

Properties of Rochelle Salt

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In a qualitative way the anomalous properties of Rochelle salt can be explained on the basis of four different theories: (a) on the dipole theory, (b) by assuming polymorphic transitions at the Curie points, (c) by postulating an anomalous piezoelectric effect, and (d) with an interaction theory which assumes that the structure and the fundamental properties of the crystal have no unusual characteristics and which ascribes the observed anomalies to an accidental degeneration of the piezoelectric interaction between the elastic deformation and the electric polarization. The existence of a polymorphic transition at the upper Curie point is demonstrated in a new experiment and it is shown that this transition is a spontaneous elastic deformation. It can be explained on the basis of either

one of the four theories. A quantitative analysis of the experimental data, which leads to a new interpretation of the elastic and piezoelectric measurements, shows that the theories (b) and (c) are not valid for Rochelle salt. The experimental data verify the conclusions of the dipole theory insofar as they lead to the result that Rochelle salt would show an abnormal temperature dependence of the dielectric constant even if the crystal were not piezoelectric or if the piezoelectric deformations could be suppressed. However, it is doubtful whether the clamped crystal has a Curie point. The observed Curie points of the free crystal result from the lattice-dipole coupling as described by the interaction theory.

THE DIPOLE THEORY OF ROCHELLE SALT

THREE theories have been advanced to account for the well-known anomalous properties¹ of Rochelle salt. The commonly accepted theory, due to Kurtschatow² and Fowler,³ assumes that the phenomena are due to the Lorentz interaction between rotating polar molecules and that the lower Curie point is caused by the gradual freezing-in of the dipoles. Against this theory several objections can be raised.⁴ We possess no conclusive evidence that the anomalies are due to free dipoles. On the contrary, the discovery of electric Curie points in H_2KPO_4 and H_2KAsO_4 ⁵ shows that they occur also in crystals which contain no polar molecules. The most serious deficiency of Fowler's theory (and also of Onsager's⁶ theory for H_2KPO_4) lies in the fact that it assumes a rigid lattice structure. It

neglects the large piezoelectric effects which occur in all ferroelectric crystals.⁷ The theory, therefore, does not relate to the commonly measured properties of Rochelle salt but rather to the properties of the strain free crystals, i.e., of crystals which are clamped rigidly in such a way that no piezoelectric deformations can take place. The measured quantities, however, are those of free crystals in which the stresses are zero. Sawyer and Tower,⁸ David⁹ and the writer¹⁰ have shown that a partial suppression of the piezoelectric deformations greatly reduces the dielectric constant in the para-electric state and almost completely suppresses the hysteresis loops in the ferroelectric temperature range. The properties of the clamped crystals differ so radically from those of the free crystals that it is doubtful whether a rigidly clamped crystal would show any anomalies whatever, and hence it is questionable whether the dipole theory of Rochelle salt in its present form can be justified.

POLYMORPHISM OF ROCHELLE SALT

The second theory, due to Jaffe,¹¹ postulates that Rochelle salt undergoes a polymorphic

¹ For reviews see: I. V. Kurtschatow, *Seignette Electricity* (Moscow, 1933). French translation entitled: *Le champs moléculaire dans les diélectriques* (Paris, 1936). H. Staub, *Naturwiss.* **23**, 728 (1935). W. G. Cady, *Am. Phys. Teacher* **6**, 227 (1938). P. Scherrer, *Zeits. f. Elektrochem.* **45**, 171 (1939) and the forthcoming review by the writer in the *Annals New York Academy of Science*.

² P. Kobeko and J. Kurtschatow, *Zeits. f. Physik* **66**, 192 (1930).

³ R. H. Fowler, *Proc. Roy. Soc.* **A149**, 1 (1935).

⁴ Other deficiencies of Fowler's theory have been pointed out by Busch, Hablützel and Scherrer, *Helv. Phys. Acta* **10**, 330 (1937).

⁵ G. Busch, *Helv. Phys. Acta* **11**, 269 (1938).

⁶ L. Onsager, Symposium on Dielectrics, to appear in *Annals New York Academy of Science*.

⁷ W. Lüdy, *Zeits. f. Physik* **113**, 302 (1939) shows that H_2KPO_4 has a piezoelectric anomaly similar to that of Rochelle salt.

⁸ C. B. Sawyer and C. H. Tower, *Phys. Rev.* **35**, 269 (1930).

⁹ R. David, *Helv. Phys. Acta* **8**, 431 (1935).

¹⁰ H. Mueller, *Phys. Rev.* **47**, 175 (1935).

¹¹ H. von R. Jaffe, *Phys. Rev.* **51**, 43 (1937); **53**, 917 (1938).

transition at the Curie points. It assumes that the normally orthorhombic structure becomes monoclinic through a slight change of the angle between the b and c axes. Jaffe estimated that at 0°C this angle should deviate from 90° by about $2.7'$. To test this hypothesis we have measured this angle as a function of temperature. Four plane mirrors were glued to the b and c faces of a rectangular block of Rochelle salt of the dimensions $l_a = 4$ cm, $l_b = l_c = 1$ cm. Two electrodes were attached to the a faces and connected together to avoid electric fields due to pyroelectric charges. The crystal was mounted, with the a axis vertical, within a small temperature bath with four windows and placed on the prism table of a Geneva precision spectrometer. By the usual method of autocollimation, employing a Huygens ocular, it was possible to measure the angles between the mirrors to an accuracy of $5''$. The crystal was kept for over 10 hours at constant temperature, namely at 0° , 11° , 25° , 34° and 45°C . The measurements were repeated twice with increasing and decreasing temperatures, the results agreed within $15''$. Although the mirrors on opposite faces were not exactly parallel ($180 \pm 1.5^\circ$) the angles between them varied with temperature by less than $20''$. The angles between neighboring faces, however, showed a very marked temperature variation. They stayed approximately ($\pm 20''$) constant between 45° and 25°C , but below the Curie point the angle between the $+b$ and $+c$ directions diminished (and the other angles increased or decreased accordingly) by about $3'$ at 11°C and by $3'45''$ at 0°C .¹² These deviations are considerably larger than the experimental errors of maximal $30''$. The results must be considered as the first direct verification of Jaffe's hypothesis.

The polymorphic transition of Rochelle salt is of a very unusual type. According to the x-ray evidence¹³ it does not involve any marked structural changes, it has no latent heat of transition and it is not accompanied by a sudden change of

the optical properties. It is a transition of the second kind in which the specific heat¹⁴ and the temperature gradient of the birefringence¹⁰ have a discontinuity at the Curie point. Especially significant is the fact that one can produce artificially, at temperatures above the Curie point, the same type of polymorphic transition which occurs spontaneously below the Curie point. This can be accomplished by applying either an electric field in the direction of the a axis or a shearing strain in the b, c plane. In either case the angle between the b and c axes is slightly changed, the optical properties are altered and the crystal becomes pyroelectric. To realize that the latter statement is true we recall that above the Curie point the dielectric and piezoelectric constants show a large temperature variation. Hence if a constant field or stress is applied the electric polarization of the crystal varies with temperature. The writer has shown¹⁰ that the relation between the spontaneous polarization and the change of birefringence (spontaneous Kerr effect) is the same as between dielectric polarization and Kerr effect¹⁵ above the Curie point. It appears most likely that also the relation between deformation and polarization is the same. A comparison of the dielectric and piezoelectric (static) measurements indicates that above the Curie point the relation $y_z = \delta \cdot P_x$ is valid, where $\delta = 1 \pm 0.4 \times 10^{-6}$. Within the accuracy of the available data this relation holds also for the spontaneous polarization and deformation. For instance, at 0°C we found $y_z = 3'45'' = 0.001$ and the spontaneous moment is $P = 800$ e.s.u. (from the hysteresis loops), whence $\delta = 1.2 \times 10^{-6}$.

We conclude therefore that the polymorphic transition is simply a spontaneously occurring elastic deformation. It can be explained on the basis of the dipole theory: The spontaneous deformation is the inverse piezoelectric effect produced by the spontaneous polarization. However, this argument can also be reversed, and

¹² Jaffe expected that these angular changes could be detected only if the crystals were grown at temperatures below the Curie point. Our determination was carried out on a crystal which had previously been used to measure the pyroelectric effect. More accurate measurements by a different method are in progress.

¹³ H. M. Krutter and B. E. Warren, *Phys. Rev.* **43**, 500 (1933); H. Staub, *Physik. Zeits.* **34**, 292 (1933); *Helv. Phys. Acta* **7**, 1, 480 (1934).

¹⁴ P. Kobeko and J. Nelidow, *Physik. Zeits. Sowjetunion* **1**, 382 (1932); A. Rusterholz, *Helv. Phys. Acta* **8**, 39 (1935); A. J. C. Wilson, *Phys. Rev.* **54**, 1103 (1938); J. F. G. Hicks and J. G. Hooley, *J. Am. Chem. Soc.* **60**, 2994 (1938).

¹⁵ It is questionable whether the name "Kerr effect" is appropriate. The observed change of birefringence could also be termed a quadratic photoelastic effect. Actually, in view of Pockels' results on other piezoelectric crystals, the optical changes are most probably the result of both, mechanical and electrical, deformations.

since we have, so far, no means of deciding whether the polarization or the elastic deformation is the primary effect, we can explain the phenomena also as follows:

At the Curie points the orthorhombic lattice of Rochelle salt becomes unstable against elastic deformations, i.e., an elastic anomaly is the intrinsic cause of the abnormal properties. Our experimental results imply indeed, since the crystal gets a shearing strain without a stress being applied, that the elastic modulus s_{44} becomes infinitely large at the Curie point. Below the Curie point the lattice has two elastically stable states. An alternating field can force it to flop from one position into the other, hence the hysteresis loops. If this interpretation of Jaffe's theory is correct, the final solution of the problem of Rochelle salt must be found in its lattice structure and the lattice forces, and not in the dipole-dipole interaction.

THE PIEZOELECTRIC THEORY OF ROCHELLE SALT

The third theory of Rochelle salt makes the abnormally large piezoelectric effect responsible for the anomalies. This theory was first proposed by Cady¹⁶ and has been the guiding idea in the work of Schulwas-Sorokin and Posnov.¹⁷ Cady pointed out that the electric susceptibility κ_F in the a direction of a free crystal is larger than that, κ_{cl} , of a clamped crystal. In a free crystal the piezoelectric deformation gives rise to an additional polarization $P' = e_{14}y_z$, where $y_z = d_{14}E$ is the deformation caused by the electric field. Hence $P_F = \kappa_F E = P_{cl} + P' = (\kappa_{cl} + e_{14}d_{14})E$. By writing this equation in the form

$$P_F = \kappa_{cl} [E + (e_{14} \cdot d_{14} P_F / \kappa_{cl} \cdot \kappa_F)]$$

one recognizes the analogy with the Lorentz equation $P = N\alpha(E + fP)$, which leads to a Curie point when $N\alpha f = 1$.

The lattice theory offers a simple physical interpretation of Cady's formal theory. According

¹⁶ W. G. Cady, *Phys. Rev.* **33**, 278 (1929). Some writers have, erroneously, credited this theory to me. Professor Cady apparently has abandoned this theory in favor of the dipole theory (see reference 1). Partly as a matter of convenience, we shall here nevertheless refer to it as "Cady's theory."

¹⁷ R. D. Schulwas-Sorokin, *Zeits. f. Physik* **77**, 541 (1932); *Physik. Zeits. Sowjetunion* **12**, 685 (1937); and M. V. Posnov, *Phys. Rev.* **47**, 166 (1935).

to Born¹⁸ the piezoelectric effect is the result of the so-called "inner displacements" of ions. Another way of stating the conclusions of this theory is: An elastic deformation produces a reversible change of the equilibrium orientation and magnitude of the dipole moment of the unit cell, and vice versa, a change of this moment creates an elastic deformation (homogeneous disturbance in Born's notation). The dipole moment of the unit cell is not necessarily due to the presence of polar molecules; the basic cell of most ionic lattices (NaCl) has a moment. If now an electric field is applied on a free crystal the following changes in the basic cell occur successively: First the moment is oriented; this creates an elastic deformation which in turn alters the equilibrium position of the dipole in such a way that the field can orient it still further. An additional polarization creates additional deformation and shifts the equilibrium position still further, and so on, and it is readily seen how such an "autocatalytic" reaction might eventually result in a spontaneous alignment of the moments.

This type of mechanism is essentially different from that of the dipole or the elastic theory. Though polar molecules might be involved, they are not necessary. In any case no free or hindered rotation must be assumed. In the piezoelectric theory of Rochelle salt the dipole-lattice interaction is responsible for the observed anomalies.

THE INTERACTION THEORY OF ROCHELLE SALT

To these three older theories we now can add a fourth one. This fourth theory is a special case of Cady's theory. The formulation of this new aspect of the problem of Rochelle salt also furnishes the basis on which it is possible to decide which theory is the correct one.

The following considerations apply to the state of Rochelle salt above the upper and below the lower Curie point where the structure is orthorhombic. We consider the change Φ of the free energy of 1 cc when the crystal is deformed by a uniform strain with the components x_x , y_z , and simultaneously polarized in an arbitrary direction

¹⁸ M. Born and M. Göppert-Mayer, *Handbuch der Physik*, Vol. 24, 634-8, or M. Born, *Problems of Atomic Dynamics* (Mass. Inst. of Tech., 1926), pp. 139-154. Born's discussion of zinc blende can be generalized to fit the case of Rochelle salt and leads to the formulation given in the next section.

by a uniform electric field. By referring all quantities to a system of axes in which the x, y, z directions coincide with the crystallographic a, b, c axes, respectively, and by taking into account the symmetry properties of the orthorhombic class we obtain, in first approximation,

$$\begin{aligned} \Phi = & \frac{1}{2}(c_{11}x^2 + c_{22}y^2 + c_{33}z^2) \\ & + (c_{23}y_z z_x + c_{31}z_x x_x + c_{12}x_x y_y) \\ & + \frac{1}{2}(c_{44}y_z^2 + c_{55}z_x^2 + c_{66}x_y^2) \\ & + (f_{14}y_z P_x + f_{25}z_x P_y + f_{46}x_y P_z) \\ & + \frac{1}{2}(\chi_1 P_x^2 + \chi_2 P_y^2 + \chi_3 P_z^2). \end{aligned} \quad (1)$$

P_x, P_y, P_z are the components of the polarization and c_{ik}, f_{ik}, χ_i are characteristic constants of the crystal. By differentiation we obtain the stresses $-Y_z = \partial\Phi/\partial y_z$, and the components of the electric field $E_x = \partial\Phi/\partial P_x$. This furnishes nine equations, three each of the following form

$$-X_x = c_{11}x_x + c_{12}y_y + c_{13}z_z, \quad (2a)$$

$$-Y_z = c_{44}y_z + f_{14}P_x, \quad (2b)$$

$$E_x = f_{14}y_z + \chi_1 P_x, \quad (2c)$$

or by solving this system of linear equations

$$-x_x = s_{11}X_x + s_{12}Y_y + s_{13}Z_z, \quad (3a)$$

$$-y_z = s_{44}Y_z + d_{14}E_x, \quad (3b)$$

$$P_x = d_{14}Y_z + \kappa_1 E_x. \quad (3c)$$

The relations between the first and second set of constants are of the following types

$$\begin{aligned} s_{23} &= (c_{12}c_{13} - c_{11}c_{23})/D_{13}, \\ c_{23} &= (s_{12}s_{13} - s_{11}s_{23})D_{13}, \end{aligned} \quad D_{13} = \begin{vmatrix} c_{11} & c_{12} & c_{13} \\ c_{12} & c_{22} & c_{23} \\ c_{13} & c_{23} & c_{33} \end{vmatrix},$$

$$\begin{aligned} s_{44} &= \chi_1/D_{14}, & (4a) \quad D_{14} &= c_{44}\chi_1 - f_{14}^2 & (4d) \\ d_{14} &= f_{14}/D_{14}, & (4b) \quad &= 1/(s_{44}\kappa_1 - d_{14}^2). \\ \kappa_1 &= c_{44}/D_{14}, & (4c) \end{aligned}$$

The two sets of six constants c_{11} to c_{23} and s_{11} to s_{23} are the elastic constants and compliance coefficients, and the three constants d_{ik} are the piezoelectric moduli, as defined in the usual theory. $\chi_i = 1/\kappa_{ei}$ are the reciprocal of the principal electric susceptibilities of the clamped crystal (when $y_z = 0$) while κ_i are the susceptibilities of the free crystal (when $Y_z = 0$). In place of the more logical¹⁹ piezoelectrical constants f_{ik}

¹⁹ It is logical to express the energy change (1) either in terms of inner parameters (z_y, P_x) or external parameters (Y_z, E_x). Voigt's definition of e_{ik} involves a mixing of

the usual theory employs the quantities e_{ik} defined by $-Y_z = e_{14}E_x$ (if $y_z = 0$) or $-P_x = e_{14}y_z$ (if $E_x = 0$). Comparison with Eqs. (2) and (3) shows that

$$f_{14} = \chi_1 e_{14} = \chi_1 d_{14}/s_{44}. \quad (5)$$

The two sets of constants c_{44}, c_{55}, c_{66} and s_{44}, s_{55}, s_{66} require special attention. They are not identical with the corresponding quantities in the usual theory, because we note that the commonly employed relation $s_{44} = 1/c_{44}$ is not valid. According to Eq. (2b) c_{44} is the elastic constant for a shearing deformation during which $P_x = 0$. In order to carry out such a deformation it would be necessary to apply simultaneously an electric field $E_x = f_{14}y_z$ in order to suppress the production of a polarization. The constant c_{44} (and similarly c_{55} and c_{66}) characterizes the "true" elastic properties of the crystal, because it relates to a deformation in which the piezoelectric effect plays no role.

The constant s_{44} , on the other hand, is the compliance for a deformation during which the applied field is zero. In order to measure this constant it is necessary to cover the crystal with a grounded electrode. Therefore we shall call s_{44} the compliance of the foiled crystal. It is not a true elastic constant, because even in a foiled crystal a deformation creates a piezoelectric polarization. The foil serves only to compensate for the induced surface charges but does not suppress the polarization.

We have previously pointed out that the susceptibilities κ_i of the free crystal depend on the elastic deformation. They are therefore not suitable constants to characterize the true dielectric properties of the crystal. In their stead we must use the constants χ_i . For similar reasons we consider f_{ik} as the true piezoelectric constants, because d_{14} is the moment P_x for a stress $Y_z = 1$ when $E_x = 0$ and depends therefore on the deformation.

The problem of finding the origin of the anomalous properties of Rochelle salt consists therefore in determining which one of the three quantities c_{44}, f_{14} or χ_1 shows an abnormal behavior.

parameters (E, y_z). This inconsistency of the usual theory is the root of many misunderstandings, particularly in connection with the problem of Rochelle salt. The f_{ik} constants were introduced by Mason, Phys. Rev. 55, 783 (1939).

(We know that none of the other quantities has an unusual value.) Thus the decision between the three theories depends simply on which one of these three constants has an abnormal temperature dependence.

Unfortunately neither c_{44} , f_{14} nor χ_1 has been measured in a direct way. The experiments furnish s_{44} , d_{14} and κ_1 . It is well known that κ_1 and d_{14} become extremely large at the Curie point, and our new experiment shows that also s_{44} reaches an infinite value at this temperature. According to Eqs. (4) these facts permit only one interpretation, namely, that none of the fundamental constants becomes zero or infinite at the Curie point, but that the determinant $D_{14} = c_{44}\chi_1 - f_{14}^2$ vanishes at this critical temperature. This can occur even if all three parameters have normal values²⁰ and normal temperature gradients. Thus we are led to a fourth theory of Rochelle salt, which assumes that the structure and the properties of the crystal have no unusual characteristics. The occurrence of the anomalies is accidental. It is the result of an unusual combination of circumstances and has its origin in the lattice-dipole interaction as discussed in the preceding section. This fourth theory does not exclude any of the earlier theories, because it is possible that D_{14} vanishes because either c_{44} or χ_1 becomes unusually small or because f_{14} is abnormally large.

In a qualitative way any one of the four theories is able to account for the dielectric, piezoelectric, pyroelectric, optical, elastic, caloric and electrocaloric anomalies of Rochelle salt. Only a quantitative analysis of the experimental data can decide which one is valid. For this purpose we shall calculate the fundamental quantities c_{44} , χ_1 and f_{14} from the measured values of s_{44} , κ_1 and d_{14} , by using Eqs. (4). But before we can do this, it is necessary to clarify the interpretation of the experimental results.

²⁰ For most crystals, in particular also for ammonium-sodium tartrate which is isomorphous with Rochelle salt, $c_{44} \sim 10^{11}$, $\chi_1 \sim 1.5$, $f_{14} = 3$ to $7 \cdot 10^4$. Hence D_{14} differs only slightly from $c_{44}\chi_1$ and the usual relations $s_{44} = 1/c_{44}$, $\chi_1 = 1/\kappa_1$ are good approximations. But if for instance $c_{44} = 2 \times 10^{10}$ (in some crystals it is even smaller) $\chi_1 = 0.5$ (corresponds to a dielectric constant of 25) the determinant D_{14} vanishes when $f_{14} = 10^6$, and this is not an unusually large value.

THE GAP EFFECT IN ROCHELLE SALT

A crystal of Rochelle salt at a constant temperature above the Curie point is a system with, mainly, two independent variables: The shearing stress Y_z and the electric field E_x . In such a system the dielectric properties depend on the stress, and the elastic properties depend on the electric field. The role of external stresses in the dielectric measurements of Rochelle salt is now generally recognized, but the influence of electric fields on the elastic constants has not been taken into account in the correct manner.²¹ For other piezoelectric crystals Cady²² has discussed this problem in connection with the so-called gap effect. In Rochelle salt this gap effect is unusually large and it can readily be calculated for the experimentally most important cases as follows.

We consider a thin plate of Rochelle salt of thickness T , cut normal to the a direction, and placed between the parallel plates of a condenser with a plate separation $(D+T)$. D is the gap width. V denotes the potential difference between the condenser plates and $E_0 = V/(D+T)$ is the field when the crystal is removed. The crystal is deformed by a uniform strain y_z and has therefore a uniform polarization P_x which creates a charge density $\pm P_x$ on the surfaces of the plate. If σ denotes the charge density on the condenser plates, the field intensity in the gap is $E_x' = 4\pi\sigma$, and in the crystal $E_x = 4\pi(\sigma - P_x)$. Whence $V = 4\pi[\sigma D + (\sigma - P_x)T]$. By eliminating σ from the last two equations we obtain

$$E_x = E_0 - 4\pi P_x D / (D + T). \quad (6)$$

For the special cases of a foiled or plated crystal, $D = 0$, and $E_x = V/T$. For an isolated crystal, $D = \infty$, the surface charges give rise to a depolarization field $E_x = -4\pi P_x$. By inserting E_x from Eq. (6) into Eqs. (3b) and (3c) it is found that these relations can be written

$$-y_z = s_{44}^* Y_z + d_{14}^* E_0, \quad (3b')$$

$$P_x = d_{14}^* Y_z + \kappa_1^* E_0, \quad (3c')$$

²¹ W. P. Mason, Phys. Rev. **55**, 775 (1939). A. N. Holden and W. P. Mason, Phys. Rev. **57**, 54 (1940). While the experimental work reported in these papers is of superior quality, the writer cannot agree with the theoretical interpretation of the results. It will be shown here that their calculations of the dielectric constant of the clamped crystal and of d_{14} are not justified.

²² W. G. Cady, Physics **7**, 245 (1936).

where

$$s_{44}^* = s_{44} - 4\pi d_{14}^2 D / (\epsilon_F D + T), \quad (7a)$$

$$d_{14}^* = d_{14}(D + T) / (\epsilon_F D + T) \quad (7b)$$

$$\kappa_1^* = \kappa_1(D + T) / (\epsilon_F D + T), \quad (7c)$$

and where $\epsilon_F = 1 + 4\pi\kappa_1$ is the dielectric constant in the a direction of the free crystal. Eq. (7c) expresses the well-known fact that a small gap between electrode and crystal gives rise to a large error in the determination of the dielectric constant. Eq. (7b) shows that a gap has a similar influence on the determination of the piezoelectric modulus d_{14} . According to Eq. (7a) the elastic compliance coefficient s_{44} is smaller for a crystal held in an air-gap holder than it is for a foiled crystal. Since ϵ_F and d_{14} assume very large values in Rochelle salt, especially near the Curie point, all these changes are enormous, even for a small gap.

Of special interest is the case of an isolated crystal, i.e. when $\epsilon_F D \gg T$. Denoting by s_{44}^i the compliance coefficient of an isolated crystal, one finds from Eqs. (7a) and (4)

$$s_{44}^i = s_{44} - 4\pi d_{14}^2 / \epsilon_F = s_{44} \epsilon_{cl} / \epsilon_F = 1/c_{44} + d_{14}^2 / \kappa_1 \epsilon_F, \quad (8)$$

where ϵ_{cl} is the dielectric constant of the clamped crystal. We can show later²³ that in Rochelle salt $d_{14}^2 / \kappa_1 \epsilon_F$ is a small correction term, amounting to less than 0.4 percent of $1/c_{44}$. Hence we arrive at the important result that the elastic measurements on the isolated crystal furnish very closely the true elastic properties of Rochelle salt. This is due to the fact that in an isolated crystal the depolarization field $E_x = -4\pi P_x$ prevents almost completely the production of a piezoelectric polarization.

THE ELASTIC PROPERTIES OF ROCHELLE SALT

The above considerations are valid only if the electrical conductivity of the crystal and its surface can be neglected. The relations hold therefore if the elastic constants are determined by a dynamic method. For static measurements, as carried out by Mandell,²⁴ the crystal is neither

²³ The relation $s_{44}^i = 1/c_{44}$ is obtained if one approximates $\epsilon_F = 4\pi\kappa_1$. Since above the Curie point ϵ_F is nowhere smaller than 70, this approximation involves a very small error.

²⁴ W. Mandell, Proc. Roy. Soc. **A116**, 623 (1927). Mandell's data are derived from bending and twisting

isolated nor foiled, and it is therefore not surprising that the results differ from those obtained by dynamic methods. The static methods furnish reliable results only if the crystals are foiled or if the applied stress contains no shearing components Y_z, Z_x, X_y . Static measurements of this type have been carried out by Hinz.²⁵ As shown in Table I his results are in satisfactory agreement with those of Mason.²⁶

Elastic measurements by the dynamic method have been made by Davies,²⁷ Cady,²² Mikhailov,²⁸ Mattiat,²⁹ Hiltcher³⁰ and Mason.²⁶ The constant s_{44} is calculated from the resonance frequency $f = \frac{1}{2}(E/\rho)^{\frac{1}{2}}$ of a plate, 1 cm long, for longitudinal vibrations in the direction at 45° to the b and c axes. The density ρ is 1.775 (acc. to Mason) and Young's modulus E for this direction is

$$1/E = S = \frac{1}{4}(s_{22} + s_{33} + 2s_{23} + s_{44}^*), \quad (9)$$

whereby s_{44}^* must be replaced by s_{44} if the electrodes are attached to the crystal, or by s_{44}^i if the plate is mounted in a sufficiently wide air-gap holder. Since $s_{44} > s_{44}^* > s_{44}^i$ (Eq. (7a)) the isolated crystal has the highest resonance frequency, f^i , and the foiled crystal has the lowest, f . The data of the various observers differ because many have neglected to take into account the large gap effect. The best data³¹ are those of Mason, who

experiments on thin plates, in which it is difficult or impossible to avoid shearing stresses. Mandell reports that the crystals reached a state of constant deformation only after some minutes and he ascribes this to the slow electrical conduction along the surface. However, this leakage was not large enough to eliminate all potential differences, otherwise he would have found the large change of s_{44} at the Curie point of the foiled crystal. Mandell's data, therefore, refer to a crystal in an unknown electric field and cannot be used for a quantitative analysis.

²⁵ H. Hinz, Zeits. f. Physik **111**, 617 (1938). The values of $s_{11}, s_{22}, s_{33}, s_{23}, s_{31}, s_{12}$ are obtained from measurements of the longitudinal and transversal strains for stresses parallel to the crystallographic axes which create no piezoelectric effects in Rochelle salt. Hinz's values of s_{44}, s_{55} and s_{66} are subject to the same objections as raised against Mandell's data.

²⁶ W. P. Mason, reference 21. His dynamic measurements on unplated crystals, cut normal to the a axis, furnish s_{11}, s_{22}, s_{33} and $(2s_{23} + s_{44}^i), (2s_{31} + s_{66}^i), (2s_{12} + s_{66}^i)$. Mason's determination of c_{44}, c_{66}, c_{66} neglects the gap effect and is therefore open to criticism. We shall therefore not use his values of s_{23}, s_{31} and s_{12} .

²⁷ R. M. Davies, Phil. Mag. **16**, 97 (1933).

²⁸ G. Mikhailov, Tech. Physik USSR **3**, 652 (1936).

²⁹ O. Mattiat, Hoch: tech. u. Elek: akus. **50**, 115 (1937).

³⁰ R. Hiltcher, Zeits. f. Physik **104**, 672 (1937).

³¹ Other investigators, using a wide gap, find similar values, e.g., Hiltcher finds $f^i = 2.1 \times 10^6$, Mikhailov 2.12×10^6 ; others find smaller values, Mattiat 1.9, Davies 2.07×10^6 . In Mason's notation $f^i = f_M, f = f_R$.

TABLE I. *Static and dynamic compliance coefficients of Rochelle salt.*

	s_{11}	s_{22}	s_{33}	s_{12}	s_{13}	s_{23}
Static values (Hinze)	5.23×10^{-12}	3.43	3.24	-2.18	-1.68	-1.33
Dynamic values (Mason)	5.18×10^{-12}	3.49	3.34	(-1.53)	(-2.11)	(-1.03)

finds at 30°C $f^i = 2.105 \times 10^5$. This value furnishes $S = 3.16 \times 10^{-12}$ and with the data in Table I and Eq. (8) one derives

$$c_{44} = 1/s_{44}^i = 11.6 \times 10^{10}.$$

The value of f^i decreases at a uniform rate³² with increasing temperature. The temperature gradient is somewhat larger than in other crystals, but this can be ascribed to the fact that the crystal is near its melting point. We conclude that the elastic constant c_{44} of Rochelle salt has a normal value and a normal temperature variation. Consequently Jaffe's theory must be discarded. The spontaneous elastic deformation at the Curie point is not caused by an elastic anomaly but it is a secondary effect.

From Mason's data of f , the resonance frequency of the plated crystal, we have calculated in Fig. 1 (see also Table II) the compliance coefficient s_{44} of the foiled crystal. The result confirms our previous conclusion that s_{44} becomes infinite at the Curie point. As shown by the dotted curve in Fig. 1 s_{44} follows a Curie-Weiss law of the form

$$s_{44} - 1/c_{44} = \sigma/(t - t_c) \quad (10)$$

with $t_c = 23^\circ\text{C}$ and $\sigma = 66.7 \times 10^{-12}$. σ will be called the "elastic Curie constant." According to Eq. (8) its value is related to the dielectric and piezoelectric constants by the equation

$$\sigma = (t - t_c)d_{14}^2/\kappa_1 = C(d_{14}/\kappa_1)^2, \quad (11)$$

where C is the electric Curie constant in the law $1/\kappa_1 = (t - t_c)/C$.

Mason has established an interesting relation between f , f^i and the anti-resonance frequency f_A of a foiled crystal plate, for longitudinal vibra-

tions at 45° to the b and c direction; namely,

$$\frac{\pi f_A}{2f} \cot \frac{\pi f_A}{2f} = 1 - (f^i/f)^2 = -k^2/(1 - k^2). \quad (12)$$

As shown in the appendix this relation can be derived on the basis of the fundamental relations (3). Mason's derivation is not acceptable and the correct expression for the electromechanical coupling coefficient is (according to Eqs. (12), (9) and (8))

$$k^2 = 1 - (f/f^i)^2 = 4\pi d_{14}^2/\epsilon_F(s_{22} + s_{33} + 2s_{23} + s_{44}) \\ = 4\pi \rho d_{14}^2 f^2/\epsilon_F. \quad (13)$$

THE PIEZOELECTRIC PROPERTIES OF ROCHELLE SALT

In this section we shall prove that the true piezoelectric properties of Rochelle salt are normal. According to Eqs. (4)

$$d_{14}/\kappa_1 = f_{14}/c_{44}. \quad (14)$$

Since we have already shown that c_{44} is very nearly constant, a normal behavior of f_{14} is ascertained if we can show that the ratio d_{14}/κ_1 has a constant value in the temperature range above the Curie point.

The results of the dielectric measurements at audiofrequencies of the writer,¹⁰ Bancroft,³³ Mason²¹ and Hablützel³⁴ are in satisfactory agreement. The susceptibility κ_1 of the free crystal is therefore known with a good degree of accuracy, but it would be desirable to have further data at radiofrequencies.

The constant d_{14} has been measured by Norgorden³⁵ by a dynamic method from the inverse piezoelectric effect. He found that in the temperature range between 24° to 33° the piezoelectric effect for small fields (frequency 700 cycles/sec.) follows a Curie-Weiss law

$$-y_2 = d_{14}E_x = \Delta E_x/(t - t_c), \quad (15)$$

where $t_c = 23^\circ\text{C}$ and $\Delta = 4.25 \times 10^{-5}$ (from Norgorden's Fig. 11). For the same temperature range the writer¹⁰ has shown that κ_1 (for 1000 cycles) is given by $\kappa_1 = C/(t - t_c) = 178/(t - 23)$.

³² f^i decreases from 2.12 at 25° to 2.07×10^5 at 50°C . Our consideration is restricted to the temperature range above the Curie point. To explain the small discontinuity of f^i at the Curie point it is necessary to enlarge the present theory.

³³ D. Bancroft, Phys. Rev. **53**, 587 (1938).

³⁴ J. Hablützel, Helv. Phys. Acta **12**, 489 (1939).

³⁵ O. Norgorden, Phys. Rev. **49**, 820 (1936); **50**, 782 (1936).

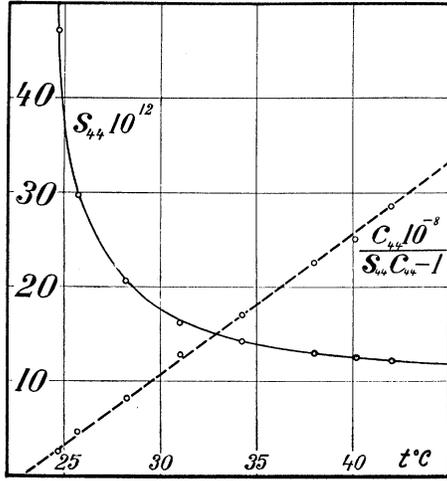


FIG. 1. The Curie-Weiss law for the elastic compliance coefficient s_{44} of a foiled crystal of Rochelle salt. $C_{44}10^{-8}$ should read $C_{44}10^{-10}$.

Hence

$$d_{14}/\kappa_1 = \Delta/C = 2.4 \times 10^{-7}$$

is constant and $f_{14} = c_{44}\Delta/C = 2.8 \times 10^4$ has no unusually large value and varies but little with temperature.

This result is confirmed by the data of Mikhailov.³⁶ This investigator measured the change δf of the resonance frequency of a crystal plate with a change $\delta D = D_1 - D_2$ of the gap width. The plate is cut normal to the a axis and the vibrations are longitudinal at 45° to the b and c direction. According to Eqs. (9) and (7)

$$\delta f / \delta D = 2\pi\rho T l^2 f^3 [d_{14}/(T + \epsilon_F D)]^2, \quad (16)$$

where l is the length of the plate and f is the resonance frequency for an intermediate gap D defined by $(T + \epsilon_F D)^2 = (T + \epsilon_F D_1)(T + \epsilon_F D_2)$, or,

³⁶ G. Mikhailov, *Tech. Physik USSR* **4**, 461 (1937).

approximately,

$$(T + \epsilon_F D) = 4\pi\kappa_1(D_1 D_2)^{\frac{1}{2}}$$

and hence

$$(d_{14}/\kappa_1)^2 = \frac{8\pi D_1 D_2}{\rho T l^2 f^3} \frac{\delta f}{\delta D}. \quad (16')$$

The experiments (Mikhailov's Fig. 2) show that in the entire temperature range δf is practically constant for a fixed δD . By inserting Mikhailov's data $\delta f = 280 \pm 20$, $D_1 = 1.4 \times 10^{-2}$, $D_2 = 1 \times 10^{-2}$, $f = 1.195 \times 10^5$, $l = 1.447$, $T = 0.2588$ we find $d_{14}/\kappa_1 = 3.5 \times 10^{-7}$, and $f_{14} = 4 \times 10^4$.

Finally we have Mason's data, from which, according to Eq. (13), we obtain

$$d_{14}^2 = k^2 \epsilon_F / 4\pi\rho f^2. \quad (13')$$

The coupling factor k can be evaluated, according to Eq. (12) either from f and f^i or from f and f_A . Table II presents a complete set of data. f , f^i and f_A are Mason's values,³⁷ $4S = s_{22} + s_{33} + 2s_{23} + s_{44}$ is obtained from f , k_1 results from f and f^i , k_2 from f and f_A . The dielectric data are taken from the writer's measurements. This set of data shows once more that f_{14} is approximately constant and gives $f_{14} = 7.2 \times 10^4$. The three methods lead to different values of f_{14} , though all are of the same order of magnitude. The difference is most probably due to the fact that the first value is based on data obtained at audiofrequencies, the second involves only measurements at radiofrequencies, while in the calculation of the third value data from high and low frequency measurements have been mixed. The static measurements³⁸ of d_{14} lead to a still larger value of f_{14}

³⁷ The writer is indebted to Dr. Mason for communicating the original data.

³⁸ R. D. Schulwas-Sorokin, *Zeits. f. Physik* **73**, 700 (1932); H. Hinz, *Zeits. f. Physik* **111**, 617 (1938).

TABLE II. Elastic, dielectric and piezoelectric data for Rochelle salt above the upper Curie point.

$t^\circ\text{C}$	$f \times 10^{-1}$	$f_A \times 10^{-1}$	$f^i \times 10^{-1}$	$4S \times 10^{12}$	k_1	k_2	ϵ_F	κ_1	$d_{14} \times 10^6$	$s_{44} \times 10^{12}$	χ_1	$(d_{14}/\kappa_1) \times 10^7$
24.7	10,473	16,434	21,220	51.34	0.868	0.870	1490	119	67.7	47.2	0.046	5.7
25.7	12,916	18,350	21,200	33.76	0.796	0.793	810	64.3	37.2	29.7	0.054	5.8
28.2	15,046	19,380	21,144	24.88	0.704	0.703	430	34.2	20.6	20.8	0.071	6.0
31.0	16,626	19,960	—	20.38	0.617	—	265	21.0	12.8	16.3	0.090	6.1
34.2	17,461	20,160	21,100	18.48	0.557	0.561	181	14.3	9.1	14.4	0.117	6.3
38.0	18,167	20,263	—	17.08	0.493	—	134	10.6	6.65	13.0	0.142	6.3
40.2	18,351	20,270	20,878	16.74	0.473	0.477	116	9.1	5.88	12.6	0.160	6.4
42.0	18,656	20,290	—	16.20	0.438	—	104	8.2	5.07	12.1	0.171	6.2
47.5	18,962	20,320	20,712	15.69	0.400	0.402	80	6.3	4.0	11.6	0.214	6.3
Average $d_{14}/\kappa_1 = 6.2 \times 10^{-7}$												

of about 10×10^4 . Compared with other piezoelectric crystals the value of f_{14} is not unusually large. Hence the anomalous properties of Rochelle salt cannot be ascribed to an abnormal piezoelectric effect and we can eliminate Cady's theory.

According to Eq. (8) the relation $s_{44}^i = 1/c_{44}$ is not exact but involves a percental error $100 \times c_{44} d_{14}^2 / \kappa_1 \epsilon_F$. This quantity is smaller than $(d_{14}/\kappa_1)^2 c_{44} / 4\pi$ and the data above show that the error is smaller than 0.35 percent and probably even less than 0.1 percent.

The elastic Curie constant, as defined in Eqs. (10) and (11), is $\sigma = C(d_{14}/\kappa_1)$, where $C = 178$ for temperatures near the Curie point. Since here again we mix low and high frequency data, we chose the larger value $(d_{14}/\kappa_1) = 6.2 \times 10^{-7}$ and obtain $\sigma = 68 \times 10^{-12}$. The close agreement with the previously determined value shows that all data are consistent.

Finally it should be pointed out that the commonly used relation $e_{14} = d_{14}/s_{44}$ is valid only if s_{44} is the compliance coefficient of the foiled crystal. All previous calculations of e_{14} are based on s_{44}^i and lead therefore to excessive values.

THE DIELECTRIC PROPERTIES OF THE CLAMPED CRYSTAL

We have already eliminated the elastic and piezoelectric theory of Rochelle salt and have now to make a decision between the dielectric and interaction theories. This is achieved by calculating the reciprocal susceptibility χ_1 of the clamped crystal. According to Eqs. (4a) and (4c) $\chi_1 = c_{44} s_{44} / \kappa_1$, and can be calculated from the experimental data in Table II. The results are given in the table and Fig. 2 shows that the susceptibility of the clamped crystal follows a Curie-Weiss law

$$\chi_1 = 1/\kappa_{cl} = (t - t_c^*)/C^* \quad (17)$$

with $t_c^* = 18.5^\circ\text{C}$ and $C^* = 136$. All the data which are used to find χ_1 , with the exception of s_{23} , have been verified by at least two observers or two methods.³⁹ A small error in s_{23} does not alter the results.⁴⁰

³⁹ κ_1 and f^i have been verified by at least three observers, s_{22} and s_{33} by two. The close agreement between k_1 and k_2 (Table II) is ample proof that Mason's values of f are accurate. Only these values and s_{23} are used to find χ_1 .

⁴⁰ For any value of s_{23} between -1 and -2×10^{-12} the Curie point t_c^* is between 18° and 19° and C^* is unchanged.

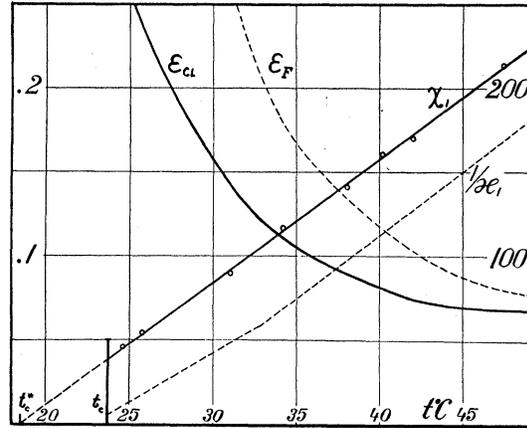


FIG. 2. The dielectric constants and the reciprocal susceptibilities of Rochelle salt for the free and the clamped crystal.

The results in Fig. 2 prove conclusively that the true dielectric properties of the clamped crystal of Rochelle salt are anomalous. However, at the Curie point $t_c = 23.7^\circ\text{C}$ of the free crystal, ϵ_{cl} has a finite value of about 300. The interaction theory is therefore correct insofar as the free crystal becomes spontaneously polarized at a temperature at which the true dielectric, elastic and piezoelectric properties are normal.

Of special interest is the fact that the Curie constant $C^* = 136$ of the clamped crystal coincides with that, C , of the free crystal for temperatures above 34°C .¹⁰ That this is not a coincidence is shown by the following consideration: If the dielectric susceptibility of the clamped crystal satisfies a Curie-Weiss law $\chi_1 = (t - t_c^*)/C^*$, then according to Eq. (4)

$$1/\kappa_1 = (t - t_c^* - C^* f_{14}^2 / c_{44}) / C^* = (t - t_c) / C,$$

i.e., the clamped and the free crystal have the same Curie constant

$$C^* = C, \quad (18)$$

We have used Hinz's values $s_{22} + s_{33} + 2s_{23} = 4 \times 10^{-12}$; Mason's value 4.9×10^{-12} gives the same C^* and $t_c = 18.3$, even Mandell's value 9.4×10^{-12} produces no appreciable change of C^* , but it shifts t_c^* to about 14°C . We have calculated under what circumstances the anomalies could be explained with a constant value of the dielectric constant of the clamped crystal. This would occur if $\epsilon_{cl} = 200$ and if $s_{22} + s_{33} + 2s_{23} = 13 \times 10^{-12}$. The latter value is incompatible with the measurements because it would require $s_{23} > 3 \times 10^{-12}$. But, since $2s_{23} + 1/c_{44} < 6 \times 10^{-12}$ is definitely established by a large number of experiments, this hypothesis would lead to an infinite or negative value of c_{44} . Hence a "pure" interaction theory is excluded.

but the Curie temperature t_c^* of the clamped crystal is lower than that, t_c , of the free crystal by

$$t_c - t_c^* = \delta t = C f_{14}^2 / c_{44} = C c_{44} (d_{14} / \kappa_1)^2. \quad (19)$$

Since we have no reliable value for (d_{14} / κ_1) , we cannot test Eq. (19), but it is noteworthy that the value from Table II, when applied to the temperature range above 34° , where $C = 136$, $t_c = 25^\circ$, furnishes $\delta t = 6^\circ$, whence $t_c^* = 19^\circ$. Equations (18) and (19) make it possible to discuss the behavior of the clamped crystal below the lower Curie point, in spite of the fact that no elastic and piezoelectric data are available for this temperature range. If the assumption is justified that c_{44} and f_{14} have approximately the same values as they have above the upper Curie point, then the shift of the lower Curie point is found from $\delta t' / \delta t = C' / C$, where $C' = -93.8$ is the Curie constant at the lower Curie point.¹⁰ The lower Curie point of the clamped crystal is therefore higher than that of the free crystal.

The writer¹⁰ has shown that the dielectric data can be represented by a set of Curie-Weiss laws, whereby various temperature ranges give the values C and t_c shown in Table III. Eq. (19) serves to find the corresponding values of δt and t_c^* and we are therefore able to construct the approximate course of the $\chi_1(t)$ curve as shown in Fig. 3.

Figure 3 shows that the difference $\chi_1 - 1/\kappa_1 = 0.05$ is practically constant over the entire temperature range. This result is a consequence of $\chi_1 = c_{44} s_{44} / \kappa_1$ and $s_{44} = 1/c_{44} + d_{14}^2 / \kappa_1$, (from Eq. (8)), whence

$$\chi_1 - 1/\kappa_1 = (d_{14} / \kappa_1)^2 c_{44}. \quad (20)$$

By using Eqs. (4) and (5) it is readily shown that (20) is equivalent to Cady's relation $\kappa_1 - \kappa_{cl} = d_{14} e_{14}$. Eq. (20) offers the most convenient method for the determination of the dielectric

TABLE III. Curie constants and Curie temperatures for the free and clamped crystal of Rochelle salt.

TEMPERATURE RANGE	C	δt	t_c	t_c^*
above 34	136	6.8	25.3	18.5
32 to 24	178	8.9	23.0	14.1
- 18 to - 28	-93.8	-4.7	-17.9	-13.2
- 28 to - 42	-68.5	-3.4	-20.6	-17.2
- 42 to - 80	-47.9	-2.4	-27.1	-24.7
-100 to -140	-80.6	-4.0	16.6	12.6

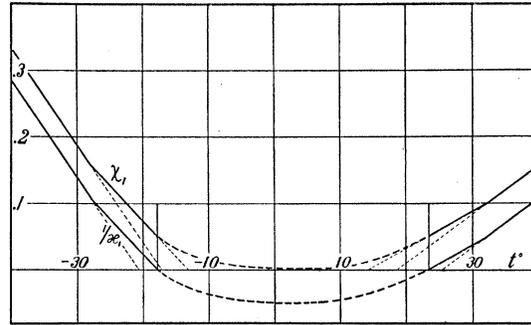


FIG. 3. The reciprocal susceptibility of the free crystal and the approximate course of the $\chi_1(t)$ curve for the clamped crystal of Rochelle salt in the ferroelectric temperature range.

properties of the clamped crystal. The value of χ_1 is obtained by displacing all points of the measured $1/\kappa_1(t)$ curve by an amount $(d_{14} / \kappa_1)^2 c_{44}$. This shift usually will vary with temperature. Its magnitude can be found from elastic measurements, since, with good approximation (use $\epsilon_F = 4\pi\kappa_1$)

$$(d_{14} / \kappa_1)^2 = (1/f^2 - 1/f'^2) / \rho\kappa_1. \quad (21)$$

Our theory is valid only for the temperature range where the crystal is orthorhombic; i.e., above the upper and below the lower Curie point. In order to give a theory for the ferroelectric state it is necessary to enlarge the present theory by taking into account higher terms in the expression (1) for the free energy. We shall discuss this extension in another paper, in which we shall prove that the relationships between the properties above and below the upper Curie point are essentially those given in an earlier paper.¹⁰ There, (Eq. (23) of our 1935 paper) we have shown that $-1/2\kappa_0 = (t - t_c) / C$, where κ_0 is the susceptibility corresponding to the slope of the saturation branch of the hysteresis loop. Hence by plotting $-1/2\kappa_0$ versus t we can interpolate between the two branches of the $1/\kappa_1$ curve in Fig. 3 and obtain the approximate $\chi_1(t)$ curve for the ferroelectric range. According to the result in Fig. 3 it appears most likely that the clamped crystal of Rochelle salt does not become ferroelectric, although its dielectric constant reaches extremely large values between -10° and 10°C .

We conclude therefore that the true dielectric properties of Rochelle salt are anomalous and this anomaly is largely responsible for the spon-

taneous polarization and deformation of the free crystal. The clamped crystal, however, most probably does not become ferroelectric, or if it does, the two Curie points are only a few degrees apart and the clamped crystal will never show a large hysteresis loop. This result is confirmed by the experiments on crystals in which the deformation is suppressed. The large hysteresis loop of the free crystals is mainly due to the piezoelectric interaction between dielectric polarization and elastic deformation.

APPENDIX

Anti-resonance of a vibrating crystal

We consider the case of a foiled plate of Rochelle salt, 1 cm long, cut normal to the a axis, and in the state of longitudinal vibration in the direction at 45° to the b and c axes. We refer all quantities to a new system of axes in which $x' = x$ and the y' axis points in the direction of vibration. The stress tensor associated with a longitudinal wave has only one component $Y_{y'}$ and the elastic equations (3) in the new system are⁴¹

$$\begin{aligned} -y_{y'} &= s_{22}' Y_{y'} + d_{12}' E_x, \\ P_x &= d_{12}' Y_{y'} + \kappa_1 E_x, \end{aligned} \quad (A)$$

where

$$\begin{aligned} s_{22}' &= \frac{1}{4}(s_{22} + s_{33} + 2s_{23} + s_{44}), \\ d_{12}' &= \frac{1}{2}d_{14}, \end{aligned} \quad (B)$$

and $E_x = E \cos \omega t$ is the field applied across the condenser plates. If u denotes the displacement in the direction of vibration of a volume element of the crystal, $y_{y'} = \partial u / \partial y'$, and the principles of mechanics furnish

$$\rho \partial^2 u / \partial t^2 = -\partial Y_{y'} / \partial y'. \quad (C)$$

Since for a foiled crystal $\partial E / \partial y' = 0$, (A) and (C)

⁴¹ For the equations of transformation see W. P. Mason, Phys. Rev. **55**, 781 (1939).

lead to the differential equation of a wave

$$s_{22}' \rho \partial^2 u / \partial t^2 = \partial^2 u / \partial y'^2.$$

The solution which satisfies the boundary conditions $Y_{y'}(\pm \frac{1}{2}) = 0$ is

$$u = a \sin \omega y' / v \cos \omega t, \quad (D)$$

i.e., a standing wave with the amplitude

$$a = (-v d_{12}' E / \omega) \cos \omega / 2v, \quad (E)$$

and traveling with the velocity $v = (\rho s_{22}')^{-\frac{1}{2}}$.

The field produces within the crystal a displacement current of density

$$i = (1/4\pi)(\partial D / \partial t) = (1/4\pi)(\partial E_x / \partial t) + \partial P_x / \partial t.$$

By inserting u from (D) into $y_{y'} = \partial u / \partial y'$ and substituting the result in Eqs. (A) one finds after elimination of $Y_{y'}$

$$P_x = [(\kappa_1 - d_{12}'^2 / s_{22}') E - (a \omega d_{12}' / v s_{22}') \cos \omega y' / v] \cos \omega t.$$

If W is the width of the crystal the total current I passing through the condenser is

$$I = W \int_{-1}^1 i dy',$$

and this leads to the final result

$$I = (\epsilon_F / 4\pi) W (dE_x / dt) \times \left[\left(\frac{2v}{\omega} \tan \frac{\omega}{2v} - 1 \right) \pi d_{14}'^2 / s_{22}' \epsilon_F + 1 \right].$$

Resonance occurs when $\omega / 2v = \frac{1}{2}\pi$; i.e., for the frequency $f = \omega / 2\pi = \frac{1}{2}v = \frac{1}{2}(\rho s_{22}')^{-\frac{1}{2}} = \rho^{-\frac{1}{2}}(s_{22}' + s_{33} + 2s_{23} + s_{44})^{-\frac{1}{2}}$. This is the result used in Eq. (9). Anti-resonance occurs when $I = 0$, hence for a frequency $f_A = \omega / 2\pi$ for which

$$(2f / \pi f_A) \tan (\pi f_A / 2f) = 1 - s_{22}' \epsilon_F / \pi d_{14}'^2,$$

and comparison with Eqs. (12) and (13) shows that this is identical with Mason's relation, but the value of k is that given in Eq. (13).