CHAPTER 5

EMPIRICAL WORK IN THE 1890s

Experiments played a major role in the development of the piezoelectric research in the pretheoretical phase. The formulation of Voigt's general theory followed empirical findings and it was designed to account for the experimental results. Unlike this theory, however, the *later* theoretical developments during the 1890s, which I described in the previous two chapters, were virtually independent of the experiment. Among the issues they raised, only the theoretical question about the relations between related phenomena like piezoelectricity and electro-optics invited experimental resolution. These relationships were first studied theoretically and later, as will be shown below, examined in the laboratory. Thus, while Voigt's 1890 theory shaped most experiments performed in the 1890s, the theoretical developments after its introduction had little influence on the experiments performed at the time. This is also true of the molecular theories, with the sole exception of Voigt's molecular theory, which motivated the construction of one experiment and was in the background of another.

Following Jacques and Pierre Curie's announcement of the discovery of piezoelectricity, there was much interest in the new phenomenon and experimental work on its properties commenced. The publication of Voigt's theory had a similar influence. However, this time the work was focused on theory; only few experiments were done. This might be surprising for anyone who thinks that the central role of experiments is to confirm or refute theories. Moreover, all the empirical tests of the theory were done at Göttingen, where Voigt had suggested the general theory, and were related to him personally. Still, one should remember that the theory had an empirical basis from its introduction in the experiments performed during the 1880s.

VOIGT AND RIECKE'S DETERMINATION OF PIEZOELECTRIC CONSTANTS

The confirmation of the theory

The only experiment constructed in order to test Voigt's general theory was performed by Voigt himself with his colleague Riecke in 1891. In this work they had taken upon themselves to not only confirm the theory but also determine the piezoelectric coefficients of quartz and tourmaline. Since the coefficients make sense only in the realm of the theory, this step displays a confidence in the validity of the theory. Their confidence in the theory was at least partly based on the agreement between its results and the empirical data collected during the 1880s, i.e., before its formulation. However, Riecke and Voigt wrote, "since the former measurements were conducted with no consideration of a theory and in many cases in only a *qualitative* way, they are not suitable for a completely satisfactory examination of the theory. It, therefore, remained to perform extended (*ausgedehntere*) quantitative determinations of several cases that were accessible (*zugänglichen)* to theoretical treatment and after calculating each substance's individual piezoelectric constants to compare them with the theoretical laws." They did this on tourmaline and quartz.[1]

Probably no one was better suited for this research than Riecke and Voigt. I have mentioned more than once their interest in piezoelectricity. Voigt's interest in his general theory is obvious. Since 1885 Riecke had done a few experiments on pyroelectricity and also exhibited theoretical interest in piezo- and pyroelectricity. The skills needed to confirm Voigt's theory were different from those required in examining unknown physical behavior as in Röntgen's experiments. In the former case one had to carry out exact measurements with crystals, a practice in which Riecke and Voigt had expertise. They exhibited a high degree of precision in their experiments and mastery of physical-mathematical techniques in analyzing their results. Voigt had performed experiments on elasticity of crystals since his student years, while Riecke carried out electromagnetic measurements from his early researches in 1871. Voigt and Riecke belonged to two different schools of German physics (Neumann and Weber), yet exact measurements in absolute units and the elimination of experimental error were regarded essential in both.[2] The friendly relationship between Riecke and Voigt (which was not the usual case with the relationships between the experimental and theoretical physicist in the German universities) facilitated their collaboration.[3]

Indeed Riecke and Voigt made much effort to get precise results and to eliminate experimental errors. For example, they concluded that they could not simply apply weights by a lever on the crystal they wished to press, since repeated readings for the same weights did not yield steady values (they attributed that to uneven distribution of pressure in such an arrangement). Instead, they devised a more complicated arrangement in which weights (W in Figure 5.1) were loaded in a pan of a balance. The pan was connected by a rigid vertical hanger to a small steel block (S), placed above the middle of the pressed surface on a brass plate covered with rubber. In this way they applied unidirectional pressure on rectangular crystal plates. One surface of the plate was connected to a Thomson's electrometer (EM—with its other side grounded)

---

[1] E. Riecke und W. Voigt, "Die Piëzoelectrischen Constanten des Quarzes und Turmalines," *Ann. Phy.* 45 (1892):523–552, on p. 524, my italics. Page references in parentheses in this section refer to this paper.

[2] Jungnickel and McCormmach, *Intellectual Mastery of Nature*, vol. 1, *passim* and Olesko, *Physics as a Calling*, *passim*. See there on Voigt's early works pp. 287–297. On Riecke's see Wiechert, "Eduard Riecke," p. 47. For a view of the two traditions similar to the one presented here see Darrigol, *From Ampère to Einstein*, p. 75.

[3] They were heads of two independent institutes, Riecke for experimental and Voigt for theoretical physics. This uncommon administrative arrangement probably contributed to their good working relations.

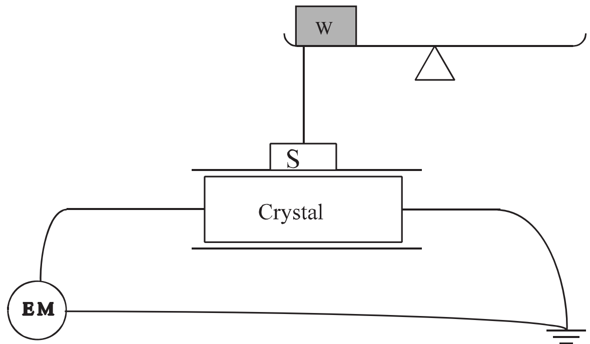

Figure 5.1: A schematic description of Riecke and Voigt's experiment (my reconstruction).

and the other surface to the ground (through a gas pipe).[4] The entire arrangement was set on a stable table in a glass box. A net of brass wire lined the inner part of the box and the surface of the table was covered with silver foil, so that the external electric field would not influence the apparatus (pp. 531–2). Riecke and Voigt measured the deviations of the electrometer needle due to the electrification of the crystals on an arbitrary scale. Like Czermak four years earlier, they compared these readings after each measurement to the deviation caused by a known electric tension. They used a "Clark cell" (1.435 V at 15°C), which was considered steadier and more reliable than a "Daniell cell," which Czermak had employed.

Their apparatus enabled them to load and unload weights and to measure the effects, assumed to be equal, of both increasing and decreasing the pressure. Between measurements, they probably connected both faces to the ground. This setting enabled them to make several measurements with the same pressure, reducing the influence of a single error. However, they noticed a deviation in the position of the electrometer needle between successive measurements. After deciding that the deviation was due to unavoidable damping and diffusion of electricity, they formulated a mathematical expression that corrected the reading of the needle. They confirmed it with 70 measurements of both loading and unloading (pp. 533–6). This sequence demonstrated their meticulous efforts to reach precision by eliminating experimental errors and their use of mathematical techniques to do so.

Previous quantitative experiments measured the effect of pressure in a direction that involved only one piezoelectric modulus. The confirmation of the general theory required the comparison of the effects of various situations in which more than one modulus was involved. For simplicity, Riecke and Voigt chose to apply unidirectional rather than more complicated pressures. Still, they had to apply them in various

[4] Gas pipes were used for grounding electric instruments since they were connected to the ground to protect them from lightning. Usually, like in this experiment, the gas pipe was also a convenient way to close the electric circuit (as was usually done by grounding), so that the electrometer measured the tension between the edges of the crystal. The arrangement when the examined face was the pressed one was somewhat more complicated.

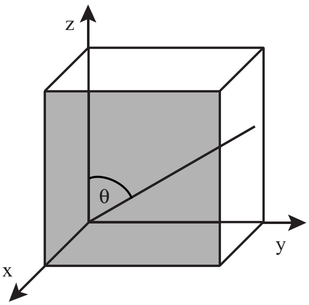

Figure 5.2: Pressure in Riecke and Voigt's experiment was applied along directions that form an angle with the z axis in the yz plane. The electrodes were connected to the yz planes—the shaded plane in the figure and the one parallel to it.

directions corresponding to the crystals' piezoelectric constants. For quartz, which has two moduli, equal pressures in five different directions in the same plane, perpendicular to a polar axis (the yz plane, see Figure 5.2) were sufficient. They applied these pressures on three bars of quartz cut from the same plate. Voigt had already used the same plate to determine quartz's elastic constants in 1887. The bars' long edges (from 11 to 17 mm) were at angles of 22.5°, 45°, 112.5°, and 135° from the principal (z) axis in the yz plane. Pressure of two-kg in weight was applied in the directions of the long edges, perpendicularly to the polar axis $-x$. The electric effect was always measured by connecting the yz face (i.e., perpendicular to the polar axis) to an electrometer. Comparing the reading of an electrometer with the reading of one cell, they calculated "an electric moment in Clark" $-m_x$. From the piezoelectric equation of quartz (Chapter 2. Equation (6)) they derived an equation that expresses the electric moment in terms of the two sought moduli and the geometry of the plate:[5]

$$-\frac{m_x}{p}\frac{q}{q_x} = -\delta_{11}\sin^2\theta + \delta_{14}\sin\theta\cos\theta \qquad (1)$$

where q is the area of the pressed face q_x that of the yz face, whose voltage was read, p the weight and y is the angle between the direction of pressure and the principal axis in the yz plane as shown in Figure 5.2.

In each direction of pressure they made three to six measurements and found the average value for the expression on the left side of equation (1). From these averages, they used the least squares method to calculate the values of the moduli in arbitrary "Clark scale" (they did not elaborate on this calculation and the mean deviation found by this procedure). They used these values, in turn, to calculate the theoretical predictions for induced electric tension in their experiment and to compare them with the observed values, concluding that the agreement "is satisfactory" (p. 539).[6] In

[5] The equation is valid only for the polarization in a polar axis, i.e. it can be applied only in this case when a surface perpendicular to that axis is connected to the electrometer.

[6] Indeed, the maximum deviation is less than 3% (0.191 calculated against 0.186 observed). Unlike the electric moments observed, the values of the moduli taken directly from different observations deviates

showing the agreement of equation (1) derived from Voigt's theory with the observations, they confirmed the general theory for the first time. Since former experiments examined only one piezoelectric coefficient in quartz (δ_{11}), this was the first quantitative examination of the dependence of the electric effect on the direction of the stress.

The measurements of tourmaline were somewhat more complex. Since it has four rather than two piezoelectric coefficients, applying pressure in different directions in one plane would not suffice to find the value of all its coefficients. Riecke and Voigt therefore measured eight different combinations of directions of pressure and the faces on which the effect was observed in four crystal bars.[7] This time, they did not develop a general expression for all the cases but compared each measurement with its specific theoretical expression. In each measurement, they expressed the potential in Clark units and found the average for each combination. These averages led to eight equations with four unknowns. The piezoelectric moduli were derived directly from this system of equations. In such a derivation, they could not use an error analysis method like the method of least squares. Instead, they showed that independent determinations of the coefficients led to similar results. However, they determined the value of one moduli (δ_{15}) only once, though they could have determined it twice. Instead, they determined the value another three times. This choice somewhat weakened the confirmation. Still they concluded that the agreement between their values "can be described as satisfactory."[8] Thus, their observations corroborated the relations deduced from Voigt's general theory and confirmed it. Still, the use of the method of least squares for quartz made the confirmation in that case more satisfactory (also by Riecke and Voigt's own standards) than that of tourmaline (pp. 539–44).

Riecke and Voigt confirmed the theory for only two species, which represent only two classes of crystals out of the 20 that, according to Voigt's theory, should show piezoelectric behavior. Apparently, they and others regarded this as satisfactory. Later, the theory was regarded as confirmed, as shown, for example, in the review articles of Riecke and Pockels. From the various cases studied in Voigt's general theory, Riecke and Voigt discussed only that of unidirectional pressure derived for a cylindrical bar. The prisms they examined were not cylinders but their dimensions enabled the use of the equations that Voigt had found for this case. Evidently, they saw no need for a confirmation of Voigt's predictions for various geometrical circumstances, since they

---

significantly from their mean value. For example a calculation of δ_{14} from one observation (either in 45° or 135°) with the found value of δ_{11} (from a direct measurement) deviates by almost 10% from its mean value given by least squares. The deviation has a smaller influence on the value of the expression displayed by the experimentalists since δ_{14} is significantly smaller than δ_{11} (pp. 537–9). They did not comment on the large deviation in the values of δ_{14}. This deviation did not weaken the confirmation of the theory (which accounted for the observations) but did weaken the determination of the coefficients.

7 As with quartz, they used crystal specimens that Voigt had already used for elastic experiments (this time in experiments that he performed in 1890).

8 The values of two moduli (δ_{22} and δ_{31}) vary in about 10% between their determinations. Yet since their values are one order of magnitude smaller the other two, an error of 1% in the values of one of the others can lead to an error of 10% in the smaller moduli. Thus, Riecke and Voigt could regard the confirmation as satisfactory. The deviation in the values of the small moduli is parallel to the deviation in δ_{14} of quartz whether the latter is calculated directly and not by the method of least squares (footnote). Riecke and Voigt, however, did not mention this similarity (or the deviation in the quartz's modulus).

were derived mathematically from the basic equations, whose confirmations were the subject of their research. This reveals a known and by then virtually universal confidence in mathematical deductions in physics.

German versus French methods of determination

The measurements in arbitrary units were sufficient for the confirmation of the piezoelectric theory. Determination of its coefficients in absolute units did not add to its confirmation but demonstrated that they are true constants of the crystals by comparing them with previous observations. Nevertheless, Riecke and Voigt regarded this determination as an important task of their piezoelectric experiment, an aim independent of the confirmation of the theory. As mentioned, determination of theoretical coefficients in absolute units was an important theme in the work of both.[9]

However, the determination turned out to be more complicated than they had expected. As in the previous measurements by the Curies and Czermak, voltage was the electric quantity read in the experiment. Voigt's piezoelectric moduli, however, related elastic pressure or stress to polarization. Polarization was known to be equal to the charge surface density, which could be calculated from the voltage (in absolute measurements) and the capacity of the system. Like their predecessors, to this end they used an external condenser, whose capacity was calculated from its dimensions, but in a somewhat different way from both Czermak and the Curies. Voigt and Riecke connected the condenser to the apparatus and compared voltage readings due to the piezoelectric effect with and without the condenser, finding the ratio between the capacity of the system in the two states. From their ratio and the capacity of the condenser, they calculated the capacity of the apparatus (p. 534, 544–5). With its value, they found that $\delta_{11} = 5.31 \times 10^{-8}$ statcoulomb/dyne for quartz and $\delta_{33} = -4.70 \times 10^{-8}$ for tourmaline.[10]

Their experimental method was closer to Czermak's than to the Curies'. In measuring coefficients of quartz and tourmaline, the Curies determined only the electric charge due to an additional weight on a known condenser by a null deviation of an electrometer needle (above p. 21). Their method bypassed the measurement of the capacity of the system and translation of a deviation of an electrometer dial to voltage. Czermak and Riecke and Voigt, on the contrary, measured and accounted for all the magnitudes involved in their experiment. They measured the capacity of the system rather than bypassing it, and they read a deviation in the electrometer dial and compared it with a standard cell rather than perform a "null experiment." Czermak tried to account for all parts of the apparatus, but less rigorously. For example, in measuring the capacity of the system, he neglected the small capacity of the electrometer (p. 98). Moreover, Riecke and Voigt reduced systematic and accidental sources of errors mathematically. They accounted for the divergence from the correct position of their electrometer dial (an error that did not arise in the Curie's setting); they carried

[9] See the references in note 2.

[10] E. Riecke und W. Voigt, "Die Piëzoelectrischen Constanten des Quarzes und Turmalins," *Göttingen Nachrichten*, 1891 (No. 8; 11 Nov.): 247–255, on p. 254.

out observations under several conditions; and they used the method of least squares for error analysis. Riecke and Voigt's experiment was more meticulous than that of the Curies as they examined every detail of their apparatus.

Yet, whether it was really more accurate was a matter of opinion. They surely agreed with most of the German measuring physicists that their experiment would yield more precise and accurate results. German measuring physicists thought that one should account for external influences on experimental results rather than bypass them. Among the students of Neumann like Voigt, this was even clearer. "Neumann and his seminar students did not believe that redesigning an instrument could reduce all errors. In their view, it would be futile to pursue the material perfection of instruments over the accurate mathematical determination of errors."[11]

A controversy in 1860s about the appropriate way to reach exact and valid results between Carl Pape, another member of Neumann's school, and the influential French experimentalist Henri-Victor Regnault illustrates their attitude. Would accuracy be achieved by noting all errors and accounting for them through mathematical analysis, as Pape claimed, or through elimination of errors by an experimental arrangement that would permit their neglect, as Regnault claimed? Regnault considered mathematical techniques unsuitable for the examination of experiments because they were too far from the realities of the laboratory. "With his so-called *methode directe* Regnault tried to obtain data directly by varying experimental apparatuses and arrangements *a priori* rather than calculating errors of experimental data *a posteriori*." For him, the skill and mastery of the experimentalist produce reliable and accurate results, evident through their consistency. While Pape favored carrying out experiments under various conditions, Regnault preferred comparing results of experiments performed under the same conditions. Errors, except accidental errors, should be reduced in the experiment itself by modifying the setting, the apparatus and the target according to the judgment of the experimentalist, not in its data analysis. In the words of Jean Baptiste Dumas, "A severe critic, he allows no causes of error to escape him; an ingenious spirit, he discovers the art of avoiding all of them."[12] Pape pointed out that Regnault was and would be unable to avoid significant experimental errors. Pape thought that by accounting mathematically for errors, a scientist could reach more accurate and valid results than in an attempt to eliminate them. The scientist could not rely on the personal mastery of the experimentalist but on physical-mathematical analysis. Dörries noted that Regnault's "whole measuring enterprise became artistic to an extent where subjective judgment prevailed at the expense of objectively reproducible measurements."[13]

---

[11] Olesko, *Physics as a Calling*, p. 302.

[12] Matthias Dörries, "Vicious Circles, or, The Pitfalls of Experimental Virtuosity," in Heidelberger and Steinle (eds.), *Experimental Essays - Versuche zum Experiment*, Baden-Baden: Nomos, 1998: 123–140, on p.124. Dumas is quoted in Hasok Chang, "Spirit, air, and quicksilver: The search for the "real" scale of temperature," *HSPS* 31 (2001): 251–286, on 274.

[13] Olesko, *Physics as a calling*, pp. 378–382; Matthias Dörries, 'Easy Transit: Crossing Boundaries between Physics and Chemistry in mid-Nineteenth-Century France' in C. Smith and J. Agar (eds.), *Making Space for Science,* Houndmills: Macmillan, 1998, pp. 248–262 on p. 260, quotation from "Vicious Circles," p. 137.

Pape and Regnault present two attitudes toward experimentation: a mathematical versus an artisanal approach. The former used common procedures in locating possible errors and reducing them; the latter employed more particular solutions to specific experimental settings and their modification. They resemble analytic and synthetic geometry. Nothing in the "artisanal" approach was intrinsically more artistic than synthetic geometry. Experimentation in both the approaches involved theoretical considerations and assumptions about the working of the apparatus, even if Regnault attempted to eliminate them. In the "artisanal approach" these were primarily applied in designing the experiment before its performance while in the "mathematical," primarily after it was performed.

Like Pape, Voigt and Riecke displayed a high degree of confidence in their analysis of experimental instruments and their systematic and accidental errors. Like him, they preferred the mathematical analysis of all the experimental components to bypassing measurements. Other German measuring physicists, which included most theoreticians, revealed the same tendency. Data analysis and mathematical theory of measuring instruments and their deviations were central to both Neumann's and Weber's schools. This centrality indicates that German measuring physicists trusted their method of analyzing complicated results more than experimental methods for bypassing complexities.[14] Czermak, who belonged to neither of these schools but was educated as a theoretical physicist in the German sphere, displayed a similar approach in his experiment. He, however, put less emphasis on error analysis. The Curies, on the other hand, proved themselves true and successful followers of Regnault. By appropriate design of their apparatus, they measured the sought magnitude almost directly, without a need for elaborate data analysis and mathematical elimination of error. Jacques Curie continued using this method (reaching excellent results) well after Riecke and Voigt's experiment. Pierre Curie continued to use it in other fields like radioactivity (below p. 214). This example suggests that French physicists were right in acknowledging Regnault's lasting influence.[15] Elisabeth Garber claims that the disciplinary borders between experimental physics and mathematics were more rigid and defined in France than in Germany and Britain. "Experimental physicists in France [she further claims] regarded their work as purely empirical and devoid

---

[14] For example, Friedrich Kohlrausch, who was an influential teacher of Riecke (Voigt, *"Riecke als Physiker," Physikalische Zeitschrift* ***16*** (1915), 219–221) considered calculation of the effect of the earth's magnetic moment necessary for exact measurement of electric resistance standards. "The British, aware of the difficulties involved [in the magnetic measurements], tried to develop alternative methods that would bypass it. Kohlrausch did not"). See Kathryn M. Olesko, "Precision, Tolerance, and Consensus: Local Cultures in German and British Resistance Standards," *Archimedes: New Studies in the History and Philosophy of Science and Technology*, 1996:117–156, p. 138. Olesko's work demonstrates the centrality of data analysis for German physicists in both Weber's and Neumann's schools. Olesko reveals differences between German and British attitudes towards practices of exact measurements. The examples of the Curies' experiment and Regnault indicate that the French were closer to the British than to the Germans in their preference for bypassing the complicated mathematical analysis of unnecessary influences.

[15] Chang, "search for 'real' scale," p. 273, Dörries, "Easy Transit," p. 260.

of all hypotheses."[16] The German measurements in piezoelectricity did not involve more hypotheses than the French, but clearly did apply more mathematics. If Garber is right about the status of mathematics in French physics, its consequences should be most conspicuous in quantitative measurements, as suggested by the example of piezoelectricity.

Determining the constants

Riecke and Voigt's results, presented to the Göttingen Society for Science on August 1, 1881, did not agree with those of the Curies. They were lower by 16% (for quartz, 5.31 compared to 6.32) and 13% (for tourmaline, 4.7 compared to 5.4) than the Curies'. In the published version of the communication, dated November 11, these results were given alongside those of the Curies, without any further comment.[17] Yet before they sent a more complete report of their experiment to the *Annalen der Physik*, dated "autumn 1881," they realized that the value calculated for the capacity of the system given earlier "was however surely too small" (p. 545). Therefore, their figures for the moduli were also too small.

The estimation of the capacity was too small, they explained, because shellac on the external condenser increased its capacity while it was not accounted for by the calculation. Moreover, the particular state of the condenser did not permit a theoretical calculation of the capacity. They had to find it experimentally. They used an electromagnetic method of alternating current suggested by Maxwell in his *Treatise of Electricity and Magnetism*.[18] Here, the capacitor was connected by a tuning fork to a battery that charged it and a galvanometer through which it was discharged. This method required a special series of complicated measurements to find the capacity of the external condenser.[19] With the new value for the condenser, Riecke and Voigt recalculated the capacity of the experimental apparatus (pp. 546–9). The long procedure

[16] Elisabeth Garber, *The Language of Physics,* p. 314.

[17] Riecke and Voigt quoted 6.3 and 5.3 respectively. I presume that they did not attribute to the Curies' experiment higher precision than that (the Curies themselves published a value of 6.32 in 1889). The error in the latter number is probably due to a simple mistake. Riecke and Voigt, "Die Piëzoelectrischen Constanten," *Göttingen Nachrichten*, pp. 254–55.

[18] Maxwell, *Treatise,* (3rd ed.) pp. 420–425.

[19] The tuning fork alternates between the battery and the galvanometer, acting as oscillating switch. At a certain frequency of oscillation (in their experiment, 31.47 times a second) the needle of the galvanometer is steady. To measure this frequency exactly, they used a special apparatus with photographic paper. The capacity is then expressed as a function of the resistance of the galvanometer, the frequency of steady current, and the ratio between the current that discharges the condenser and that in a "branch circuit" in which a resistance of 22,000Ω was connected to the battery. (The measurement of the current in the "branch circuit" actually indirectly gives the voltage of the cell, which is not expressed directly by the formula. In this way they measured the voltage of the pile rather than relying on their "book values" as the Curies did with the same kind of "Daniell cell.") The last two were measured in the experiment. They made about twenty measurements of the two currents with and without the measured condenser. In each case they calculated the capacity of the system. From these measurements, they obtained the mean values of the capacities of the "tuning fork circuit," and of the circuit without the condenser. The difference between those two values gave the capacity of the condenser.

required to determine the capacity is a good example of the effort needed for exact measurements.

Only after this lengthy procedure they could calculate the absolute magnitudes of the piezoelectric moduli of quartz and tourmaline. Their values were now little higher than those Jacques and Pierre Curie had found a decade earlier. For δ_{11} of quartz they found 6.45 versus 6.32; for δ_{33} of tourmaline, they found -5.71 compared to -5.4, all multiplied by 10^{-8}. This time, Riecke and Voigt stated that the smaller discrepancy "might well be especially due to that we took into our account loss of electricity that took place during the observation. In Messrs Curie's not the least remark relating to this is found" (pp. 549–50). In particular, they probably had in mind the corrections they made in the reading of the electrometer. Yet, their critique was not limited to a specific procedure. It also revealed their uneasiness with the brief and general descriptions of the Curies' experiments, in which only the end results, but not the values of the various observations, were given. In this they did not follow Regnault. Riecke and Voigt probably shared Wilhelm Weber's ideal of an experimental account. Weber argued that the "'surety and certainty of the result' was founded in good part on the investigator's thoroughness in reporting the experiment's instruments, how they were used, how the trials were performed and what changes were made, and how the data was taken and reduced."[20] The Curies' reports lacked this thoroughness and thus did not give German physicists the desired certainty.[21]

According to Riecke and Voigt, their earlier determination of the condenser's capacity was "surely too small" because the calculation disregarded the accidental shellac that increased its capacity. Thus, they implied that no external stimulus was required to convince them of the need to reexamine the capacity that was "surely" wrong. However, this was not obvious to them when first analyzing the results of the experiment. Even in a public announcement of its results, and in its later written version, they gave results based on "surely too small" capacity. Only a close reexamination of the apparatus, including the condenser, made it clear that the earlier values were wrong. A new set of measurements to replace those made on a mistaken premise was necessary. Evidently, a surface examination of the condenser was not part of the procedure that they applied in this experiment.

But why did Riecke and Voigt take the trouble to return to the laboratory and start inspecting apparatus that they had already checked, and from which they had even published experimental results? I think the answer lies in the disagreement with the earlier results of the Curies and, to a lesser degree, those of Czermak.[22] In spite of their greater trust in their own method, Riecke and Voigt did not dismiss the Curies' method and results—results confirmed, though unsatisfactorily, by Czermak.[23] The

---

20 Olesko, "Precision, Tolerance, and Consensus," p. 119.

21 The presentation of the Curie's results also leaves much to be desired by the historian, especially considering the absence of their laboratory notes.

22 The published sources are silent about the reason for the re-determination. I failed to locate any manuscript that illuminates the question.

23 Riecke and Voigt did not mention Czermak's determination, but they knew the paper (Voigt quoted results from it as early as 1890, Voigt, "Allgemeine Theorie"). They probably disregarded Czermak's result because they depended on his mistaken theory. Yet, despite the problematic determination of

higher accuracy that they attributed to their own method was not sufficient to account for the large gap of 16% between the results. The errors accounted for by their analysis were much smaller than this gap, which suggested a fault in one of the experiments. Since Riecke and Voigt could not examine the Curies' apparatus, they probably decided to reexamine their own. An error was indeed found in the value ascribed to the capacity. It is common to reexamine experiments and even to perform them again in cases of discrepancy with a theory. This was not the case here, since the piezoelectric theory was indifferent to the magnitude of the moduli. Here the results of an earlier experiment offered grounds for comparison and thus influenced the results of the later experiment.[24] It is unlikely that Riecke and Voigt would have noticed a little shellac on a condenser had their results agreed with those of the Curies or had the Curies not performed any previous measurements.

Pyroelectricity

Correcting the values of the moduli was important not only for the records and agreement with the Curies' results but also for inferring the existence of a genuine direct pyroelectric effect. Following others, Voigt assumed in his general theory that pyroelectricity is an electric effect of strain, due to thermal deformation of the crystals, rather than a direct thermal effect. Thus, the theory expressed the electric effect of temperature change as a function of the coefficient of thermal expansion and the piezoelectric constants in the relevant crystal classes (above p. 92). If pyroelectricity was only a secondary phenomenon of piezoelectricity, the constant calculated from these two coefficients would be equal to the one obtained from direct measurements. Riecke and Voigt compared the calculated constant from this experiment with the one obtained by Riecke from direct measurements on another specimen a year earlier. Since Voigt had already measured the elastic constants for the same tourmaline specimen in 1890, calculating the value of the piezoelectric constants from them and the moduli was straightforward (p. 550). The coefficients for the thermal expansion of tourmaline were determined by Pfaff in 1861, though on another specimen. From this they calculated 1.34 (statcoulomb/cm^2 per degree C) for the electric charge due to piezoelectricity caused by thermal expansion. Riecke's direct measurement led to an average value of only 1.13 for the total effect. Yet the results pointed out an additional second-order term, i.e., a term that was dependent on the square of the temperature. Adjustment of the value from 18°C, at which it was originally determined, to 28°C, in which the piezoelectric measurements were taken, raised the value to 1.23. Considering that a number of constants were involved in the determination of the theoretical value, they concluded that the agreement between the results confirmed the basic assumptions of the theory. In the future thus, they wrote, "one will have no need to distinguish between pyroelectricity and piezoelectricity as two different

Czermak, one could use the measurements that he did not need to modify (those on the plates with parallel surfaces) to reach results that are close to the Curies'.

[24] It should be clear that the contingent historical way in which the experimental results were attained does not alter the validity of the methods eventually used, or their results.

phenomena. Both have their common origin in deformations that occur inside the crystals." (p. 552)

Interestingly, the correction of the piezoelectric moduli did not change their conclusion that pyroelectricity is a secondary effect of piezoelectricity. They also found reasonable agreement with their earlier mistaken values, though these were lower by 20% than the corrected values. In their earlier report Riecke and Voigt calculated a lower value for the secondary pyroelectric effect of only 1.08. However, they still claimed that it agreed with Riecke's value, which this time they cited, without discussion, as 1.18.[25] In this publication they did not refer to any second-order term. The arrival at the same expected conclusion from two different sets of values revealed flexibility in analyzing a precise qualitative experimental result. Their conclusion is very close to the position that Riecke had taken already in 1885 and that Voigt adopted somewhat more cautiously in 1890. Perhaps the flexibility in interpreting the experimental results contributed to Voigt's retreat from the conclusive statement in his 1894 theoretical work (Chapter 4, p. 177) and his return to empirical examination of the existence of a direct pyroelectric effect in tourmaline in 1898. I will discuss his later experiment below.

HANKEL AND LINDENBERG'S EXPERIMENTS

Piezoelectric and pyroelectric phenomena were also studied empirically by W. G. Hankel. Hankel maintained his view that experiments on heating and pressing crystals involve three independent effects with different characteristics: pyro-, piezo-, and actino-electricity (Chapter 1). After his retirement from teaching at Leipzig University in 1887, Hankel continued his old research program on the pyroelectricity of crystals, publishing treatises 19 to 21 on his "electric researches" in the 1890s. In 1892 and 1895 he published two accounts of electric examinations of 13 different crystals, done in collaboration with a certain H. Lindenberg. Pyroelectricity, which he called thermoelectricity, continued to play the leading role in these experiments. In discussing each crystal they started with its pyroelectric behavior, then discussed its piezoelectric behavior and compared them with each other regarding the directions and kinds of effects. Perhaps the only change in the methods and aims of Hankel's experiments from the 1860s was the introduction of piezoelectric experiments in 1881. As in Hankel's previous experiments, Hankel and Lindenberg did not cut the crystals to plates or bars along polar axes or axes in which they were particularly interested, as others did, but left the crystal in an essentially natural form. In a few cases they cut a crystal to have a plane surface but then the "interesting" part of the mineral was left in its natural form (e.g., they cut strontium sulfate parallel to its hexagonal shape). They were more interested in the various properties of the crystals they examined than in general properties of pyro- and piezoelectricity. Thus, they discussed at length the

---

[25] Without their explanation for the cited value I can offer only speculations. The value they quoted might be an adjustment of Riecke's original value to 23°. This was also the value of one of the five specimens that Riecke had measured, so perhaps they decided that it is more reliable then other values. *Nachrichten*, p. 255.

specific forms of the specimens and investigated crystals of special form like twin crystals.[26]

Reading only Hankel and Lindenberg's papers, one cannot even guess that a theory of the examined phenomena was suggested a few years earlier. They made no reference to Voigt's general theory or to any of the theoretical discussions in the field. Examining many different crystals they could have contributed much to the confirmation (or refutation) of the theory by comparing their results with the theoretical expectations, as Riecke and Voigt did for quartz and tourmaline. Hankel and Lindenberg, however, did not make the measurements needed for such examination. Using crystals in their natural form they pressed them in directions dictated by their form and not by theory and did not make sure that the pressure was uniform. They indicated numeric results of the potential of the crystals on an arbitrary scale, which was compared with a known cell. However, this is not enough for an examination of the mathematical theory. To examine whether the coefficients given by the theory are sufficient to account for the phenomena, one needs to have more quantitative, systematic information about the directions of pressure and the measured surfaces and about the capacity in different settings. Clearly, this did not concern Hankel and Lindenberg, who did not relate their finding to the theory even when they could.

Two years later, Pockels indicated that two qualitative observations that they made on Rochelle Salt can be seen as a confirmation of the general theory. Their observations on the appearance of electric charge due to pressure in various directions were in accordance with its predictions.[27] Hankel and Lindenberg themselves indicated that crystals of the same classes show the same electric behavior. This observation supports Voigt's general theory. Yet, this assertion was not particular to Voigt's theory. The connection between the crystallographic and electric properties of crystals has been accepted since the work of Haüy a century earlier. That crystals of the same class should show the same kind of pyroelectric effect had already been assumed when Hankel had started his researches in the subject in 1839. Another of their experimental findings contradicted both Voigt's general theory and the assumption of workers in the field for decades. Hankel and Lindenberg found that pyroelectricity is not limited to hemihedral crystals. They observed a pyroelectric effect in potassium dichlorate, a crystal that has a center of symmetry. However, the observational results were not consistent; the side that became positive in most specimens became negative in others. Such behavior suggests that the phenomenon observed is either due to irregularities

[26] Wilhelm G. Hankel und H. (Heinrich?) Lindenberg, "Ueber die thermo- und piëzoelektrischen Eigenschaften der Krystalle des chlorsauren Natrons, des unterschwefelsauren Kalis, des Seignettesalzes, des Resorcins, des Milchzuckers und des dichromsauren Kalis," *Leipzig Abhandlungen* 18 (1892): 363–405; id., "Ueber die thermo- und piezoelektrischen Eigenschaften der Krystalle des brom- und überjodsauren Natrons, des Asparagins, des Chlor- und Brombaryums, sowie des unterschwefelsauren Baryts und Strontians," *ibid.,* 21 (1895):11–42. W.G. Hankel, "Ueber die thermo- und piezoelektrischen Eigenschaften der Krystalle des ameisensauren Baryts, Bleioxyds, Strontians und Kalkes, des salpetersauren Baryts und Bleioxyds, des schwefelsauren Kalis, des Glycocolls, Taurins und Quercits," *ibid.*, 24 (1898): 469–496.

[27] F. Pockels, "Ueber den Einfluss des elektrostatischen Feldes auf das optische Verhalten piëzoelektrischer Krystalle." *Göttingen Abhandlungen* 39 (1894) 204 pp. on p. 161.

in the specimens or to another electric effect. Such reasoning could justify the neglect of this result by later workers in the field. The marginal place of these researches, which were only published in the transactions of the Leipzig Academy, perhaps also played a role in this neglect. Hankel's continuous work on the electricity of crystals is an example of research that stagnated at a point in time—no later than the beginning of the 1880s—and was not influenced by later major developments in the field. His research became not only marginal but almost irrelevant to the scientific community.

POCKELS'S STUDY OF THE RELATION BETWEEN PIEZOELECTRICITY AND ELECTRO-OPTICS

Pockels studied piezoelectricity empirically in order to determine its relation to the related phenomenon of electro-optics, which is the effect of electric fields on double refraction in crystals. I have already discussed his 1890 theoretical treatment of the relation between the two phenomena, in which he showed that the joint effect of (converse) piezoelectricity and piezo-optics accounted qualitatively for electro-optics, but he left open the possibility of a direct effect. To decide whether such a direct effect existed, it would be necessary to examine whether the joint effects accounted quantitatively for the whole of the observed effect of electro-optics (Chapter 4, p. 152). The coefficients of the three phenomena and of elasticity had to be known for this experiment. A few years later Pockels took on the task himself, determining the values of the coefficients. He measured all the coefficients (except those of elasticity, which he took from the literature) on the same specimens to make sure that the results would not be influenced by differences between specimens of the same crystal, publishing his detailed results in 1894. He determined the three coefficients in question in absolute units. In such units the coefficients could be inserted into the same equation and compared. Exactitude was, thus, central to Pockels's empirical work. He presented a long discussion of the instruments of measurement and their theory. For example, he developed a mathematical expression for the variations of the electrometer dial to eliminate the error in its reading.[28]

The relations between the coefficients of the three phenomena were expressed according to their theoretical treatment by Pockels in 1890. For the empirical comparison he developed an expression for the value of the indirect electro-optic coefficient e'_{mn}, i.e., the optic effect due to piezoelectricity and piezo-optics:

$$e'_{mn} = \frac{1}{x_n} \sum_{1}^{6} a_{mh} \delta_{nh} \qquad (2)$$

where χ_n is the dielectric constant, a_{mn} the piezo-optic constant, and δ_{nh} the piezoelectric modulus. e'_{mn} are the coefficients that determine the effect of the electric moment on the refraction of light in the crystal according to Pockels's electro-optic

[28] *Ibid*. The discussion of the instruments is on pp. 13–29. Page references in parentheses hereinafter refer to this paper.

theory (Chapter 4, equation (2)). If the whole optic effect is due to piezoelectricity, e'_{mn} should be equal to value of the electro-optic constant—e_{mn} calculated from the observation. In the electro-optic experiments Pockels did not find e_{mn}, but rather its multiplication by the dielectric constant χ. Thus, the value of the dielectric constant did not enter the comparison and its measurement was therefore saved. On the other hand, Pockels needed to find the elastic coefficient, though it does not appear in equation (2). It was needed for the calculation of the piezo-optic constant, since the measurements were made in known stress, but the constant a_{mn} is relative to strain rather than stress. However, the elastic coefficients had been determined before and were known to be steady in various specimens of the same crystal.

The need to determine four different constants on the same crystal considerably diminished the number of species that Pockels could examine. "The crystals must not only be free from cracks, inclusions, and optical disturbances, but must also have large dimensions." In addition, the optical effect in the specific crystals should be observable. These constraints reduced the number of the crystals that he investigated to three: quartz, sodium-chlorate, and Rochelle salt. Even tourmaline was inappropriate for quantitative examination since optical measurements could not be taken due to the high absorption of light of Brazilian tourmaline. He tried without success to examine qualitatively a few other crystals (pp. 2–3). Pockels's difficulty in finding additional crystals that suited his experimental examination suggests one reason for the use of essentially the same crystals in these quantitative studies. That physicists were satisfied with a confirmation of the theory limited to a small number of crystal classes, was probably based at least partly on the technical difficulties in examining other crystals. These difficulties did not encourage other researchers to enter the field.

Pockels's experimental set-up for measuring the piezoelectric coefficients was similar to that of Riecke and Voigt. This was expected from a *privatdozent* at Göttingen who kept working connections with Voigt, his former teacher. Like his professors he measured deviations of the electrometer's needle and compared them with the readings of a Clark cell but not before he had adjusted the reading to the correct value by a mathematical expression he developed for the oscillations of the needle somewhat differently for each kind of crystal. The capacity of the system was again determined by adding an external air-condenser. Like Czermak, Pockels determined the capacity of the external capacitor theoretically by a method due to Kirchhoff. He did not need to use an experimental method like Maxwell's tuning fork (pp. 69–73, 131–2, 137–43).

Although the piezoelectric coefficients of quartz had already been measured, Pockels considered it worthwhile to remeasure the moduli's values on the same specimen on which he had measured the other constants, since he assumed that their magnitude might vary from one quartz specimen to another. Like Voigt and Riecke, he applied unidirectional pressures in the yz plane (perpendicular to their polar direction x), but only in three directions: in the direction of the y axis (this is a transverse effect) and at angles of 45° and −45° (Figure 5.3).

With such a small number of observations he could not analyze the data in a method like that of least squares but calculated the values directly from the expressions for the three pressures he applied. The piezoelectric equations of quartz (Chapter 2, equation

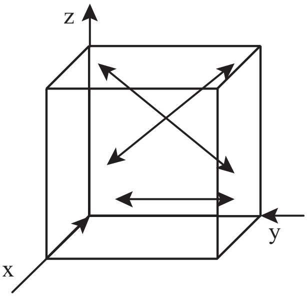

Figure 5.3: Directions of pressures in Pockels experiment with quartz. The arrows show the directions in which Pockels applied pressure, all in the *yz* plane.

(6)) provide for these three cases:

$$\frac{a_{90}}{p} = \delta_{11}, \quad \frac{a_{+45}}{p} = \frac{1}{2}(\delta_{11} - \delta_{14}), \quad \frac{a_{-45}}{p} = \frac{1}{2}(\delta_{11} + \delta_{14}) \tag{3}$$

where a_{90}, a'_{+45} and a_{-45} are correspondingly the polarizations due to pressures in 90°, +45°, and −45° directions. A simple manipulation led to the following expressions for the values of the moduli:

$$\delta_{11} = \frac{1}{3}\left(\frac{a_{+45}}{p} + \frac{a_{-45}}{p}\right) + \frac{2}{3}\frac{a_{90}}{p}, \quad \delta_{14} = \frac{a_{-45}}{p} - \frac{a_{+45}}{p} \tag{4}$$

Pockels calculated the values of the electric polarizations from those of the observed voltage and the capacity of the system. Inserting these values in equation (4), he got: $\delta_{11} = -6.27\times10^{-8}$, $\delta_{14} = +1.925 \times 10^{-8}$.

Yet equations (4), from which Pockels found the values of the moduli, are not unique expressions for the moduli and thus are not necessary. The value of δ_{11} could have been deduced directly from the polarization a_{90} or only from the other two measurements, or from any combination of the two. The weight Pockels ascribed to the various measurements is arbitrary. It does not reflect any obvious reason. Moreover, a calculation of δ_{14} from the value of δ_{11} (with either of the last two equations in (3)) gives a result that deviates by more than 10% from the value that Pockels found.[29] The value that Pockels found is a mean, but he did not justify it as such. He did not refer to this question. One could do a similar calculation with Riecke and Voigt's measurements. However, their use of the method of least squares to determine the value of the moduli made their determination superior to any arbitrary direct calculation, like that of Pockels. The latter justified the values he obtained by comparing the observational data to figures calculated with these values. He found an agreement within 4%. The procedure showed that the values are at least rough mean values (pp. 131–44).[30] Pockels's results agree with Voigt's general theory, but after Riecke and

[29] From eq. 3 one can get for example $\delta_{14} = \delta_{11} - \frac{2a_{+45}}{p}$. Inserting the value of δ_{11} from the direct measurement gives $\delta_{14} = 1.65. \times 10^{-8}$. A similar equation with a_{-45} gives a value of 2.2×10^{-8}.

[30] An alternative determination of the moduli, on the other hand, gives a deviation of almost 10%.

Voigt's more thorough confirmation in a similar situation, this corroboration added very little. Pockels was, however, not interested in the confirmation of the theory, which he considered confirmed, but in the value of the quartz moduli, which he needed to determine the relation between piezoelectricity and electro-optics. His results differ from those of Riecke and Voigt. The agreement for δ_{11} is satisfactory; Pockels's value is smaller by 2.9%. It is in excellent agreement with that of the Curies', a difference of less than 1%. The value Pockels got for δ_{14} is "considerably larger" than that found by Riecke and Voigt: 1.925 in comparison to 1.45, a difference of about 30%. Pockels did not explain this gap; he probably did not know how. Later measurements were closer to Pockels's, finding values even higher than his.

According to Voigt's theory, only shear stresses electrify sodium-chlorate, which has only one piezoelectric coefficient, by the equations:

$$a = -\delta_{14} Y_z, \quad b = -\delta_{14} Z_x, \quad c = -\delta_{14} X_y. \tag{5}$$

Pockels first derived the value of the modulus δ_{14} by an experiment that involved only the shear stress X_y. This was a very limited confirmation of Voigt's theory, since he did not examine whether the coefficients of the other stresses have the same value, as followed from the theory.[31] Pockels was probably aware of this limitation since he carried out additional experiments. The second experiment was not required for the determination of the constant (he did not even use it for that purpose). However, it was needed for the confirmation of Voigt's theory. In the second arrangement, he applied equal stress in the three relevant directions of stress (Y_z, Z_x, X_y) and measured their joint contribution. He compared the experimental results with their theoretical value assuming the value for δ_{14} previously determined, and found "satisfactory agreement" (pp. 73–8). The agreement was needed not only to confirm Voigt's theory, but also to justify the use of the value of the piezoelectric modulus in all directions in calculating the secondary piezoelectric optic effect.

While Pockels's measurements of sodium chlorate largely confirmed the general theory, the test of theoretical relations for Rochelle salt (also called Seignette salt—$KNaC_4H_4O_6\ 4H_2O$) was more problematic. Like sodium-chlorate it is electrified only by shear stress, but it has three independent coefficients rather than one. Its basic piezoelectric equations are:

$$a = -\delta_{14} Y_z, \quad b = -\delta_{25} Z_x, \quad c = -\delta_{36} X_y. \tag{6}$$

Pockels first tried to measure the value of δ_{14}. To this end, he applied pressure in the yz plane at an angle of about 45° from both axes and measured the electric moment—a in the x direction. However, he soon encountered unprecedented difficulties. First, he observed a much stronger electrical activity than before, about two orders of magnitude stronger than that shown by quartz. That was simply solved by the applications of smaller weights of little more than 100 g instead of 1000 g used in the previous experiments. Second, he found that after loading weights on the crystal the electrometer's dial did not stabilize but continued increasing in a way that precluded him from

[31] Pockels did not examine the assumption of linear effect as he applied the same weight in all measurements.

finding a correct time for taking the measurement. Thus, instead of a fixed value he could only state a range between 340 and 1180 $\times$ 10^{-8} (statcoul/dyne) for δ_{14}, concluding that its value was "left undetermined" (pp. 183–9).

The values that Pockels got for the moduli δ_{14} contradict the assumption that it is a constant. Still, he continued to refer to the coefficient as undetermined constant implying that one would eventually be able to determine its constant value. He suggested an ad hoc explanation for his inability to observe the true value of the constant and thus for the apparent contradiction with piezoelectric theory. He thought that the source of the continuous rise in electric tension measured by the electrometer might be in the high magnitude of the effect. Therefore, he conjectured that the connection to the ground and the electrometer do not supply enough electric charge to the metal plates attached to the crystal. In such a case, the tension between them is smaller than the inner electric field in the crystal, so a net electric field remains in the crystal. This field produces electric current (in the crystal) that raises the tension between the metallic plates. This explanation is not based on any special property of Rochelle salt but on its strong electric effect. Pockels himself showed reservations about his hypothesis. He still suggested an experimental arrangement to examine it. To the best of my knowledge, no one tried to construct it.[32]

The other two moduli of Rochelle salt did show a constant value. Pockels measured this directly in directions that involved only one modulus. He also measured the value of δ_{25} in another experiment in which he applied pressure in a direction that involved the value of $\delta_{14.}$ However, since the latter's value was undetermined, he preferred the value he found in the measurement that involved only δ_{25}. This is a sound decision, but it weakens the confirmation of the theory in Rochelle salt by reducing the number of different cases in which it was quantitatively tested. It left Pockels with measurements that according to the theory involved only one modulus. Still, the rejected measurement of a more complex effect provided qualitative confirmation of the theoretical relations between the piezoelectric and the crystallographic axes. His initial confidence in Voigt's general theory helped Pockels to regard his experiments and Hankel and Lindenberg's qualitative findings as a confirmation of the theory in Rochelle salt. He relied on the theory in his comparison between piezoelectricity and electro-optics (pp. 190–3).

The comparison between the compound effect of piezoelectricity and piezo-optics and the total electro-optic effect in Rochelle salt did not yield clear conclusions. One coefficient (e_{41}) was undetermined in both effects; the calculated and the observed values of another were very close; but in a third one the optic effects were of opposite directions. Still Pockels was cautious not to regard the last case as a proof of the existence of a genuine effect due to the smallness of the optic effect in this direction

[32] In hindsight one can conclude that Pockels probably observed for the first time an effect of ferro-electricity. Indeed δ_{14} is not constant in Rochelle salt. Though Pockels's experiment left an open question about the piezoelectric behaviour of the crystal, he did not suggest it as a subject for further research. Its experimental examination was resumed only in the 1920s by Joseph Valasek, who formerly worked with Voigt. A decade later physicists in the USSR realized that Rochelle salt crystal exhibits an unrecognized electric phenomenon that they named after the crystal "Seignette- electricity," which is today usually called ferro-electricity since it is analogous to ferromagnetism.

(p. 203). Quartz and sodium-chlorate provided clearer results. The secondary effect of piezoelectricity contributes only 1/12 of the total electro-optic effect in sodium chlorate (p. 82). In quartz it accounts for less than half of the observed electro-optic principal coefficient (e_{11}).[33] This is the same electro-optic effect that Röntgen and Kundt had regarded as a secondary effect of piezoelectricity. Thus, the research demonstrated "that electrostatic forces [fields] exert [*ausüben*] a direct influence on the transmission of light [*lightbewegung*] in piezoelectric crystals" (p. 204). Thereby, it justified Pockels's "positivistic" approach to study the phenomenon "without any hypothesis" about its sources.

This demonstration was based on the acceptance of Pockels's theoretical analysis of the phenomenon, whose piezoelectric part was based on Voigt's theory. Following Lippmann, his analysis tacitly assumed that piezoelectricity is reciprocal and thus that the piezoelectric constants are the same for both the direct and the converse effects. This is a crucial implicit assumption for Pockels since he measured the constant in the **direct** effect, and used these values in calculating a secondary (optic) effect of the **converse** effect. As I discussed in Chapter 4, the assumption of reciprocity was essential for any consideration of the relations between the converse and direct effect and it was implicit in the thermodynamic formulation. However, it was quantitatively confirmed only once by the Curies in 1882. No one else tried to measure the converse effect, or to examine in any other way that the phenomena are really reversible.[34] The observations of the multiplied effects of loading and unloading weights indicated that the direct effect itself does not suffer from any kind of hysteresis (*Nachwirkung*), but did not show the existence of a full Carnot cycle. Interestingly, I did not find any reference to this shortcoming in the literature. Probably due to experimental difficulties, Curies' confirmation, which Pockels cited (p. 84), satisfied the contributors to the field.

THE RELATION BETWEEN PIEZOELECTRICITY AND PYROELECTRICITY

Riecke and Voigt's 1891 examination of the relation between piezoelectricity and pyroelectricity did not provide conclusive results like those Pockels found regarding electro-optics. This was partly due to the nature of negative results. Demonstrating inexistence is harder than demonstrating existence. That an effect smaller than the experimental error existed was still a possibility. Such an effect was likely since the theoretical and the observed results deviated by about 10% and involved reinterpretation. Furthermore, unlike Pockels in the electro-optic experiments, Riecke and Voigt did not measure all the coefficients on the same specimen. Thus, as mentioned (above p. 177) in his 1894 theory, Voigt retreated to a more cautious position assuming the

[33] Piezoelectricity and piezo-optics account for about 72% of the value of the other constant—e_{14}, Pockels, "Einfluss des elektrostatischen Feldes," pp. 148–49.

[34] True, both are difficult tasks. Yet, one could examine, for example, whether the piezoelectric effect produces heat, which theoretically it should not.

possible existence of direct pyroelectricity. In addition to general cautiousness, like that Pockels showed about electro-optics, Voigt had molecular arguments in favor of a direct effect. According to his model, a change of temperature should induce electricity in two ways: one by the piezoelectric effect due to thermal displacement, the other by the thermal motion of the electric poles inside the molecules. Yet regarding the 1891 experimental results, in 1897 he was still cautious in public about the existence of a direct effect in tourmaline, writing that "probably, true pyroelectricity in that case does not exist."[35] A few months later he carried out new measurements to check the existence of a direct effect of heat. To this end he compared the joint effects of thermal displacement and piezoelectricity with the total pyroelectric effect. This time he measured all the relevant coefficients on the same specimen.[36] His findings supported his supposition that a genuine direct effect of temperature change exists, and thereby his molecular hypothesis. He left the last conclusion to the reader.

Voigt used the same tourmaline specimen on which he had already determined the values of the elastic and piezoelectric constants in 1890 and 1891. Unlike his and Riecke's experiment in 1891, this time he measured the thermal deformation constants, using a special instrument and method of a certain Hr. C. Pulfrich from the Carl Zeiss company. He found that the constants were considerably smaller (20 and 60%) than those given by Pfaff, which he and Riecke had used in 1891. Hence the secondary effect of piezoelectricity that they had calculated in 1891 was too high. With the new values for the thermal constants, he reanalyzed the data of the 1891 experiment. He now calculated 0.98 (statcoulomb/cm^2 per degree) for the indirect pyroelectric effect, instead of 1.34 in 1891. A comparison with the value that Riecke had found for the total pyroelectric effect -1.23 shows the existence of a direct effect. However, Voigt was not satisfied with that but measured again the total pyroelectric effect on four prisms of the same specimen on which he had made the other measurements. As in previous experiments he observed the electric tension on an electrometer. He compared these readings with the readings due to piezoelectricity with the same arrangement. Thus, he could show that the secondary piezoelectric effect accounts for only 80% of the total effect, before translating the results to absolute units. He used readings of the piezoelectric effect to translate the results into absolute units in terms of charge density, relying on the values that he and Riecke had determined for the piezoelectric moduli. Thereby, he bypassed a complicated measurement of the absolute charge on the hot tourmaline.[37] The value of the pyroelectric constant Voigt found was 1.21, a good agreement with Riecke's value. That leaves for what he called the true effect, i.e., direct pyroelectricity, a value of 0.234, which is above the experimental error. He therefore concluded that direct pyroelectricity exists in

[35] Woldemar Voigt, *Die fundamentalen physikalischen Eigenschaften der Krystalle in elementarer Darstellung*, Leipzig, Veit & Comp., 1898, p. 121.

[36] W. Voigt. "Lässt sich die Pyroelectricität der Krystalle vollständig auf piëzoelectrische Wirkungen zurückführen?" *Ann. Phy.* 66 (1898): 1030–1060. On the molecular consideration p. 1034.

[37] Voigt's method differed from Reicke's. To avoid heat current the latter had not measured the charge directly on the tourmaline but only its induction on an electroscope, from which he calculated the charge on the specimen, Eduard Riecke, "Ueber die Pyroelectricität des Turmalins," *Ann. Phy.*, 28 (1886): 43–80.

tourmaline, and might also exist in all similar crystals, i.e., crystals with a unique hemihedral (asymmetric) crystallographic axis. He repeated the claim, central to his theory, that the electric effect of temperature changes in the other crystals (like quartz) is in reality an effect of piezoelectricity.[38] Despite his efforts, Voigt's conclusions were not accepted as conclusive. In 1914 Röntgen still claimed that the existence of true pyroelectricity seems possible on theoretical grounds, but had not been experimentally established.[39]

Research on the relations between the kindred phenomena of piezoelectricity, pyroelectricity, and electro-optics revealed the fertility of measuring physics. Only precise quantitative measurements whose design and interpretation were based on the mathematical theory of the effects could tell whether the last two were genuine phenomena. In 1909, in a lecture about "the struggle for the decimal in physics," Voigt asserted that this kind of research raised questions that could be neither known nor resolved without precise measurements.[40] He did not mention the rather complicated examples from the study of piezoelectricity, but his and Pockels' experiments were excellent examples for his claim. Though Röntgen and Kundt had observed electro-optic effects as early as 1883, they did not realize that they had observed a new, genuine phenomenon. They did not even raise the question of whether such a phenomenon existed, as the theoretically oriented Pockels did seven years later. He later succeeded in answering this question with precise measurements. In the study of pyroelectricity, Voigt showed that a more thorough and accurate experiment in which all the variables were examined on the same specimen could reveal a phenomenon that earlier experiments had overlooked. Both examples display the exploratory power of exact experimental work in the tradition of Neumann.[41]

VOIGT'S EXAMINATION OF THOMSON'S HYPOTHESIS

Two years before his study of the relation between pyroelectricity and piezoelectricity, Voigt constructed an experiment in order to observe the internal polarization of tourmaline, first suggested by Thomson in 1860. According to Thomson's hypothesis, pyroelectric crystals, like tourmaline, have permanent internal polarization whose effect is compensated by charge density on the crystal surfaces. This hypothesis was adopted by the major contributors to the study of piezoelectricity. It led Jacques and Pierre Curie to the discovery of the phenomena, and it was a necessary consequence of the general theory. However, as Voigt pointed out, though changes in the polarization due to variations in temperature and pressure were measured in the laboratory,

---

[38] *Ibid.* pp. 1054–1058. Since considerations of symmetry ruled out the possibility of an effect due to uniform change of temperature, a contradictory assertion would contradict one of the two basic assumptions of the general theory.

[39] W.C. Röntgen, "Pyro- und Piezoelektricität Untersuchungen" *Ann. Phy.* 45(1914): 737–800.

[40] Woldemar Voigt, "Die Kampf die Dezimale in der Physik," *Deutsche Revue*, 34 (Juli 1909): 71–85.

[41] One the other hand Darrigol claims that Neumann's followers "hardly discovered any new effects." *Ampère to Einstein*, p. 75.

the natural electric polarization was not observed.[42] Although Voigt claimed that all students of the subject adopted the hypothesis, it was not the case. Duhem's early thermoelectric theory of pyro- and piezoelectricity, which I discussed in Chapter 3, is a good example of a theory that did not adopt the hypothesis. Riecke's pyroelectric experiments refuted Duhem's theory, and he retreated from it before 1892. Yet Duhem was not alone in rejecting Thomson's hypothesis and the opposition did not disappear after the publication of Voigt's theory. In his handbook on electricity, Gustav Wiedemann objected to Thomson's hypothesis, claiming that when a pyroelectric crystal, e.g., tourmaline, in uniform temperature is broken, its two halves do *not* show the existence of any free electricity, as should follow from the hypothesis. His objection implied that such an experiment had been performed, but he did not indicate who, if any, performed the experiment.[43] In 1901 Thomson, now Lord Kelvin, correctly pointed out that "Wiedemann mentions an experiment without fully describing it." He further claimed that "it would be very difficult to get trustworthy results by breakages [of tourmaline], because it would be almost impossible to avoid irregular electrifications by the appliances used for making the breakage." However, this is exactly what Voigt had done five years before Kelvin wrote this.[44]

Voigt used the same tourmaline specimen that had served him in the determination of the elastic and piezoelectric constants. He made sure that the crystal was free of external stress or variation in temperature. Then he cut it into four and connected the pieces' edges to a Nernst–Dolezalek's electrometer, all that in a quarter of a second, and read the tension on the electrometer. To translate the reading to absolute units he compared it to that due to pressure on the same prism, known by the piezoelectric moduli, as he would do two years later in determining the pyroelectric constants. For the internal polarization at 24°C, he found an average value of 33.4 (statcoulomb/cm^2) with deviations of about 10%. Compared with Riecke's value for the pyroelectric effect (1.23 statcoulomb/cm^2 per degree), this is not large natural polarization. Moreover, the pyroelectric effect of heating is in the opposite direction to that of the natural polarization. On the basis of these two values he wrote an equation for the total electric moment of tourmaline at any temperature as: $\mu = 33.4 - 1.32(\theta - 24)$, where θ is the temperature (in degrees Celsius). According to this equation, the natural electric moment of tourmaline should equal zero around 50°C and should have an opposite direction at higher temperatures. Voigt tried to measure the internal polarization at 60°C but succeeded in getting only a weak unmeasurable effect.

Voigt was aware that one can question whether the electric tension that he measured is really due to the internal electric moment of the crystal and not to another effect. In

---

[42] W. Voigt, "Versuch zur Bestimmung des wahren specifischen electrische Momentes eines Turmalins," *Ann. Phy.*, 60 (1897): 368–375 (first appeared in *Göttingen Nachrichten* 1896, Heft 3.), pp. 368–9.

[43] Wiedemann, *Die Lehre von der Elektricität*, 1st edition (1883), Vol. II, pp. 337–8. The objection appears also in the second edition of 1893. It is interesting to note that both Duhem and Wiedemann thought that the phenomena of both pyro and piezoelectricity are excited by heat.

[44] Kelvin, "Aepinus atomized," p. 560 in a footnote. As in other cases, Kelvin was ignorant of Voigt's work though it was published in the *Annalen der Physik*. He assumed that one could still rely on Canton's more than a century old results. However Canton merely observed that all the pieces of the same crystal maintain the same polar axis. Priestly, *History and Present State*, Vol. I. pp. 377–78.

order to defend his conclusion he negated other possible sources of the effect. First, he noted that the similarity of the results in the four pieces makes implausible an assumption that the electric effect observed was due to electrification in the process of breaking the crystal. The latter process is not uniform and thus its effects on four different pieces are highly unlikely to be close to each other. Second, the measured value is too high to be explained by conductivity of the air in such a short period. Moreover, he assumed that the true value of the polarization is a little higher than his results, since the conductivity of the air probably diminished the effect. Furthermore, he rejected possibilities of considerable electrification by friction or from a piezo- or pyroelectric effect because their electric effect in tourmaline is of an opposite sign to the one observed in the experiment.[45]

Voigt's interest in the permanent polarization of crystals went beyond his wish to confirm Thomson's hypothesis and thereby his general theory. He thought that the magnitude of the permanent internal polarization could shed light on the obscure question of the molecular structure and the process that produces the piezoelectric effect. Riecke's molecular theory requires the assumption of high inner polarization (much higher than that induced by piezo- and pyroelectricity), while no such assumption is needed in Voigt's model. The latter further assumed that in some attainable state of equilibrium the internal electric moment could equal zero.[46] Riecke's assumption of "exorbitant large permanent specific moments" [polarization] adds according to Voigt complications that have no justification in the observations, and it is "unpleasant."[47] Voigt left the reader to conclude that the experimental determination of the internal polarization supports his, rather than Riecke's molecular model.[48]

Thus, considerations of the molecular theory were a major motivation for Voigt's measurement of permanent polarization. They motivated also his search for direct pyroelectricity. However, they were not the experiments' sole motivation. The general phenomenological theory also supplied reasons for them. In measuring internal polarization, Voigt verified a consequence of the general theory. Although the existence of a direct pyroelectric effect was not a consequence of the general theory (neither is it a rigorous deduction from the molecular theory), Voigt inclusion of this effect in the mathematical theory of the subject followed from a cautious phenomenological approach. Pockels's phenomenological theory of piezo-optics and his examination of its direct effect show that molecular assumptions were not necessary for Voigt's study of genuine pyroelectricity. Notwithstanding the role of molecular considerations in this case, such a significant influence of the molecular models was exceptional in the theoretical phase of the piezoelectric research.

---

[45] Voigt, "wahren electrischen Momentes," pp. 370–5. Voigt apparently considered the piezoelectric effect of decreasing the pressure, which agrees in signs with that of pyroelectricity. One might suppose that cutting the crystal would reduce its inner pressure.

[46] On these theories see Chapter 3 pp. 122–129.

[47] *Ibid.*, pp. 369–70, quotation on p. 370.

[48] Riecke ignored Voigt's finding and the question of the magnitude of the molecules' polarization when he returned to his molecular suggestion in 1912. Riecke, "Zur Molekularen Theorie der Piezoelectrizität des Tourmalines."

In another sense, the detection of internal electric polarization is exceptional in that phase. This was the only piezoelectric experiment in the 1890s that aimed to directly observe a property, or even an entity, that had not been observed before. The existence of permanent polarization was not deduced from a comparison between precise measurements of kin phenomena but was observed directly. It was an experiment of discovery rather than of measurement. In this sense it better fits the experimental physics of Röntgen and Kundt that characterizes the pretheoretical phase. Precision was still important in the experiment in order to validate its results and to dismiss alternative explanations for their origins. Yet, the difficulties in such an experiment characterize experimental physics—how to break the crystal without electrifying it, how to eliminate external influences, and how to dismiss alterative explanations? Still, characteristic to his own tradition of measuring physics, Voigt was not satisfied with relative values but measured the electric moment in absolute units. Though he did not directly rely on any complicated mathematical device, he indirectly relied on these methods in using the values of the piezoelectric constants that he had measured and calculated five years earlier. The categories of experimental and measuring physics are useful analytical tools, but as this example indicates, physicists did not see themselves obligated to one or other of these.

THE MONOPOLY OF GÖTTINGEN AND THE PLACE OF PIEZOELECTRIC RESEARCH IN A WIDER CONTEXT

Empirical work on piezoelectricity in the 1890s was done almost exclusively at Göttingen University. The only experiments performed elsewhere were those of Hankel in Leipzig. However, these were outdated and did not take account of the recent theoretical developments. A decade earlier the geography of the empirical work on piezo- and pyroelectricity was very different. Experiments were carried out in Paris (by Jacques and Pierre Curie and Friedel), Strasbourg (by Kundt and his students), Giessen and Würzburg (by Röntgen), as well as in Leipzig and in Göttingen. Göttingen's "monopoly" of the piezoelectric experiments raises a historical question, which I would like to address in the following.

The experiments on piezoelectricity, and especially precise experiments, required means that were not available in many departments or institutes of physics. Such experiments demanded skills that mostly came with experience in similar kinds of research like that involving the use of crystals according to their crystallographic axes (e.g., in elasticity and optics). Not many physicists had such experience. Crystallographers, who had experience with crystals, usually lacked experience with precise electric measurements, which were also needed for these experiments. Furthermore, they rarely revealed much interest in such physical questions.[49] Instruments probably posed a minor problem, since most experiments required only standard instruments

[49] Questions of general electric and elastic behaviour like piezoelectricity attracted less attention from crystallographers, who were primarily interested in the structure of crystals and their characteristics. Even a text on *physical* crystallography like that of Groth of 1885 discusses briefly the electric

that were available in virtually all university laboratories. Crystal specimens for the experiments, however, were not available everywhere. Prisms of crystals cut in various directions were available for purchase from known firms for affordable prices for an average university laboratory.[50] However, larger prisms, which were needed at least for some experiments,[51] were more expensive. Voigt needed support from the Royal Scientific Society of Göttingen to purchase the "precious" tourmaline specimen on which he carried out four different experiments, including three on piezo- and pyroelectricity, during the 1890s. Pockels mentioned the help he got from Voigt in obtaining Rochelle salt crystals.[52] Apparently, the use of the same specimens for various experiments was not only a scientific but also an economic need. The use of the same specimen reveals another hindrance for newcomers, which is the cumulative character of some experiments. Voigt based part of his research on previous observations on the same specimens. Experimentalists in other places could not use Voigt's precise results in the same manner, since they were determined for the same specimen. While the relations between phenomena and constants that were found in Göttingen were regarded as universal, the precise values of certain coefficients were dependent on the specific specimen. Thus, in another laboratory one had to launch a new series of measurements on other specimens, as Pockels did in his electro-optic experiment.

These (in a wide sense) practical obstacles made experimentation in other places more difficult. Yet, they clearly did not prevent interested scientists from constructing piezoelectric experiments. Apparently, physicists were not interested enough in the field to make such an effort. Voigt observed that piezoelectricity as part of the general physics of crystals was "far from the problems that ha[d] occupied the larger number of physicists."[53] True as it is, Voigt's observation gives only a partial picture of the interest in piezoelectricity. In the pretheoretical phase the field attracted experimental and theoretical work from quite a few physicists. In the theoretical phase, contributions to the subject were confined neither to scientists preoccupied with the physics of

properties of crystals and dedicates only one paragraph to piezoelectricity; Paul Groth, *Physikalische Krystallographie.*

50 Crystal from "Steeg und Reuter" company (which supplied Röntgen with his crystals) costed 3–30 Marks a piece (of a few millimetres), while a larger quartz prism costed 15–75 DM (Groth, *Physikalische Krystallographie*, pp. 695–99). The average annual budget for equipment in Germany circa 1900 was a little less than 4,000 DM (Forman, Heilbron and Weart, "Physics Circa 1900," pp. 58–66, especially table c.2.).

51 Large crystals enable the use of the piezoelectric theory's relatively simple equations for unidirectional stress. With the equipment of the period applying an exactly unidirectional pressure in a precise direction on small crystals bars (of a few mm) is very difficult. Moreover, in such cases surface effects become too strong and do not permit the use of the theoretical equations which do not account for any surface effects. In addition, larger crystals facilitate the application of greater pressures that produce greater electric tension, and thus make the measurements more reliable. Larger crystals become requisite when one cuts a crystal specimen to a few (necessarily smaller) prisms in order to compare the pressure in various directions.

52 Voigt thanked the Göttingen Society in 1898 ("Lässt sich die Pyroelektricität auf piëzoelektricität," p. 1034). In breaking the tourmaline specimen two years before, Voigt explained that "except the preciousness of the materials," [i.e. the tourmaline] the experiment does not entail difficulties (Voigt, "specifischen electrischen Momentes," p.370); Pockels, "Einfluss des elektrostatischen" p. 161.

53 Voigt, "Rede," p. 39.

crystals nor to Göttingen (though much originated from that university). The field also received attention in handbooks and more tellingly gained official recognition with a prize that Jacques and Pierre Curie received in 1895 for its discovery.[54]

These facts indicate that piezoelectricity attracted more attention from physicists than Voigt suggested and that experimentalists refrained from working in the field at the second phase due to other factors. One can point out at least two important factors that preclude work on the field: the kind of laboratory work it offered and the conclusions one might have drawn from it. Kundt and Röntgen may be taken as examples of physicists who left the subject. Both performed experiments aiming at observing expected piezoelectric phenomena and discovering new ones in the pretheoretical phase. Testing theories and accurate measurements were neither central interests nor a special expertise of experimental physicists like them. In their laboratory work they were attracted to unexplained phenomena about which experiments could reveal new properties, more than to phenomena that were already accounted for by a detailed mathematical theory.[55] Experiments like those of Riecke, Voigt, and Pockels were unlikely to attract experimental physicists like Kundt.[56] Not surprisingly, these experiments were done by physicists who were identified with measuring rather than with experimental physics; experimental physicists did not participate in the experiments of the theoretical phase.[57]

Thus, measuring physicists would have been better candidates for the experimental study of piezoelectricity in the theoretical phase. Yet, no measuring physicist outside of Göttingen was engaged with piezoelectricity in the 1890s.[58] Göttingen's physics community had a direct interest in the validity of the general theory, which was conceived in it. For others, piezoelectric experiments did not promise much. Voigt's general theory was not controversial. It was a theory of what Thomas Kuhn called "normal science" based on substantial grounds in the general physics of crystals and in previous experiments. The known phenomena, moreover, yielded to this theory. Therefore, its test was expected to confirm the theory, and thus to add very little to the knowledge of the world. This was even more so after Riecke and Voigt confirmed it for

---

54 The Curies received the second biannual "prix Planté" from the French Academy. Hurwic, *Pierre Curie*,p. 44.

55 Yet at a later period (in the 1910s) Röntgen carried out also exact measurements of pyroelectric and piezoelectric constants, Röntgen, "Pyro- und Piezoelektricität," and below.

56 Of course many contingent causes were involved in determining the empirical research of each physicist. For example, from 1895 Röntgen was fully occupied with the study of X-rays, and needed no other reason to leave piezoelectricity for the time being. He returned to it in the second decade of the 20th century. Another example is Jacques Curie's leaving Paris in 1883 for Montpellier, which probably contributed to draw a practical end to his and his brother's contribution to the piezoelectric research. Still, I maintain that such contingent factors did not determine the fate of the research programmes examined in this study.

57 Hankel and Lindenberg should be identified with the experimentalists, but as explained, though performed after the introduction of the general theory, their experiments belong to the pre-theoretical phase.

58 Jacques Curie might be regarded as an exception, since he continued carrying out measurement of quartz's coefficients probably also then. However his results were published only in 1910 and more importantly it is difficult to characterize him - a lecturer for mineralogy in Montpellier, as a measuring physicist in the common (German) sense of the term.

two cases. Had one failed to confirm the theory, its empirical test would have attracted much attention and excitement. Since that was not the case, its confirmation was not a very exciting procedure for one who had no direct interest in the theory; yet it still demanded high skill and much work. Obviously, Voigt himself and his colleagues had such an interest. Ironically, the high precision of the piezoelectric measurements made further research even less attractive, since it suggested that considerable improvement on their values would not be possible. The practical obstacles, the marginality of piezoelectricity in physical research and the lack of known technological implications of the field, with the low probability of observing an unaccounted phenomenon, also made piezoelectricity unattractive for measuring physicists.

Göttingen did not become a center for the study of piezoelectricity only by default. The conditions in Germany in general, and at that university in particular were better suited than those in other places for such work. At the institutional level a professor in a German university could employ many resources, both financial and human, in pursuit of his research program. The dependence of students, assistants, and *privatdocenten* on the director of the institute enabled him to draw more forces to his work.[59] In the pretheoretical phase Kundt used his institute in Strasbourg to promote the experimental study of crystals' electric properties using his powdering method. No less than eight researchers in his institute worked on related questions in the second half of the 1880s.[60] Neither Riecke nor Voigt directed a similar collective effort in Göttingen. Yet, Pockels's work originated from his dissertation under Voigt on a subject that was close to his supervisor's interests, and it continued to be connected to the latter's theoretical and experimental work during the first half of the 1890s, when he was an assistant and *privatdocent* at the university. Still, the study of piezoelectricity in Göttingen benefited more from the conjunction of the interests in the subject of the two university professors than from the structure of German physical institutes. Their common interest in the subject surely encouraged its research.

Riecke and Voigt's common interest in the subject was not totally accidental but reflected a preoccupation with exact measurements that characterizes German physics. The combination of a mathematical theory with exact measurements was stronger in Germany than in other countries. Due to this combination German physicists were good candidates for the execution of experiments that required both mathematical and observational expertise. Moreover, Göttingen, or more exactly its physicists, was especially suited for such study. Voigt and Riecke succeeded the two traditions that excelled in precise measurements, those of Franz Neumann in Königsberg and of Gauss, Weber and Kohlrausch in Göttingen. These traditions ascribed merit to precision in experiments based on reliable instruments and even more on mathematical accounts of all possible experimental errors.[61] This ideal of exactitude can be found in

[59] On the junior German scientists as "the disciplined research army of the German professor" see Forman, Heilbron and Weart "Physics *Circa* 1900;" the term is quoted from p. 53.

[60] Most of the experiments at Kundt's institute dealt with pyroelectricity. For the experiments that used its dusting method see Chapter 1 note 112. Czermak's experiments were also connected to this research.

[61] On the combination of mathematical theory and exact measurements in these traditions and in Germany see Olesko, "Precision, Tolerance, and Consensus" and Garber, *The Language of Physics*. On Neumann and his seminar see Olesko, *Physics as a Calling*.

the piezoelectric experiments carried out in Göttingen.[62] However, since the research program in Göttingen was directed by only two individuals, it is difficult to attribute an understanding of their actions to traditions and general characteristics of German physics alone. One should consider their specific areas of interest and scientific attitudes, especially their previous work on crystals that attracted them to the study of piezoelectricity in the first place, as I did in examining their motivations for individual researches. According to this perspective, Voigt's personal fascination with the physics of crystals seems the crucial factor that made Göttingen rather than another (probably German) institute the center of piezoelectric research from 1890 onward.

RÖNTGEN'S AND J. CURIE'S LATER DETERMINATION OF QUARTZ'S PIEZOELECTRIC CONSTANT

After Pockels's determination, physicists continued measuring quartz's piezoelectric constant. The exact value of the constant attracted special interest due to the use of "piezo-quartz" in sensitive electric measurements of charge and current. Already in their first publication of the quartz principal piezoelectric constant (δ_{11}) in 1881, Jacques and Pierre Curie had suggested its use as an instrument for electric measurements. During the 1880s, with the help of instrument makers they improved their invention, making it applicable also for the measurement of current in addition to charge. Jacques employed the device, known as "piezo-quartz," to measure specific induction and conductivity in dielectric crystals in his 1888 dissertation.[63] In 1898 Marie Curie employed the "piezo-quartz" in the first quantitative study of radioactivity, and it then became a central tool in the laboratory of Marie and Pierre Curie.[64] The "piezo-quartz" made possible the employment of the method of "null deviation" in these studies. In this device a known voltage due to a charge generated by piezoelectricity from the quartz balanced an unknown electrical tension induced by the electric process under study, be it conductivity of crystal or radioactive rays. The use of the transverse piezoelectric effect in long and narrow plates made the apparatus sensitive to a very small charge. Clearly, Pierre Curie maintained his preference for the null method, which enables "measuring an *absolute value* of the quantity of electricity." Marie Curie joined in her husband's preference for that method, which involved little mathematics but required experience and skill. As they remarked about maintaining the needle at the zero point continuously as the charge

---

[62] The combination of physicists skilled in complicated mathematics with interests in phenomena that appear in the laboratory (which was not unique to Göttingen) might be a partial explanation for the centrality of that university also in the theoretical contribution to piezoelectricity.

[63] J. Curie "Quartz piézo-electrique," in *OPC*, pp. 554–563.

[64] Pierre and Marie Curie, "Les nouvelles substances radioactives et les rayons qu'elles émettent," *OPC*, pp. 374–409, on pp, 375–76. Marie Curie, *Traité de radioactivité*, Vol 1, Paris: Gauthier-Villars, 1910, pp. 96–106. M. Curie, "Rayons émis par les composés de l'uranium et du thorium,"*Comptes rendus* 126 (1898): 1101–1103.

increases, "with a little practice one acquires the precise dexterity necessary for this operation."[65] Such an attitude is clearly artisanal rather than mathematical.

The values of Marie Curie's radioactive measurements after 1898 suggest that Jacques Curie had already redetermined the value of quartz's piezoelectric constant before that year (but after 1893). Still, the use of quartz for electric measurement and probably also the new study of radioactivity was behind his new determination of the constant. The results of his measurements and their description appeared only in Marie Curie's book on radioactivity in 1910. The text indicates that Jacques Curie continued measuring quartz in the first decade of the twentieth century.[66] He measured the piezoelectric constant of the transverse effect, the same one used in the "piezo-quartz balance." That his determination was closely associated with Marie Curie's research on radioactivity is shown by the similarity between their experimental arrangements, as a comparison of the schematic figures of the two readily reveals (see Figures 5.4 and 5.5).

In his later measurements, Jacques Curie modified the experimental arrangement employed by him and his brother in 1881, based in the same basic idea of electric balance (Chapter 1, p. 21). Apparently, he regarded this method as more suitable than the "mathematical." He connected the battery and the crystal to the same side of the electrometer, and grounded its other side, keeping its needle at zero, rather than connecting the two to opposite sides of the electrometer as was done in the brothers' early determinations. One face of the quartz (Q in Figure 5.4) was grounded, the other (P) connected to the electrometer, a known cylindrical plate condenser (with a guard ring) (A) and via a commutator to the earth. The condenser's other plate (B) was connected to a battery of 10 known "Weston cells" (cadmium cells), invented in 1892 and more reliable than both the "Daniell cell" previously used by the Curies and the Clark cell used by later experimentalists. While AP was grounded, a weight was loaded on the crystal and induced a charge q on P due to piezoelectricity; due to the voltage of the cells, a charge q' was induced on A. These are totally independent of each other. Then a commutator simultaneously disconnected AP from the earth and connected the other plate of the condenser (B) to the ground instead of the battery, while the weight was unloaded from the piezo-quartz. The electrometer's needle would stay at the zero point only if the total charge on the conductor AP was zero, i.e., when $q = q'$. The charge q' is calculable from the voltage of the battery and the capacity of the condenser, known from the condenser's geometry. By varying the weight, Jaques Curie found the

---

[65] M. and P. Curie, "Les nouvels substances," p.375, and footnote on p. 376. They further claimed, with some exaggeration, that "the measurement is independent of the sensitivity of the electrometer." Yet the more sensitive the electrometer the smaller the change needed to move the needle from the zero point. Röntgen later discussed the sensitivity of the electrometer in such a measurement, which is high but still limited, as in any other measurement.

[66] On J. Curie's experiment see M. Curie, *Traité de radioactivité*, Vol 1, pp. 104–105. J. Curie probably did not publish the results himself. Marie Curie referred to "the newest" measurements of J. Curie. In earlier publications M. and P. Curie did not mention the new values. Yet, in 1910 Marie Curie repeats the values for radioactive measurement from 1900, which are almost identical to those of 1898 (there is no systematic difference between the two sets). M. Curie, "Rayons émis par les composés de l'uranium," p. 1102; M. & P. Curie "nouvelles substances radioactives," p. 377. In 1890 Jacques and Pierre Curie quoted the older value for the constant. Lord Kelvin published their short pamphlet after meeting Pierre Curie in 1893 without further comment, Kelvin, "Piezo-electric Property of Quartz," p. 321.

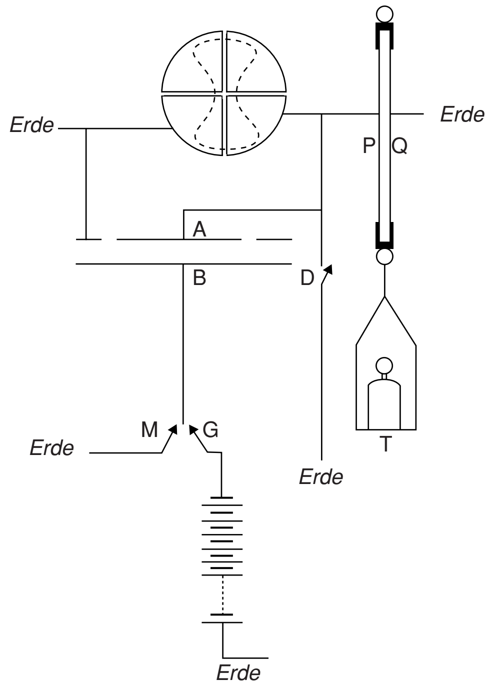

Figure 5.4: J. Curie's experiment for measuring quartz's piezoelectric constant (from the German translation of M. Curie, *Traite de radioactivité*).

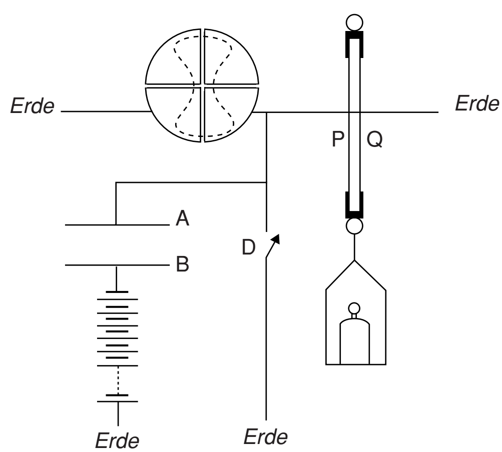

Figure 5.5: M. Curie's experiment for measuring low electric currents induced by radioactive pulverized materials spread on the inner side of B (from the German translation of M. Curie, *Traite de radioactivité*).

weight needed to leave the needle at zero, i.e., the weight needed to induce a known charge by the piezoelectric effect.[67] From measurements on several specimens, until 1910 he determined a value of 6.90×10^{-8} (statcoul/dyne), equal to the current value. Later experts attributed the higher value of Jacques Curie's result to more attention to the apparatus (improved insulation) and the target specimens (purity of the specimens and their orientation) rather than to improvements in the method of measurement.[68]

Wilhelm Röntgen also considered it helpful to have "a trustworthy (*sicher*) value" for the quartz piezoelectric constant due to his interest in measurement of another phenomenon. Like Jacques Curie in the 1880s, he was interested in the conductivity of dielectric crystals. In particular he studied the influence of X-rays on their conductivity. Also like Jacques Curie, Röntgen preferred the null method in this study. He showed in detail that the deviation of the electrometer needle, which other methods employed, suffers from uncontrollable fluctuations.[69] Therefore, he employed the Curies's "piezo-quartz" and their apparatus. Unfamiliar with Jacques Curie's latest measurement,[70] Röntgen turned to a new determination of quartz's principal piezoelectric constant (δ_{11}).

Röntgen exhibited much care in preparing the samples of the experiment in order to avoid experimental errors. He employed an optical method to measure their dimensions. He made sure that their orientations are like those assumed, and that they are well isolated.[71] For the determination itself he first employed a "less reliable" method, in which the deviations of the electrometer due to a load applied in a transverse direction (y axis) on the quartz specimens were compared to those due to a "standard cadmium element" (Weston cell). The crystal was connected to the experimental system designed for the measurements of conductivity, whose capacity Röntgen had already measured. With the latter value and the normalized reading of the electrometer he found very close values for the piezoelectric coefficients of the three crystal plates examined 6.85 and twice 6.86×10^{-8} [statcoul/dyne]. It is "very conspicuous," Röntgen noted, that these results disagree with the earlier values for the constant (of 6.27 to 6.45×10^{-8}).[72] He "discover[ed] neither in the method, nor in the performance of the measurements an error, that could cause the considerable

---

67 *Ibid.*, Marie Curie does not comment on the reasons for the modification of the experimental design. One advantage of the new design is in eliminating any oscillation of the needle. In the earlier arrangement oscillations were inevitable since the electrometer could not have been connected simultaneously to the cell on one side and the crystal and the condenser on the other.

68 Cady, *Piezoelectricity*, pp. 216–219.

69 W.C. Röntgen "Über die Elektrizitätsleitung in einigen Kristallen und über den Einfluß der Bestrahlung darauf," *Ann. Phy.* 41 (1913): 449–498, quotation on p. 473. Since the measurement of feeble current is a continuous process, one cannot compare the reading of the electrometer during the measurement to the deviation due to a standard cell (as was done in experiments on piezoelectricity).

70 As mentioned, J. Curie's results were buried in Marie Curie's book on radioactivity. Röntgen was privately informed only later by Voigt about Curie's measurements, about which Voigt himself had been notified by Marie Curie. W. C. Röntgen, "Pyro- and piezoelektrische Untersuchungen," *Ann. Phy.* 45 (1914): 737–800, footnote on p. 799.

71 Röntgen, "Elektrizitätsleitung in einigen Kristallen," pp. 474–479.

72 *Ibid.*, pp. 480–82. Röntgen mentioned the results quoted above except for that of J. Curie, of which he was ignorant, and a measurement by F. Hayashi from 1912 that lead to the value of $6.31. \times 10^{-8}$.

difference between the earlier values and mine." Nevertheless, he could not dismiss an "unfounded" (*nicht begründt*) doubt that an error had fallen in the value given to the scalar deviation of the electrometer.[73]

To remove any doubt and to obtain "more accurate values," Röntgen carried out an additional set of measurements with the very same "null method" of the Curies. Interestingly, his arrangement is almost identical to Jacques Curie's later experiment (Figure 5.4). As in Curie's experiment, the side of a quartz plate covered with silver foil (P) and a condenser's plate (A) were connected to an electrometer (whose other side was grounded) and to the ground. Then they were disconnected while the other side of the condenser was disconnected from the cadmium cells. The only difference in the experiment was that Röntgen loaded the weights on the plate after it had been disconnected from the ground, rather than stressing the quartz while P is grounded as in Curie's experiment. In Röntgen's arrangement, the electrometer would stay at the zero point only if the charge in the system exactly balanced the tension induced by the piezoelectric effect, in other words, when the charge due to the cells equals the charge induced by piezoelectricity. The value of the charge is directly given from the known tension of the reliable cell and the capacity of the condenser, calculable from its geometry. Röntgen noted that the null method enabled high precision. A change of 0.2 g generated a visible deviation of the electrometer, while he employed weights of about 300 g. This leaves an observational error of less than 0.1%.[74]

This high precision allowed Röntgen to seriously examine a deviation of 0.3% between values derived from different measurements on the same specimen with varied distances between the condenser plates. Thereby, he discovered a systematic error in the values taken for the distance between the condenser plates (needed for calculation of capacity), which he initially determined directly by an optical instrument (Abbe's thickness gauge). He corrected the systematic error by mathematical determination of the constant required to be added to the value of length in order to reach agreement among the values derived from different measurements on the same specimens. The elimination of the systematic error increased the average value of the constant by about 0.5%, and brought it closer to those of his earlier experiment. While the detection and elimination of error were done in this case by mathematical analysis, Röntgen pointed out another possible source of error that could be neither detected nor eliminated after performing the experiment. He suggested that a gap might exist between the silver foil and the crystal. Such a gap would reduce the value of the constant detected. In order to eliminate this source of error, he carried out a new series of measurements in which he silvered (*versilbern)* the three specimens previously examined, once again employing the null-method. Indeed, this procedure led him to a value of 6.94×10^{-8} [statcoul/dyne], higher by about 1% than the previous one and very close to that obtained by Jacques Curie.[75] As mentioned, Röntgen did not know of Curie's result so he found his results significantly higher than earlier ones (Table 5.1). Discussing possible sources for this disagreement, he concluded that it

[73] *Ibid.*, p. 483.
[74] *Ibid.*, 484–486.
[75] *Ibid.*, 487–490.

Table 5.1: Comparison of the six experimental determinations of piezoelectric coefficients

	Curies'	Czermak's	Riecke and Voigt's	Pockels'	Röntgen's	J. Curie's
Crystals and coefficients measured	Quartz (δ_{11}), tourmaline (δ_{33})	Quartz (δ_{11})	Quartz (δ_{11}, δ_{14}), tourmaline (δ_{15}, $\delta_{22}, \delta_{31}, \delta_{33}$)	Quartz (δ_{11}, δ_{14}), Rochelle salt (δ_{14}, δ_{25}, δ_{36}), sodium-chlorate (δ_{14})	Quartz (δ_{11})	Quartz (δ_{11})
Value of quartz's δ_{11} (in statcoul/dyne $\times 10^{-8}$)	6.32	6.27	1st 5.31 2nd 6.45	6.27	1st 6.86 2nd 6.94	6.9
Number of different settings by which it was determined	2	2	5	3	2	1
Measurement of system's capacity	No	Yes	Yes	Yes	1st yes 2nd no	No
Determination of a capacitor's capacity	Theoretical	Theoretical	1st theoretical 2nd experimental	Theoretical	Theoretical	Theoretical
Voltage reading	Null experiment—needle at zero	Compared with a Daniell cell	Compared with a Clark cell	Compared with a Clark cell	1st compared with a Weston cell 2nd null experiment	Null experiment
Elaborate statistical analysis of the results	No	No	For quartz	No	Yes	No

originated in experimental flaws in the previous experiments. He suggested that they might arise from mistaken orientation, lack of homogeneity in pressing the crystal, existing deformations in them, an underestimation of the capacity or [electric] tension (*Spannungen*), failure of isolation or from fluctuations in the value of the Clark cells. "All these flaws, [he concluded,] . . . would have reduced the value of k [the piezoelectric constant] found."[76]

Thus, Röntgen explained his higher values by his attention to various sources of error in preparing the apparatus and the target. His meticulousness marked his approach in almost every aspect: the isolation of the condenser, the correct orientation of the quartz plates, the measurement of their dimensions etc. Apparently, Jacques Curie employed similar thoroughness in his measurements.[77] Röntgen's determination was carried out over a long period. The early measurements were performed during the winter of 1911–12, those with the null-method in the summer of that year, and the last one with the silvered specimen probably only toward the end of that year. Röntgen could have carried out the measurement with silvered plates from the beginning and saved himself additional work. Apparently, the possibility of this gap occurred to him only later. As with Riecke and Voigt's determination of the constant, the long history of Röntgen's determination (until it "ended") is rooted in the disagreement between his and earlier results. Had they agreed, he would have probably been satisfied with his first "less reliable" determination using a comparison to a standard cell. Had he suspected in advance that he would find a considerable deviation, he would have probably employed the more reliable null method. The experiment also had its own dynamics. When analyzing the results, examining them and continuously reflecting on the experiment, Röntgen considered additional sources of error.

In retrospect, Röntgen's first set of measurements based on the reading of an electrometer reading were accurate enough. They deviate from those obtained by the null method by no more than 0.3%, practically below the experimental error. Their difference from the final value is rooted in the later elimination of an error in the target (due to a gap between the crystal and the foil), which is independent of the method of measurement. Nevertheless, Röntgen saw a need to repeat the determination of the constant with the null method, which he considered more reliable. He trusted more the null method, which bypasses corrections of the electrometer reading and complicated calculations of the capacity of the system. That he did not apply the null method at first suggests that its application was more complicated and time-consuming. It required more care in conducting the experiment itself. Marie and Pierre Curie mentioned the dexterity needed in such experiments. In Röntgen's arrangement, similar to Jacques Curie's, skill was needed to quickly disconnect and connect the different components of the apparatus between the two stages of the experiment. Like the Curies, Röntgen preferred the null method over others in additional studies. Yet,

---

[76] *Ibid.*, 492–493, quotation on p. 493. Among other possibilities Röntgen raised the assumption that Voigt's theory did not account well for the phenomena. So the value of the coefficient for the transverse effect was not equal to that of the longitudinal effect. However that seemed to him implausible.

[77] This meticulosity is suggested by the value that J. Curie attained for the constant, his return to the determination and the high number of specimens that he examined. As mentioned he did not publish a description of his experiment.

Röntgen also employed the "mathematical" method, which characterized German theoreticians. Although he did not share their view that it leads to more certainty, he found it valid and useful enough to employ it. Moreover, in analyzing the "artisanal" null-method experiment, Röntgen employed mathematical manipulation to reduce error. Still, to reduce another error he returned to an "artisanal" approach, in which he manually changed the connection to the target. In viewing null method experiments as superior to experiments that need much mathematical error analysis, the German experimental physicist Röntgen placed himself closer to the French experimentalists than to the German theoreticians. His work, however, suggests that a combination of the two approaches was evolving at the beginning of the twentieth century, in addition to separate use of the two in different experiments by the same scientists. Combining the two approaches Röntgen enjoyed advantages of both in eliminating experimental error. Mathematical analysis alone reduced an error occurring in a careful manual measurement of the distance between the condenser plates, while the use of the null method in the same experiment bypassed major sources of error. Of course, mathematical analysis could not eliminate an error originating in a gap between the specimens and silver foil. Manual work is needed in every experiment. So, Riecke and Voigt, for example, like Röntgen, needed to prepare their targets before any mathematical analysis. Mathematics was used also in the "artisanal" approach. Still, among the experiments discussed here, only Röntgen's really combined the two approaches. That he, rather than another scientist, carried out the combination is not completely accidental. Due to their working connection with their theoretical colleagues, German experimentalists were the best candidates to combine the two traditions.[78]

CONCLUSIONS: EXPERIMENTS AND THEIR ROLES IN A THEORETICAL PHASE

The formulation of a general quantitative theory of piezo- and pyroelectricity did not limit the function of the experiment to its test. Clearly, testing mathematical theories was one function of the laboratory in the "theoretical phase," though apparently not so central as one might have expected. Physicists were satisfied with few experimental confirmations limited to a few cases. Collecting information about nature by finding the precise mathematical relations and coefficients that characterized physical processes was another function. The quantitative measurements of constants differed from experiments like those of Hankel and Lindenberg's in their dependence on mathematical laws, which give the constants meaning. Finally, experiments indicated the existence of natural phenomena, through precise measurements. The precise determination of a constant to the highest degree possible was not only an end in itself but also a means to reveal relations between phenomena and to discern whether genuine

[78] This one example can at best indicate on a general process that still need to be studied.

physical interactions existed.[79] Pockels and Voigt were concerned with the particular (e.g., a constant of a specific material) mostly as a way to reach the general (e.g., the existence of a direct electro-optic effect). Precise measurements, as Voigt claimed, raised and answered questions inaccessible through qualitative experiments.[80] Exactitude was conceived as an indispensable means to a superior end.

Considerable effort to attain high precision and eliminate even small experimental errors was evident in all the determinations of piezoelectric constants, including the earlier ones of the Curies and Czermak. Apparently, the seven scientists engaged in these measurements trusted the precision of their determinations. They all shared an "ethos of exactitude." Still, they presented different methods of reaching exactitude. While the Curies bypassed potentially complicated determinations and eliminated any significant source of error, the German "measuring physicists" preferred to measure all quantities and base the elimination of error on theoretical-mathematical analysis.[81]

In the tradition of Regnault, the Curies reduced potential errors in their measurements by manipulating the apparatus. German "measuring physicists" regarded the mathematical method of reducing errors as superior to other methods. They did not adopt the Curies' earlier method of null experiment,[82] nor did the Curies adopt theirs. Today, the mathematical analysis of error has become a virtually inseparable part of experimentation. Yet, the choice between experimental designs that bypass some measurements and those that do not still exists. Years later, Jacques Curie's null experiment was regarded as most reliable, more than those of Riecke, Voigt, and Pockels.[83]

The two attitudes toward precise measurements characterized two different traditions—that of French experimentalists and German theoreticians. However, nationality was not the decisive factor in the difference between the two attitudes. Affiliation with a particular school or tradition was more important. Indeed, these schools were each related to a specific national, regional, institutional, educational, and linguistic setting. Weber and Neumann found their followers in Germany, Regnault in France. Although, the tradition of "measuring physics," with its emphasis on mathematical reduction of errors, was probably unique to Germany, it had its roots in the French mathematical sciences of the early nineteenth century, on which Gauss, Weber, and Neumann based their work. On the other hand, Regnault suggested an

---

[79] Thus I do not accept the dichotomy implied in Olesko's claim that Neumann's school's "investigative strategy . . . emphasized primarily, although not exclusively, the eradication of error rather than the discovery of new truths or the construction of comprehensive theories." At least in Voigt's and Pockels's research, error reduction was a mean to discoveries, and did not exclude formulation of theories.

[80] Voigt, "Die Kampf der Dezimale," p. 73.

[81] Yet all the measurements were based on mathematical laws, which gave the constants meaning.

[82] In addition to the experiments mentioned above Franz Nachtikal, a student of Voigt, applied the method of his teacher and Riecke in measuring the piezoelectric moduli and their change with pressure "Ueber die Proportionalität zwischen den piëzoelektrischen Momenten und den sie hervorrufenden Drucken," *Göttingen Nachrichten*, 1899, 109–118.

[83] Cady, *Piezoelectricity*, pp. 217–218.

alternative methodology to that of Biot and his generation.[84] These schools, moreover, did not include all German or French physicists. Germany had its own two separate traditions of "experimental" and "measuring physics." Experimental physicists in Germany did not share the attitude of their compatriot "measuring physicists." In 1912 Röntgen, a prominent representative of the experimental tradition, considered the null experiment as more reliable than the mathematical reduction of error. Röntgen showed an inclination toward the artisanal rather than the mathematical approach to precise measurements. Still, his work combined the two previously separated approaches.

The tests of Voigt's general theory are examples of experiments that did not require "systematic theories" in their analysis. Of course, the experimentalists used theoretical claims, i.e., assumptions about the relations between different magnitudes, such as the relation between electric tension and charge, between gravity and elasticity etc. They also trusted the reliability of experimental instruments like Thomson's electrometer or Clark's cell. Yet the claims they used were based on and justified by many experiments in a variety of conditions and were not dependent on the validity of a particular theory. Thereby, they belong to what is sometimes termed "a low-order theory," i.e., they are shared by a few systematic and encompassing "high-level" theories. For example, the relations between capacity, charge, and voltage are the same in Maxwell's field theory and in its competing corpuscular and potential theories.

More importantly, the analysis of these experiments did not require the piezoelectric theory under examination. One sole exception is Czermak's experiment, which was consequently regarded as unreliable. These experiments not only confirmed intrinsic relations between the variables in the phenomena under question, like the linearity of the effect (these might be called phenomenological regularities), but also general principle. The confirmations of Voigt's theory focused on the relations of effects in different directions. A refutation of its predictions would have entailed a contradiction with the law of symmetry, with major implications to the growing awareness of its role in contemporary physics. Thus, the test of Voigt's relations had consequences that extended well beyond the limited field of piezoelectricity.[85] Although even Quine clarified that some theoretical claims can be tested independently, and Hacking furthermore claimed that "seldom is the modeling of a piece of apparatus or an instrument the same as the theory in question or the systematic theory," pointing out the independence of experiment from the theory being tested still seems noteworthy.[86]

---

[84] Chang, "search for 'real' scale," p. 274.

[85] Indeed whether piezoelectric coefficients are linear or not or even whether they are constant did not have much relevancy to other branches. This can explain the indifference to Pockels's finding of non linear behaviour in Rochelle Salt.

[86] Willard Quine, *Theories and Things*, Cambridge MA: Belknap Press, 1981, p. 71; Ian Hacking, "The Self-Vindication of the Laboratory Sciences," in *Science as Practice and Culture*, edited by Andrew Pickering, Chicago: Chicago University Press, 1992, pp. 29–64, on p. 45. I borrowed a few terms (like systematic and low-level theories) from the writing of and on the socalled "New Experimentalism." See for example papers in Heidelberger and Steinle (eds.) Experimental Essays - Versuche zum Experiment.

Riecke and Voigt's research illustrates the complexity of the experiment and its analysis. It also exhibits its flexibility and the ability of the experimentalists to modify and adjust it. In this case, the modification of the experiment did not involve reconsideration of its theory but a fresh inspection of its equipment revealed an accidental technical problem. The experiment was modified by the addition of a complicated measurement of capacity. Consequently, the results were changed, but not the other components of the experiment. This episode supports the claim reemphasized by "New Experimentalism" that theory does not give complete directions for practical experimental decisions.[87] Theory could not tell Riecke and Voigt which part of the experiment needed modification and how to modify it. The solution of the problem was based more on experimental methods than on theoretical ones. For measuring the capacity, they adopted the "tuning fork method" from Maxwell's treatise. Although regarded as the epitome of his electromagnetic field theory, Maxwell's book was far from being a systematic presentation of the theory and was not limited to its presentation. It was also a detailed presentation of the experimental method. Despite the method's reliance on more advanced theory than was needed for the theoretical calculation of capacity, it did not require field theory and its specific concepts. Maxwell's analysis of the charging and discharging of condensers was also accepted by physicists who rejected his system. Riecke and Voigt themselves were not Maxwellians. I presume that even Duhem was forced to accept this analysis of Maxwell, despite his manifested objection to the latter's theory.

Peter Galison has called historians' attention to the freedom experimentalists have in deciding when to end an experiment.[88] One can always suggest further measurements of components of the apparatus, the measuring instruments themselves, or the target in order to check possible systematic and accidental errors. Galison examined episodes from the history of particle physics in the twentieth century; this story shows that "ending an experiment" was also sometimes a long and complicated process in the study of bulk matter at the end of the previous century. Experiments were not over once the measurements had been made. Neither data analysis nor publication of results terminated the research. The Curies were quick to pronounce their determination of the piezoelectric constants. Yet they continued to measure them, returning to the same experiment for many years: Jacques pronounced modified results for basically the same measurement almost 30 years after the initial publication. Voigt's experiments on the existence of direct pyroelectricity, with Riecke and alone, showed that a conclusion from an experiment (not only a determination of a magnitude) can be changed a few years after its performance. In 1898, theoretical concerns combined with dissatisfaction with the precision and method of the former experiment (which did not measure all variables on the same specimen), led Voigt to complete the experimental investigation that had apparently been concluded in 1891.[89] Like the

---

[87] For a statement of this claim see David C. Gooding, "Experiment," in *A Companion to the Philosophy of Science*, edited by W.H. Newton-Smith, Oxford: Blackwell, 2000, pp. 117–126.

[88] Peter Galison, *How Experiments End*, Chicago: University of Chicago Press, 1987.

[89] Voigt's 1898 experiment might be seen as independent of the previous one, but since it was done on the same specimen and since Voigt used the same piezoelectric measurements and re-analysed the old experiment with new data obtained in 1898, I maintain that both experiments can also be regarded as

Curies, Riecke and Voigt announced their determination of piezoelectric moduli soon after they obtained numerical results, but the publication did not end the experiment. They returned to the laboratory soon after to correct their findings. This example shows that, in the absence of theoretical expectations, earlier experimental results can influence a new experiment; they can even determine when it would end. Röntgen's choice to carry out a second determination of quartz's piezoelectric coefficient reveals the same influence of earlier results. Perhaps this influence characterizes more direct measurements than other experiments (e.g., those that test theories).

Ending an experiment following a previous experiment's results contains a paradoxical element: the new experiment was designed, among other aims, to examine exactly the correctness of the previous results, and to find more accurate and valid results. Nevertheless, the circularity is only apparent. Although the ending of the new experiment was done in view of the previous one, the justification for the correction of the results and the procedures of their reexamination were independent of the preceding results. This is most apparent in Röntgen's case as his end results still diverge from earlier values. True, in the case of Riecke and Voigt's experiment the new experimental results were influenced by the previous ones, but were not determined by them. Results that disagreed with previous ones were published by Riecke and Voigt as long as no error was found in the experiment and its analysis. Plausibly, without the Curies' previous results, the faulty results would have remained standing.[90] However, the methods and procedures used by Riecke and Voigt in measuring the correct capacity, and their confidence in them, provide excellent reasons to believe that had their results led to disagreement with the Curies', they would not have hesitated to publish them.

---

one. This semantic choice can help to recognize that the analysis of the experiment and its conclusions can be changed even years after they have found their way to a scientific journal.

90 Since Riecke and Voigt needed to measure the capacity of the specific condenser used in the experiment, they probably would not have found this fault a few years later, when further measurements were made.