observed is either due to irregularities

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[26] Wilhelm G. Hankel und H. (Heinrich?) Lindenberg, "Ueber die thermo- und piëzoelektrischen Eigenschaften der Krystalle des chlorsauren Natrons, des unterschwefelsauren Kalis, des Seignettesalzes, des Resorcins, des Milchzuckers und des dichromsauren Kalis," *Leipzig Abhandlungen* 18 (1892): 363–405; id., "Ueber die thermo- und piezoelektrischen Eigenschaften der Krystalle des brom- und überjodsauren Natrons, des Asparagins, des Chlor- und Brombaryums, sowie des unterschwefelsauren Baryts und Strontians," *ibid.,* 21 (1895):11–42. W.G. Hankel, "Ueber die thermo- und piezoelektrischen Eigenschaften der Krystalle des ameisensauren Baryts, Bleioxyds, Strontians und Kalkes, des salpetersauren Baryts und Bleioxyds, des schwefelsauren Kalis, des Glycocolls, Taurins und Quercits," *ibid.*, 24 (1898): 469–496.

[27] F. Pockels, "Ueber den Einfluss des elektrostatischen Feldes auf das optische Verhalten piëzoelektrischer Krystalle." *Göttingen Abhandlungen* 39 (1894) 204 pp. on p. 161.

in the specimens or to another electric effect. Such reasoning could justify the neglect of this result by later workers in the field. The marginal place of these researches, which were only published in the transactions of the Leipzig Academy, perhaps also played a role in this neglect. Hankel's continuous work on the electricity of crystals is an example of research that stagnated at a point in time—no later than the beginning of the 1880s—and was not influenced by later major developments in the field. His research became not only marginal but almost irrelevant to the scientific community.

POCKELS'S STUDY OF THE RELATION BETWEEN PIEZOELECTRICITY AND ELECTRO-OPTICS

Pockels studied piezoelectricity empirically in order to determine its relation to the related phenomenon of electro-optics, which is the effect of electric fields on double refraction in crystals. I have already discussed his 1890 theoretical treatment of the relation between the two phenomena, in which he showed that the joint effect of (converse) piezoelectricity and piezo-optics accounted qualitatively for electro-optics, but he left open the possibility of a direct effect. To decide whether such a direct effect existed, it would be necessary to examine whether the joint effects accounted quantitatively for the whole of the observed effect of electro-optics (Chapter 4, p. 152). The coefficients of the three phenomena and of elasticity had to be known for this experiment. A few years later Pockels took on the task himself, determining the values of the coefficients. He measured all the coefficients (except those of elasticity, which he took from the literature) on the same specimens to make sure that the results would not be influenced by differences between specimens of the same crystal, publishing his detailed results in 1894. He determined the three coefficients in question in absolute units. In such units the coefficients could be inserted into the same equation and compared. Exactitude was, thus, central to Pockels's empirical work. He presented a long discussion of the instruments of measurement and their theory. For example, he developed a mathematical expression for the variations of the electrometer dial to eliminate the error in its reading.[28]

The relations between the coefficients of the three phenomena were expressed according to their theoretical treatment by Pockels in 1890. For the empirical comparison he developed an expression for the value of the indirect electro-optic coefficient e'_{mn}, i.e., the optic effect due to piezoelectricity and piezo-optics:

$$e'_{mn} = \frac{1}{x_n} \sum_{1}^{6} a_{mh} \delta_{nh} \tag{2}$$

where χ_n is the dielectric constant, a_{mn} the piezo-optic constant, and δ_{nh} the piezoelectric modulus. e'_{mn} are the coefficients that determine the effect of the electric moment on the refraction of light in the crystal according to Pockels's electro-optic

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[28] *Ibid.* The discussion of the instruments is on pp. 13–29. Page references in parentheses hereinafter refer to this paper.

theory (Chapter 4, equation (2)). If the whole optic effect is due to piezoelectricity, e'_{mn} should be equal to value of the electro-optic constant—e_{mn} calculated from the observation. In the electro-optic experiments Pockels did not find e_{mn}, but rather its multiplication by the dielectric constant χ. Thus, the value of the dielectric constant did not enter the comparison and its measurement was therefore saved. On the other hand, Pockels needed to find the elastic coefficient, though it does not appear in equation (2). It was needed for the calculation of the piezo-optic constant, since the measurements were made in known stress, but the constant a_{mn} is relative to strain rather than stress. However, the elastic coefficients had been determined before and were known to be steady in various specimens of the same crystal.

The need to determine four different constants on the same crystal considerably diminished the number of species that Pockels could examine. "The crystals must not only be free from cracks, inclusions, and optical disturbances, but must also have large dimensions." In addition, the optical effect in the specific crystals should be observable. These constraints reduced the number of the crystals that he investigated to three: quartz, sodium-chlorate, and Rochelle salt. Even tourmaline was inappropriate for quantitative examination since optical measurements could not be taken due to the high absorption of light of Brazilian tourmaline. He tried without success to examine qualitatively a few other crystals (pp. 2–3). Pockels's difficulty in finding additional crystals that suited his experimental examination suggests one reason for the use of essentially the same crystals in these quantitative studies. That physicists were satisfied with a confirmation of the theory limited to a small number of crystal classes, was probably based at least partly on the technical difficulties in examining other crystals. These difficulties did not encourage other researchers to enter the field.

Pockels's experimental set-up for measuring the piezoelectric coefficients was similar to that of Riecke and Voigt. This was expected from a *privatdozent* at Göttingen who kept working connections with Voigt, his former teacher. Like his professors he measured deviations of the electrometer's needle and compared them with the readings of a Clark cell but not before he had adjusted the reading to the correct value by a mathematical expression he developed for the oscillations of the needle somewhat differently for each kind of crystal. The capacity of the system was again determined by adding an external air-condenser. Like Czermak, Pockels determined the capacity of the external capacitor theoretically by a method due to Kirchhoff. He did not need to use an experimental method like Maxwell's tuning fork (pp. 69–73, 131–2, 137–43).

Although the piezoelectric coefficients of quartz had already been measured, Pockels considered it worthwhile to remeasure the moduli's values on the same specimen on which he had measured the other constants, since he assumed that their magnitude might vary from one quartz specimen to another. Like Voigt and Riecke, he applied unidirectional pressures in the yz plane (perpendicular to their polar direction x), but only in three directions: in the direction of the y axis (this is a transverse effect) and at angles of 45° and −45° (Figure 5.3).

With such a small number of observations he could not analyze the data in a method like that of least squares but calculated the values directly from the expressions for the three pressures he applied. The piezoelectric equations of quartz (Chapter 2, equation

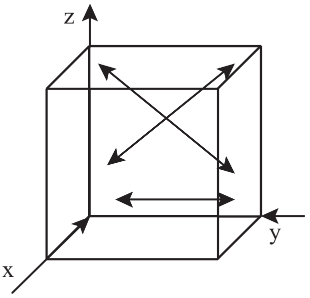

Figure 5.3: Directions of pressures in Pockels experiment with quartz. The arrows show the directions in which Pockels applied pressure, all in the *yz* plane.

(6)) provide for these three cases:

$$\frac{a_{90}}{p} = \delta_{11}, \qquad \frac{a_{+45}}{p} = \frac{1}{2}(\delta_{11} - \delta_{14}), \qquad \frac{a_{-45}}{p} = \frac{1}{2}(\delta_{11} + \delta_{14}) \tag{3}$$

where a_{90}, a'_{+45} and a_{-45} are correspondingly the polarizations due to pressures in 90°, +45°, and −45° directions. A simple manipulation led to the following expressions for the values of the moduli:

$$\delta_{11} = \frac{1}{3}\left(\frac{a_{+45}}{p} + \frac{a_{-45}}{p}\right) + \frac{2}{3}\frac{a_{90}}{p}, \qquad \delta_{14} = \frac{a_{-45}}{p} - \frac{a_{+45}}{p} \tag{4}$$

Pockels calculated the values of the electric polarizations from those of the observed voltage and the capacity of the system. Inserting these values in equation (4), he got: $\delta_{11} = -6.27\times10^{-8}$, $\delta_{14} = +1.925 \times 10^{-8}$.

Yet equations (4), from which Pockels found the values of the moduli, are not unique expressions for the moduli and thus are not necessary. The value of δ_{11} could have been deduced directly from the polarization a_{90} or only from the other two measurements, or from any combination of the two. The weight Pockels ascribed to the various measurements is arbitrary. It does not reflect any obvious reason. Moreover, a calculation of δ_{14} from the value of δ_{11} (with either of the last two equations in (3)) gives a result that deviates by more than 10% from the value that Pockels found.[29] The value that Pockels found is a mean, but he did not justify it as such. He did not refer to this question. One could do a similar calculation with Riecke and Voigt's measurements. However, their use of the method of least squares to determine the value of the moduli made their determination superior to any arbitrary direct calculation, like that of Pockels. The latter justified the values he obtained by comparing the observational data to figures calculated with these values. He found an agreement within 4%. The procedure showed that the values are at least rough mean values (pp. 131–44).[30] Pockels's results agree with Voigt's general theory, but after Riecke and

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[29] From eq. 3 one can get for example $\delta_{14} = \delta_{11} - \frac{2a_{+45}}{p}$. Inserting the value of δ_{11} from the direct measurement gives $\delta_{14} = 1.65. \times 10^{-8}$. A similar equation with a_{-45} gives a value of 2.2×10^{-8}.

[30] An alternative determination of the moduli, on the other hand, gives a deviation of almost 10%.

Voigt's more thorough confirmation in a similar situation, this corroboration added very little. Pockels was, however, not interested in the confirmation of the theory, which he considered confirmed, but in the value of the quartz moduli, which he needed to determine the relation between piezoelectricity and electro-optics. His results differ from those of Riecke and Voigt. The agreement for δ_{11} is satisfactory; Pockels's value is smaller by 2.9%. It is in excellent agreement with that of the Curies', a difference of less than 1%. The value Pockels got for δ_{14} is "considerably larger" than that found by Riecke and Voigt: 1.925 in comparison to 1.45, a difference of about 30%. Pockels did not explain this gap; he probably did not know how. Later measurements were closer to Pockels's, finding values even higher than his.

According to Voigt's theory, only shear stresses electrify sodium-chlorate, which has only one piezoelectric coefficient, by the equations:

$$a = -\delta_{14} Y_z, \quad b = -\delta_{14} Z_x, \quad c = -\delta_{14} X_y. \tag{5}$$

Pockels first derived the value of the modulus δ_{14} by an experiment that involved only the shear stress X_y. This was a very limited confirmation of Voigt's theory, since he did not examine whether the coefficients of the other stresses have the same value, as followed from the theory.[31] Pockels was probably aware of this limitation since he carried out additional experiments. The second experiment was not required for the determination of the constant (he did not even use it for that purpose). However, it was needed for the confirmation of Voigt's theory. In the second arrangement, he applied equal stress in the three relevant directions of stress (Y_z, Z_x, X_y) and measured their joint contribution. He compared the experimental results with their theoretical value assuming the value for δ_{14} previously determined, and found "satisfactory agreement" (pp. 73–8). The agreement was needed not only to confirm Voigt's theory, but also to justify the use of the value of the piezoelectric modulus in all directions in calculating the secondary piezoelectric optic effect.

While Pockels's measurements of sodium chlorate largely confirmed the general theory, the test of theoretical relations for Rochelle salt (also called Seignette salt—$KNaC_4H_4O_6\ 4H_2O$) was more problematic. Like sodium-chlorate it is electrified only by shear stress, but it has three independent coefficients rather than one. Its basic piezoelectric equations are:

$$a = -\delta_{14} Y_z, \quad b = -\delta_{25} Z_x, \quad c = -\delta_{36} X_y. \tag{6}$$

Pockels first tried to measure the value of δ_{14}. To this end, he applied pressure in the yz plane at an angle of about 45° from both axes and measured the electric moment—a in the x direction. However, he soon encountered unprecedented difficulties. First, he observed a much stronger electrical activity than before, about two orders of magnitude stronger than that shown by quartz. That was simply solved by the applications of smaller weights of little more than 100 g instead of 1000 g used in the previous experiments. Second, he found that after loading weights on the crystal the electrometer's dial did not stabilize but continued increasing in a way that precluded him from

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[31] Pockels did not examine the assumption of linear effect as he applied the same weight in all measurements.

finding a correct time for taking the measurement. Thus, instead of a fixed value he could only state a range between 340 and 1180×10^{-8} (statcoul/dyne) for δ_{14}, concluding that its value was "left undetermined" (pp. 183–9).

The values that Pockels got for the moduli δ_{14} contradict the assumption that it is a constant. Still, he continued to refer to the coefficient as undetermined constant implying that one would eventually be able to determine its constant value. He suggested an ad hoc explanation for his inability to observe the true value of the constant and thus for the apparent contradiction with piezoelectric theory. He thought that the source of the continuous rise in electric tension measured by the electrometer might be in the high magnitude of the effect. Therefore, he conjectured that the connection to the ground and the electrometer do not supply enough electric charge to the metal plates attached to the crystal. In such a case, the tension between them is smaller than the inner electric field in the crystal, so a net electric field remains in the crystal. This field produces electric current (in the crystal) that raises the tension between the metallic plates. This explanation is not based on any special property of Rochelle salt but on its strong electric effect. Pockels himself showed reservations about his hypothesis. He still suggested an experimental arrangement to examine it. To the best of my knowledge, no one tried to construct it.[32]

The other two moduli of Rochelle salt did show a constant value. Pockels measured this directly in directions that involved only one modulus. He also measured the value of δ_{25} in another experiment in which he applied pressure in a direction that involved the value of $\delta_{14.}$ However, since the latter's value was undetermined, he preferred the value he found in the measurement that involved only δ_{25}. This is a sound decision, but it weakens the confirmation of the theory in Rochelle salt by reducing the number of different cases in which it was quantitatively tested. It left Pockels with measurements that according to the theory involved only one modulus. Still, the rejected measurement of a more complex effect provided qualitative confirmation of the theoretical relations between the piezoelectric and the crystallographic axes. His initial confidence in Voigt's general theory helped Pockels to regard his experiments and Hankel and Lindenberg's qualitative findings as a confirmation of the theory in Rochelle salt. He relied on the theory in his comparison between piezoelectricity and electro-optics (pp. 190–3).

The comparison between the compound effect of piezoelectricity and piezo-optics and the total electro-optic effect in Rochelle salt did not yield clear conclusions. One coefficient (e_{41}) was undetermined in both effects; the calculated and the observed values of another were very close; but in a third one the optic effects were of opposite directions. Still Pockels was cautious not to regard the last case as a proof of the existence of a genuine effect due to the smallness of the optic effect in this direction

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[32] In hindsight one can conclude that Pockels probably observed for the first time an effect of ferro-electricity. Indeed δ_{14} is not constant in Rochelle salt. Though Pockels's experiment left an open question about the piezoelectric behaviour of the crystal, he did not suggest it as a subject for further research. Its experimental examination was resumed only in the 1920s by Joseph Valasek, who formerly worked with Voigt. A decade later physicists in the USSR realized that Rochelle salt crystal exhibits an unrecognized electric phenomenon that they named after the crystal "Seignette- electricity," which is today usually called ferro-electricity since it is analogous to ferromagnetism.

(p. 203). Quartz and sodium-chlorate provided clearer results. The secondary effect of piezoelectricity contributes only 1/12 of the total electro-optic effect in sodium chlorate (p. 82). In quartz it accounts for less than half of the observed electro-optic principal coefficient (e_{11}).[33] This is the same electro-optic effect that Röntgen and Kundt had regarded as a secondary effect of piezoelectricity. Thus, the research demonstrated "that electrostatic forces [fields] exert [*ausüben*] a direct influence on the transmission of light [*lightbewegung*] in piezoelectric crystals" (p. 204). Thereby, it justified Pockels's "positivistic" approach to study the phenomenon "without any hypothesis" about its sources.

This demonstration was based on the acceptance of Pockels's theoretical analysis of the phenomenon, whose piezoelectric part was based on Voigt's theory. Following Lippmann, his analysis tacitly assumed that piezoelectricity is reciprocal and thus that the piezoelectric constants are the same for both the direct and the converse effects. This is a crucial implicit assumption for Pockels since he measured the constant in the **direct** effect, and used these values in calculating a secondary (optic) effect of the **converse** effect. As I discussed in Chapter 4, the assumption of reciprocity was essential for any consideration of the relations between the converse and direct effect and it was implicit in the thermodynamic formulation. However, it was quantitatively confirmed only once by the Curies in 1882. No one else tried to measure the converse effect, or to examine in any other way that the phenomena are really reversible.[34] The observations of the multiplied effects of loading and unloading weights indicated that the direct effect itself does not suffer from any kind of hysteresis (*Nachwirkung*), but did not show the existence of a full Carnot cycle. Interestingly, I did not find any reference to this shortcoming in the literature. Probably due to experimental difficulties, Curies' confirmation, which Pockels cited (p. 84), satisfied the contributors to the field.

THE RELATION BETWEEN PIEZOELECTRICITY AND PYROELECTRICITY

Riecke and Voigt's 1891 examination of the relation between piezoelectricity and pyroelectricity did not provide conclusive results like those Pockels found regarding electro-optics. This was partly due to the nature of negative results. Demonstrating inexistence is harder than demonstrating existence. That an effect smaller than the experimental error existed was still a possibility. Such an effect was likely since the theoretical and the observed results deviated by about 10% and involved reinterpretation. Furthermore, unlike Pockels in the electro-optic experiments, Riecke and Voigt did not measure all the coefficients on the same specimen. Thus, as mentioned (above p. 177) in his 1894 theory, Voigt retreated to a more cautious position assuming the

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[33] Piezoelectricity and piezo-optics account for about 72% of the value of the other constant—e_{14}, Pockels, "Einfluss des elektrostatischen Feldes," pp. 148–49.

[34] True, both are difficult tasks. Yet, one could examine, for example, whether the piezoelectric effect produces heat, which theoretically it should not.

possible existence of direct pyroelectricity. In addition to general cautiousness, like that Pockels showed about electro-optics, Voigt had molecular arguments in favor of a direct effect. According to his model, a change of temperature should induce electricity in two ways: one by the piezoelectric effect due to thermal displacement, the other by the thermal motion of the electric poles inside the molecules. Yet regarding the 1891 experimental results, in 1897 he was still cautious in public about the existence of a direct effect in tourmaline, writing that "probably, true pyroelectricity in that case does not exist."[35] A few months later he carried out new measurements to check the existence of a direct effect of heat. To this end he compared the joint effects of thermal displacement and piezoelectricity with the total pyroelectric effect. This time he measured all the relevant coefficients on the same specimen.[36] His findings supported his supposition that a genuine direct effect of temperature change exists, and thereby his molecular hypothesis. He left the last conclusion to the reader.

Voigt used the same tourmaline specimen on which he had already determined the values of the elastic and piezoelectric constants in 1890 and 1891. Unlike his and Riecke's experiment in 1891, this time he measured the thermal deformation constants, using a special instrument and method of a certain Hr. C. Pulfrich from the Carl Zeiss company. He found that the constants were considerably smaller (20 and 60%) than those given by Pfaff, which he and Riecke had used in 1891. Hence the secondary effect of piezoelectricity that they had calculated in 1891 was too high. With the new values for the thermal constants, he reanalyzed the data of the 1891 experiment. He now calculated 0.98 (statcoulomb/cm^2 per degree) for the indirect pyroelectric effect, instead of 1.34 in 1891. A comparison with the value that Riecke had found for the total pyroelectric effect -1.23 shows the existence of a direct effect. However, Voigt was not satisfied with that but measured again the total pyroelectric effect on four prisms of the same specimen on which he had made the other measurements. As in previous experiments he observed the electric tension on an electrometer. He compared these readings with the readings due to piezoelectricity with the same arrangement. Thus, he could show that the secondary piezoelectric effect accounts for only 80% of the total effect, before translating the results to absolute units. He used readings of the piezoelectric effect to translate the results into absolute units in terms of charge density, relying on the values that he and Riecke had determined for the piezoelectric moduli. Thereby, he bypassed a complicated measurement of the absolute charge on the hot tourmaline.[37] The value of the pyroelectric constant Voigt found was 1.21, a good agreement with Riecke's value. That leaves for what he called the true effect, i.e., direct pyroelectricity, a value of 0.234, which is above the experimental error. He therefore concluded that direct pyroelectricity exists in

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[35] Woldemar Voigt, *Die fundamentalen physikalischen Eigenschaften der Krystalle in elementarer Darstellung*, Leipzig, Veit & Comp., 1898, p. 121.

[36] W. Voigt. "Lässt sich die Pyroelectricität der Krystalle vollständig auf piëzoelectrische Wirkungen zurückführen?" *Ann. Phy.* 66 (1898): 1030–1060. On the molecular consideration p. 1034.

[37] Voigt's method differed from Reicke's. To avoid heat current the latter had not measured the charge directly on the tourmaline but only its induction on an electroscope, from which he calculated the charge on the specimen, Eduard Riecke, "Ueber die Pyroelectricität des Turmalins," *Ann. Phy.*, 28 (1886): 43–80.

tourmaline, and might also exist in all similar crystals, i.e., crystals with a unique hemihedral (asymmetric) crystallographic axis. He repeated the claim, central to his theory, that the electric effect of temperature changes in the other crystals (like quartz) is in reality an effect of piezoelectricity.[38] Despite his efforts, Voigt's conclusions were not accepted as conclusive. In 1914 Röntgen still claimed that the existence of true pyroelectricity seems possible on theoretical grounds, but had not been experimentally established.[39]

Research on the relations between the kindred phenomena of piezoelectricity, pyroelectricity, and electro-optics revealed the fertility of measuring physics. Only precise quantitative measurements whose design and interpretation were based on the mathematical theory of the effects could tell whether the last two were genuine phenomena. In 1909, in a lecture about "the struggle for the decimal in physics," Voigt asserted that this kind of research raised questions that could be neither known nor resolved without precise measurements.[40] He did not mention the rather complicated examples from the study of piezoelectricity, but his and Pockels' experiments were excellent examples for his claim. Though Röntgen and Kundt had observed electro-optic effects as early as 1883, they did not realize that they had observed a new, genuine phenomenon. They did not even raise the question of whether such a phenomenon existed, as the theoretically oriented Pockels did seven years later. He later succeeded in answering this question with precise measurements. In the study of pyroelectricity, Voigt showed that a more thorough and accurate experiment in which all the variables were examined on the same specimen could reveal a phenomenon that earlier experiments had overlooked. Both examples display the exploratory power of exact experimental work in the tradition of Neumann.[41]

VOIGT'S EXAMINATION OF THOMSON'S HYPOTHESIS

Two years before his study of the relation between pyroelectricity and piezoelectricity, Voigt constructed an experiment in order to observe the internal polarization of tourmaline, first suggested by Thomson in 1860. According to Thomson's hypothesis, pyroelectric crystals, like tourmaline, have permanent internal polarization whose effect is compensated by charge density on the crystal surfaces. This hypothesis was adopted by the major contributors to the study of piezoelectricity. It led Jacques and Pierre Curie to the discovery of the phenomena, and it was a necessary consequence of the general theory. However, as Voigt pointed out, though changes in the polarization due to variations in temperature and pressure were measured in the laboratory,

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[38] *Ibid.* pp. 1054–1058. Since considerations of symmetry ruled out the possibility of an effect due to uniform change of temperature, a contradictory assertion would contradict one of the two basic assumptions of the general theory.

[39] W.C. Röntgen, "Pyro- und Piezoelektricität Untersuchungen" *Ann. Phy.* 45(1914): 737–800.

[40] Woldemar Voigt, "Die Kampf die Dezimale in der Physik," *Deutsche Revue*, 34 (Juli 1909): 71–85.

[41] One the other hand Darrigol claims that Neumann's followers "hardly discovered any new effects." *Ampère to Einstein*, p. 75.

the natural electric polarization was not observed.[42] Although Voigt claimed that all students of the subject adopted the hypothesis, it was not the case. Duhem's early thermoelectric theory of pyro- and piezoelectricity, which I discussed in Chapter 3, is a good example of a theory that did not adopt the hypothesis. Riecke's pyroelectric experiments refuted Duhem's theory, and he retreated from it before 1892. Yet Duhem was not alone in rejecting Thomson's hypothesis and the opposition did not disappear after the publication of Voigt's theory. In his handbook on electricity, Gustav Wiedemann objected to Thomson's hypothesis, claiming that when a pyroelectric crystal, e.g., tourmaline, in uniform temperature is broken, its two halves do *not* show the existence of any free electricity, as should follow from the hypothesis. His objection implied that such an experiment had been performed, but he did not indicate who, if any, performed the experiment.[43] In 1901 Thomson, now Lord Kelvin, correctly pointed out that "Wiedemann mentions an experiment without fully describing it." He further claimed that "it would be very difficult to get trustworthy results by breakages [of tourmaline], because it would be almost impossible to avoid irregular electrifications by the appliances used for making the breakage." However, this is exactly what Voigt had done five years before Kelvin wrote this.[44]

Voigt used the same tourmaline specimen that had served him in the determination of the elastic and piezoelectric constants. He made sure that the crystal was free of external stress or variation in temperature. Then he cut it into four and connected the pieces' edges to a Nernst–Dolezalek's electrometer, all that in a quarter of a second, and read the tension on the electrometer. To translate the reading to absolute units he compared it to that due to pressure on the same prism, known by the piezoelectric moduli, as he would do two years later in determining the pyroelectric constants. For the internal polarization at 24°C, he found an average value of 33.4 (statcoulomb/cm^2) with deviations of about 10%. Compared with Riecke's value for the pyroelectric effect (1.23 statcoulomb/cm^2 per degree), this is not large natural polarization. Moreover, the pyroelectric effect of heating is in the opposite direction to that of the natural polarization. On the basis of these two values he wrote an equation for the total electric moment of tourmaline at any temperature as: $\mu = 33.4 - 1.32(\theta - 24)$, where θ is the temperature (in degrees Celsius). According to this equation, the natural electric moment of tourmaline should equal zero around 50°C and should have an opposite direction at higher temperatures. Voigt tried to measure the internal polarization at 60°C but succeeded in getting only a weak unmeasurable effect.

Voigt was aware that one can question whether the electric tension that he measured is really due to the internal electric moment of the crystal and not to another effect. In

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[42] W. Voigt, "Versuch zur Bestimmung des wahren specifischen electrische Momentes eines Turmalins," *Ann. Phy.*, 60 (1897): 368–375 (first appeared in *Göttingen Nachrichten* 1896, Heft 3.), pp. 368–9.

[43] Wiedemann, *Die Lehre von der Elektricität*, 1st edition (1883), Vol. II, pp. 337–8. The objection appears also in the second edition of 1893. It is interesting to note that both Duhem and Wiedemann thought that the phenomena of both pyro and piezoelectricity are excited by heat.

[44] Kelvin, "Aepinus atomized," p. 560 in a footnote. As in other cases, Kelvin was ignorant of Voigt's work though it was published in the *Annalen der Physik*. He assumed that one could still rely on Canton's more than a century old results. However Canton merely observed that all the pieces of the same crystal maintain the same polar axis. Priestly, *History and Present State*, Vol. I. pp. 377–78.

order to defend his conclusion he negated other possible sources of the effect. First, he noted that the similarity of the results in the four pieces makes implausible an assumption that the electric effect observed was due to electrification in the process of breaking the crystal. The latter process is not uniform and thus its effects on four different pieces are highly unlikely to be close to each other. Second, the measured value is too high to be explained by conductivity of the air in such a short period. Moreover, he assumed that the true value of the polarization is a little higher than his results, since the conductivity of the air probably diminished the effect. Furthermore, he rejected possibilities of considerable electrification by friction or from a piezo- or pyroelectric effect because their electric effect in tourmaline is of an opposite sign to the one observed in the experiment.[45]

Voigt's interest in the permanent polarization of crystals went beyond his wish to confirm Thomson's hypothesis and thereby his general theory. He thought that the magnitude of the permanent internal polarization could shed light on the obscure question of the molecular structure and the process that produces the piezoelectric effect. Riecke's molecular theory requires the assumption of high inner polarization (much higher than that induced by piezo- and pyroelectricity), while no such assumption is needed in Voigt's model. The latter further assumed that in some attainable state of equilibrium the internal electric moment could equal zero.[46] Riecke's assumption of "exorbitant large permanent specific moments" [polarization] adds according to Voigt complications that have no justification in the observations, and it is "unpleasant."[47] Voigt left the reader to conclude that the experimental determination of the internal polarization supports his, rather than Riecke's molecular model.[48]

Thus, considerations of the molecular theory were a major motivation for Voigt's measurement of permanent polarization. They motivated also his search for direct pyroelectricity. However, they were not the experiments' sole motivation. The general phenomenological theory also supplied reasons for them. In measuring internal polarization, Voigt verified a consequence of the general theory. Although the existence of a direct pyroelectric effect was not a consequence of the general theory (neither is it a rigorous deduction from the molecular theory), Voigt inclusion of this effect in the mathematical theory of the subject followed from a cautious phenomenological approach. Pockels's phenomenological theory of piezo-optics and his examination of its direct effect show that molecular assumptions were not necessary for Voigt's study of genuine pyroelectricity. Notwithstanding the role of molecular considerations in this case, such a significant influence of the molecular models was exceptional in the theoretical phase of the piezoelectric research.

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[45] Voigt, "wahren electrischen Momentes," pp. 370–5. Voigt apparently considered the piezoelectric effect of decreasing the pressure, which agrees in signs with that of pyroelectricity. One might suppose that cutting the crystal would reduce its inner pressure.

[46] On these theories see Chapter 3 pp. 122–129.

[47] *Ibid.*, pp. 369–70, quotation on p. 370.

[48] Riecke ignored Voigt's finding and the question of the magnitude of the molecules' polarization when he returned to his molecular suggestion in 1912. Riecke, "Zur Molekularen Theorie der Piezoelectrizität des Tourmalines."

In another sense, the detection of internal electric polarization is exceptional in that phase. This was the only piezoelectric experiment in the 1890s that aimed to directly observe a property, or even an entity, that had not been observed before. The existence of permanent polarization was not deduced from a comparison between precise measurements of kin phenomena but was observed directly. It was an experiment of discovery rather than of measurement. In this sense it better fits the experimental physics of Röntgen and Kundt that characterizes the pretheoretical phase. Precision was still important in the experiment in order to validate its results and to dismiss alternative explanations for their origins. Yet, the difficulties in such an experiment characterize experimental physics—how to break the crystal without electrifying it, how to eliminate external influences, and how to dismiss alterative explanations? Still, characteristic to his own tradition of measuring physics, Voigt was not satisfied with relative values but measured the electric moment in absolute units. Though he did not directly rely on any complicated mathematical device, he indirectly relied on these methods in using the values of the piezoelectric constants that he had measured and calculated five years earlier. The categories of experimental and measuring physics are useful analytical tools, but as this example indicates, physicists did not see themselves obligated to one or other of these.

THE MONOPOLY OF GÖTTINGEN AND THE PLACE OF PIEZOELECTRIC RESEARCH IN A WIDER CONTEXT

Empirical work on piezoelectricity in the 1890s was done almost exclusively at Göttingen University. The only experiments performed elsewhere were those of Hankel in Leipzig. However, these were outdated and did not take account of the recent theoretical developments. A decade earlier the geography of the empirical work on piezo- and pyroelectricity was very different. Experiments were carried out in Paris (by Jacques and Pierre Curie and Friedel), Strasbourg (by Kundt and his students), Giessen and Würzburg (by Röntgen), as well as in Leipzig and in Göttingen. Göttingen's "monopoly" of the piezoelectric experiments raises a historical question, which I would like to address in the following.

The experiments on piezoelectricity, and especially precise experiments, required means that were not available in many departments or institutes of physics. Such experiments demanded skills that mostly came with experience in similar kinds of research like that involving the use of crystals according to their crystallographic axes (e.g., in elasticity and optics). Not many physicists had such experience. Crystallographers, who had experience with crystals, usually lacked experience with precise electric measurements, which were also needed for these experiments. Furthermore, they rarely revealed much interest in such physical questions.[49] Instruments probably posed a minor problem, since most experiments required only standard instruments

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[49] Questions of general electric and elastic behaviour like piezoelectricity attracted less attention from crystallographers, who were primarily interested in the structure of crystals and their characteristics. Even a text on *physical* crystallography like that of Groth of 1885 discusses briefly the electric

that were available in virtually all university laboratories. Crystal specimens for the experiments, however, were not available everywhere. Prisms of crystals cut in various directions were available for purchase from known firms for affordable prices for an average university laboratory.[50] However, larger prisms, which were needed at least for some experiments,[51] were more expensive. Voigt needed support from the Royal Scientific Society of Göttingen to purchase the "precious" tourmaline specimen on which he carried out four different experiments, including three on piezo- and pyroelectricity, during the 1890s. Pockels mentioned the help he got from Voigt in obtaining Rochelle salt crystals.[52] Apparently, the use of the same specimens for various experiments was not only a scientific but also an economic need. The use of the same specimen reveals another hindrance for newcomers, which is the cumulative character of some experiments. Voigt based part of his research on previous observations on the same specimens. Experimentalists in other places could not use Voigt's precise results in the same manner, since they were determined for the same specimen. While the relations between phenomena and constants that were found in Göttingen were regarded as universal, the precise values of certain coefficients were dependent on the specific specimen. Thus, in another laboratory one had to launch a new series of measurements on other specimens, as Pockels did in his electro-optic experiment.

These (in a wide sense) practical obstacles made experimentation in other places more difficult. Yet, they clearly did not prevent interested scientists from constructing piezoelectric experiments. Apparently, physicists were not interested enough in the field to make such an effort. Voigt observed that piezoelectricity as part of the general physics of crystals was "far from the problems that ha[d] occupied the larger number of physicists."[53] True as it is, Voigt's observation gives only a partial picture of the interest in piezoelectricity. In the pretheoretical phase the field attracted experimental and theoretical work from quite a few physicists. In the theoretical phase, contributions to the subject were confined neither to scientists preoccupied with the physics of

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properties of crystals and dedicates only one paragraph to piezoelectricity; Paul Groth, *Physikalische Krystallographie.*

[50] Crystal from "Steeg und Reuter" company (which supplied Röntgen with his crystals) costed 3–30 Marks a piece (of a few millimetres), while a larger quartz prism costed 15–75 DM (Groth, *Physikalische Krystallographie*, pp. 695–99). The average annual budget for equipment in Germany circa 1900 was a little less than 4,000 DM (Forman, Heilbron and Weart, "Physics Circa 1900," pp. 58–66, especially table c.2.).

[51] Large crystals enable the use of the piezoelectric theory's relatively simple equations for unidirectional stress. With the equipment of the period applying an exactly unidirectional pressure in a precise direction on small crystals bars (of a few mm) is very difficult. Moreover, in such cases surface effects become too strong and do not permit the use of the theoretical equations which do not account for any surface effects. In addition, larger crystals facilitate the application of greater pressures that produce greater electric tension, and thus make the measurements more reliable. Larger crystals become requisite when one cuts a crystal specimen to a few (necessarily smaller) prisms in order to compare the pressure in various directions.

[52] Voigt thanked the Göttingen Society in 1898 ("Lässt sich die Pyroelektricität auf piëzoelektricität," p. 1034). In breaking the tourmaline specimen two years before, Voigt explained that "except the preciousness of the materials," [i.e. the tourmaline] the experiment does not entail difficulties (Voigt, "specifischen electrischen Momentes," p.370); Pockels, "Einfluss des elektrostatischen" p. 161.

[53] Voigt, "Rede," p. 39.

crystals nor to Göttingen (though much originated from that university). The field also received attention in handbooks and more tellingly gained official recognition with a prize that Jacques and Pierre Curie received in 1895 for its discovery.[54]

These facts indicate that piezoelectricity attracted more attention from physicists than Voigt suggested and that experimentalists refrained from working in the field at the second phase due to other factors. One can point out at least two important factors that preclude work on the field: the kind of laboratory work it offered and the conclusions one might have drawn from it. Kundt and Röntgen may be taken as examples of physicists who left the subject. Both performed experiments aiming at observing expected piezoelectric phenomena and discovering new ones in the pretheoretical phase. Testing theories and accurate measurements were neither central interests nor a special expertise of experimental physicists like them. In their laboratory work they were attracted to unexplained phenomena about which experiments could reveal new properties, more than to phenomena that were already accounted for by a detailed mathematical theory.[55] Experiments like those of Riecke, Voigt, and Pockels were unlikely to attract experimental physicists like Kundt.[56] Not surprisingly, these experiments were done by physicists who were identified with measuring rather than with experimental physics; experimental physicists did not participate in the experiments of the theoretical phase.[57]

Thus, measuring physicists would have been better candidates for the experimental study of piezoelectricity in the theoretical phase. Yet, no measuring physicist outside of Göttingen was engaged with piezoelectricity in the 1890s.[58] Göttingen's physics community had a direct interest in the validity of the general theory, which was conceived in it. For others, piezoelectric experiments did not promise much. Voigt's general theory was not controversial. It was a theory of what Thomas Kuhn called "normal science" based on substantial grounds in the general physics of crystals and in previous experiments. The known phenomena, moreover, yielded to this theory. Therefore, its test was expected to confirm the theory, and thus to add very little to the knowledge of the world. This was even more so after Riecke and Voigt confirmed it for

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[54] The Curies received the second biannual "prix Planté" from the French Academy. Hurwic, *Pierre Curie*,p. 44.

[55] Yet at a later period (in the 1910s) Röntgen carried out also exact measurements of pyroelectric and piezoelectric constants, Röntgen, "Pyro- und Piezoelektricität," and below.

[56] Of course many contingent causes were involved in determining the empirical research of each physicist. For example, from 1895 Röntgen was fully occupied with the study of X-rays, and needed no other reason to leave piezoelectricity for the time being. He returned to it in the second decade of the 20th century. Another example is Jacques Curie's leaving Paris in 1883 for Montpellier, which probably contributed to draw a practical end to his and his brother's contribution to the piezoelectric research. Still, I maintain that such contingent factors did not determine the fate of the research programmes examined in this study.

[57] Hankel and Lindenberg should be identified with the experimentalists, but as explained, though performed after the introduction of the general theory, their experiments belong to the pre-theoretical phase.

[58] Jacques Curie might be regarded as an exception, since he continued carrying out measurement of quartz's coefficients probably also then. However his results were published only in 1910 and more importantly it is difficult to characterize him - a lecturer for mineralogy in Montpellier, as a measuring physicist in the common (German) sense of the term.

two cases. Had one failed to confirm the theory, its empirical test would have attracted much attention and excitement. Since that was not the case, its confirmation was not a very exciting procedure for one who had no direct interest in the theory; yet it still demanded high skill and much work. Obviously, Voigt himself and his colleagues had such an interest. Ironically, the high precision of the piezoelectric measurements made further research even less attractive, since it suggested that considerable improvement on their values would not be possible. The practical obstacles, the marginality of piezoelectricity in physical research and the lack of known technological implications of the field, with the low probability of observing an unaccounted phenomenon, also made piezoelectricity unattractive for measuring physicists.

Göttingen did not become a center for the study of piezoelectricity only by default. The conditions in Germany in general, and at that university in particular were better suited than those in other places for such work. At the institutional level a professor in a German university could employ many resources, both financial and human, in pursuit of his research program. The dependence of students, assistants, and *privatdocenten* on the director of the institute enabled him to draw more forces to his work.[59] In the pretheoretical phase Kundt used his institute in Strasbourg to promote the experimental study of crystals' electric properties using his powdering method. No less than eight researchers in his institute worked on related questions in the second half of the 1880s.[60] Neither Riecke nor Voigt directed a similar collective effort in Göttingen. Yet, Pockels's work originated from his dissertation under Voigt on a subject that was close to his supervisor's interests, and it continued to be connected to the latter's theoretical and experimental work during the first half of the 1890s, when he was an assistant and *privatdocent* at the university. Still, the study of piezoelectricity in Göttingen benefited more from the conjunction of the interests in the subject of the two university professors than from the structure of German physical institutes. Their common interest in the subject surely encouraged its research.

Riecke and Voigt's common interest in the subject was not totally accidental but reflected a preoccupation with exact measurements that characterizes German physics. The combination of a mathematical theory with exact measurements was stronger in Germany than in other countries. Due to this combination German physicists were good candidates for the execution of experiments that required both mathematical and observational expertise. Moreover, Göttingen, or more exactly its physicists, was especially suited for such study. Voigt and Riecke succeeded the two traditions that excelled in precise measurements, those of Franz Neumann in Königsberg and of Gauss, Weber and Kohlrausch in Göttingen. These traditions ascribed merit to precision in experiments based on reliable instruments and even more on mathematical accounts of all possible experimental errors.[61] This ideal of exactitude can be found in

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[59] On the junior German scientists as "the disciplined research army of the German professor" see Forman, Heilbron and Weart "Physics *Circa* 1900;" the term is quoted from p. 53.

[60] Most of the experiments at Kundt's institute dealt with pyroelectricity. For the experiments that used its dusting method see Chapter 1 note 112. Czermak's experiments were also connected to this research.

[61] On the combination of mathematical theory and exact measurements in these traditions and in Germany see Olesko, "Precision, Tolerance, and Consensus" and Garber, *The Language of Physics*. On Neumann and his seminar see Olesko, *Physics as a Calling*.

the piezoelectric experiments carried out in Göttingen.[62] However, since the research program in Göttingen was directed by only two individuals, it is difficult to attribute an understanding of their actions to traditions and general characteristics of German physics alone. One should consider their specific areas of interest and scientific attitudes, especially their previous work on crystals that attracted them to the study of piezoelectricity in the first place, as I did in examining their motivations for individual researches. According to this perspective, Voigt's personal fascination with the physics of crystals seems the crucial factor that made Göttingen rather than another (probably German) institute the center of piezoelectric research from 1890 onward.

RÖNTGEN'S AND J. CURIE'S LATER DETERMINATION OF QUARTZ'S PIEZOELECTRIC CONSTANT

After Pockels's determination, physicists continued measuring quartz's piezoelectric constant. The exact value of the constant attracted special interest due to the use of "piezo-quartz" in sensitive electric measurements of charge and current. Already in their first publication of the quartz principal piezoelectric constant (δ_{11}) in 1881, Jacques and Pierre Curie had suggested its use as an instrument for electric measurements. During the 1880s, with the help of instrument makers they improved their invention, making it applicable also for the measurement of current in addition to charge. Jacques employed the device, known as "piezo-quartz," to measure specific induction and conductivity in dielectric crystals in his 1888 dissertation.[63] In 1898 Marie Curie employed the "piezo-quartz" in the first quantitative study of radioactivity, and it then became a central tool in the laboratory of Marie and Pierre Curie.[64] The "piezo-quartz" made possible the employment of the method of "null deviation" in these studies. In this device a known voltage due to a charge generated by piezoelectricity from the quartz balanced an unknown electrical tension induced by the electric process under study, be it conductivity of crystal or radioactive rays. The use of the transverse piezoelectric effect in long and narrow plates made the apparatus sensitive to a very small charge. Clearly, Pierre Curie maintained his preference for the null method, which enables "measuring an *absolute value* of the quantity of electricity." Marie Curie joined in her husband's preference for that method, which involved little mathematics but required experience and skill. As they remarked about maintaining the needle at the zero point continuously as the charge

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[62] The combination of physicists skilled in complicated mathematics with interests in phenomena that appear in the laboratory (which was not unique to Göttingen) might be a partial explanation for the centrality of that university also in the theoretical contribution to piezoelectricity.

[63] J. Curie "Quartz piézo-electrique," in *OPC*, pp. 554–563.

[64] Pierre and Marie Curie, "Les nouvelles substances radioactives et les rayons qu'elles émettent," *OPC*, pp. 374–409, on pp, 375–76. Marie Curie, *Traité de radioactivité*, Vol 1, Paris: Gauthier-Villars, 1910, pp. 96–106. M. Curie, "Rayons émis par les composés de l'uranium et du thorium,"*Comptes rendus* 126 (1898): 1101–1103.

increases, "with a little practice one acquires the precise dexterity necessary for this operation."[65] Such an attitude is clearly artisanal rather than mathematical.

The values of Marie Curie's radioactive measurements after 1898 suggest that Jacques Curie had already redetermined the value of quartz's piezoelectric constant before that year (but after 1893). Still, the use of quartz for electric measurement and probably also the new study of radioactivity was behind his new determination of the constant. The results of his measurements and their description appeared only in Marie Curie's book on radioactivity in 1910. The text indicates that Jacques Curie continued measuring quartz in the first decade of the twentieth century.[66] He measured the piezoelectric constant of the transverse effect, the same one used in the "piezo-quartz balance." That his determination was closely associated with Marie Curie's research on radioactivity is shown by the similarity between their experimental arrangements, as a comparison of the schematic figures of the two readily reveals (see Figures 5.4 and 5.5).

In his later measurements, Jacques Curie modified the experimental arrangement employed by him and his brother in 1881, based in the same basic idea of electric balance (Chapter 1, p. 21). Apparently, he regarded this method as more suitable than the "mathematical." He connected the battery and the crystal to the same side of the electrometer, and grounded its other side, keeping its needle at zero, rather than connecting the two to opposite sides of the electrometer as was done in the brothers' early determinations. One face of the quartz (Q in Figure 5.4) was grounded, the other (P) connected to the electrometer, a known cylindrical plate condenser (with a guard ring) (A) and via a commutator to the earth. The condenser's other plate (B) was connected to a battery of 10 known "Weston cells" (cadmium cells), invented in 1892 and more reliable than both the "Daniell cell" previously used by the Curies and the Clark cell used by later experimentalists. While AP was grounded, a weight was loaded on the crystal and induced a charge q on P due to piezoelectricity; due to the voltage of the cells, a charge q' was induced on A. These are totally independent of each other. Then a commutator simultaneously disconnected AP from the earth and connected the other plate of the condenser (B) to the ground instead of the battery, while the weight was unloaded from the piezo-quartz. The electrometer's needle would stay at the zero point only if the total charge on the conductor AP was zero, i.e., when $q = q'$. The charge q' is calculable from the voltage of the battery and the capacity of the condenser, known from the condenser's geometry. By varying the weight, Jaques Curie found the

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[65] M. and P. Curie, "Les nouvels substances," p.375, and footnote on p. 376. They further claimed, with some exaggeration, that "the measurement is independent of the sensitivity of the electrometer." Yet the more sensitive the electrometer the smaller the change needed to move the needle from the zero point. Röntgen later discussed the sensitivity of the electrometer in such a measurement, which is high but still limited, as in any other measurement.

[66] On J. Curie's experiment see M. Curie, *Traité de radioactivité*, Vol 1, pp. 104–105. J. Curie probably did not publish the results himself. Marie Curie referred to "the newest" measurements of J. Curie. In earlier publications M. and P. Curie did not mention the new values. Yet, in 1910 Marie Curie repeats the values for radioactive measurement from 1900, which are almost identical to those of 1898 (there is no systematic difference between the two sets). M. Curie, "Rayons émis par les composés de l'uranium," p. 1102; M. & P. Curie "nouvelles substances radioactives," p. 377. In 1890 Jacques and Pierre Curie quoted the older value for the constant. Lord Kelvin published their short pamphlet after meeting Pierre Curie in 1893 without further comment, Kelvin, "Piezo-electric Property of Quartz," p. 321.

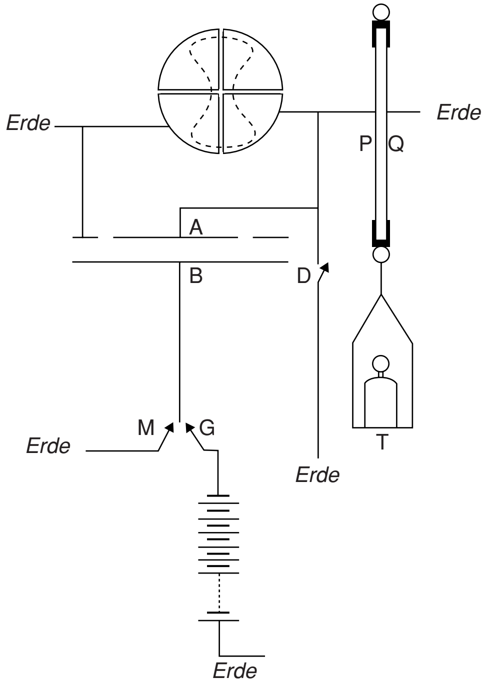

Figure 5.4: J. Curie's experiment for measuring quartz's piezoelectric constant (from the German translation of M. Curie, *Traite de radioactivité*).

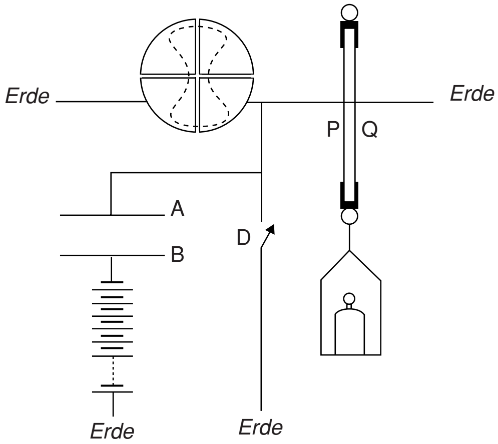

Figure 5.5: M. Curie's experiment for measuring low electric currents induced by radioactive pulverized materials spread on the inner side of B (from the German translation of M. Curie, *Traite de radioactivité*).

weight needed to leave the needle at zero, i.e., the weight needed to induce a known charge by the piezoelectric effect.[67] From measurements on several specimens, until 1910 he determined a value of 6.90 × 10^{-8} (statcoul/dyne), equal to the current value. Later experts attributed the higher value of Jacques Curie's result to more attention to the apparatus (improved insulation) and the target specimens (purity of the specimens and their orientation) rather than to improvements in the method of measurement.[68]

Wilhelm Röntgen also considered it helpful to have "a trustworthy (*sicher*) value" for the quartz piezoelectric constant due to his interest in measurement of another phenomenon. Like Jacques Curie in the 1880s, he was interested in the conductivity of dielectric crystals. In particular he studied the influence of X-rays on their conductivity. Also like Jacques Curie, Röntgen preferred the null method in this study. He showed in detail that the deviation of the electrometer needle, which other methods employed, suffers from uncontrollable fluctuations.[69] Therefore, he employed the Curies's "piezo-quartz" and their apparatus. Unfamiliar with Jacques Curie's latest measurement,[70] Röntgen turned to a new determination of quartz's principal piezoelectric constant (δ_{11}).

Röntgen exhibited much care in preparing the samples of the experiment in order to avoid experimental errors. He employed an optical method to measure their dimensions. He made sure that their orientations are like those assumed, and that they are well isolated.[71] For the determination itself he first employed a "less reliable" method, in which the deviations of the electrometer due to a load applied in a transverse direction (y axis) on the quartz specimens were compared to those due to a "standard cadmium element" (Weston cell). The crystal was connected to the experimental system designed for the measurements of conductivity, whose capacity Röntgen had already measured. With the latter value and the normalized reading of the electrometer he found very close values for the piezoelectric coefficients of the three crystal plates examined 6.85 and twice 6.86 × 10^{-8} [statcoul/dyne]. It is "very conspicuous," Röntgen noted, that these results disagree with the earlier values for the constant (of 6.27 to 6.45 × 10^{-8}).[72] He "discover[ed] neither in the method, nor in the performance of the measurements an error, that could cause the considerable

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[67] *Ibid.*, Marie Curie does not comment on the reasons for the modification of the experimental design. One advantage of the new design is in eliminating any oscillation of the needle. In the earlier arrangement oscillations were inevitable since the electrometer could not have been connected simultaneously to the cell on one side and the crystal and the condenser on the other.

[68] Cady, *Piezoelectricity*, pp. 216–219.

[69] W.C. Röntgen "Über die Elektrizitätsleitung in einigen Kristallen und über den Einfluß der Bestrahlung darauf," *Ann. Phy.* 41 (1913): 449–498, quotation on p. 473. Since the measurement of feeble current is a continuous process, one cannot compare the reading of the electrometer during the measurement to the deviation due to a standard cell (as was done in experiments on piezoelectricity).

[70] As mentioned, J. Curie's results were buried in Marie Curie's book on radioactivity. Röntgen was privately informed only later by Voigt about Curie's measurements, about which Voigt himself had been notified by Marie Curie. W. C. Röntgen, "Pyro- and piezoelektrische Untersuchungen," *Ann. Phy.* 45 (1914): 737–800, footnote on p. 799.

[71] Röntgen, "Elektrizitätsleitung in einigen Kristallen," pp. 474–479.

[72] *Ibid.*, pp. 480–82. Röntgen mentioned the results quoted above except for that of J. Curie, of which he was ignorant, and a measurement by F. Hayashi from 1912 that lead to the value of $6.31.\times 10^{-8}$.

difference between the earlier values and mine." Nevertheless, he could not dismiss an "unfounded" (*nicht begründt*) doubt that an error had fallen in the value given to the scalar deviation of the electrometer.[73]

To remove any doubt and to obtain "more accurate values," Röntgen carried out an additional set of measurements with the very same "null method" of the Curies. Interestingly, his arrangement is almost identical to Jacques Curie's later experiment (Figure 5.4). As in Curie's experiment, the side of a quartz plate covered with silver foil (P) and a condenser's plate (A) were connected to an electrometer (whose other side was grounded) and to the ground. Then they were disconnected while the other side of the condenser was disconnected from the cadmium cells. The only difference in the experiment was that Röntgen loaded the weights on the plate after it had been disconnected from the ground, rather than stressing the quartz while P is grounded as in Curie's experiment. In Röntgen's arrangement, the electrometer would stay at the zero point only if the charge in the system exactly balanced the tension induced by the piezoelectric effect, in other words, when the charge due to the cells equals the charge induced by piezoelectricity. The value of the charge is directly given from the known tension of the reliable cell and the capacity of the condenser, calculable from its geometry. Röntgen noted that the null method enabled high precision. A change of 0.2 g generated a visible deviation of the electrometer, while he employed weights of about 300 g. This leaves an observational error of less than 0.1%.[74]

This high precision allowed Röntgen to seriously examine a deviation of 0.3% between values derived from different measurements on the same specimen with varied distances between the condenser plates. Thereby, he discovered a systematic error in the values taken for the distance between the condenser plates (needed for calculation of capacity), which he initially determined directly by an optical instrument (Abbe's thickness gauge). He corrected the systematic error by mathematical determination of the constant required to be added to the value of length in order to reach agreement among the values derived from different measurements on the same specimens. The elimination of the systematic error increased the average value of the constant by about 0.5%, and brought it closer to those of his earlier experiment. While the detection and elimination of error were done in this case by mathematical analysis, Röntgen pointed out another possible source of error that could be neither detected nor eliminated after performing the experiment. He suggested that a gap might exist between the silver foil and the crystal. Such a gap would reduce the value of the constant detected. In order to eliminate this source of error, he carried out a new series of measurements in which he silvered (*versilbern)* the three specimens previously examined, once again employing the null-method. Indeed, this procedure led him to a value of 6.94×10^{-8} [statcoul/dyne], higher by about 1% than the previous one and very close to that obtained by Jacques Curie.[75] As mentioned, Röntgen did not know of Curie's result so he found his results significantly higher than earlier ones (Table 5.1). Discussing possible sources for this disagreement, he concluded that it

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[73] *Ibid.*, p. 483.

[74] *Ibid.*, 484–486.

[75] *Ibid.*, 487–490.

Table 5.1: Comparison of the six experimental determinations of piezoelectric coefficients

	Curies'	Czermak's	Riecke and Voigt's	Pockels'	Röntgen's	J. Curie's
Crystals and coefficients measured	Quartz (δ_{11}), tourmaline (δ_{33})	Quartz (δ_{11})	Quartz (δ_{11}, δ_{14}), tourmaline ($\delta_{15}, \delta_{22}, \delta_{31}, \delta_{33}$)	Quartz (δ_{11}, δ_{14}), Rochelle salt ($\delta_{14}, \delta_{25}, \delta_{36}$), sodium-chlorate ($\delta_{14}$)	Quartz (δ_{11})	Quartz (δ_{11})
Value of quartz's δ_{11} (in statcoul/dyne × 10^{-8})	6.32	6.27	1st 5.31 2nd 6.45	6.27	1st 6.86 2nd 6.94	6.9
Number of different settings by which it was determined	2	2	5	3	2	1
Measurement of system's capacity	No	Yes	Yes	Yes	1st yes 2nd no	No
Determination of a capacitor's capacity	Theoretical	Theoretical	1st theoretical 2nd experimental	Theoretical	Theoretical	Theoretical
Voltage reading	Null experiment—needle at zero	Compared with a Daniell cell	Compared with a Clark cell	Compared with a Clark cell	1st compared with a Weston cell 2nd null experiment	Null experiment
Elaborate statistical analysis of the results	No	No	For quartz	No	Yes	No

originated in experimental flaws in the previous experiments. He suggested that they might arise from mistaken orientation, lack of homogeneity in pressing the crystal, existing deformations in them, an underestimation of the capacity or [electric] tension (*Spannungen*), failure of isolation or from fluctuations in the value of the Clark cells. "All these flaws, [he concluded,] . . . would have reduced the value of k [the piezoelectric constant] found."[76]

Thus, Röntgen explained his higher values by his attention to various sources of error in preparing the apparatus and the target. His meticulousness marked his approach in almost every aspect: the isolation of the condenser, the correct orientation of the quartz plates, the measurement of their dimensions etc. Apparently, Jacques Curie employed similar thoroughness in his measurements.[77] Röntgen's determination was carried out over a long period. The early measurements were performed during the winter of 1911–12, those with the null-method in the summer of that year, and the last one with the silvered specimen probably only toward the end of that year. Röntgen could have carried out the measurement with silvered plates from the beginning and saved himself additional work. Apparently, the possibility of this gap occurred to him only later. As with Riecke and Voigt's determination of the constant, the long history of Röntgen's determination (until it "ended") is rooted in the disagreement between his and earlier results. Had they agreed, he would have probably been satisfied with his first "less reliable" determination using a comparison to a standard cell. Had he suspected in advance that he would find a considerable deviation, he would have probably employed the more reliable null method. The experiment also had its own dynamics. When analyzing the results, examining them and continuously reflecting on the experiment, Röntgen considered additional sources of error.

In retrospect, Röntgen's first set of measurements based on the reading of an electrometer reading were accurate enough. They deviate from those obtained by the null method by no more than 0.3%, practically below the experimental error. Their difference from the final value is rooted in the later elimination of an error in the target (due to a gap between the crystal and the foil), which is independent of the method of measurement. Nevertheless, Röntgen saw a need to repeat the determination of the constant with the null method, which he considered more reliable. He trusted more the null method, which bypasses corrections of the electrometer reading and complicated calculations of the capacity of the system. That he did not apply the null method at first suggests that its application was more complicated and time-consuming. It required more care in conducting the experiment itself. Marie and Pierre Curie mentioned the dexterity needed in such experiments. In Röntgen's arrangement, similar to Jacques Curie's, skill was needed to quickly disconnect and connect the different components of the apparatus between the two stages of the experiment. Like the Curies, Röntgen preferred the null method over others in additional studies. Yet,

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[76] *Ibid.*, 492–493, quotation on p. 493. Among other possibilities Röntgen raised the assumption that Voigt's theory did not account well for the phenomena. So the value of the coefficient for the transverse effect was not equal to that of the longitudinal effect. However that seemed to him implausible.

[77] This meticulosity is suggested by the value that J. Curie attained for the constant, his return to the determination and the high number of specimens that he examined. As mentioned he did not publish a description of his experiment.

Röntgen also employed the "mathematical" method, which characterized German theoreticians. Although he did not share their view that it leads to more certainty, he found it valid and useful enough to employ it. Moreover, in analyzing the "artisanal" null-method experiment, Röntgen employed mathematical manipulation to reduce error. Still, to reduce another error he returned to an "artisanal" approach, in which he manually changed the connection to the target. In viewing null method experiments as superior to experiments that need much mathematical error analysis, the German experimental physicist Röntgen placed himself closer to the French experimentalists than to the German theoreticians. His work, however, suggests that a combination of the two approaches was evolving at the beginning of the twentieth century, in addition to separate use of the two in different experiments by the same scientists. Combining the two approaches Röntgen enjoyed advantages of both in eliminating experimental error. Mathematical analysis alone reduced an error occurring in a careful manual measurement of the distance between the condenser plates, while the use of the null method in the same experiment bypassed major sources of error. Of course, mathematical analysis could not eliminate an error originating in a gap between the specimens and silver foil. Manual work is needed in every experiment. So, Riecke and Voigt, for example, like Röntgen, needed to prepare their targets before any mathematical analysis. Mathematics was used also in the "artisanal" approach. Still, among the experiments discussed here, only Röntgen's really combined the two approaches. That he, rather than another scientist, carried out the combination is not completely accidental. Due to their working connection with their theoretical colleagues, German experimentalists were the best candidates to combine the two traditions.[78]

CONCLUSIONS: EXPERIMENTS AND THEIR ROLES IN A THEORETICAL PHASE

The formulation of a general quantitative theory of piezo- and pyroelectricity did not limit the function of the experiment to its test. Clearly, testing mathematical theories was one function of the laboratory in the "theoretical phase," though apparently not so central as one might have expected. Physicists were satisfied with few experimental confirmations limited to a few cases. Collecting information about nature by finding the precise mathematical relations and coefficients that characterized physical processes was another function. The quantitative measurements of constants differed from experiments like those of Hankel and Lindenberg's in their dependence on mathematical laws, which give the constants meaning. Finally, experiments indicated the existence of natural phenomena, through precise measurements. The precise determination of a constant to the highest degree possible was not only an end in itself but also a means to reveal relations between phenomena and to discern whether genuine

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[78] This one example can at best indicate on a general process that still need to be studied.

physical interactions existed.[79] Pockels and Voigt were concerned with the particular (e.g., a constant of a specific material) mostly as a way to reach the general (e.g., the existence of a direct electro-optic effect). Precise measurements, as Voigt claimed, raised and answered questions inaccessible through qualitative experiments.[80] Exactitude was conceived as an indispensable means to a superior end.

Considerable effort to attain high precision and eliminate even small experimental errors was evident in all the determinations of piezoelectric constants, including the earlier ones of the Curies and Czermak. Apparently, the seven scientists engaged in these measurements trusted the precision of their determinations. They all shared an "ethos of exactitude." Still, they presented different methods of reaching exactitude. While the Curies bypassed potentially complicated determinations and eliminated any significant source of error, the German "measuring physicists" preferred to measure all quantities and base the elimination of error on theoretical-mathematical analysis.[81]

In the tradition of Regnault, the Curies reduced potential errors in their measurements by manipulating the apparatus. German "measuring physicists" regarded the mathematical method of reducing errors as superior to other methods. They did not adopt the Curies' earlier method of null experiment,[82] nor did the Curies adopt theirs. Today, the mathematical analysis of error has become a virtually inseparable part of experimentation. Yet, the choice between experimental designs that bypass some measurements and those that do not still exists. Years later, Jacques Curie's null experiment was regarded as most reliable, more than those of Riecke, Voigt, and Pockels.[83]

The two attitudes toward precise measurements characterized two different traditions—that of French experimentalists and German theoreticians. However, nationality was not the decisive factor in the difference between the two attitudes. Affiliation with a particular school or tradition was more important. Indeed, these schools were each related to a specific national, regional, institutional, educational, and linguistic setting. Weber and Neumann found their followers in Germany, Regnault in France. Although, the tradition of "measuring physics," with its emphasis on mathematical reduction of errors, was probably unique to Germany, it had its roots in the French mathematical sciences of the early nineteenth century, on which Gauss, Weber, and Neumann based their work. On the other hand, Regnault suggested an

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[79] Thus I do not accept the dichotomy implied in Olesko's claim that Neumann's school's "investigative strategy... emphasized primarily, although not exclusively, the eradication of error rather than the discovery of new truths or the construction of comprehensive theories." At least in Voigt's and Pockels's research, error reduction was a mean to discoveries, and did not exclude formulation of theories.

[80] Voigt, "Die Kampf der Dezimale," p. 73.

[81] Yet all the measurements were based on mathematical laws, which gave the constants meaning.

[82] In addition to the experiments mentioned above Franz Nachtikal, a student of Voigt, applied the method of his teacher and Riecke in measuring the piezoelectric moduli and their change with pressure "Ueber die Proportionalität zwischen den piëzoelektrischen Momenten und den sie hervorrufenden Drucken," *Göttingen Nachrichten*, 1899, 109–118.

[83] Cady, *Piezoelectricity*, pp. 217–218.

alternative methodology to that of Biot and his generation.[84] These schools, moreover, did not include all German or French physicists. Germany had its own two separate traditions of "experimental" and "measuring physics." Experimental physicists in Germany did not share the attitude of their compatriot "measuring physicists." In 1912 Röntgen, a prominent representative of the experimental tradition, considered the null experiment as more reliable than the mathematical reduction of error. Röntgen showed an inclination toward the artisanal rather than the mathematical approach to precise measurements. Still, his work combined the two previously separated approaches.

The tests of Voigt's general theory are examples of experiments that did not require "systematic theories" in their analysis. Of course, the experimentalists used theoretical claims, i.e., assumptions about the relations between different magnitudes, such as the relation between electric tension and charge, between gravity and elasticity etc. They also trusted the reliability of experimental instruments like Thomson's electrometer or Clark's cell. Yet the claims they used were based on and justified by many experiments in a variety of conditions and were not dependent on the validity of a particular theory. Thereby, they belong to what is sometimes termed "a low-order theory," i.e., they are shared by a few systematic and encompassing "high-level" theories. For example, the relations between capacity, charge, and voltage are the same in Maxwell's field theory and in its competing corpuscular and potential theories.

More importantly, the analysis of these experiments did not require the piezoelectric theory under examination. One sole exception is Czermak's experiment, which was consequently regarded as unreliable. These experiments not only confirmed intrinsic relations between the variables in the phenomena under question, like the linearity of the effect (these might be called phenomenological regularities), but also general principle. The confirmations of Voigt's theory focused on the relations of effects in different directions. A refutation of its predictions would have entailed a contradiction with the law of symmetry, with major implications to the growing awareness of its role in contemporary physics. Thus, the test of Voigt's relations had consequences that extended well beyond the limited field of piezoelectricity.[85] Although even Quine clarified that some theoretical claims can be tested independently, and Hacking furthermore claimed that "seldom is the modeling of a piece of apparatus or an instrument the same as the theory in question or the systematic theory," pointing out the independence of experiment from the theory being tested still seems noteworthy.[86]

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[84] Chang, "search for 'real' scale," p. 274.

[85] Indeed whether piezoelectric coefficients are linear or not or even whether they are constant did not have much relevancy to other branches. This can explain the indifference to Pockels's finding of non linear behaviour in Rochelle Salt.

[86] Willard Quine, *Theories and Things*, Cambridge MA: Belknap Press, 1981, p. 71; Ian Hacking, "The Self-Vindication of the Laboratory Sciences," in *Science as Practice and Culture*, edited by Andrew Pickering, Chicago: Chicago University Press, 1992, pp. 29–64, on p. 45. I borrowed a few terms (like systematic and low-level theories) from the writing of and on the socalled "New Experimentalism." See for example papers in Heidelberger and Steinle (eds.) Experimental Essays - Versuche zum Experiment.

Riecke and Voigt's research illustrates the complexity of the experiment and its analysis. It also exhibits its flexibility and the ability of the experimentalists to modify and adjust it. In this case, the modification of the experiment did not involve reconsideration of its theory but a fresh inspection of its equipment revealed an accidental technical problem. The experiment was modified by the addition of a complicated measurement of capacity. Consequently, the results were changed, but not the other components of the experiment. This episode supports the claim reemphasized by "New Experimentalism" that theory does not give complete directions for practical experimental decisions.[87] Theory could not tell Riecke and Voigt which part of the experiment needed modification and how to modify it. The solution of the problem was based more on experimental methods than on theoretical ones. For measuring the capacity, they adopted the "tuning fork method" from Maxwell's treatise. Although regarded as the epitome of his electromagnetic field theory, Maxwell's book was far from being a systematic presentation of the theory and was not limited to its presentation. It was also a detailed presentation of the experimental method. Despite the method's reliance on more advanced theory than was needed for the theoretical calculation of capacity, it did not require field theory and its specific concepts. Maxwell's analysis of the charging and discharging of condensers was also accepted by physicists who rejected his system. Riecke and Voigt themselves were not Maxwellians. I presume that even Duhem was forced to accept this analysis of Maxwell, despite his manifested objection to the latter's theory.

Peter Galison has called historians' attention to the freedom experimentalists have in deciding when to end an experiment.[88] One can always suggest further measurements of components of the apparatus, the measuring instruments themselves, or the target in order to check possible systematic and accidental errors. Galison examined episodes from the history of particle physics in the twentieth century; this story shows that "ending an experiment" was also sometimes a long and complicated process in the study of bulk matter at the end of the previous century. Experiments were not over once the measurements had been made. Neither data analysis nor publication of results terminated the research. The Curies were quick to pronounce their determination of the piezoelectric constants. Yet they continued to measure them, returning to the same experiment for many years: Jacques pronounced modified results for basically the same measurement almost 30 years after the initial publication. Voigt's experiments on the existence of direct pyroelectricity, with Riecke and alone, showed that a conclusion from an experiment (not only a determination of a magnitude) can be changed a few years after its performance. In 1898, theoretical concerns combined with dissatisfaction with the precision and method of the former experiment (which did not measure all variables on the same specimen), led Voigt to complete the experimental investigation that had apparently been concluded in 1891.[89] Like the

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[87] For a statement of this claim see David C. Gooding, "Experiment," in *A Companion to the Philosophy of Science*, edited by W.H. Newton-Smith, Oxford: Blackwell, 2000, pp. 117–126.

[88] Peter Galison, *How Experiments End*, Chicago: University of Chicago Press, 1987.

[89] Voigt's 1898 experiment might be seen as independent of the previous one, but since it was done on the same specimen and since Voigt used the same piezoelectric measurements and re-analysed the old experiment with new data obtained in 1898, I maintain that both experiments can also be regarded as

Curies, Riecke and Voigt announced their determination of piezoelectric moduli soon after they obtained numerical results, but the publication did not end the experiment. They returned to the laboratory soon after to correct their findings. This example shows that, in the absence of theoretical expectations, earlier experimental results can influence a new experiment; they can even determine when it would end. Röntgen's choice to carry out a second determination of quartz's piezoelectric coefficient reveals the same influence of earlier results. Perhaps this influence characterizes more direct measurements than other experiments (e.g., those that test theories).

Ending an experiment following a previous experiment's results contains a paradoxical element: the new experiment was designed, among other aims, to examine exactly the correctness of the previous results, and to find more accurate and valid results. Nevertheless, the circularity is only apparent. Although the ending of the new experiment was done in view of the previous one, the justification for the correction of the results and the procedures of their reexamination were independent of the preceding results. This is most apparent in Röntgen's case as his end results still diverge from earlier values. True, in the case of Riecke and Voigt's experiment the new experimental results were influenced by the previous ones, but were not determined by them. Results that disagreed with previous ones were published by Riecke and Voigt as long as no error was found in the experiment and its analysis. Plausibly, without the Curies' previous results, the faulty results would have remained standing.[90] However, the methods and procedures used by Riecke and Voigt in measuring the correct capacity, and their confidence in them, provide excellent reasons to believe that had their results led to disagreement with the Curies', they would not have hesitated to publish them.

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one. This semantic choice can help to recognize that the analysis of the experiment and its conclusions can be changed even years after they have found their way to a scientific journal.

[90] Since Riecke and Voigt needed to measure the capacity of the specific condenser used in the experiment, they probably would not have found this fault a few years later, when further measurements were made.

CONCLUDING REMARKS

PRETHEORETICAL AND THEORETICAL PHASES OF STUDY

Piezoelectricity grew as a new field of research in the last quarter of the nineteenth century. During a short period the subject received a theory that systematized the knowledge about the phenomena and transformed the field from a pretheoretical to a theoretical phase. The early phase seems typical of young fields. It was characterized by a combination, even a mixture, of experiment and theoretical notions, thoughts, and suggestions some of them informed by theories from other fields. Experiments examined either unpublished assumptions or speculations of the experimentalists themselves, or theoretically suggested a short time earlier. The Curies' discovery of the direct effect is an example of the first kind, their discovery of the converse effect of the second. Röntgen's examination of the direction of the phenomena in quartz is an even better example of a study in which separation between theoretical assumptions and experimental design and practice is almost impossible. These can be more easily distinguished in his and J. Curie and Friedel's experiments on the relations between the electric effects of variations of temperature and pressure. Similar analytical separation can be made for Kundt's optical experiment and for many of Hankel's experiments. However, in all these examples the experimentalists tested assumptions that had not been articulated before they designed their experiments (at least not in public). The articulation of the assumption was connected to its experimental study. For example, the articulation of the idea that heating a crystal from the center would have the same electric effect as cooling it from the circumference took place only when it was thought to be demonstrable in the laboratory. Though Czermak examined his theory himself, and published the theory and its experimental confirmation together, his case suggests a wider distance between experiment and assumption. He designed the experiment to examine the consequences of a mathematical theory rather than one claim or assumption. His work, the work of a trained theoretician, was a step in the mathematization of the field, and in the shift from a pretheoretical to a theoretical phase.

In the pretheoretical phase, experiments were used directly to supply new information about the properties of the phenomenon, to deduce laws, and to decide between competing claims. Their interpretation was not free of theory; however, the results of these experiments had a direct bearing on specific questions. Their consequences to claims about nature did not need the mediation of an elaborated mathematical form. Properties like the directions of the effects in particular crystals were shown immediately in the experiments. Even when interpreted through a nontrivial optic theory in Kundt's and Röntgen's early experiments, their meaning was clear once observations had been made. The laws of the development of charge by pressure were deduced by the Curies from their experiments, without any intermediary piezoelectric theory. The competing theoretical claims about the relation between piezo- and pyroelectricity were put to an empirical test by the adherents of both claims and the experimental results in this controversy were connected directly to theoretical claims. In Hankel's experiment, the results seemed to be the claim itself: the effects of cooling and pressing are not the same. His opponents had to construct more delicate experiments to show what they considered to be the true effects of heating and cooling and that Hankel's results were an outcome of another process, which he failed to perceive. Yet, the results of these experiments were also directly manifested in the laboratory as in Röntgen's experiment of heating from the center and the circumference and to a lesser degree by Curie and Friedel's demonstration of the nonuniform temperature of the specimen.

Experimental design at the pretheoretical phase involved theoretical considerations both of piezoelectricity and other fields (not just electromagnetic, optic, and elastic, but even piezo-optic). Yet these considerations were not based on an elaborate theory of the field that determines what kinds of effects appear and in what circumstances one is supposed to observe them. Moreover, while in some experiments experimentalists examined questions that followed hypotheses grounded on theoretical understanding, in others the questions examined were independent of a systematic theory. The discovery of piezoelectricity and the study of the relations between piezo- and pyroelectricity are good examples of the first kind. Röntgen's torsion experiment is probably the best example of an important discovery that originated in experimental procedure rather than in a theoretical notion. This is true about most experiments on the direction of the phenomena. On the other hand, Voigt's general theory does not leave similar phenomena unaccounted. It predicted whether any kind of strain on any crystal would induce an electric effect or not. Thus, any later attempt at examining the existence of such an effect was also made a test of the general theory.

Most experiments in the pretheoretical phase appealed to numeric indicators, but the results sought were qualitative effects rather than quantitative relations. Numeric values were expressed (if at all) in arbitrary units and were not part of the experimental report. Hankel's very detailed accounts well illustrate this kind of practice. In figures appended to his publications he quoted numeric results (in arbitrary units), but they were seldom mentioned in the text. Qualitative notions like a more or less extensive effect and its sign were sufficient. The existence or nonexistence of an electric effect was all that the Curies needed in order to ascertain which crystals are piezoelectric and along which axes. In addition, Röntgen needed to measure the direction of the pressure. In a more quantified experiment, using a simple calorimeter Curie and Friedel had to measure the quantity of heat released from a crystal. These experiments did not require high precision, neither was more accuracy required than was enough to distinguish between no effect, some effect, and a large effect.

The precise magnitudes were inconsequential for the validity of the experimental results. This well exemplifies the difference between what German physicists called experiments and measurements. Measurements required exact quantitative results and thus higher precision. Such quantitative experiments or measurements were also carried out in the pretheoretical phase. Jacques and Pierre Curie's determination of the law of the development of charge required such precision and even more so theirs and Czermak's measurements of piezoelectric constants. Yet, this kind of experiment was in the minority in the early phase, but they became dominant in the theoretical phase. Qualitative experiments that were prevalent in the pretheoretical phase virtually disappeared in the later phase.

Later experiments were embedded in a mathematical theory of piezoelectricity that was used to interpret the physical meaning of the results, and in a theory of other phenomena that was used to analyze the data. In the theoretical phase experiments neither deduced new laws, nor exhibited directly the existence of an effect, instead they confirmed theories and determined mathematical magnitudes. These precise determinations revealed the existence of genuine, otherwise undetected, phenomena. Compared with the former experiments, the latter experiments were more complicated, both in the experimental apparatus and in the analysis of the results. Though, as claimed in Chapter 5, the results of the experimental testing of the general theory were independent of this, the experimental design followed the elaborate piezoelectric theory. The theory was used to select the shape of the crystal specimens and the kind of stresses exercised on them. Examining the existence of direct pyroelectricity or electro-optics made sense only in the realm of a quantitative theory.

Between the two phases, not only did experimentation itself change, the relationship between theory and experiment also underwent change—a gap was created between the two. The development of the theory became almost independent of the laboratory, rather than an outcome of new findings as in the pretheoretical phase. This was probably a consequence of the more general character of Voigt's theory. Particular assumptions that could be tested separately and then added to the knowledge of the phenomena in the pretheoretical phase (e.g., the direction of the electric moment induced by pressure in a particular direction) were later consequences of the general theory. An experiment on the directions of the effect in untested crystal species could only confirm or contradict the theory. Once the laboratory supplied sufficient information for the construction of a theory (a few observations on a few crystals were sufficient for that), the theory could be developed without a need for additional experimental results. Nonetheless, Voigt's general theory did not encompass all possible questions. For example, it provided no guidance about the magnitude of the effect in different directions and crystals (the value of the piezoelectric coefficients). That could have been a subject of a systematic experimental study aiming at finding empirical regulations. But it was not. Neither experimentalists nor theoreticians studied this nor similar questions unaccounted for by mathematical theory. General issues like the theory's thermodynamical underpinnings, its bearing on electromagnetic theory, and its possible molecular explanation as opposed to the experimental results, shaped the development of piezoelectric theory at that phase. Experimental evidence was almost inconsequential for these questions. It was more relevant to questions that originated in the nonrigorous explanatory models, which were still open to changes. Unlike the phenomenological theory, neither the assumptions on which these were based nor their consequences were grounded in experiment.

Clearly, an accepted comprehensive mathematical theory was a prerequisite for a theoretical phase of study. This, however, was not a sufficient condition. Such a phase also required a basic consensus about the central phenomena: their identification, their major properties, and their description. In addition, it required an agreement that the theory describes at least the most important and interesting phenomena.[1] Otherwise the theory could not direct the study of the field, e.g., experiments would study mainly relations that are beyond the scope of the theory. So, the division between pretheoretical and theoretical phases seems inadequate for revolutionary and controversial fields, which cannot be directed by united theory.

NATIONAL OR INTERNATIONAL SCIENCE?

At a personal level an almost complete reshuffle took place between the two phases. French and German experimentalists predominated both the speculative and the experimental work in the pretheoretical phase (e.g., the Curies, Lippmann, Röntgen). In the theoretical phase, the lead was taken by German theoreticians who combined mathematical analysis with exact experiments (e.g., Voigt, Pockels). At the same time the field became less accessible to physicists outside the field who had not been engaged in similar research earlier. The shift from experimentalists to theoreticians coincided with a change in the respective contributions of scientists working in different countries. While in the pretheoretical phase French scientists produced 17 publications, they published only two in the theoretical phase. The number of German publications, on the other hand, rose from 13 in the early phase to 21 in the later (see Table A.3). However, the map of the research had already changed earlier. An early French lead with the works of the Curies and Lippmann was taken over shortly by Germans with the works of Röntgen and to a lesser extent Hankel and Kundt. While no center of piezoelectricity was formed in the 1880s,[2] Göttingen became such a center in the 1890s. It almost monopolized the experimental work and was prominent in the theoretical realm. Duhem was the only French physicist who contributed to the mathematical elaboration of the theory, which was mostly carried out by Germans.

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[1] Voigt general theory of piezoelectricity satisfied these requirements. Earlier qualitative rules like those suggested by the Curies between pressure and electric charge were not comprehensive enough.

[2] Despite the concentration of work on piezoelectricity in Paris in the early 1880, it was too short-lived and personal (i.e. based on the works of the Curies) to be considered a real centre. Lippmann's and Duhem's works were unrelated to the small centre around Friedel's laboratory.

However, unlike all German contributors, he did not carry out experimental work in the field.

In their study of piezoelectricity French and German physicists revealed different styles and attitudes. As discussed in Chapter 5, the quantitative measurements well display such differences. German experimental work involved more mathematics and analysis. In eliminating systematic and accidental errors it relied on the objective method of data analysis rather than on the skill and ingenuity of the experimentalist. German measuring physicists preferred accounting for and measuring all experimental magnitudes and errors to an attempt to bypass complicated determinations of these magnitudes preferred by the French. The British and Italian contributions also had their own characteristics. These agree with the general notions about physics in these countries. Mathematical physics in Italy was then more mathematical than physical. It was concerned mainly with the mathematical solution of problems derived from physics. Kelvin's work well exemplified the British interest in mechanical models. However, since only one physicist from each country contributed to the field, one cannot generalize about national styles.[3]

Yet, even in the case of France and Germany, the one example of piezoelectricity leads any attempt at defining a national style into difficulties. Jacques and Pierre Curie and Friedel advocated the molecular view. Their compatriot Duhem rejected it.[4] East of the border, Röntgen shared the molecular explanation, though more cautiously; Czermak adopted while Voigt criticized it and suggested a theory that avoided molecular assumptions. Mathematical and thermodynamic theories were suggested on both sides of the border. Duhem's thermodynamic approach, based on a potential function due to Helmholtz, a German, was shared by his German colleagues. It was not that the Germans believed in the merits of molecular assumption and the French did not, or vice versa, but that different physicists in both countries (and in others) held both approaches. Even the experiments did not show a clear division between German and French physics. Hankel's, Kundt's, and Röntgen's experiments of the 1880s were more similar to those of the Curies and Friedel than to those of Czermak, Voigt, and Pockels. The first did not involve elaborate mathematical error analysis or determination of exact numerical results. German qualitative experiments resembled French experiments more than German precise measurements. Thus, the differences in style of experimentation can be better traced to differences between various schools and approaches than to national differences. Kundt and Röntgen were part of the German experimental school, while later experiments were made by physicists of German

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[3] Lodge's attempt to explain pyroelectricity shows a tendency, similar to Kelvin's, to models, but his work was not a direct contribution to piezoelectricity.

[4] Piezoelectricity supplies a counterexample to the claim that French scientists did not adopt speculations in general and molecular hypotheses in particular. These, I showed, played a significant role in the thought of Jacques and Pierre Curie and Friedel. Still, claims like Garber's that "French experimental physicists were skeptical of 'speculation' and hypotheses," may be correct overall (Garber, *The Language of Physics*, p. 313). Friedel was a mineralogist and a chemist rather than a physicist. So he and his assistants were perhaps atypical of French physicists.

theoretical schools. The above-mentioned characteristics of German experiments do not fit all German schools but only theoretical ones and more precisely, those of Weber and Neumann.

However, if the study of piezoelectricity suggests that the styles and approaches to the practice of physics were more a question of a local school of physics than of a nationality, it does indicate other national differences. The shift of the research from France to Germany and its successful pursuit there suggests that the German system was more fertile for such research. Since its discovery, French science had made essential contributions to the study of the phenomenon. The French system enabled two junior researchers to speculate and examine their speculation. However, German physicists were better at elaborating the work done by the Curies, both experimentally and theoretically. The German system probably had better resources (both human and material) to conduct research that included systematic experimentation, elaboration of a mathematical theory, and its quantitative examination. The case of piezoelectricity suggests that the French were better at discovery and initial research free of an elaborate theory, than at the elaboration of a systematic theory. This is one case; the study of X-rays provides another example.[5] Yet, more research is needed to find out whether this was characteristic of French physics of the time.

From the second half of the nineteenth century, French scientists had sensed a decline of science in their country. The issue of the alleged decline in French science in general, and in physics in particular has continued to entangle historians and sociologists. Quantitative evaluation of French physics shows that its productivity was surprisingly similar to that of German and British physics relative to the size of their populations. Quantitative evaluations based on prestige, like national number of Nobel prizes, show a similar pattern. French physics continued to produce important discoveries and famous physicists. Piezoelectricity is but one example. However, as Nye claimed, quantitative evaluation of French science and these examples of its quality are not enough to ascertain whether a decline actually occurred. If all was well, what was the source of decline?[6] The clear drop in the French contribution to piezoelectricity suggests a reason for that feeling. If the example of piezoelectricity is indeed characteristic, it indicates a sense in which French science lagged behind contemporary German and British science, not so much in either quantity or quality but in the kind of research undertaken. Apparently, French science was better at a more traditional kind of research than in the more modern combination of mathematical theory and analysis and experimentation. This conclusion agrees with Garber's view that French science receded from central subjects that had become mathematical during

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[5] Wheaton's data taken from *Fortschritte der Physik* shows a marked decline in the contribution of French scientists to the study of x-rays after 1902, that is a few years after its discovery, Bruce R. Wheaton, *The Tiger and the Shark: Empirical roots of wave-particle dualism*, Cambridge: Cambridge University press, 1983, 241, note 28.

[6] Contemporary feelings surely reflected a pessimistic atmosphere and fears of the advance in British and German science, after the loss of the hegemony that the French had at the beginning of the century (due to the rise of science in these countries). Yet it probably reflected also a genuine inability to compete with other countries in some fields or realms.

the nineteenth century.[7] Whether this should be termed a decline or not becomes a question of definition.

MOLECULAR AND PHENOMENOLOGICAL THEORIES

Jacques and Pierre Curie's discovery of the piezoelectric effect originated in molecular considerations. Their assumption that such an effect should exist evolved from a specific mechanical-molecular view of pyroelectricity grounded on Thomson's hypothesis of permanent internal polarization. The Curies later explicitly expressed their molecular interpretation of the effect as originating in variations in distances between polarized molecules. Yet, soon after, Lippmann predicted the existence of the converse effect based on thermodynamic-analytical considerations rather than on molecular. Although Lippmann's argument could not be supported by molecular notions, it did not contradict the molecular suggestion of the Curies. Molecular notions and the Curies' suggestion in particular continued to direct the study of the phenomena as shown in the contributions of Jacques Curie and Friedel, Röntgen, and Czermak. Though the molecular explanation of the Curies agreed with the observations at the beginning of the 1880s, later observations revealed inconsistencies. The contradiction was implicit and still hidden in the experimental error in Czermak's study, which was tacitly based on the molecular hypothesis. Röntgen's torsion experiment made the contradiction apparent. He himself concluded that the current molecular account could not explain this experiment.

The failure of the molecular explanation to account for Röntgen's results led to the construction of a phenomenological theory by Voigt. Voigt's theory assumed only that the phenomena are a linear effect of strain and that they are subject to the rules of symmetry, without assuming any specific structure of matter. Logically, the theory could have been formulated just after the establishment of the linearity of piezoelectricity in 1881. Moreover, a part of Voigt's objections to the molecular theory was valid from the time of its introduction. Yet the experimental evidence was essential for the formulation of Voigt's theory. Not only did it demonstrate the limitations of the molecular account, it was also necessary for the recognition of the complexity of the phenomena. For example, the experiments on the directions of the effects in the early 1880s revealed the need to connect the electric effect to specific components of elastic strain; only Röntgen's 1889 torsion experiment displayed its dependence on shear strain.

The phenomenological theory replaced the molecular as the dominant exposition of piezoelectricity due to the latter's failure to account for the later experiments and the failure of explanatory attempts to suggest a highly plausible or promising theory

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[7] On the issue of the decline in French science see Mary Jo Nye, "Scientific Decline: Is Quantitative Evaluation Enough?" *ISIS*, 75 (1984): 697–708; Garber, *The language of physics,* pp. 312–316; Harry W. Paul, "The Issue of Decline in Nineteenth–Century French Science."*French Historical Studies*, 7 (1972): 416–450 and Terry Shinn, "The French Science Faculty System, 1808-1914: Institutional Change and Research Potential," *HSPS* 10 (1979): 271–323, esp. pp. 274, 329 (Tables 1–3).

with either solid premises or an ability to explain unaccounted relations. While the hypothetical nature of the molecular theory was apparent, the general phenomenological theory was not itself free of any supposition. Its suppositions, however, were based on experiment (linearity) and on a general principle of crystal physics (subordination to symmetry), which itself was a generalization of numerous observations of various phenomena. Scientists often employed symmetry considerations to avoid hypothetical structures and explanations. Voigt's theory did not assume either unobserved properties or mechanisms. Obviously, it employed theoretical entities and relations from the theories of elasticity and electricity, but those were related to observational magnitudes.[8] Only for pyroelectricity did the theory assume a mechanism, through strain, which was not experimentally grounded. In that sense (and only in that), it was not completely phenomenological. Four years later this was amended by the consideration of the existence of a direct effect. It is ironic that the removal of the speculative assumption from the phenomenological theory was done with reference to a hypothetical molecular theory.

One might suppose that the introduction of a phenomenological theory that exposed the shortcomings of molecular suggestions would dissuade physicists from such hypotheses. This, however, did not happen. On the contrary, the introduction of the new theory stimulated conjectures about the sources and mechanisms of the phenomena. The new speculations were more elaborate than the previous ones. Most of them were formulated by referring to the phenomenological theory rather than to raw observational results. Yet, as explained, these explanatory theories were left as speculations and were marginal to further research; none of them was adopted by the scientific community. While explanatory theories were suggested, a central effort was dedicated to the elaboration of the phenomenological theory. Yet the same physicists contributed to both efforts. Riecke and Voigt, who developed molecular theories, participated in the elaboration of the phenomenological theory. The scientists who proposed both explanatory and phenomenological theories, Duhem, Riecke, and Voigt, presented three different approaches regarding the relation between the two kinds of theories. In the 1890s Duhem rejected explanatory models for thermodynamic descriptive theories. Riecke, on the contrary, preferred corpuscular explanatory theories. For him, phenomenological theory was a stage in the road toward explanatory models, a stage that teaches us about laws of nature and thereby enables suggesting their causes. Voigt presented an intermediate position: satisfied in phenomenological theories but not avoiding explanatory speculations and allowing an accepted explanatory theory in the far future.

In the elaboration of phenomenological theory, Duhem, Riecke, and Voigt took another step away from an explanatory theory with the thermodynamic formulation of the theory between 1892 and 1894. This formulation enabled a combined treatment of the direct and converse effects and proved a useful device to study secondary

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[8] I refer here only to relations used in the theory of piezoelectricity. These were either experimentally based like Coulomb's law, or a kind of definition like the equality of electric moment to superficial charge. Relations such as those between Maxwell's displacement and electric fields were not adopted.

effects. With that formulation piezoelectricity became part of a larger domain embraced by thermodynamics, an approach that excluded explanatory hypotheses. Yet, as explained in Chapter 4, this formulation did not involve fewer assumptions than did Voigt's original phenomenological approach. Only the admission of a possible direct pyroelectric effect reduced the number of assumptions. Thereby, the theory was free from hypotheses that were not justified experimentally.

In the study of piezoelectricity, most physicists did not commit themselves to a particular theory or even to a particular approach. In their scientific work they revealed a pragmatic attitude toward the questions of the true constitution of matter and the right way to carry out scientific research and argument. Moreover, theoretical approaches alone did not determine the piezoelectric research. Experimental tradition and previous experience of the researchers exerted considerable influence. Thus, while molecular speculations led to the discovery of the effect, further studies were no longer dependent on the molecular hypothesis, but followed experimental procedures and examples from pyroelectric research. The Curies chose the crystal species they examined from known pyroelectric crystals (and a "control group" from nonpyroelectric crystals), and they examined them along known pyroelectric axes. Next, they studied the development of electricity by variations of pressure following Gaugain's study of the development of electricity by temperature differences in the same crystal.[9] In a good experimentalist fashion the Curies examined various properties of the new phenomenon: the materials in which it appear, the relation between the electric effect, the variation of pressure and the dimensions of the specimen, and the magnitude of the coefficient that characterizes this relation, once it was found to be linear. These experiments did not derive guidance from any molecular hypothesis. Moreover, the fact that Lippmann predicted the converse effect on thermodynamics did not prevent the Curies from testing and confirming his prediction. What was true of the Curies' experiments was also true for later experiments like those of Kundt and most of Röntgen's and Hankel's, including Röntgen's torsion experiment.

Only the combination of both molecular and phenomenological approaches gave the theoretical background for the establishment of piezoelectric knowledge; experimental study, of course, was essential for the development of the subject. The molecular approach was fruitful in leading to the discovery of the direct effect, but it failed to direct the Curies to the existence of the converse effect. The discovery of the latter effect originated in a thermodynamical theoretical discussion of electric phenomena. One could not infer the existence of the piezoelectric effect from this approach. Yet once the direct effect was known, the existence of the converse effect was deduced through the thermodynamic-analytical approach and not by the molecular. In this episode the two approaches complemented each other. It is interesting to note that the order of their application was crucial—a reverse order could not have led to

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[9] Yet this study was probably motivated also from molecular speculation, since they used its results to support their molecular model. The model, which was published soon after the communication of the experimental results, predicted the observed relations between the charge, the dimensions of the crystal and the variations of pressure.

the discovery. Later, molecular-mechanistic considerations led to the recognition by Röntgen and Jacques Curie and Friedel that crystals like quartz are not electrified by uniform temperature change. On the other hand, a positivistic-quantitative approach was fertile for the discovery of direct electro-optics by Pockels. Voigt's discovery of direct pyroelectricity in tourmaline profited from both the molecular assumption that it should exist and the phenomenological theory that quantitatively expressed its relation with the indirect effect. Thus, the early history of piezoelectricity displays the flexibility of physicists in their application of molecular, phenomenological and thermodynamic approaches, and the fertility of their combination.

After the introduction of Voigt's general theory, the paths of the explanatory and the phenomenological theories diverged. Both, of course, related to Voigt's theory: the one took it as a starting point for further elaborations, the other suggested explanatory theories that yielded the equations of that theory. Yet, the elaboration of the phenomenological theory did not alter the explanatory models, while the molecular explanations were not mentioned in the works on phenomenological theory. The two efforts were hardly related either conceptually or technically. They seem to be two parallel realms: one hypothetical, whose relation to reality is unknown, the other rigorous and firmly based on observations. John Heilbron claimed that "in order to recapture the spirit of fin-de-siècle physics it will be necessary to admit a sort of professional schizophrenia, whose two personalities correspond to the physicist as practicing scientist and the physicist as philosopher of science." As a physicist one believed in the existence of entities like atoms and molecules, which he doubted as a philosopher. Physicists' cautious, sceptical philosophical claims about the reality of physical concepts, Heilbron showed, contradicted their practice and comments in scientific papers.[10] Notwithstanding the usefulness of this picture to the historical understanding of fin-de-siècle physics, it fails to consider differences between various *practices* of the physicists. In phenomenological-thermodynamical research the physicists seem closer to their "philosophical persona" than to their "scientific" one. In this research physicists refrained from the speculative assumptions of molecular theories. The separation between the two realms of research resembles the two personalities discussed by Heilbron. Yet, this indicates that the division between the physicist *qua* philosopher and the physicist *qua* scientist is problematic. Was Voigt's theory of secondary phenomena a work of a physicist *qua* philosopher and his molecular theories those of a physicist *qua* scientist?

Furthermore, considering various practices in physics, one finds that the separation between two kinds of attitudes—the molecular-atomistic and the phenomenological-positivistic—was not complete. The contribution of Voigt's molecular view to his decision to consider direct pyroelectricity reveals the significance of the molecular for

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[10] John L. Heilbron, "Atomic Concepts and mechanical Models in the Physical Sciences of the Early 1890's," chapter 1 in *A History of the Problem of Atomic Structure from the discovery of the Electron to the Beginning of Quantum Mechanics*, PhD. Dissertation, University of California, Berkeley, 1964, pp. 1–58. On the two personalities see the quotation on pp. 26–27 and the following discussion. John L. Heilbron, "'Fin-de-siècle' physics," in *Science, Technology, and Society in the Time of Alfred Nobel*, C.G.Bernhard, E.Crawford, and P. Sörböm (eds.), Oxford: Pergamon Press, 1982: pp. 51–73 p. 56, for another expression of the idea.

the phenomenological theory. Thus, the two theoretical efforts were not independent of each other.[11] This connection though fragile, suggests that physicists did embody the same persona in elaborating a "positivistic" theory as in elaborating a molecular one. A physicist like Voigt was well aware of the hypothetical nature of the atoms and molecules of his explanatory theory, yet he did not vitiate the value of this theory for his phenomenological theory, which he considered a true and valid description of relations between the phenomena.[12] Overall, the phenomenological theory well represented his philosophical view of physics as accounting for relations between observable magnitudes. Thus, even in the work of a physicist with a positivistic inclination like Voigt, there existed a relation between the philosophical, phenomenological and molecular tiers of thought.

Whether they had a more positivistic-phenomenological attitude, like Voigt, or a molecular or mechanistic inclination like Riecke and Thomson, the physicists who worked on piezoelectricity seemed to believe in the existence of atoms (excluding Duhem). This position had gained ever more credibility at the time. They all knew that the evidence for the existence of these corpuscles was not conclusive, and that their molecular theories could be regarded at best as plausible. While most physicists assumed the existence of such corpuscles, they disputed their properties. The arrangement of such corpuscles in a complex matter like a crystal was another issue for speculations. Since none of the explanatory theories of piezoelectricity could suggest any new predictions that did not follow the general phenomenological theory, they could not use the experimental evidence to support their hypothetical premises. Further obstacles to an explanatory theory of piezoelectricity that would correspond to reality were not hidden from some participants. Voigt explained that even proof of the existence of atoms and their general structure, does not supply enough grounds for the construction of a unique molecular explanation; furthermore, such a theory would be based on the phenomenological theory.[13]

Based on controversial and insecure premises and unable to attain unaccounted relations, the molecular models were doomed to remain hypothetical. Still the shortcomings of the models did not negate the possibility of the existence of molecular structures and mechanisms that induced the observed phenomena. Physicists had various reasons to advance molecular models, although they were aware of their hypothetical nature. They wanted to show the compatibility of the molecular assumption with new findings, to gain a better understanding of the phenomena and to advance their ideas about the structure of matter. This was also a possible way to examine the consequences of hypothetical assumptions that could not be tested directly.

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[11] Olivier Darrigol reveals a stronger link between the two approaches half a century earlier in the study of hydrodynamics and elasticity. He shows that physicists moved with ease from one kind of argument to another. Those who preferred continuum-phenomenological theory continued to believe in the molecular structure of matter and to consider it in their arguments. Olivier Darrigol, "Between hydrodynamics and elasticity theory: the first five births of the Navier-Stokes equation," *AHES, 56* (2002), 95–150.

[12] Still, the assumption that Voigt adopted from the molecular theory in its weak form (that direct pyroelectricity ***might*** exist) did not add any unobservable claim to the theory.

[13] Voigt, "Phänomenologische und atomistische." See the discussion above p. 96.

In one case at least such an experiment was carried out. Voigt succeeded in comparing the plausibility of his and Riecke's molecular models with measurements of the permanent electric polarization of tourmaline. Still, in some cases the attempts to construct molecular theories probably also revealed a hope that such a theory would eventually be found to correspond with reality. Since both molecular and phenomenological realms seemed to suggest potential benefits, advancing simultaneously in both directions was a reasonable strategy. Progressing in parallel layers, hoping that both would contribute to the knowledge of piezoelectricity and matter in general, was reasonable as long as one recognized the hypothetical character of the one versus the firmer ground of the other. The combinations of applying tentative molecular models and the use of a firmer phenomenological approach suggest a belief in the possibility of discovering the true reality of piezoelectricity, even if not in the foreseeable future. Apparently, in their physics, the participants did not seek immediately for the ultimate structure and mechanism of nature but a better knowledge of natural behavior that would enable description and, if possible, understanding of nature.

APPENDIX 1

EARLIER APPEARANCES OF ELECTRICITY BY PRESSURE

The Curies were not the first to observe electricity generated by pressure. More than 60 years earlier, Haüy had electrified crystals by pressure and in the process commenced a short research tradition that appears to be related to the study of piezoelectricity. Wiedemann assumed such a connection in 1894 when he opened the description of the piezoelectric research with Haüy. He still pointed to some uncertainty in the conditions of the latter's experiment that makes its relation to the Curies' discovery unclear.[1] According to the *Britannica*, however, Haüy observed piezoelectricity.[2] If this is correct, the discovery of the piezoelectric effect should be attributed to Haüy, and dated to the first quarter of the nineteenth century rather than to the last. This would require significant changes in the story told in this book. One should give an account of how and why the effect had to be rediscovered in 1880 and what was the fate of the earlier research tradition. Moreover, even if Haüy observed effects of another nature one should consider whether a knowledge of these effects influenced the discovery of piezoelectricity. Therefore, this appendix examines the reports on the electric effects of pressure published before 1880, in order to study the nature of these effects, the way they were understood historically at the time, and the relation of that research tradition to the later study of piezoelectricity.

Indeed in 1817, René-Just Haüy was the first to observe electrification that clearly originated from pressure, without rubbing. Already 30 years earlier, Coulomb "drew this consequence that compression, or a transitory [*passagére*] dilatation, has an influence on the quantity or on the nature of electricity that is developed by mutual rubbing of bodies." However, he did not suggest that pressure by itself induce electricity. That was suggested by Antoine Libes in 1804. He reported on an electrification by pressing a disc of isolated metal to cloth or rubber. However, according to a later physicist the peculiarities of the experiment made it "isolated and unfruitful."[3] Haüy did not refer

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[1] Gustav Wiedemann, *Die Lehre von der Elektricität*, Second edition, 1894, Vol. 2 p. 417.

[2] It claims that "he [Haüy] was also known for his studies of pyroelectricity and piezoelectricity in crystals." "Haüy, René-Just," *Britannica CD,* Version 97, Encyclopaedia Britannica, Inc., 1997.

[3] B. [Biot?] "Sur la développement de l'électricité dans les corps par la pression et la dilatation," *Bulletin société philomathaique Paris*, 7 (1820): 149–155, quotations from pp. 150, 151. This is a report on

to any of these predecessors; he examined the effect of pressure on a few crystal species.

Haüy simply pressed a crystal specimen between his fingers for a short period, and then observed its electricity, **after** its release. To his "good fortune" he first examined Iceland Spar (calcite) that among the species examined presented the strongest electric effect. Iceland Spar with its conspicuous double refraction had been a paradigmatic crystal for Haüy since his early work on crystallography, so its choice for the new experiment was natural for him. His reasons to suppose that pressure might induce electricity, however, are less clear. Once discovered, his reasons to study the effect became clearer. In his comprehensive study of minerals, Haüy revealed a genuine interest in their various physical properties. Electric phenomena were not missing from his studies. Regarding the general interest in electricity at the time this is not surprising. Moreover, generation of electricity occupied an important part in the study of electricity by contemporaries. So, the possibility of generating electricity by a new method, related to the known rubbing method, seemed worth a study. Since the mechanism by which rubbing generates electricity was unknown, the discovery of any new method carried a promise for better understanding of the processes in which electricity is released.

In his experiment Haüy made special efforts to eliminate any friction in the processes of pressing. The crystals were always pressed between two plastic materials like fingers and cloth. A pressure by rigid matter or fluids on the same crystals did not generate electric effect nor did all the crystals examined electrify under pressure of the fingers. Those that were, especially Iceland Spar, were all electrified with a positive charge and kept their electricity for up to a few days after being pressed.[4]

Clearly, the effect that Haüy observed was not piezoelectricity. Unlike piezoelectricity, the effect did not appear while pressure was applied but only after the pressed bodies were disconnected. Second, the effect did not involve polarization of the crystal; instead, all its faces were charged in the same manner. Lastly, it was dependent on both the pressing and the pressed materials. Haüy himself did not connect the discovered effect to the polar phenomenon of pyroelectricity, but to electrification by rubbing. He suggested that the fingers cause invisible displacements of the crystal's molecules. In their return to the original position, the motion of the molecules generates an electric effect analogous to that of rubbing. Thus, he saw the result as a surface effect of contact between the two bodies.

Antoine César Becquerel's memoir given to the *Académie de Sciénce* probably by Biot who was a member of both the *Academy* and the philomatic society and an editor in the latter's bulletin in which it appeared. In another place following Priestly, Becquerel mistakenly claimed that already Aepinus had observed electrification by pressure by pressing two glasses without rubbing. However, Priestly did not claim that the experiment was of pure pressure. Moreover, according to the modern translation of Aepinus, the experiment was of rubbing two glass plates one on the other. A.C. Becquerel, "Du dégagement de l'électricité par pression," *Traité expérimental de l'électrcicité et du magnétisme*, Tome deuxième, Paris: Firmin Didot Frères, 1834: pp. 97–111, on p. 97; Joseph Priestly, *The History and Present State of Electricity,* Reprinted from the third edition, London, 1755, p. 276; Aepinus, *Theory of Electricity and Magnetism*, pp. 274–5 (sections 55–57). I have not had a similar opportunity to consult Libes's and Coulomb's original writings (Becquerel does not specified Coulomb's publication).

[4] Haüy, "Sur l'Électricité Produite dans les Minéraux á l'aide de la pression," *Mémoires du Muséum d'Histoire Naturelle*, 3 (1817): 223–228, also in *Annales de chimie et de physique* 5(1817): 95–101.

Antoine César Becquerel contested Haüy's assertion that electrification by pressure is limited to a few crystal species. Specifically, he claimed that the crystals that did not show the effect in Haüy's experiment become electrified by pressure in a more sensitive experiment, which he designed to this end. The effect, he declared, is universal: "All the substances of nature whatsoever, isolated and pressed one against the other, would emerge of the pressure with different states of electricity, the one with an excess of vitreous electricity, the other with correspondent excess of resinous electricity." This, he claimed, is true even for conductors and fluids, as he concluded from observing electricity in nonconductors after they were pressed to conductors. However, in pressing two of these materials to each other, one is unable to observe the phenomenon since the charges pass quickly from the one to the other.[5]

Unlike Haüy, who relied on simple pressure by fingers, Becquerel constructed an apparatus for pressing specimens by weights of a known value. He shaped a specimen, usually of a crystal, to a small circular disc fixed by an insulator to a shank of glass the other side of which was connected to a copper tube (b in Figure A.1), put inside a close electric torsion balance of Coulomb (a kind of electroscope). In that way he made sure that the specimen was not electrified before it was pressed. The whole apparatus was put in a stable frame and was electrically isolated. The pressed specimen was put between two circular plates (cc in the main Figure and q in Figure 42 bis of A.1). The lower plate had a hollow center (2 cm in diameter, shown on the upper left side of Figure A.1), which enabled the insertion of a small glass tube varnished by gum-lac from below. On its edge, this glass tube carried a small disc of cork or a similar material. It was firmly connected to a balance of weights that pressed it upward once weight was hung on the farther hook (the balance at the lower right-hand part of the main figure). This way it pressed the circular specimen in cc. The pressure was released very quickly and without rubbing with a special arrangement designed by Becquerel (seen in the figure left of the weight balance directly under the electric balance). After their separation he pulled out the crystal specimen and measured the charge on the **cork**. He did not measure the charge on the specimen at all. Contacting the cork with a disc of the electric balance of the same dimensions, he measured their separation from which he calculated the charge. The effect was very small; a regular Coulomb's balance with a silver wire was not sensitive enough. Becquerel used platinum, which is more sensitive but less reliable. Since both the cork and the specimen were isolated, he took the charge on the specimen to be equal in size and inverse in sign to that of the cork.[6]

With this device he measured the effect due to a few different weights of a few kilograms on four crystal species (Iceland spar, barytes, quartz, and lime) and found a linear relation between the pressure and the electric charge. In these and in more quantitative measurement, he observed wide differences in the magnitude of the effect. All crystals became vitreous after pressed by cork; fruits, on the other hand, became resinous. He concluded that all materials can be ordered in a list according

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[5] A.C. Becquerel ,"Expériences sur le développement de l'électricité par la pression; Lois de ce développement," *Annales de chimie et de physique*, 22 (1823): 1–34, p. 13, 34 and [Biot] "Développement de l'électricité," quotation from p. 152.

[6] Becquerel, "Du dégagement de l'électricité," Traité expérimental , pp. 101–103.

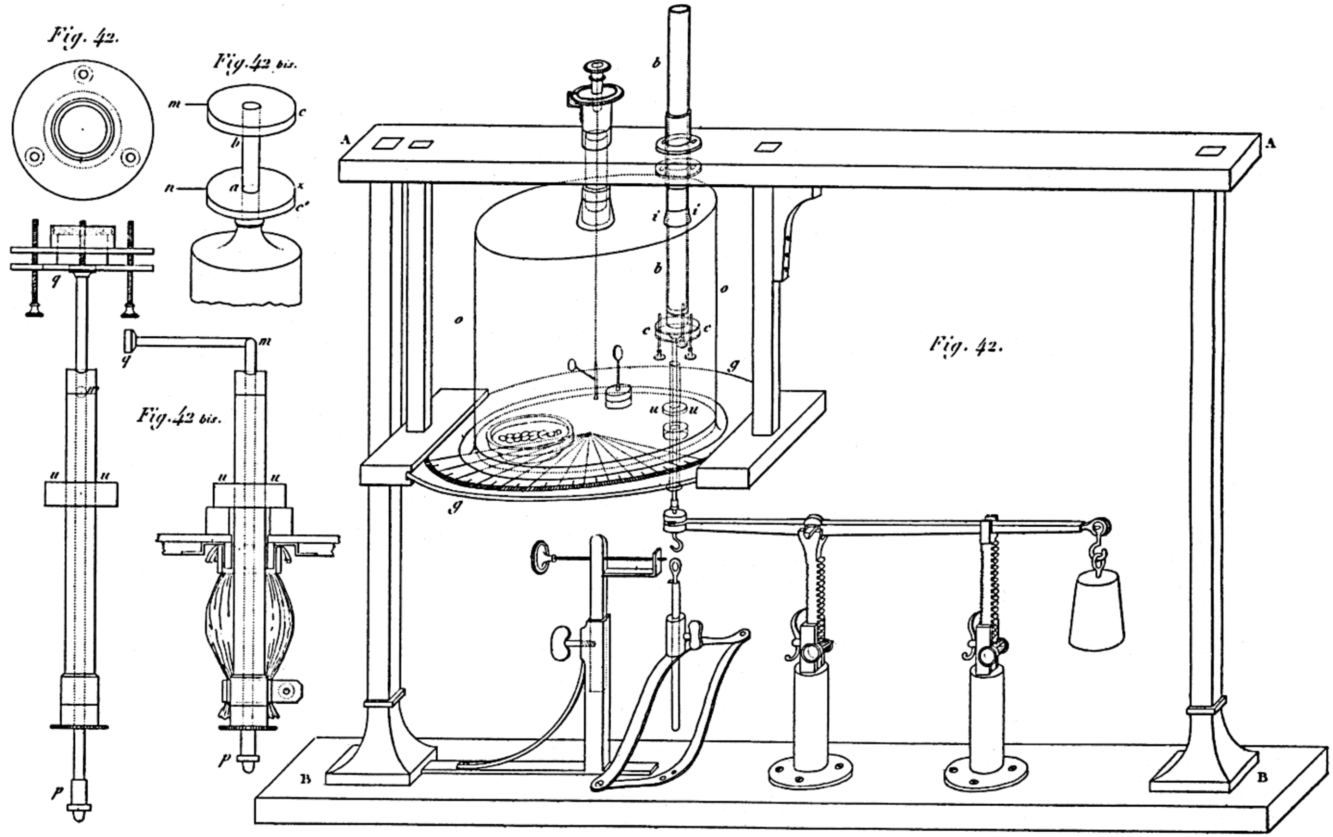

Figure A.1: Becquerel's instrument for measuring electricity by pressure. The specimen was pressed to cork between the two circular plates cc (inside the cylinder at the center of the figure and in details in the left hand side). The balance on the lower right side pressed the specimen by the glass tube ab in Figure 42 bis on the higher left-hand side of the figure. From Becquerel "déveloment de l'electricité pur la pression".

to their tendency to gain positive or negative electricity by pressing, like the list of their tendency to become positive or negative by rubbing. A material with a higher tendency to become positive pressed to any material with a lower tendency would gain positive charge. Metals, for example, became positive when pressed with cork, but negative when pressed by crystals.[7]

Becquerel found that the magnitude of the observed effect depends on several variables. He therefore kept the smoothness of the crystals, the temperature and the humidity constant in all measurements. The dependence on the smoothness of the specimen and the need of a soft pressing material for an observable effect suggested that the phenomenon is due to the outer layers of the bodies. As such, Becquerel pointed at a possible relation between this and the appearance of electricity and light by exfoliation of mica. In both adjacent layers are separated from each other (in the case of pressing after its release). Both phenomena are caused in his suggestion by the breaking of molecular attraction between these layers.[8] In two different materials pressed to each other, this is a kind of contact electricity in which pressure is intensified. It seems, he wrote, "that at the instance in which one applies the pressure, a new state of equilibrium between the two fluids that compose the natural electric fluid of the molecules in contact is formed." To form this equilibrium electricity flows from one substance to the other: positive electricity occupies the surface of one material and negative that of the other. The charge on both is observable only after their separation, as was indeed done in the experiment. Since the number of molecules in contact increases with the pressure applied, and more so in soft materials, one might expect that the effect increases with pressure, as observed. Still, Becquerel assumed that the effect would stop increasing at a certain pressure; "since it arrives at a point in which they [the molecules] can be further compressed only with great difficulty." He rejected a conjecture that the phenomenon is an effect of the heat produced during the pressure. To demonstrate the shortcomings of this conjecture, he pressed a crystal and then diminished the pressure to half, waited a short while and measured the charge. The effect was half that of the original pressure, while it should be about the same according to the heat assumption.[9] Thus, the view of the effect as a result of interaction between the outer layers of the pressed materials seemed well supported by the evidence.

Becquerel also examined whether the stretching of bodies has an electric effect. According to a report from 1820 on his work to the *Académie de Sciénces*, probably by Biot, "M. Becquerel believed to recognize that stretching of certain bodies, of rubber, for example, also developed electricity; however, his experiments in this respect are needed to be repeated with new precautions, and to rely on delicate and precise means of measurement." According to Jean-Baptiste Biot, Becquerel's research should be only a beginning.

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[7] Becquerel, "Expériences sur le Développement de l'électricité par la pression." pp. 8–9.

[8] *Ibid*., pp. 11–17.

[9] Becquerel, "Du dégagement de l'électricité," pp. 99–101, 109–111, quotations on pp. 99 and 110. In refuting the hypothesis that the experimental findings arouse from heat in 1834, Becquerel replied to a recent claim of Péclet. In his answer he used previous experimental results from 1823, which he then reported without reference to the heat hypothesis. E. Péclet, "Mémoire sur l'Electricité produite par le Frottement," *Annales de chimie et de physique*, 57 (1834): 337–398.

> It would be interesting to know [he continued] whether this development and that produced by compression, is progressive or sudden, whether the electricity developed in each of these operations is the same or different, what part the molecules in the interior of the body and those of the surface take in the total production; it would be especially interesting and perhaps rather easy to investigate in crystalline minerals, where the aggregation of the particles, however regular in its assembly, presents in the different directions in the crystal known differences that can influence the great or small ease, with which the electricity is separated. It is needed to measure also the influence that can exist between them and the quantity of heat released or absorbed during the compression and expansion, all these things are necessary to know for discovering how and by which force electricity withdrawn and hidden in the bodies is released and set free by various mechanic means exercised on them.[10]

At first glance this can be seen as a call to find a phenomenon like piezoelectricity—an electric effect of expansion and compression in crystals. However, Biot did not refer to piezoelectricity but to a phenomenon of another nature observed by Haüy and Becquerel. Indeed, he assumed that the geometric structure of crystal might influence the effect, modifying its properties but not its mere existence. He did not suggest that the effect be only of crystals. Why should he? Becquerel had shown that the effect is not limited to crystals. Further studies along the lines quoted here might have led to a discovery of piezoelectricity, but none of its specific properties (polarity, connection to special axes) is predicted here.[11] These suggestions are embedded in the theories of electricity that regard it as a special kind of fluid (or two fluids) that can be hidden and released from matter. Though the relations between matter and electricity remained obscure during the nineteenth century, they were expressed in different terms circa 1880. At that time these suggestions, left in an old journal article, were surely unknown. Becquerel's experiment on the electric effect of stretching was not repeated, the questions raised by Biot were not examined and the one indecisive observation was probably forgotten.

Nor was the effect of pressing two materials further studied after Becquerel. His findings had quite wide circulation in his own publications between 1820 and 1834, in reports in French and foreign languages and later in survey books on electricity.[12] Yet an interest in the phenomenon did not emerge. It was still mentioned in a few texts but was quite neglected. Peter Th. Riess's widely used handbook *Die Lehere von der Reibungselektricität* from 1853 briefly describes the findings of Haüy and Becquerel. About the same time the phenomenon was summarized with more details by Auguste de la Rive in his textbook on electricity written in French and translated to

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[10] [Biot], "Dévloppement de l'électricité," p.154–155, parts of the translation are based on Cady's translation, Cady, *Piezoelectricity*, p. 177. For the identification of Biot see note 3.

[11] However, in a brief summary on the history of piezoelectricity Arthur Ballato viewed the text (which following Cady he attributed to Becquerel) as conjecturing the appearance of electric effect due to the anisotropy of the crystals, implying a forecast of piezoelectricity. Arthur Ballato, "Piezoelectricity: History and New Thrusts," *IEEE Ultrasonic Symposium* 1996: 575–583.

[12] In addition to the publications mentioned the research was described in Brandes. Gmelin. Horner. Muncke. and Pfaff. *Gehler's Physikalisches Wörterbuch*, neu bearbeitet, Leipzig: E.B. Scheickert, 1827: Vol. 3, pp. 255–59.

English. During the 1860s the effect was described in Daguin's textbook and briefly in *Encyclopédie Moderne*.[13] Although the effect was not totally forgotten, it was not well known among scientists circa 1880.[14]

The Curies had probably learnt about the effect from a brief mention in a secondary source. In their first publication on the discovery of piezoelectricity they noted that "it had been said" that pressure is capable of electrifying a few holohedral crystals. They distinguished between this effect and their discovery. Nearly six months later in their note to the Academy of Sciences they expressed the relations between the two phenomena more clearly: "The hemihedral crystals with inclined faces are the only pyroelectric crystals; they are also the only ones capable of attaining electric polarity by pressure. Certain holohedral crystals, like Iceland Spar, are also charged by pressure, but of one electricity; this is a phenomenon of the surface, totally different [from piezoelectricity], furthermore [*et don't*] the effect is insensible in the conditions of our experiments."[15] That the older effect did not appear in the Curies' experiment is not accidental, as they designed their apparatus to detect electric polarity while a pressure is applied on the crystal. None of the effects observed by Haüy and Becquerel were expected to appear in such an experimental arrangement. Jacques and Pierre Curie connected the discovered phenomenon to pyroelectricity and hemihedral crystals, which, as shown in Chapter 1 provided enough stimulation for their discovery. The knowledge of an effect of pressure in other crystals was very unlikely to direct them to their conjecture that pressure along hemihedral crystallographic axes generates electric polarity. The effect observed by Haüy and Becquerel was related to contact electricity and rubbing, which do not appear at all in the Curies' considerations of piezoelectricity.

Hence, the electric effect of pressure observed in the first three decades of the nineteenth century does not reveal a solid historical relation to piezoelectricity and its development. Physically, the effect disagrees with piezoelectricity. The phenomenon was not limited to piezoelectric species. It depended on both the pressing and the

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[13] Peter Theophil Riess, *Die Lehre von der Reibungselektricität*, Berlin, August Hirschwald, 1853, pp. 403–404; Auguste de La Rive, *A Treatise on Electricity in Theory and Practice*, translated by Charles V. Walker, London, Longmann, 1856, Vol 2, pp. 640–44. In the same decade Becquerel himself mentioned again the effect in a history of electricity he wrote with his son, Antoine César Becquerel and Edmond Becquerel, *Résumé de l'histoire de l'électricité et du magnétisme*, Paris(?), 1858; Pierre Adolphe Daguin, *Traité élémentaire de physique théorique et expérimentale: avec les applications à la météorologie et aux arts industriels à l'usage des facultés, des établissements d'enseignement secondaire et des écoles spéciales du gouvernement*, 3rd ed. Paris, 1866, pp. 291–93; *Encyclopédie moderne*, 1861 vol. 13, p. 636. I located the last two references through Christine Blondel, "Haüy et l'électricité: De la demonstration-spectacle à la diffusion d'une science newtonienne," *Revue d'histoire des sciences* 50 (1997): 265–282.

[14] After consulting the literature for his comprehensive textbook, Mallard in 1884 still failed to mention Becquerel's experiment and referred only to Haüy's, which he thought needed further verification (*Crystallographie Physique*, pp. 554–555). As mentioned, Wiedemann in the second edition of his handbook on electricity of 1894 also referred to Haüy's experiment and its limitations. That the phenomenon observed by Haüy and Becquerel was almost forgotten can be inferred from its neglect in the first edition of Wiedemann's book of 1883.

[15] The addition of details in their second publication suggests that they might have learnt more about the earlier observations after the first article was written. J. and P. Curie, "Développement par pression," (Curie, *Oeuvres*), p. 7, "Développement par compression," (*Bulletin Société minéralogique*), p. 93.

pressed materials rather than only the specimen under examination. More telling pressure did not generate polar electricity but electric charge of the same sign in the entire specimen. Furthermore, the electricity appeared only after the release of pressure rather than while it was applied. Historically, the protagonists understood the phenomenon as connected to surface effects like electricity by contact, rubbing or exfoliation rather than to a polar inner phenomenon like pyroelectricity, and they thought that it originated in the outer layers of the matter. This is how the effect was later presented. Thus, one does not need to assume any influence of the older effect on Curie's discovery.

Notwithstanding its loose connection to piezoelectricity, the phenomenon of electrification by pressure is historically interesting due to its neglect. The phenomenon faded from the physical texts. It is not recognized today, and in a sense does not exist, though Becquerel's experiments were neither shown to be problematic, nor to be incorrect by the results of later more accurate experiments. The scientific phenomenon simply disappeared. Indeed, the existence of such an effect appeared to be explainable by current physics and it does not seem to raise a threat to current theories. It seems to be a secondary and tertiary effect rather than a genuine effect, which usually attracts more attention. Nevertheless, physics lost a knowledge about a physical phenomenon and by that one piece of information about the natural world. One can wonder how many other phenomena were discovered only to be forgotten in outdated handbooks.

APPENDIX 2

MATHEMATICAL WORKS ON VOIGT'S GENERAL THEORY

In a sense the most direct continuation of Voigt's original memoir was made in 1892 by Carlo Somigliana (1860–1955) in his solution of Voigt's equations for a specific case. Introducing the general theory Voigt had applied its equations to crystals of various shapes subject to different stresses. One of the cases examined was that of a cylinder subject to stress on the bases in the direction of its principal axis.[1] Somigliana examined the effect of stress on the lateral surface of a cylinder, while its bases are free. This mathematical problem is a piezoelectric version of a known problem in the mathematical theory of elasticity, named by Alferd Clebsch in 1860 the problem of Saint-Venant. In his French translation of Clebsch's *Theorie der Elasticität der fester Körper* (1862),[2] Jean Claude Saint-Venant generalized the theory from isotropic to what was called transverse (*trasversale*) isotropic matter.

Somigliana knew his elasticity well. In the late 1880s he had published a few important contributions to the mathematical study of the field, which continued to attract his attention for many years. His discussion of piezoelectricity was based on the results from the parallel elastic problem and was part of his research on elasticity. This research attracted the attention of mathematicians rather than physicists. For example, physicists did not refer to Clebsch's work.[3] Like most Italian mathematical physicists, Somigliana, who was appointed that year to the mathematical physics chair in Pavia, oriented his work more toward solutions of mathematical problems in physics than toward physical theory and experiments. Most of his contributions, including that on piezoelectricity, were thus published in mathematical journals.[4]

Somigliana's choice of mathematical techniques for solving the piezoelectric problem is evident. Yet, he made the effort to explain his solutions and their physical

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[1] Voigt, "Allgemeine Theorie," pp. 37–43.

[2] Carlo Somigliana, "Ricerche sulla deformazione ed i fenomeni piezoelettrici in un cilindron cristallino," *Annali di matematica puira ed applicata*, 20 (1892): 61–99. On Saint-Venant's problem see Todhunter and Pearson *History of Elasticity*, Vol. 2 pt. 2 p. 109.

[3] Garber, *The Language of Physics*, p. 268.

[4] Livia Gicardi and Clara Silvia Roero, *Bibliotheca Mathematica: Documenti per la storia della matematica nelle biblioteche Torinesi*, Umberto Allemandi, Torino, 1987, p. 155.

meaning. In particular, he observed that uniform pressure on the lateral surface (when no pressure is applied on the bases) induces an electric effect only in those crystals that are electrified by uniform pressure (p. 83). He also found an expression for the observable potentials produced on the cylinder's surfaces by simple stresses. This voltage can be observed, he claimed, by applying Kundt's dusting method. Still, Saint-Venant's problem was much more interesting from a mathematical than from an experimental perspective. It required a complicated apparatus to produce the assumed stresses and to simultaneously measure their electric effect. Thus, physicists neglected Somigliana's contribution. It was only mentioned in Pockels's survey article in Winkelmann's *Handbuch*: "The piezoelectric excitement of a cylinder in the indeed practically less important case of deformation by mechanical influence on the cover (*Mantelfläche*) was treated by Somigliana."[5]

More practical mathematical problems were treated independently by Voigt and Riecke. In 1891 both studied what Voigt called "the surface of total moment." This is the surface described by the end point of the electric moment vector due to a longitudinal pressure of one unit. "The radius vector of these points [of the surface, Riecke explained] gives the direction of the piezoelectric moments, and the lengths give its magnitude."[6] These surfaces were introduced in order to supply a geometric picture for the piezoelectric effects. Voigt discussed the surfaces of three simple groups of crystals, including that of quartz. Riecke discussed only those of tourmaline (his "hobby horse" crystal), which is much more complicated than those discussed by Voigt. Both were interested in developing concrete expressions of surfaces for specific crystal classes.

Voigt used "models" made of crystals from the discussed classes to display the surfaces to a scientific audience in the meeting of the German scientists and physicians. Still the surfaces were mathematical entities derived from the equations of the general theory. Their development was part of an effort to illustrate [*veranschaulichen*] the complicated and abstract mathematical expressions of elasticity and piezoelectricity. Though it contains less information, a surface is a better geometrical illustration than a set of equations. The surfaces were a subject of further and more general study in F. Bidlingmaier's dissertation of 1900 at Voigt's university of Göttingen. In 1897 Voigt suggested another geometrical way to illustrate the tensorial expressions of stresses and strains in the piezoelectric and elastic theory, which though different, was related to the surfaces of total moment. In the same year he finished his first book on the physics of crystals, in which he invented the term tensor and laid the foundations of tensor analysis.[7]

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[5] Pockels, "Pyro- und Piezoelectrizität," in Winkelm, *Hanbuch der Physik*, p. 784.

[6] E. Riecke, "Ueber eine mit electrischen Eigenschaften des Turmalins zusammenhängende Fläche," *Ann,. Phy.* (49) 1893: 421–429. (Originally in *Göttingen Nachrichten*, 1891), quotation from p. 421. W. Voigt, "Modelle zur Theorie der Piëzo- und Pyro-ëlektricität," *Verhandlungen der Gesellschaft Deutscher Naturforscher und Ärzte*," 1891: 35–39.

[7] F. Pockels, "Pyro- und Piezoelectrizität," pp. 777–8, W. Voigt, "Beiträge zur geometrischen Darstellung der physikalischen Eigenschaften der Krystalle," *Ann. Phy.* 63(1897): 376–385. Woldemar Voigt, *Die fundamentalen physikalischen Eigenschaften der Krystalle in elementarer Darstellung*, Leipzig: Veit & Comp., 1898. On the development of tensor analysis and Voigt's published contributions see Karin Reich, *Die Entwicklung des Tensorkalküls: von absoluten Differentialkalkül zur Relativitätstheorie*, Basel: Birkhäuser Verlag, 1994. Unfortunately Reich does not discuss the relations between Voigt's previous work concerning the mathematics of tensors and his explicit formulation of tensor analysis after 1897.

APPENDIX 3

VOIGT'S CONCEPTS OF ELECTRIC CHARGE

Voigt's short derivation of the surface charge density from the equation for the electric moment (for a plate under electric field and pressure equation (24), Chapter 4) can teach us about his concepts of electric charge. According to commonly used equations, the free charge density σ' takes the expression:

$$-4\pi\sigma' = \frac{\partial V_i}{\partial n_i} + \frac{\partial V_a}{\partial n_a} = \frac{V_1 - V_0}{H} \tag{1}$$

where the subscripts i and a, respectively, represent the magnitudes inside and outside the crystal. The derivative of the potential in the conductor is, of course, zero. Now Voigt explained: "σ' is located partly in the dielectric, partly in the conductor. We know the first part σ'' from the following fact that the constant moment α of the excited dielectric is equivalent to the surface charge of the density: $\sigma'' = \sum \alpha_i \cos(n_i, x_i)$; this gives in our case $\sigma'' = \alpha_3$." The surface density of the conductor σ located at its boundary is the difference between the total density and that of the dielectric. Considering equation (24), Chapter 4 for the electric moment Voigt obtained:

$$\sigma = \sigma' - \sigma'' = \frac{1 + 4\pi\gamma_{33}}{4\pi H}(V_1 - V_0) + \delta_{33}\Pi \tag{2}$$

> These results show that the bound [charge] densities of the conductors at the surface boundary with the dielectric and the [charge densities] of the dielectric located at the same surface, are generally by no means equal and exactly opposite [to each other]; this is found, moreover, only in the state when $V_1 = V_0$, both charges are thus connected by conductor. (p. 358)

Since at the end of this paper Voigt discussed Maxwell–Hertz's electromagnetic equations in view of piezoelectric theory, it is interesting to compare his concepts of charge with that of Heinrich Hertz. Hertz differentiated between three kinds of charge (he called it quantity of electricity): true, free, and bound electricity. True electricity is the divergence of the electric displacement (polarization in his terms);[1]

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[1] "[T]he quantity of true electricity contained in any space, multiplied by 4π, is equal to the excess of the number of lines of force which enter the surface over the number which leave it." In a note Hertz differentiates between this polarization of the ether (displacement) and polarization of matter. Heinrich

free electricity is the divergence of the electric field; and bound electricity is the difference between the first and the second. The last is what is usually associated with the electric polarization, or electric moment. Hertz's bound electricity is parallel to Voigt's "dielectric part," (σ'') but Voigt attributed to it the opposite sign as was common in continental theories.[2] σ', which, according to Voigt, has parts in both the dielectric and the conductor, equals Hertz's free charge, since it is the divergence of the electric field.[3] The charge on the conductor (σ) is therefore equal to the true charge. Voigt's equation shows that this charge has contributions from both the electric potential and the piezoelectric effect. In Voigt's scheme this charge is not connected directly to any electromagnetic magnitude, while its connection to the displacement is central in Hertz's Maxwellian theory.

Hertz, "On the fundamental Equations of Electromagnetics for Bodies at Rest," in *Electric Waves*, translated by D. E. Jones, London: MacMillan and Co., 1893, pp. 195–240, on p. 215.

[2] This difference explains why Voigt expected the charge to be opposite to σ when the conductors are connected. Note that in Hertz's notation Voigt's relation is written $\sigma = \sigma' + \sigma''$. Olivier Darrigol, "The Electrodynamic Revolution in Germany as Documented by early German Expositions of 'Maxwell's Theory'," *AHES*, 45 (1993): 196–280, on pp. 201–2.

[3] Indeed this concept was adopted by Hertz from Helmholtz's theory, which was used here by Voigt.

APPENDIX 4

TABLES

TABLE A.1. CHRONOLOGICAL TABLE OF MAJOR EVENTS IN THE HISTORY OF PIEZOELECTRICITY

The table lists major events categorized into experimental and theoretical. The theoretical events are further divided into those based on a molecular/atomistic assumption and those based on phenomenological or thermodynamic considerations. The sign **(M)** indicates an experiment whose idea was influenced by molecular notions or theory.

		Theory	
Year	Experiment	Phenomenological-thermodynamic	Molecular/ explanatory
1756	Aepinus's discovery that pyroelectricity is an electric phenomenon		
1860			Thomson's suggestion that pyroelectricity is an effect of inner electric polarization
1880	J. and P. Curie's discovery of direct piezoelectricity **(M)**		
1881	J. and P. Curie's empirical rules for the development of charge that show the linearity of the effect		J. and P. Curie's model of piezoelectricity in tourmaline
	Determination of quartz and tourmaline constants by the Curies	Lippmann's prediction of the converse effect	
	Hankel contests the connection suggested by the Curies between piezo- and pyro-electricity		
	J. and P. Curie's detection of the converse effect		

(*Cont.*)

(*Continued*)

		Theory	
Year	Experiment	Phenomenological-thermodynamic	Molecular/explanatory
1882	J. and P. Curie's confirmation of the converse effect's magnitude		
1883	Röntgen and Kundt detect converse piezoelectricity by changes in double refraction (first observation of electro-optics)		
	Röntgen's study of the geometry of the direct and converse effects in quartz		
	Röntgen, J. Curie, and Friedel show that piezoelectricity and pyroelectricity are both effects of strain in quartz. **(M)**		
1884			Mallard's systematic presentation of piezoelectricity
1886			Duhem's thermo-electric theory of piezoelectricity
1887	Czermak's quantitative measurements and determination of quartz constant		Czermak's mathematical account for quartz
1889	Röntgen's discovery of the electric effect of torsion in quartz		
1890		Voigt's general phenomenological theory	
1891	Riecke and Voigt's confirmation of the general theory and first determination of quartz and tourmaline constants		
		Pockels's theory of the converse effect and electro-optics	Riecke's molecular theory of piezoelectricity
1892	Riecke and Voigt's second determination of quartz and tourmaline constants	Duhem's thermodynamic theory of piezoelectricity	
		Duhem's analysis of the reciprocity of the phenomena	
		Pockels's correction of Duhem's analysis	
1893		Riecke's thermodynamic formulation of piezoelectricity in tourmaline	Voigt's elaboration of Riecke's molecular theory and his own suggestion for such a theory
			Kelvin's models of piezoelectricity

(*Continued*)

Year	Experiment	Theory	
		Phenomenological-thermodynamic	Molecular/explanatory
1894		Voigt's theory of secondary phenomena with full thermodynamic formulation	
	Pockels's measurements of the direct electro-optic effect and determination of piezoelectric constants		
1896	Voigt's detection and measurement of permanent polarization in tourmaline **(M)**		
1898	Voigt's measurement of direct pyroelectricity in tourmaline (**M**)		
1898	J. Curie redetermination of quartz's constant (continued later)		
1901			Kelvin's atomistic explanation of piezoelectricity
1912	Röntgen's determination of quartz's constant		

TABLE A.2. ANNUAL PUBLICATIONS ON PIEZOELECTRICITY 1880–99

The table contains only publications in which piezoelectricity was a central subject, or longer publications that included major contributions to that field. It lists different communications about the same research but neither republication in another journal nor translations. The publication dates are not necessarily of the time the work was done.

Year	Contributors and number of publications	Total number of publication
1880	J. and P. Curie 3, Hankel 1	4
1881	J. and P. Curie 4, Lippmann 1, Hankel 1	6
1882	J. and P. Curie 2	2
1883	Röntgen 4, Kundt 2, Friedel and J. Curie 1, Mack 1	8
1884		0
1885		0
1886	Duhem 1	1
1887	Duhem 1, Czermak 1, Hankel 1	3
1888	Czermak 1, J. and P. Curie 1	2

(*Cont.*)

(*Continued*)

Year	Contributors and number of publications	Total number of publication
1889	J. Curie 1, J. and P. Curie 2	3
1890	J. and P. Curie 1, Röntgen 1, Voigt 1	3
1891	Riecke 2, Riecke and Voigt 1, Voigt 1, Pockels 1	5
1892	Riecke 1, Riecke and Voigt 1, Pockels 1 , Duhem 2, Somigliana 1, Hankel and Lindenberg 1	7
1893	Riecke 1, Voigt 1, Pockels 1, Kelvin 4	7
1894	Voigt 1, Pockels 1	2
1895	Hankel and Lindenberg 1	1
1896	Voigt 1	1
1897	Voigt 1	1
1898	Voigt 1, Hankel 1	2
1899	Nachtikal	1

TABLE A.3. CONTRIBUTORS TO PIEZOELECTRICITY BY NATIONAL DIVISION 1880–98

The table presents the contributors to the study of piezoelectricity by the countries in which they worked and the period in which they published (in the pretheoretical or the theoretical phase). The years indicate dates of publication of papers on piezoelectricity. Names in parentheses indicate the places where the scientists worked.

	France	Germany	Britain	Italy
pre-theoretical phase	J. and P. Curie 1880–90 (Paris, Montpellier) Lippmann 1881 (Paris) Friedel 1883 (Paris) Duhem 1886–87 (Paris)	Hankel 1880–98 (Leipzig) Röntgen 1883–90 (Giessen, Würzburg) Kundt 1883 (Strasbourg) Mack 1883 (Strasbourg) Czermak 1887–88 (Strasbourg)		
Total number of publications	17	13	0	0
Theoretical phase	Duhem 1892 (Lille)	Voigt 1890–98 (Göttingen) Riecke 1891–93 (Göttingen) Pockels 1891–94 (Göttingen) Hankel and Lindenberg 1892–98 (Leipzig)	Kelvin 1893 (Glasgow)	Somigliana 1892 (Pavia)
Total number of publications	2	21	4	1

TABLE A.4. MAJOR THEORIES SUGGESTED FOR PIEZOELECTRICITY

The table does not include models or explanations that yield one of the other theories mentioned, such as Riecke's molecular theory. For these models the reader should consult Table 3.1 (above p. 101), which compares the various explanations suggested for the phenomenon.

Theory	General/ particular	Agreement with early observations to 1883	Agreement with Röntgen's torsion exper.	Inclusion of the converse effect	Molecular	Thermodynamic	Mathematical
Curies (1881)	For tourmaline but understood as more general	+	−	−	+	−	−
Duhem (1886)	General	−	−	−	−	+	+
Czermak (1887)	For quartz	+	−	+	+	−	+
Voigt general	General	+	+	−	−	−	+
Pockels (1891)[a]	General	+	+	+	−	−	+
Duhem 1892	General (specific equation for quartz only)	+	−	+	−	+	−
Riecke 1893	For tourmaline	+	Irrelevant	+	−	+	+
Voigt 1894	General	+	+	+	−	+	+

[a] As a complement of Voigt's 1890 theory.

TABLE A.5. DISCOVERIES OF THE EFFECTS OF CONVERSION IN CRYSTALS

Each cell indicates first discovery of the effect in the row on the magnitude in the column in crystals, e.g., cell row-Heat, column-Electric polarization notes that the effect of heat on electricity (pyroelectricity) was discovered in 1756 by Aepinus.

	Electric polarization	Temperature differences	Strain	Optical behavior
Electric tension		Predicted: Thomson (1878). Detected: Straubel (1902)[a]	Predicted: Lippman (1881). Detected: J. and P. Curie (1881)	Röntgen (1883) Kundt (1883)
Heat	Aepinus (1756)		From antiquity	Not detected
Stress/pressure	J. and P. Curie (1880)	From antiquity		Brewster (c. 1815)

[a] Rudolf Straubel, "Versuche über den elektrokalorischen Effekt beim Turmalin," *Göttingen Nachrichten*, 1902: 161–164. The priority of this work is mentioned in Pockels, "Pyro and Piezoelektrizität," (1905), p. 791.

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