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.

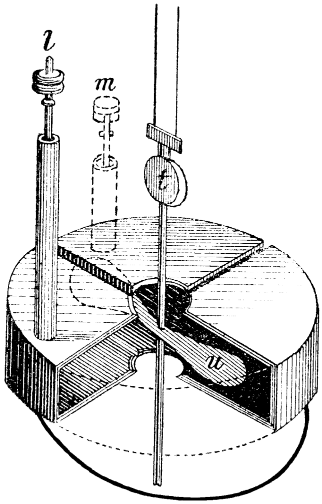

Figure 1.1: Thomson's quadratic electrometer: the two opposing quadratic sections are electrically connected and isolated from the adjacent quadrats. Usually, they are connected to two different parts of the circuit through l and m, while the needle u is electrified by a third source. The needle is suspended 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.

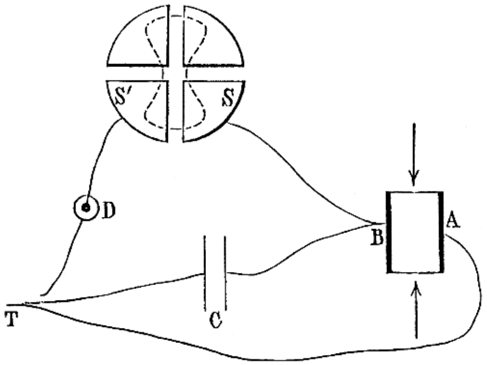

Figure 1.2: Curies' experimental measurement of piezoelectric constants (from "Phénomènes électriques," *Journal de Physique*, 1 (1882): 248.).

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 Minèralogique*) 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:

$$dm = cdx + hdp \tag{1}$$

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.

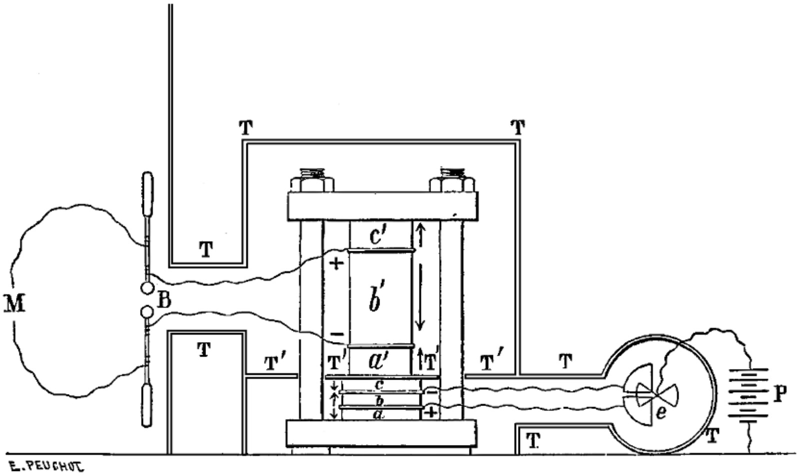

Figure 1.3: The first experiment to detect the converse effect (from J. and P. Curie, "Dilatation électrique du quartz").

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.

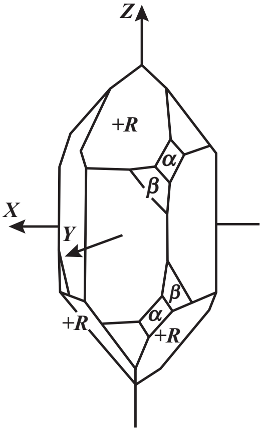

Figure 1.4: A quartz crystal with the three axes (adopted from Voigt, *Lehrbuch der Kristallphysik*).

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

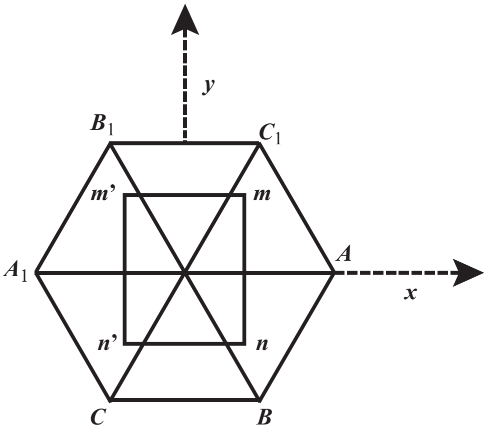

Figure 1.5: Quartz cut perpendicular to the principle axis (xy cut). AA_1 BB_1 CC_1 are its electric axes.

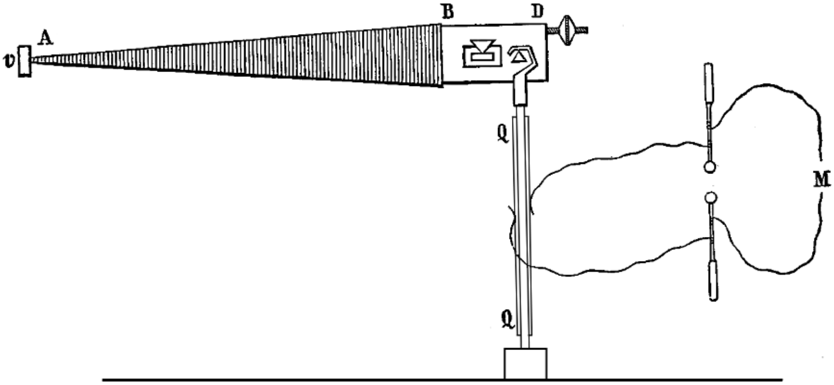

Figure 1.6: The Curies' second experiment to detect converse piezoelectricity, employing the transverse effect in quartz (from J. and P. Curie, "Dilatation électrique du quartz").

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.

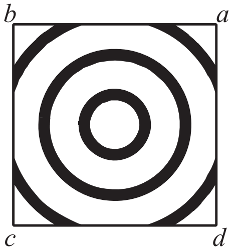

Figure 1.7: Circular rings of polarized light in quartz free from electric field.

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

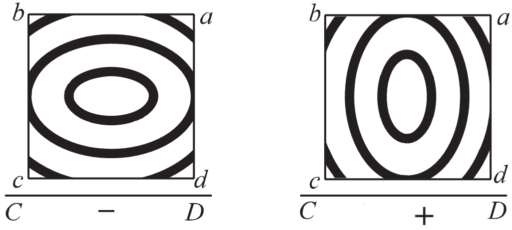

Figure 1.8: Elliptical rings due to electric field in the direction of a polar axis.

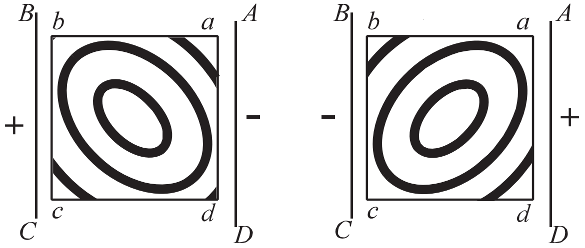

Figure 1.9: Elliptical rings due to an electric field in the *y* axis (perpendicular to a polar axis).

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.