

CHAPTER 2

THE ROAD TO THE DESCRIPTIVE THEORY

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

CZERMAK'S RESEARCH ON QUARTZ

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

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

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

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

Czermak’s theory

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

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

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

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

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

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

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

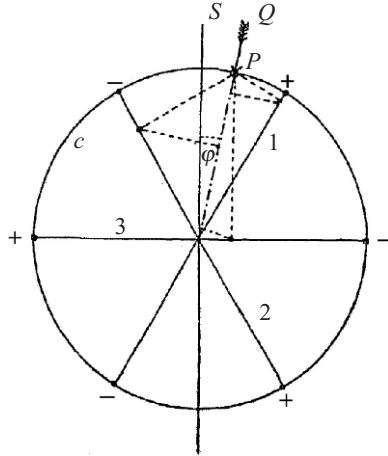


Figure 2.1: Czermak's figure for the voltage in the direction P due to pressure in the same direction. 1, 2 and 3 are quartz's polar axes (from Czermak, "elektrische Verhalten").

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

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

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

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

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

Experimental examination

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

⁵ Ibid., pp. 1228–29. This equation is valid when $0 \leq \varphi \leq 60^\circ$.

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

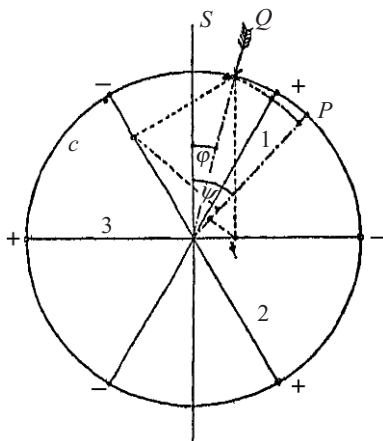


Figure 2.2: Czermak's figure for the voltage in the Q direction due to pressure in the P direction. 1, 2, 3 are the polar axes (from Czermak, "elektrische Verhalten").

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

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

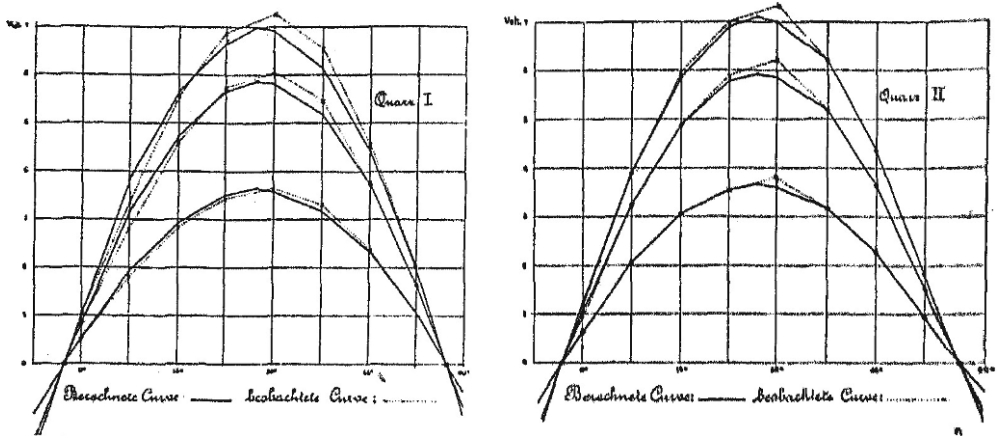


Figure 2.3: Czermak's comparison between curves computed by theory (thick lines) and those drawn between observed values (dotted lines) for two specimens (from Czermak, "elektrische Verhalten").

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

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

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

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

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

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

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

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

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

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

Absolute measurement of the piezoelectric coefficient

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

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

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

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

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

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

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

¹³ I discuss this question in chapter 5.

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

¹⁵ On Kundt see above chapter I p. 46.

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

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

THE DISCOVERY OF THE ELECTRIC EFFECT OF TORSION IN QUARTZ

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

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

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

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

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

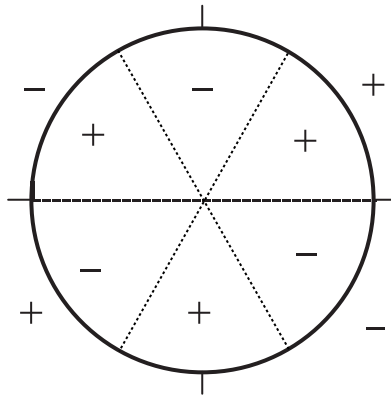


Figure 2.4: Distribution of electricity by pressure (shown inside the circle) and by torsion (shown outside the circle).

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

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

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

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

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

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

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

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

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

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

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

VOIGT'S GENERAL THEORY: MOTIVES AND BASIC ASSUMPTIONS

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

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

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

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

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

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

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

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

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

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

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

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

Voigt's piezo- and pyroelectric theory disregards the ultimate source of the phenomena. It assumes that both are effects of crystal's deformations but refrains from any further assumption on how these deformations induce electric effects. In particular, it refrains from any molecular assumption. Voigt made two objections to the assumption, basic to the molecular explanations, that all the phenomena originate in contraction and expansion along specific polarized axes. The first could have been raised already in 1881, and with supporting experimental evidence in 1883. Some

crystal species, including quartz, cannot be electrically polarized under uniform pressure, but only under nonuniform pressure. The fact, which has been known since 1883, showed that these crystals cannot be permanently polarized as required by the molecular hypothesis. On the other hand, this fact follows from considerations of the crystals' symmetry.²⁹ The second objection concerned Röntgen's latest experiment, which showed that a deformation, like torsion, which does not cause contraction or expansion generated electricity in quartz. Thus, the hypothesis that the phenomena can be reduced to contraction and expansion is invalid, and so (though Voigt does not mention them) are the molecular suggestions based on this hypothesis (pp. 5–6). Voigt suggested that any deformation can induce polarization.

THE ROOTS OF VOIGT'S EMPLOYMENT OF SYMMETRY³⁰

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

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

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

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

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

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

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

Neumann on symmetry

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

The French molecular school

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

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

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

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

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

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

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

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

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

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

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

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

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

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

For Pasteur, the optical activity of amyl alcohol demonstrated the asymmetry of its molecules. This activity, he believed, must originate in asymmetry of a primitive molecular group in the reactants that was preserved during chemical reaction. Since no reactant of the alcohol was a possible candidate, Pasteur conjectured that the alcohol is a product of a living agent that produces the asymmetry. That was the key for his celebrated experimental identification in 1857 of a new living agent of fermentation, responsible for the production of amyl alcohol. His view that any fermentation is caused by organic germs originated in that study. For him asymmetry was tightly connected to optical activity, which was more prominent in his thought during that time.⁴⁸ Pasteur's reasoning reveals two hypotheses, first that asymmetry must originate in asymmetry and second that living organisms are the only agents that can produce asymmetry. Considerations of symmetry, thus, played an essential role in the discovery of the organic agents of fermentation. Pasteur's first hypothesis was common in Haüy's tradition⁴⁹; his second was more original. In the following years he elaborated and promoted it, making asymmetry a central discriminator between "living matter" and "dead matter."⁵⁰

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

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

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

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

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

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

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

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

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

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

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

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

⁵⁴ *Ibid.*, p. 266.

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

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

Neumann's students

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

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

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

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

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

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

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

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

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

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

THE GENERAL THEORY: SCOPE AND RESULTS

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

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

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

The basic piezoelectric laws of all crystals

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

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

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

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

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

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

For quartz he found:

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

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

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

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

The effects due to various stresses

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

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

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

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

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

$$b' = -p'_x C \sin^3 \varphi, \quad c' = -p'_x C \sin^3 \varphi \quad (7)$$

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

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

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

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

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

Pyroelectricity

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

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

In the study of nonuniform heating, Voigt derived the relations between pressure and temperature change that had been stated and empirically found at the beginning of the 1880s by Jacques and Pierre Curie, and later also by Friedel, and Röntgen (above p. 56). Voigt studied the special case of heating or cooling from the center and from the circumference of a circular quartz plate, examined in the laboratory by Röntgen. Unlike Röntgen, he was not satisfied with qualitative argument but derived a mathematical expression for the charge density that accounted quantitatively for the division of the circumference to six electric zones observed by Röntgen (pp. 84–5). Voigt claimed that Röntgen's pyroelectric experiments in quartz "contain an important confirmation of the theory, while this, in turn, provides the first complete explanation of the observations" (p. 94). Voigt, we have seen, showed how the results of the previous piezoelectric experiments of Jacques and Pierre Curie, Czermak, and Röntgen derive from the general theory. Yet, he claimed that further experimental work was needed to prove it. He called for experiments on the various effects that the theory describes in different classes of crystals, including those that were not examined before (pp. 7–8). He himself would later be responsible for quantitative examinations

of the theory. However, no such experiment would be carried out to test its prediction relating various effects and classes.

CONCLUDING REMARKS TO PART I

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

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

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

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

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

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

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

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

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

⁷² On Mallard see above chapter 1 p. 61.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

⁷⁹ Voigt, “Über die Elasticitätsverhältnisse der Krystalle,” id., “L’état actuel de nos connaissances sur l’élasticité” on 289. On his piezoelectric theory see chapter 3 below.

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

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

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

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