Properties of Rochelle Salt. IV [1]

HANS MUELLER

Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received September 12, 1940)

A new class of effects in crystals, called morphic effects, is considered. They arise when elastic strains alter the symmetry of the structure. This necessitates the introduction of new coefficients, proportional to the acting strains, into the matrix of the coefficients which characterize the linear effects. The new coefficients give rise to a series of new quadratic effects in crystal physics. These morphic effects play a role in the photoelasticity of cubic crystals. They are especially large in the crystals of Rochelle salt, where they are responsible for the so-called Kerr effects and a new type of irreversible piezoelectric effects. The existence of this new effect has been verified. It creates irreversible normal strains when the crystal is polarized in the a direction, and spontaneous contractions occur when the crystal is cooled to below the Curie point. The spontaneous normal strains are responsible for the anomalous thermal expansion of Rochelle salt and for a series of other anomalies. It is suggested that these strains may also be the cause for the existence of the lower Curie point.

THE KERR EFFECT OF ROCHELLE SALT

IN 1893, in the course of his classical investigation of the relation between the piezoelectric, photoelastic and electro-optical properties of crystals, Pockels[2] discovered in Rochelle salt an irreversible electro-optical effect for electric fields parallel to the a axis. In 1930 the writer, unaware of Pockels' work, rediscovered this so-called Kerr effect and, in collaboration with Miss Groat,[3] studied its dependence on field intensity and temperature for various light directions. In contrast to all other crystals, for which the Kerr effect is too small to be observed, the quadratic change of birefringence in Rochelle salt is about a million times larger than the electro-optical double refraction in most liquids. It appears, therefore, improbable that it could be explained on the basis of the Langevin-Born theory for the Kerr effect in gases and liquids, and a lattice theory of the phenomenon cannot be attempted as long as the crystal structure of Rochelle salt is not known. Jaffé[4] has proposed an explanation based on the laws of classical crystal physics. He pointed out that at temperatures between the Curie points the crystal is not rhombic but monoclinic hemimorphic. Crystals of the latter class have, for electric fields in direction of the polar axis, a linear electro-optical effect which gives rise to the same kind of optical changes as are observed in the Kerr effect of Rochelle salt. According to this theory the Kerr effect is really a linear effect. It is not reversed by a reversal of the field because such a reversal also inverts the direction of the polar axis by the process of orientation-twinning. Although the suppositions of Jaffé's theory are correct, his explanation is not adequate, because it implies that the effect should vanish at the Curie points, while actually it is largest at these temperatures and it also exists above the upper Curie point, where the crystal is rhombic. A more satisfactory theory is obtained by the following modification of Jaffé's argument:

For crystals of the rhombic hemiedric class an electric field E_x in the a direction produces a linear electro-optical effect which is given by the equations

$$a_{11} = 1/n_a{}^2, \qquad a_{22} = 1/n_b{}^2, \qquad a_{33} = 1/n_c{}^2,$$
$$a_{23} = r_{41}P_x, \qquad a_{31} = a_{12} = 0. \tag{1}$$

n_a, n_b, n_c are the principal refractive indices of the unpolarized crystal, P_x is the electric polarization and r_{41} is an electro-optical constant.[5] The polarization constants a_{ik} determine the

[1] This is the last of a series of four papers on this subject. The previous articles, Phys. Rev. **47**, 175 (1935); **57**, 829 (1940) and **58**, 565 (1940) are referred to as papers I, II and III, respectively.

[2] F. Pockels, Abhand. d. Ges. d. Wiss. zu Göttingen, Math. Phys. Klasse **39**, 1 (1893).

[3] L. M. Groat, M. S. Thesis, 1932. Massachusetts Institute of Technology, see paper I.

[4] H. von R. Jaffé, Phys. Rev. **51**, 43 (1937).

[5] To avoid confusion with the piezoelectric constants e_{ik} we denote the electro-optical constants by r_{ik}, instead of by e_{ik}, as customary after F. Pockels, *Lehrbuch d. Kristall-optik* (Leipzig, 1905).

optical index ellipsoid $\Sigma a_{ik}yz=1$ of the polarized crystal. Equations (1) would be valid for Rochelle salt above the upper Curie point if the piezoelectric effect were small. However, since this effect is unusually large, it becomes necessary to enlarge the classical theory. The piezoelectric action of the field E_x is to create a shearing deformation $y_z = -f_{14}P_x/c_{44}$ (from Eq. (2a), III), which alters the symmetry of the crystal from rhombic hemiedric to monoclinic hemimorphic with the a axis as polar axis. For crystals of the latter class the equations for the linear electro-optical effect, for fields in the a direction[6] are

$$a_{11}-1/n_a{}^2=r_{11}P_x, \qquad a_{22}-1/n_b{}^2=r_{21}P_x,$$
$$a_{33}-1/n_c{}^2=r_{31}P_x, \qquad a_{23}=r_{41}P_x, \qquad (2)$$
$$a_{31}=a_{12}=0.$$

Since the appearance of the three new constants r_{11}, r_{21}, r_{31} is the result of the piezoelectric deformation y_z, these parameters are proportional to the strain and, therefore, also to the polarization P_x. Whence $r_{11}=s_1P_x$, $r_{21}=s_2P_x$, $r_{31}=s_3P_x$, and the final equations for the electro-optical effects in Rochelle salt for fields in the a direction take the form

$$a_{11}-1/n_a{}^2=s_1P_x{}^2, \qquad a_{22}-1/n_b{}^2=s_2P_x{}^2,$$
$$a_{33}-1/n_c{}^2=s_3P_x{}^2, \qquad (3a)$$

$$a_{23}=r_{41}P_x, \qquad a_{31}=a_{12}=0. \qquad (3b)$$

Equations (3b) describe the ordinary linear electro-optical effect which is observed when the light direction does not coincide with a crystallographic axis. If the light traverses the crystal along the b or c axis only the optical changes described by Eqs. (3a) are observed. They represent an irreversible or quadratic electro-optical effect. Since $a_{11}=1/(n_a+\delta n_a)^2$, where δn_a is the change of the refractive index, the changes of the birefringence are

$$\Delta_a = \delta(n_b-n_c)/\lambda = k_a P_x{}^2, \qquad (4a)$$

$$\Delta_b = \delta(n_c-n_a)/\lambda = k_b P_x{}^2, \qquad (4b)$$

$$\Delta_c = \delta(n_a-n_b)/\lambda = k_c P_x{}^2, \qquad (4c)$$

where $k_a = (n_c{}^3s_3 - n_b{}^3s_2)/2\lambda$, etc., $k_a+k_b+k_c=0$, and λ is the wave-length of the light. (4b) and

(4c) represent the transversal Kerr effects for light traveling in the b or c direction, (4a) gives the longitudinal Kerr effect for light parallel to the field. These equations account for the curious field and temperature dependence of the electro-optical double refraction. From the Curie-Weiss law $\kappa_1 = C/(t-t_c)$ and Eq. (3a), III, it follows that for temperatures above the Curie point

$$E_x = P_x(t-t_c)/C+BP_x{}^3. \qquad (5)$$

By substitution of $P_x = (\Delta/k)^{\frac{1}{2}}$, from Eq. (4), we arrive at the empirically verified relation (Fig. 12, I)

$$E_x/\Delta^{\frac{1}{2}} = R(t-t_c)+Q\Delta, \qquad (6)$$

where $R=1/Ck^{\frac{1}{2}}$ and $Q=B/k^{\frac{3}{2}}$, whence

$$Q/R^3 = BC^3. \qquad (7)$$

The experimental values are[7] $k_a=1.7\times10^{-7}$, $k_b=-6.4\times10^{-7}$, $k_c=4.7\times10^{-7}$, $R_b=6.9\pm0.2$, $Q_b=150\pm20$, $R_c=10.1\pm0.2$, $Q_c=307\pm10$. These data give $Q_b/R_b{}^3=4.5\pm1.0$, $Q_c/R_c{}^3=3.0\pm0.4$. The latter value is based on more accurate data and agrees quite well with the results of the dielectric measurements which give $C=178$, $B=5.8\pm0.7\times10^{-8}$, whence $BC^3=3.3\pm0.4$. The electro-optical measurements lead therefore to the same value of B as derived in paper III from the dielectric and elastic saturation effects.

Between the Curie points the spontaneous polarization $P_x{}^0$ creates a spontaneous Kerr effect $\Delta^0 = kP_x{}^{02}$. This gives rise to the anomalous temperature variation of the birefringence near the two Curie points (Figs. 18 and 19, I). The full curve in Fig. 1 presents the observed variation of $(n_a-n_c)/\lambda$ with temperature. By subtracting from these data the values of $\Delta_b{}^0$, as calculated from k_b and the values of $P_x{}^0$ from Table II in paper III, we obtain the dotted curve which represents the change of birefringence of the clamped crystal. This curve has no anomalies at the Curie points, but the slope changes markedly in the range between $-5°$ and $0°$C. Although the change is gradual and appears at a somewhat lower temperature than the minimum of the $\chi_1(t)$ curve, we suspect that it is caused by the peculiar type of transition

---

[6] We follow Jaffé's suggestion of designating the polar axis by a and not by c, as is customary in monoclinic crystals.

[7] From paper I. k is identical with ρf^2. The equation on page 189 of paper I (Phys. Rev. 47) should read $\rho_c f^2 = 4.7 \pm 1.0 \times 10^{-7}$.
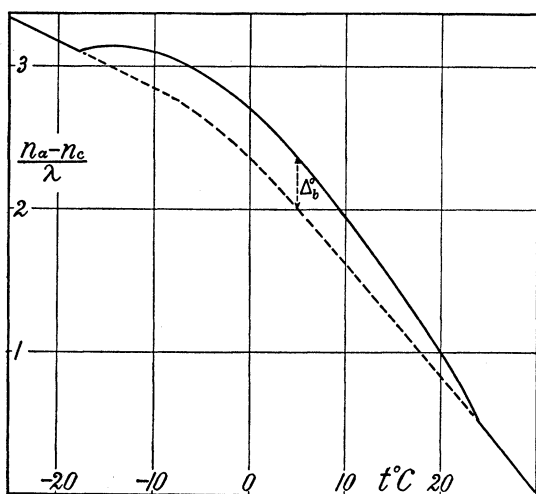
FIG. 1. Temperature dependence of the birefringence of the free crystal (full curve) and the clamped crystal (dotted curve) of Rochelle salt.

which the clamped crystal undergoes in this temperature range.

The irreversible electro-optical effect in the ferroelectric temperature range can be explained, as Jaffé proposed, as a linear effect of the monoclinic structure, but to obtain quantitative agreement with the observations it is necessary to correlate the change of birefringence with the electric polarization, and not with the field E or the inner field F. If the applied field E_x is larger than the coercive field, but not large enough to produce dielectric saturation, one can assume that it changes the polarization from $P_x{}^0$ to $P_x{}^0 + \delta P_x$, where $P_x{}^0 \gg \delta P_x$ and where $P_x{}^0$ has the same direction as the applied field. The change of birefringence is, in first approximation,

$$\Delta = k(P_x{}^0 + \delta P_x)^2 - \Delta^0 = 2kP_x{}^0\delta P_x = 2kP_x{}^0\kappa_1{}^0E_x, \quad (8)$$

where $\kappa_1{}^0$ is the susceptibility of the free crystal in the ferroelectric state. Although $P_x{}^0$ vanishes at the Curie points, the Kerr effect does not become zero, because, as was shown in paper III, $\kappa_1{}^0$ increases near these temperatures at the same rate as $1/P_x{}^{0^2}$. Hence the electro-optical effects are larger at the Curie points than at any other temperature. Theory and observations furnish at the Curie points $\Delta = (E_x/Q)^{\frac{2}{3}}$. At temperatures between, but not too close to the Curie points, Δ is proportional to the field. However, it does not reverse its sign when E_x is reversed,

because the product $P_x{}^0E_x$ is always positive, except for small fields where the $\Delta(E_x)$ curve represents a quadratic hysteresis loop (Fig. 23, I). In strong fields the change of birefringence tends toward saturation in the same manner as $P_x{}^2$. The smallest Kerr effect in the ferroelectric range occurs at the transition temperature of the clamped crystal near 5°C. Since all conclusions agree with the facts there can be little doubt that the fundamental relations (3) are correct. From the values of k, c_{44} and f_{14} one finds by a rough estimate that the electro-optical constants r_{11}, r_{21} and r_{31} reach the same order of magnitude (of about 10^{-7}) as the ordinary constant r_{41} when the shearing strain y_z is of the order of 10^{-3}. This means that, from the phenomenological point of view, a crystal of Rochelle salt must be considered to be monoclinic when the angle between the b and c axes differs from 90° by only a few minutes.

MORPHIC EFFECTS IN CRYSTAL PHYSICS

The above discussion shows that the Kerr effect in Rochelle salt belongs to a new class of effects in crystal physics which, as far as the writer knows, have not been discussed previously[8] and which we propose to call "morphic" effects. They occur when the symmetry of a crystal is altered by elastic strains. The change of symmetry calls for a change in the matrix of the coefficients which determine the linear effects. New coefficients, which were zero in the undeformed crystal, may appear, or coefficients which had originally identical values become different. Morphic effects are of higher order, but their properties can be derived from the theory of the linear effects. They are linear effects with variable coefficients. The theory of these effects is not covered by the theory of the ordinary second order effects (electrostriction, etc.), because, as is seen form the examples given below, the morphic effects do not follow the same laws of superposition which hold for quadratic effects. Since a deformation usually will not create new symmetry elements but rather reduce their number, the morphic effects can not occur in

---

[8] A similar type of effect for isotropic solids has been considered by L. Brillouin, Proc. Indian Acad. Sci. 8, 251 (1938). The name "morphic" was suggested by Dr. J. F. G. Hicks.
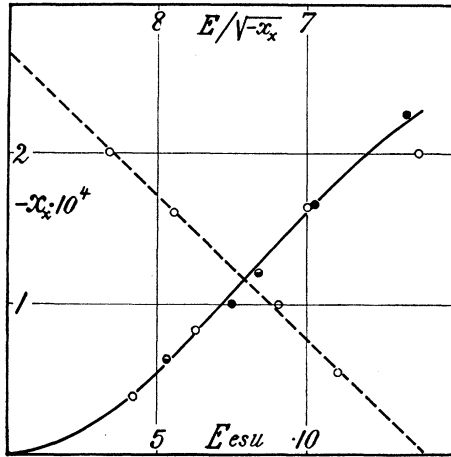
FIG. 2. The irreversible piezoelectric effect in Rochelle salt.

triclinic crystals, but they will be frequent in cubic crystals. The following consideration shows how they enter in the photoelasticity of cubic crystals.

According to the classical theory a pressure P normal to a cube face produces a birefringence

$$\delta(n_x - n_y) = \tfrac{1}{2}n^3(p_{11} - p_{12})(s_{11} - s_{12})P, \quad (9)$$

where p_{ik}'s are the elasto-optical constants and s_{ik}'s are elastic compliance coefficients. This equation is modified by morphic effects which take into account the fact that the cubic crystal becomes tetragonal under the influence of the pressure. For a tetragonal crystal the photo-elastic equation for pressure along the tetragonal axis is

$$\delta(n_x - n_y)$$
$$= \tfrac{1}{2}n^3[(p_{11} - p_{21})s_{11} - (p_{22} + p_{23} - 2p_{12})s_{12}]P.$$

The relations $p_{11} = p_{22}$ and $p_{12} = p_{21} = p_{23}$, which are valid for the undeformed cubic crystal, will not hold in the deformed crystal. Instead $(p_{11} - p_{21})$ must differ from $(p_{22} + p_{23} - 2p_{12})$ by a quantity proportional to the pressure P. The photoelastic effect in a cubic crystal follows, therefore, a law of the form

$$\delta(n_x - n_y) = AP + BP^2. \quad (10)$$

Maris,[9] and more recently Kidani,[10] have indeed shown that Eq. (10) is in better agreement with

[9] H. B. Maris, J. Opt. Soc. Am. **15**, 194 (1927).
[10] Y. Kidani, Proc. Phys.-Math. Soc. Japan **21**, 457 (1939).

the observation than the classical law (9). The quadratic term BP^2 is of morphic origin and cannot be considered as an ordinary higher order effect, because the measurements of the change of refraction by a hydrostatic pressure, which creates no symmetry changes, show no deviations from the linear law.

It appears likely that morphic effects may play a role in many fields of crystal physics. The morphic effects are smaller than the linear effects, but they seem to be larger than the ordinary quadratic effects. We shall not attempt to develop here a general theory of the morphic effects but limit our consideration to their influence on the properties of Rochelle salt.

THE QUADRATIC PIEZOELECTRIC EFFECT AND THE ANOMALOUS THERMAL EXPANSION OF ROCHELLE SALT

Since the elastic properties of a crystal are given by a tensor of the same kind as that describing its optical properties, the equations for the piezoelectric effect have the same structure as those for the electro-optical phenomena. The equations for the piezoelectric effect in Rochelle salt for a field E_x are therefore similar to Eqs. (3), namely

$$-x_x = \varphi_1 P_x^2, \quad -y_y = \varphi_2 P_x^2, \quad -z_z = \varphi_3 P_x^2, \quad (11a)$$

$$-y_z = f_{14}P_x/c_{44}, \quad z_x = x_y = 0. \quad (11b)$$

In addition to the linear effect, given by Eq. (11b), the field E_x will create a morphic effect resulting in three normal strains which cannot be reversed by inverting the direction of the field. Equations (11a) happen to be identical with those describing electrostriction. However, it should be noted that the conditions for the occurrence of the quadratic piezoelectric effect are different from those for electrostriction. The morphic piezoelectric effect occurs only if the shearing deformation y_z is not suppressed. The appearance of electrostriction is not dependent on this condition.

The existence of the quadratic piezoelectric effect has been verified in a preliminary experiment carried out in collaboration with Dr. H. T. Gerry. We measured with a Lippmann interferometer the change of length in the a direction of a Rochelle salt crystal when an electric field

E_x was applied. The change x_x was found to be a contraction and was independent of the direction of the field. The effect is many thousand times larger than any electrostrictive effect ever reported. Since it is a contraction it is impossible to account for it by heating effects due to Joule heat or to electrocaloric effects. The results obtained at a room temperature of 25.5°C are given by the full curve in Fig. 2. The field dependence of the quadratic piezoelectric effect is similar to that of the Kerr effect at the same temperature. By using the same arguments which lead to Eq. (6) one finds that above the Curie point the relation

$$E_x/(-x_x)^{\frac{1}{2}} = v(t-t_c) - wx_x \qquad (12)$$

should hold, where $v = 1/C\varphi_1^{\frac{1}{2}}$, $w = B/\varphi_1^{\frac{1}{2}}$. The dotted curve in Fig. 2 shows indeed that Eq. (12) is satisfied and gives $v(t-t_c) = 6 \times 10^2$, $w = 1.3 \times 10^6$. The value of w/v^3 is again of the same order of magnitude as Q/R^3 and BC^3, but since the temperature of the crystal was not controlled we cannot give a reliable value of v. From w and B one estimates that $\varphi_1 = 1.2 \times 10^{-9}$ cm³/erg. No crystals suitable for the determination of φ_2 and φ_3 were available. The magnitude of the quadratic piezoelectric effect is surprisingly large. Near the Curie point a field of 3000 volt/cm creates a contraction of the same magnitude as that produced by a hydrostatic pressure of about 100 atmospheres. We are unable to understand how Körner[11] could fail to notice this effect.

The result of this experiment clarifies the origin of a series of effects in Rochelle salt. It shows that the quadratic electro-optical effect is, at least in part, of photoelastic origin, i.e., the birefringence is caused by the strains x_x, y_y, z_z. The order of magnitude and the sign of the Kerr effects are compatible with this explanation. The question, whether a part of the optical effects is due to the direct action of the field, can be answered only after the photoelastic properties of Rochelle salt have been studied.[12]

In the ferroelectric temperature range the spontaneous polarization P_x^0 will create spon-

taneous strains $-x_x^0 = \varphi_1 P_x^{0^2}$, $-y_y = \varphi_2 P_x^{0^2}$, $-z_z = \varphi_3 P_x^{0^2}$, and, for fields E_x larger than the coercive field, the crystal should show a linear, but irreversible, piezoelectric effect given by equations of the form $-x_x = 2\varphi_1 P_x^0 \kappa_1^0 E_x$. The spontaneous normal strains most probably give rise to an anomalous density variation of Rochelle salt at the Curie points. The available density measurements have not been carried out with sufficient accuracy to record this effect, but the existence of the spontaneous strain x_x^0 is confirmed by Hablützel's measurements[13] of the coefficient of linear thermal expansion in the a direction. The curve in the lower part of Fig. 3 presents Hablützel's data of $\alpha_x = dx_x/dt$. From this curve the dotted curve $x_x(t)$ in the upper part of the figure was evaluated by graphical integration. This curve is to be compared with the full drawn theoretical curve which is obtained by subtracting from the normal linear $x_x(t)$ variation the spontaneous contraction $x_x^0 = \varphi_1 P_x^{0^2}$. The calculation of x_x^0 is based on the value $\varphi_1 = 1.2 \times 10^{-9}$ and the P_x^0 values in Table II of paper III. The agreement is better than could be expected from the accuracy of the data.

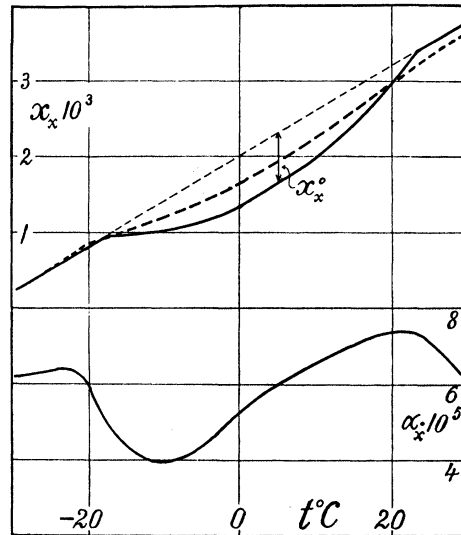Hablützel also has measured the thermal expansion in a direction at 45° to the b and c

Fig. 3. The anomalous thermal expansion of Rochelle salt. Lower curve: Coefficient of thermal expansion, according to Hablützel. Upper curves: Thermal expansion according to theory (full curve) and experiment (dotted curve).

[11] H. Körner, Zeits. f. Physik 103, 170 (1936).

[12] F. Pockels (reference 2) has measured 9 linear combinations of the photoelastic constants. Since Rochelle salt has 12 photoelastic constants, his work is not sufficient for the evaluation of all constants.

[13] J. Hablützel, Helv. Phys. Acta 8, 499 (1935).

axes and found a curve of similar shape as for the expansion in the a direction. This result, which has been confirmed in recent measurements of Dr. Gerry, indicates that either one or both of the spontaneous strains y_y^0 and z_z^0 also are contractions. Gerry,[14] furthermore, finds that the anomalous expansion is different in the (011) and (0 −1 1) directions. This, of course, is due to the spontaneous shearing deformation y_z^0.

At the Curie points the crystal of Rochelle salt undergoes, therefore, more radical changes than has heretofore been realized. These changes correspond to three spontaneous normal strains which are proportional to $P_x^{0^2}$, and a shearing strain y_z^0 which is proportional to P_x^0. These strains reach maximum values between 10^{-4} and 10^{-3} at 5°C. The production of the normal strains gives an additional contribution to the change of the specific heat. The additional energy change is $\frac{1}{2}(c_{11}x_x^{0^2}+c_{22}y_y^{0^2}+c_{33}z_z^{0^2})$ and is proportional to $(P_x^0)^4$. The conclusions drawn in paper III are, therefore, still valid. While the shearing strain is responsible for the morphic effects and leads to the introduction of new elastic and dielectric constants, the normal strains will alter slightly the values of all "normal" constants of Rochelle salt. These effects are undoubtedly responsible for the change of the value and the temperature gradient of the resonance frequencies of the isolated crystal[15] at the Curie point, of the slight variations[16] of the dielectric constants ϵ_b and ϵ_c and the change of the intensities of certain x-ray reflections.[17] They justify our conclusion in paper III that the constants c_{44}, f_{14} and B suffer small changes at the Curie points.

THE TRANSITION OF ROCHELLE SALT

The result of our discussions in papers II, III and IV may be summarized as follows: If the crystal of Rochelle salt were not piezoelectric it would show only a single transition point. The two Curie points and the large number of dielectric, piezoelectric, optical, caloric and thermal anomalies of the free crystal can all be explained on the basis of laws which are logical extensions of the laws of classical crystal physics. There remains, therefore, only the problem of understanding the nature of the transition of the clamped crystal. This transition is characterized by a high maximum of the dielectric constant, but the available evidence does not indicate any changes of the internal energy or of the structure. Figure 1 shows that the temperature gradient of the birefringence is altered but there is no sudden change of the optical constants. These peculiarities indicate that the transition can involve only a change of the position or of the dynamics of the protons of either the OH groups or the water of crystallization. The transition may be similar to those in HBr, HI, H_2S, PH_3.[18] It differs, however, from the modifications of these crystals by the fact that the transition of Rochelle salt produces no change of the specific heat. To account for this we propose the hypothesis that the transition is suppressed, i.e., with decreasing temperature the crystal approaches a transition point without actually reaching it, because in the initial stages of the transition secondary effects are created which suppress the modification and the crystal remains in its original state because at lower temperature the protons have not sufficient energy to change their positions. The nature of the suppressing agent may possibly be explained as follows.

The calculation in paper II of the dielectric susceptibility of the clamped crystal takes into account only the shearing strains y_z but neglects the normal strains. To be sure, if a crystal could be clamped so that the shearing strains are suppressed, it would also show no morphic

[14] H. T. Gerry's measurements lead to somewhat smaller values of y_z^0 than those reported in paper II, but the investigation had to be interrupted when the crystal cracked. This investigation was carried out in the Laboratories for Physical Chemistry of the Institute. I am indebted to Dr. Gerry (now with the Solvay Process Company, Hopewell, Virginia) for the permission to use his data. In contrast to Gerry's and Hablützel's results, the measurements of I. Viguess, Phys. Rev. 48, 198 (1935) indicate that y_y^0 and z_z^0 are expansions.

[15] W. P. Mason, Phys. Rev. 55, 775 (1939); G. Mikhailov, Tech. Physik U.S.S.R. 3, 652 (1936).

[16] J. Hablützel, Helv. Phys. Acta 12, 489 (1939).

[17] H. Staub, Physik. Zeits. 34, 292 (1933).

[18] These transitions, commonly ascribed to hindered rotation, are not fully understood. The fact that these crystals have two transition points suggests certain analogies with Rochelle salt. Whether they are justified could be ascertained by dielectric measurements on single crystals of these substances. Measurements on polycrystalline samples give insufficient information, because for Rochelle salt they show no Curie points. For a review of these transitions see A. Eucken, Zeits. f. Elektrochemie 45, 126 (1939).
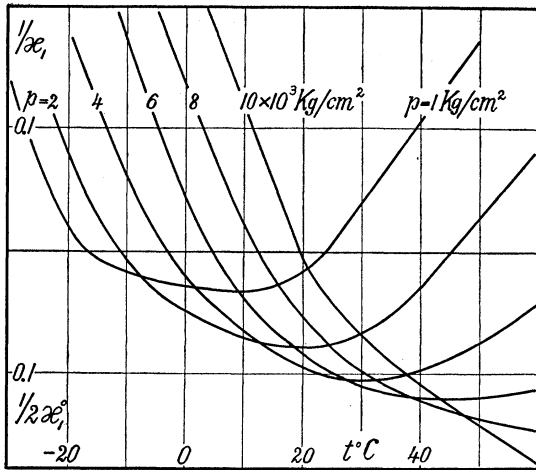
FIG. 4. Temperature dependence of the reciprocal susceptibility of Rochelle salt under hydrostatic pressure (according to the measurements of Bancroft).

effects and the normal strains would disappear. However, dielectric measurements on such a crystal would not lead to the theoretical $\chi_1(t)$ curve in Fig. 3, II. This curve applies to the experimentally unrealizable case of a crystal in which y_z is suppressed but in which the normal strains are those which occur in the free crystal. These normal strains, especially the spontaneous normal strains x_x^0, y_y^0, z_z^0, will certainly have considerable influence on the $\chi_1(t)$ curve. This follows from the investigations of Bancroft[19] who studied the influence of hydrostatic pressure on the $1/\kappa_1(t)$ curves of free crystals. Figure 4 is based on Bancroft's data. It shows, also, that at higher pressures the dielectric data can be represented by continuous curves without any discontinuities at the Curie points if one plots $1/\kappa_1(t)$ and $1/2\kappa_1^0(t)$, where κ_1 and κ_1^0 are the susceptibilities in the paraelectric and ferroelectric range, respectively. According to the results in paper II we are justified in assuming that the $\chi_1(t)$'s are parallel to those in Fig. 4, but the vertical displacement $\chi_1 - 1/\kappa_1$ will change with the pressure. Figure 4 shows that in the critical temperature range the slope of the $\chi_1(t)$ curves decreases and becomes negative,

not only when the temperature is lowered at constant pressure, but also when the pressure is raised at constant temperature. Now, it is a characteristic feature of the $\chi_1(t)$ curve that, while it has a small curvature above the Curie point, its slope decreases rapidly as soon as the temperature drops below the upper Curie point. With further temperature decrease the slope becomes negative with the result that the critical condition $\chi_1 = 0$ is avoided. Since it is known that at least two of the normal strains are contractions they must influence the $\chi_1(t)$ curve in a manner similar to that produced by a hydrostatic pressure and it seems, therefore, natural to hold these strains responsible for the peculiar course of the $\chi_1(t)$ curve and for the suppression of the transition. If this hypothesis is correct we arrive at the following explanation of the properties of the free crystal of Rochelle salt. A rigid crystal, in which all strains are suppressed, would show a transition. Probably it would occur at about 18°C where the extrapolation of the $\chi_1(t)$ curve above the Curie point intersects the zero axis (Fig. 3, II). Because of the piezoelectric interaction the free crystal becomes spontaneously polarized and deformed before this transition temperature is reached, namely at the upper Curie point at about 24°C.[20] The elastic deformation, in particular the normal strains which are of morphic origin, prevent the occurrence of the transition and the crystal returns at lower temperatures to a state of low dielectric constant. During this process the free crystal must pass through a lower Curie point. For the other ferroelectric crystals, for which an anomaly of the specific heat has been observed, there is no reason to assume that the transition is suppressed, though the interaction and morphic effect should occur also in these crystals.

[19] D. Bancroft, Phys. Rev. 53, 587 (1938).

[20] This temperature depends on the definition of the Curie point. Extrapolation of the measurements above the Curie point gives in almost all cases $t_c = 23°C$, but the maximum value of κ_1 occurs at 23.7°C. On the other hand, we find that the resonance frequencies of the foiled crystal have a minimum at 24.1°C. It is possible that this temperature differs in different crystals, depending on internal strains.