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Properties of Rochelle Salt. III[1]

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The interaction theory of Rochelle salt is extended by supplementing the expression for the free energy of the deformed and polarized crystal by a term proportional to the fourth power of the polarization in the *a* direction. This second approximation explains the dielectric and elastic saturation phenomena above the upper Curie point and the dielectric, elastic, piezoelectric and pyroelectric properties in the ferroelectric temperature range. All experimental results are compatible with the hypothesis that the clamped crystal has only one transition point at about 5° C, where its dielectric constant has a very high maximum. The two Curie points of the free crystal are due to the interaction between the elastic deformation and the electric polarization. Instead of sudden changes of the heat capacity the new theory predicts slight changes of the slope of the specific heat curve at the Curie points. The dispersion of the dielectric constant is explained without assuming a relaxation time.

THE results of paper II suggest the following explanation of the anomalous properties of Rochelle salt: If the crystal could be clamped in such a way that all elastic deformations are suppressed it would show only a single transition at about 5°C. At this temperature the dielectric constant in the *a* direction of the clamped crystal has a sharp and very high maximum, i.e., the reciprocal susceptibility χ_1 vanishes (see Fig. 3, II). This transition is not a Curie point, because below this temperature the clamped crystal is not spontaneously polarized, its dielectric behavior remains normal and χ_1 increases again to reach a normal value at low temperatures. The transition appears to be similar to those observed in other crystals, e.g. HBr, HI.[2] Most probably it is due to a modification of proton bonds or to hindered rotation of polar groups. The transition of the clamped Rochelle salt crystal does not involve changes of the crystal symmetry and it leaves the crystal structure essentially unaltered. It produces a change of the optical properties as is indicated by the fact that the temperature gradient of the birefringence $n_a - n_c$ is almost three times smaller below -20°C than it is above 25°C (see Figs. 18 and 19, I).

In the experiments on freely deformable crystals the existence of this transition is masqued by a series of other effects. As was shown in paper II these effects result from the interaction between the elastic deformation and the electric polarization. They can be accounted for by the laws of classical crystal physics. Because of this interaction the free crystal has two Curie points, one above and one below the transition temperature. Between the Curie points the free crystal is spontaneously polarized and deformed. The spontaneous deformation changes the symmetry of the crystal from rhombic hemiedric to monoclinic hemimorphic with the *a* axis as polar axis.[3] Although the interaction theory makes no use of the concept of an inner field $F = E + fP$, it furnishes an equation, $1/\kappa_1 = \chi_1(1 - f_{14}^2/\chi_1 c_{44})$ (from Eqs. (4), II), for the susceptibility κ_1 of the free crystal above the Curie point, which is analogous to that, $1/\kappa_1 = (1 - \Theta/T)fT/\Theta$ (Eq. (9), I), given by the inner field theory. A comparison of these relations shows, that the interaction gives rise to an "apparent Lorentz factor" $f = f_{14}^2/c_{44} = 0.045$, while the Curie temperature is $\Theta = f_{14}^2 T/\chi_1 c_{44}$. The Curie points of the free crystal are the temperatures $T = \Theta$ at which the determinant $D_{14} = \chi_1 c_{44} - f_{14}^2 = (T - \Theta)\chi_1 c_{44}/T$ vanishes. $c_{44} = 11.6 \times 10^{10}$ and $f_{14} = 7.2 \times 10^4$ are the true elastic and piezoelectric constants[4] for shearing strains y_z.

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[1] This is the third publication on this subject by the writer. The previous articles, Phys. Rev. **47**, 175 (1935) and Phys. Rev. **57**, 829 (1940), will be referred to as paper I and II, respectively. The numerals I and II are used also in the references to figures and equations given in these previous papers.

[2] C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **55**, 1830 (1933); G. Damköhler, Ann. d. Physik **31**, 76 (1938).

[3] H. von R. Jaffe, Phys. Rev. **51**, 43 (1937).

[4] The present investigation shows that the values of f_{14} as derived in paper II from Norgorden's or Mikhailov's measurements are too small.

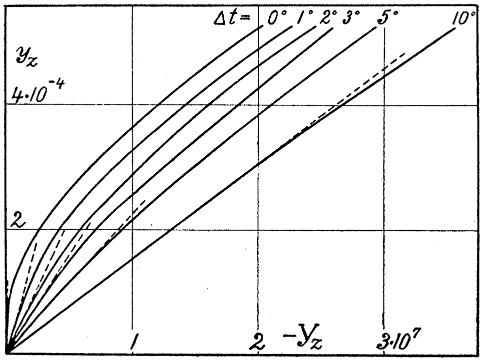

FIG. 1. Theoretical stress-strain relation for shear in the (*b*, *c*) plane of Rochelle salt above the Curie point.

The interaction theory has served to explain the relations between the dielectric, piezoelectric and elastic properties of Rochelle salt above the upper Curie point. We will show here that it can account also for the ferroelectric anomalies at temperatures between the Curie points. To this purpose it is necessary to supplement the expression (1, II) for the free energy Φ of the polarized and deformed crystal by terms of higher order. The origin of the new terms can be explained as follows: At temperatures near the transition point, where χ_1 is very small, the $P_x(E_x)$ relation for the clamped crystal must show saturation. Since the clamped crystal is orthorhombic this saturation effect introduces only terms in even powers of P_x and we shall therefore use as a second approximation

$$\Phi = \Phi^{(1)} + \tfrac{1}{4}BP_x^4, \qquad (1)$$

where $\Phi^{(1)}$ is the quadratic form (1, II). Terms involving higher powers of the strains or of P_y and P_z or mixed terms, e.g. $P_x^2 y_z^2$, are not likely to be of importance, because it was shown that the true elastic and piezoelectric properties of Rochelle salt are not unusual. A second set of correction terms arises from the change of the crystal symmetry at the Curie points. This fact would require the introduction of ten new terms involving four new elastic constants c_{14}, c_{24}, c_{34}, c_{56}, five new piezoelectric constants f_{11}, f_{12}, f_{13}, f_{26}, f_{35} and a new susceptibility χ_{23}. New experimental evidence, which will be presented in an other paper, shows that these correction terms of the second kind play an important role in the theory of the electro-optical and photoelastic effects, the anomalous thermal expansion and the electrostriction in Rochelle salt. However, these terms are small in comparison with $\frac{1}{4}BP_x^4$, and while they are not entirely negligible they play a secondary role in the following discussion of the dielectric, elastic and piezoelectric effects. The second approximation, Eq. (1), furnishes the fundamental relations

$$-Y_z = \partial\Phi/\partial y_z = c_{44}y_z + f_{14}P_x, \qquad (2a)$$

$$E_x = \partial\Phi/\partial P_x = f_{14}y_z + \chi_1 P_x + BP_x^3. \qquad (2b)$$

To test their validity we shall follow the procedure adopted in paper I by discussing first the saturation effects which occur above the Curie point, where $D_{14} = \chi_1 c_{44} - f_{14}^2 > 0$, and where the experiments furnish more reliable data because no hysteresis effects occur. These data will furnish the value of B and it will then be possible to test the theory for the ferroelectric range.

DIELECTRIC AND PIEZOELECTRIC SATURATION ABOVE THE CURIE POINT

The laws for the dielectric properties and the inverse piezoelectric effect of the free crystal are found from Eqs. (2) by setting $Y_z = 0$. The direct piezoelectric effect is obtained by elimination of y_z and by assuming $E_x = 0$. If one takes into account Eqs. ((4), II) these procedures furnish

$$E_x = P_x/\kappa_1 + BP_x^3. \qquad (3a)$$

$$-E_x = y_z/d_{14} + B(c_{44}/f_{14})^3 y_z^3, \qquad (3b)$$

$$Y_z = P_x/d_{14} + B(c_{44}/f_{14})P_x^3. \qquad (3c)$$

The $P_x(E_x)$, $y_z(E_x)$ and $P_x(Y_z)$ relations must therefore show saturation effects when $1/\kappa_1$ or $1/d_{14}$ are small, i.e., at temperatures slightly above the Curie point. At higher temperatures the cubic terms are negligible in comparison with the linear terms. This remark explains why it would be futile to search for saturation effects in the elastic or piezoelectric properties of the isolated crystal. In an isolated crystal the polarization creates a depolarization field $E_x = -4\pi P_x$ and hence the coefficient of P_x in Eq. (2b) is $(4\pi + \chi_1)$ and is about 100 times larger than $1/\kappa_1$.

The existence of saturation in the piezoelectric effects has been reported by Schulwas-Sorokin[5] and Hinz,[6] but sufficient data for the determination of B are available only from the dielectric measurements. The validity of Eq. (3a) was demonstrated by Kurtschatow[7] for static, and by the writer for dynamic measurements by the method of Sawyer and Towers (Fig. 10, I). This equation is equivalent with the relation $E=(1-\Theta/T)F+\beta f F^3$ (Eq. (7), I) of the inner field theory when the approximation $F=fP$ is valid. It leads directly, without resorting to approximations as was necessary in paper I, to the experimentally verified relation (see Fig. 8, I and Eq. (19), I)

$$E_x/X^{\frac{1}{2}}=M(t-t_c)+NX, \tag{4}$$

where $X=(\kappa_1-\kappa_E)/\kappa_1\kappa_E$, and where $\kappa_E=\partial P_x/\partial E_x$ is the reversible susceptibility. $M=1/C(3B)^{\frac{1}{2}}$, $N=1/3(3B)^{\frac{1}{2}}$ and C is the Curie constant. For small fields Eq. (4) reduces to

$$\kappa_E=\kappa_1(1-GE_x{}^2), \quad G^{-\frac{1}{3}}=g(t-t_c), \tag{4'}$$

where $g=1/C(3B)^{\frac{1}{3}}$. It was shown in paper I that the observations verify the relations $g^3=M^2/C$, $N=CM/3$, as demanded by the theory. The experimental values $g=1.05$, $N=800$, $M=13.5$, $C=178$ (near the upper Curie point) furnish $B=5.8\pm0.7\times10^{-8}$. B takes the place of βf^4 of the inner field theory. Its value may vary somewhat with temperature, but more accurate data would be required to establish this dependence.

ELASTIC SATURATION IN THE FOILED CRYSTAL

Although the true elastic properties of Rochelle salt follow Hooke's law, this law is not satisfied for shearing stresses Y_z when the crystal is covered with a grounded foil. From Eqs. (2) and the Curie-Weiss law (10, II) for the elastic compliance s_{44} one finds for the foiled crystal ($E_x=0$)

$$Y_z=(Y_z+c_{44}y_z)[1+(Y_z+c_{44}y_z)^2 \times(1+c_{44}\sigma/(t-t_c))B/\chi_1 f_{14}{}^2](t-t_c)/\sigma c_{44}. \tag{5}$$

At the Curie point, $t=t_c$, the relation is

$$Y_z=(Y_z+c_{44}y_z)^3B/\chi_1 f_{14}{}^2. \tag{5'}$$

Figure 1 presents the resulting strain-stress curves for various temperatures $t=t_c+\Delta t$. The values $B=5.8\times10^{-8}$, $c_{44}=11.6\times10^{10}$,

$$f_{14}=7.2\times10^4, \quad \chi_1=0.05+(t-t_c)/178,$$

$\sigma=66.7\times10^{-12}$ were used in the calculation. We note that large deviations from Hooke's law must be expected if the temperature of the foiled crystal is between 24° and 27°C. The elastic saturation should become apparent for shearing stresses of only a few kg/cm^2 and it should therefore not be difficult to verify this effect by ordinary elastic measurements. At higher temperatures the deviations from Hooke's law vanish.

A simpler and more accurate method for studying the elastic saturation in Rochelle salt is based on the fact that the resonance and

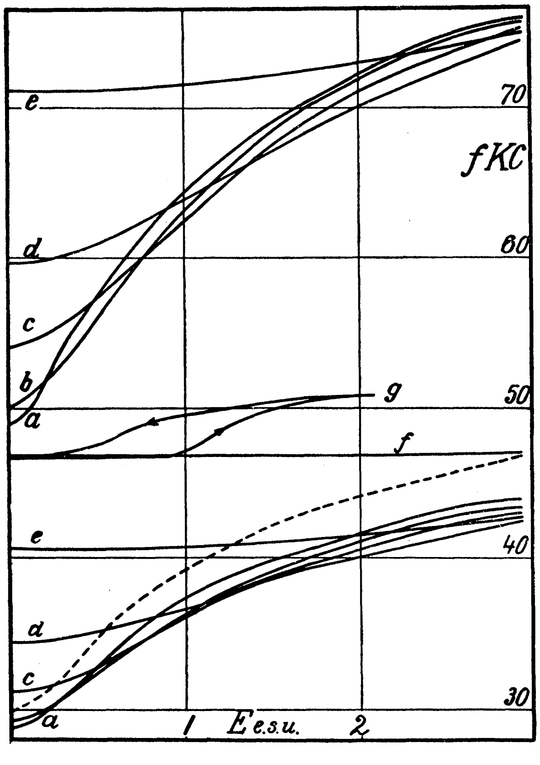

FIG. 2. Influence of a steady electric field on the resonance frequencies of a plate of Rochelle salt at various temperatures above the Curie point: (a) 24.1°, (b) 24.2°, (c) 24.5°, (d) 25.0°, (e) 26.8°, (f) 30°, (g) 18°. (f) and (g) refer to the lower resonance frequency. The dotted curve gives the change of an antiresonance frequency at 24.1°C.

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[5] R. D. Schulwas-Sorokin, Zeits. f. Physik **77**, 541 (1932).

[6] H. Hinz, Zeits. f. Physik **111**, 617 (1938).

[7] I. V. Kurtschatow, *Seignette electricity* (Moscow, 1933), Fig. 15. The isothermal static values may differ from the adiabatic dynamic values. To be exact, one should differentiate between the free energy and the enthalpy. The existence of an electrocaloric effect indicates that the difference is not negligible.

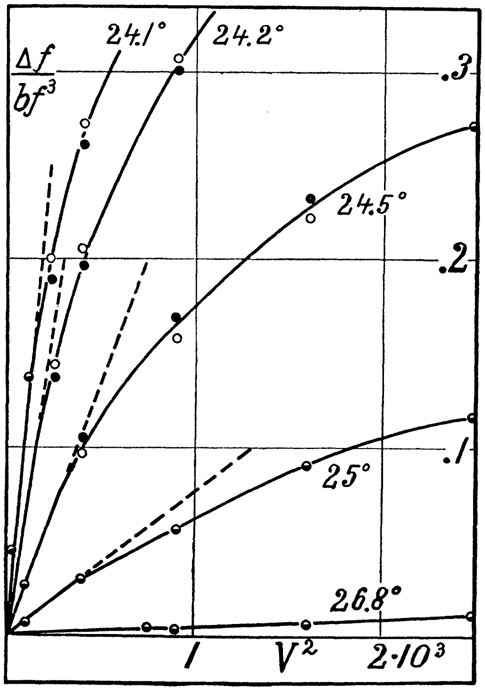

FIG. 3. Verification of the limiting law for the change of the resonance frequencies in small steady fields.

antiresonance frequencies of all those vibrations of a crystal plate, which can be excited by an alternating field in the a direction, must depend on the compliance coefficient s_{44}. For any resonance frequency f this dependence generally will be of the form $f=(\alpha+\beta s_{44})^{-\frac{1}{2}}$, or since $s_{44}-1/c_{44}=\sigma/(t-t_c)$,

$$f=[a+b/(t-t_c)]^{-\frac{1}{2}}, \qquad (6)$$

where the constants a and b depend on the mode of vibration and therefore on the size and shape of the plate and on the other elastic compliance coefficients s_{ik}, which are to be considered as temperature independent. If the plate is deformed by a constant strain $y_z{}^0$ the values of α and β remain practically unchanged, but if the electrodes are in close electrical contact with the crystal the compliance s_{44} must be replaced by the "reversible compliance" $s_{44}{}^0=-\partial y_z/\partial Y_z$, which is given by the slope of the $y_z(Y_z)$ curves in Fig. 1 and depends on $y_z{}^0$. Since a constant strain cannot be produced by mechanical means without altering the boundary conditions for the vibrations, it is more convenient to produce it by the application of a steady electric field E_0 in the a direction. A simple calculation shows that a field E_0 changes the compliance from s_{44} to $s_{44}{}^E$, where

$$1/s_{44}{}^E=c_{44}-f_{14}{}^2/(\chi_1+3BP_0{}^2),$$

and where P_0 is the polarization due to E_0 in a free crystal. Therefore, according to Eq. (3a), $3BP_0{}^2=1/\kappa_E-1/\kappa_1$, where κ_E is the reversible susceptibility in the field E_0. By combining these relations it is found that the steady field E_0 changes the resonance frequency from f to $f_E=f+\Delta f=(\alpha+\beta s_{44}{}^E)^{-\frac{1}{2}}$, and the calculation gives

$$\begin{aligned}\Delta(1/f^2)/b&=(1/f^2-1/f_E{}^2)/b\\&=(1-\kappa_E/\kappa_1)/(t-t_c).\end{aligned} \qquad (7)$$

For small fields E_0 the approximation (4^1) furnishes

$$\Delta f/bf^3=E_0{}^2/2g(t-t_c)^4. \qquad (7')$$

The change of the resonance frequencies of a foiled Rochelle salt plate by a steady field has been reported in a previous note.[8] Figure 2 gives the measurements on two resonance frequencies of a second crystal of approximately the same dimensions as the first, 3×5 cm in area and 0.096 cm thick in the a direction.[9] Table I gives

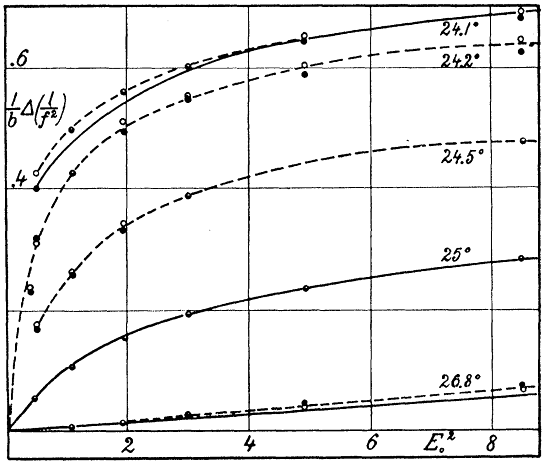

FIG. 4. Verification of the law relating the change of the resonance frequency to the change of the susceptibility of Rochelle salt in a steady electric field. The dotted curves result from the elastic measurements, the full curves for 24.1°, 25° and 26.8° are calculated from the dielectric data.

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[8] H. Mueller, Phys. Rev. **57**, 842 (1940).

[9] The crystal plates were supplied by the Brush Development Company, Cleveland, Ohio, with "graphoil" electrodes attached. The orientation of the edges could not be ascertained without damaging the electrodes.

TABLE I. *Temperature dependence of two resonance frequencies of a Rochelle salt plate.*

t°C	24.1	24.2	24.5	25.0	26.8	$a\times10^{10}$	$b\times10^{10}$
f KC	28.9	29.1	31.2	34.5	40.6_5	3.38	10.1
f KC	49.0	50.0	54.0	59.7	71.2_5	1.03	3.57

the temperature dependence of these frequencies when no steady field is acting. These data satisfy the law (6), with $t_c=23.0$°C. Thus the constants a and b can be determined in spite of the fact that the modes of vibration are not known.

Figure 3 is a plot of $2\Delta f/bf^3$ *versus* the square of the steady voltage. In accordance with Eq. (7^1) both frequencies lead to identical curves with initial slopes which vary with the temperatures in the ratios $(1/1.1)^4 : (1/1.2)^4 : (1/1.5)^4 : 2^4 : (3.8)^4$ as indicated by the dotted lines. In Fig. 4 the variation of $\Delta(1/f^2)/b$ is compared with the variation of $(1-\kappa_E/\kappa_1)/(t-t_c)$ as deduced from the dielectric data given in Fig. 7, I. This verification of Eq. (7) involves no adjustable parameter. The agreement signifies that the fundamental equations are valid and that the elastic data lead to the same value of B as the one derived from the dielectric measurements.

THE FERROELECTRIC PROPERTIES OF ROCHELLE SALT

At temperatures near the transition point χ_1 is small, and the determinant $D_{14}=\chi_1c_{44}-f_{14}^2$ is therefore negative between the two Curie points. From Eqs. (2) it follows that in this temperature range the state of minimum free energy of a free and foiled crystal ($E_x=0$; $Y_z=0$) has a spontaneous polarization P_x^0 and a spontaneous deformation y_z^0

$$P_x^0=(-D_{14}/c_{44}B)^{\frac{1}{2}};\quad y_z^0=-f_{14}P_x^0/c_{44}. \tag{8}$$

The spontaneous polarization can be directed along the $+a$ or $-a$ axis. Since it is associated with a spontaneous shearing deformation, all parts of a crystal will usually become polarized in the same direction, because, for purely geometrical reasons, different parts cannot be sheared in opposite directions without creating internal stresses. A small crystal, when cooled slowly, acts therefore as a single Weiss region and is pyroelectric, but in a large crystal it is difficult to prevent twinning, and frequently the crystals crack when they are cooled too rapidly.

The influence of the spontaneous polarization and deformation on the dielectric, elastic and piezoelectric properties of the crystal is analogous to that resulting from the application of a steady field above the Curie point. The dielectric and piezoelectric constants are decreased, and the resonance frequency of a foiled plate increases. To arrive at a theory of these effects one takes into account that a small stress δY_z and a small field δE_x change the polarization from P_x^0 to $P_x^0+\delta P_x$, and the strain from y_z^0 to $y_z^0+\delta y_z$. If one neglects all terms containing higher powers of δP_x and δy_z one finds from Eqs. (2) and (8)

$$-\delta Y_z=c_{44}\delta y_z+f_{14}\delta P_x, \tag{9a}$$

$$\delta E_x=f_{14}\delta y_z+\chi_1^0\delta P_x, \tag{9b}$$

$$\chi_1^0=\chi_1-3D_{14}/c_{44}. \tag{9c}$$

χ_1^0 is the reciprocal of the susceptibility κ_{cl}^0 of the spontaneously deformed clamped crystal, i.e., of a crystal which has been cooled without stresses to below the upper Curie point but which is prevented to deform any further if the field δE_x is applied. The solution of the linear equations (9a, b) gives

$$-\delta y_z=s_{44}^0\delta Y_z+d_{14}^0\delta E_x, \tag{10a}$$

$$\delta P_x=d_{14}^0\delta Y_z+\kappa_1^0\delta E_x, \tag{10b}$$

TABLE II. *Elastic, dielectric and piezoelectric data for Rochelle salt between the Curie points.*

t°C	$f\times10^{-5}$	k^2	κ_1^0	P_x^0	$(s_{44}^0-1/c_{44})\times10^{12}$	$d_{14}^0\times10^6$	$f_{14}\times10^{-4}$	$B\times10^8$
20	1.49	0.51	38	420	12.9	22.2	6.8	7.4
15	1.62	0.42	20	620	9.1	13.4	8.0	6.5
10	1.68	0.38	15	720	7.6	10.7	8.5	6.4
5	1.69_5	0.37	15	740	7.4	10.4	8.4	6.1
0	1.70	0.37	17.5	740	7.4	11.3	7.9	5.2
−5	1.66_5	0.40	23	700	8.3	13.7	7.4	4.4
−10	1.57	0.47	32	600	10.9	18.6	7.2	4.3
−15	—	—	80	380	—	—	—	4.3

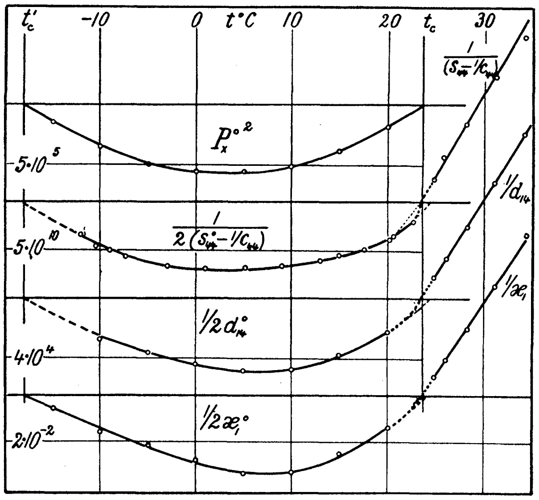

FIG. 5. Verification of the relations between the spontaneous polarization, the elastic, piezoelectric and dielectric properties of Rochelle salt between the Curie points and of their relations to the corresponding properties above the upper Curie point.

where

$$s_{44}^0 = -\chi_1/2D_{14} + 3/2c_{44}, \tag{11a}$$

$$d_{14}^0 = -f_{14}/2D_{14}. \tag{11b}$$

$$\kappa_1^0 = -c_{44}/2D_{14}. \tag{11c}$$

s_{44}^0 is the compliance coefficient of the foiled crystal, d_{14}^0 is the piezoelectric constant and κ_1^0 is the susceptibility of the free crystal in the ferroelectric state. Equations (10) hold only for small stresses and weak electric fields.

If one assumes that in a small temperature range the variation of D_{14} can be approximated by a linear law $D_{14} = (t - t_c)c_{44}/C$ Eqs. (11) can be cast into the form of Curie-Weiss laws:

$$2(s_{44}^0 - 1/c_{44}) = \sigma/(t_c - t); \quad \sigma = C(f_{14}/c_{44})^2,$$
$$2d_{14}^0 = \Delta/(t_c - t); \quad \Delta = Cf_{14}/c_{44},$$
$$2\kappa_1^0 = C/(t_c - t);$$
$$(P_x^0)^2 = h(t_c - t); \quad h = 1/CB.$$

Since the "Curie constants" vary with the temperature, we shall not use these relations, though they give a satisfactory representation of the observations near the Curie points.[10] Instead we follow the procedure adopted in paper II, i.e., we calculate the fundamental quantities c_{44}, f_{14}, χ_1 and B from the available data.

Equations (9) and (10) have the same form as the corresponding Eqs. ((2), II) and ((3), II) for temperatures above the Curie point. Hence we can use all the relations of paper II if we substitute s_{44}, d_{14}, κ_1 and χ_1 by s_{44}^0, d_{14}^0, κ_1^0 and χ_1^0, respectively. Thus it follows from Eq. ((8), II) that the compliance of the isolated crystal is[11]

$$s_{44}^i = s_{44}^0 - 4\pi d_{14}^{0\,2}/\epsilon_F^0 = 1/c_{44}$$

and the resonance frequency f^i for longitudinal vibrations at 45° to the b and c axes is

$$f^i = [\rho(s_{22} + s_{33} + 2s_{23} + 1/c_{44})]^{-\frac{1}{2}}$$

and has no anomaly at the Curie points. The resonance frequency of the foiled crystal is $f = [\rho(s_{22} + s_{33} + 2s_{23} + s_{44}^0)]^{-\frac{1}{2}}$, and it is easy to prove that Mason's[12] relation is still valid. The electromechanical coupling coefficient is

$$k^2 = 1 - (f/f^i)^2 = \rho d_{14}^{0\,2} f^2/\kappa_1^0 \tag{13}$$

and from the equations for f, f^i and (11a) it follows that

$$s_{44}^0 - 1/c_{44} = (1/f^2 - 1/f^{i2})/\rho = f_{14}^2/2c_{44}D_{14}. \tag{14}$$

According to (11b) and (11c)

$$d_{14}^0/\kappa_1^0 = f_{14}/c_{44}. \tag{15}$$

This ratio must have the same value as d_{14}/κ_1, because Eq. ((16′), II) is valid also below the Curie point and Mikhailov[13] has found that $\delta f/\delta D$ is very nearly constant at all temperatures. Eqs. (11) furnish also

$$\chi_1 + 1/2\kappa_1^0 = f_{14}^2/c_{44} = c_{44}(d_{14}/\kappa_1)^2. \tag{16}$$

This relation justifies the procedure used in Fig. 3, II for the construction of the $\chi_1(t)$ curve. It should be noted that the susceptibility κ_{cl}^0 of the spontaneously deformed clamped crystal differs from the susceptibility $\kappa_{cl} = 1/\chi_1$ of the crystal in which all deformations are suppressed. While κ_{cl} has a single and very high maximum at the transition point near 5°C, κ_{cl}^0 has at this

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[10] Paper I, Fig. 5 and O. Norgorden, Phys. Rev. **49**, 820 (1936); **50**, 782 (1936).

[11] The approximation $\epsilon_F^0 = 4\pi\kappa_1^0$ is justified also in the ferroelectric range, because the dielectric constant is nowhere smaller than 150.

[12] W. P. Mason, Phys. Rev. **55**, 775 (1939).

[13] G. Mikhailov, Tech. Physik USSR **4**, 461 (1937).

temperature a minimum $\kappa_{cl}{}^0=(\frac{2}{3})\kappa_1{}^0$. $\kappa_{cl}{}^0$ has two maxima at the Curie points, where $\kappa_{cl}{}^0=\kappa_{cl}$.

Table II gives the experimental data on Rochelle salt at temperatures between the Curie points. f and k are from Mason's[12] work. The values for $\kappa_1{}^0$ and $P_x{}^0$ are Bradford's[14] measurements. From these data $(s_{44}{}^0-1/c_{44})$, $d_{14}{}^0$ and f_{14} were calculated by using Eqs. (14), (13) and (15), respectively. The value of B is obtained from Eqs. (8) and (11c), which give

$$B=1/2\kappa_1{}^0P_x{}^{02}. \tag{17}$$

Within the rather large experimental errors f_{14} and B have the same values as were found from the data above the Curie point. Both constants seem to decrease somewhat with temperature.

The crucial test of the theory is carried out in Fig. 5. According to Eqs. (8), (11b), (11c) and (14) the quantities $(P_x{}^0)^2$, $\frac{1}{2}(s_{44}{}^0-1/c_{44})$, $\frac{1}{2}d_{14}{}^0$ and $1/\kappa_1{}^0$ are all proportional to D_{14} and should therefore have the same temperature variation, provided that c_{44}, f_{14} and B are constant. Furthermore, the last three curves should be continuations of the curves for $1/(s_{44}-1/c_{44})$, $1/d_{14}$ and $1/\kappa_1$, as given in paper II for temperatures above the Curie point. To illustrate the agreement the scales for the last three curves were adjusted so that the straight lines above the Curie point have the same slope. This procedure leads indeed to the result that the three curves become very nearly identical in the temperature range between the Curie points. They also coincide with the $P_x{}^{02}$ curve, for which the scale was chosen so as to give the same minimum at 5°C. It would not be difficult to interpolate the results on both sides of the upper Curie point by smooth curves, and to ascribe the small deviations to experimental errors, which, due to the gap effects, are particularily large near the Curie points. However, the elastic data[15] show quite clearly that the curves have a small discontinuity at the Curie point. In a later paper we can show that such anomalies are to be expected. They are the result of the neglected correction terms of the second kind and they can be explained as due to small changes of the values of the constants c_{44}, f_{14} and B at the Curie points. It is therefore not possible, on the basis of the present theory, to predict the ferroelectric properties near the Curie point from the measurements above this temperature, as was attempted with moderate success in paper I. However, since the changes of c_{44}, f_{14} and B are small, our theory is adequate in predicting the minimum or maximum values of the various quantities at the transition point. At this temperature χ_1 is very small, and the assumption $\chi_1=0$ gives $(D_{14})_{\min}=-f_{14}{}^2$. By using Eqs. (8) and (11) and the values of f_{14}, c_{44} and B as derived from the measurements above the Curie point, one finds the following approximate values:

	calculated	observed
$(P_x{}^0)_{\max}=f_{14}(c_{44}B)^{-\frac{1}{2}}$	$=860$	740 e.s.u.
$(y_z{}^0)_{\max}=f_{14}{}^2(c_{44}B)^{-\frac{1}{2}}/c_{44}$	$=5\times10^{-4}=2'$	$3.7'$
$f_{\max}=[(4\times10^{-12}+3/2c_{44})\rho]^{-\frac{1}{2}}$	$=1.85\times10^5$	1.71×10^5
$(\kappa_1{}^0)_{\min}=c_{44}/2f_{14}{}^2$	$=11.4$	12.5[16]
$(d_{14}{}^0)_{\min}=1/2f_{14}$	$=7\times10^{-6}$	10.4×10^{-6}

With the exception of $(y_z{}^0)_{\max}$, which has been measured for only one crystal, the deviations from the observed values indicate that at the transition point $\chi_1>0$. The experimental evidence, resulting from the three independent investigations of Bradford, Hablützel and Mason, supports therefore the conclusion that the

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[14] E. B. Bradford, B.S. Thesis, Massachusetts Institute of Technology, 1934. $P_x{}^0$ is obtained from the height of the hysteresis loops. Bradford's values of $P_x{}^0$ agree with those given by J. Hablützel, Helv. Phys. Acta **12**, 489 (1939), but they are larger than those resulting from the pyroelectric measurements in paper I. Bradford's values for the susceptibilities, at 1000 cycles/sec., are slightly higher than Hablützel's, but they are lower than Mason's values. The data in Table II are in e.s.u.

[15] The elastic data are more accurate than the dielectric measurements. Figure 5 is based on the original data of Dr. Mason.

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

clamped crystal has no Curie point. It possesses a transition point where the dielectric constant reaches an extremely high maximum.

The spontaneous polarization and deformation lower the free energy of the crystal by

$$\Phi=\tfrac{1}{2}c_{44}(y_z{}^0)^2+f_{14}y_z{}^0P_x{}^0+\tfrac{1}{2}\chi_1(P_x{}^0)^2 +\tfrac{1}{4}B(P_x{}^0)^4=-\tfrac{1}{4}B(P_x{}^0)^4. \quad (18)$$

The maximum energy change is about 4500 $\text{erg/cm}^3=0.017$ cal./mol. Since, near the Curie point, $(P_x{}^0)^2=h(t_c-t)$, where h is about 5×10^4, the theory does not demand a sudden change of the specific heat at the Curie points, but only a change of the slope of the specific heat curve. This change of slope is only about 3×10^{-4} cal./mol/°C ^{2} and is much too small to be detected by the usual methods. For the crystals of H_2KPO_4 and H_2KAsO_4, for which our theory should also be applicable, a large and sudden change of the specific heat has been observed,[17] but this is not necessarily in contradiction with the theory, because one might expect such a change to occur at the transition temperature, i.e., at a temperature somewhat lower than the Curie point. The experiments leave some doubt whether the temperature, where the specific heat changes, is identical with that of the Curie point. In Rochelle salt no anomaly has been found, either at the Curie points or at the transition temperature.

For large electric fields and large shearing stresses Y_z Eqs. (2) predict hysteresis curves for the electric polarization of the free crystal, for the deformation y_z of a foiled plate and for the direct and inverse piezoelectric effect. The dielectric hysteresis has been studied by numerous investigators. Bloomenthal[18] and Hinz[6] have reported hysteresis of the inverse piezoelectric effect and the existence of elastic hysteresis follows from the recent work of the writer.[8] Contrary to the theory, the hysteresis loops have not a single Barkhausen jump and the coercive field is smaller than the theoretical values. These discrepancies are not surprising if one realizes that the theoretical Barkhausen jump corresponds to a transition from an instable to a stable equilibrium state. Structural inhomogeneities, internal stresses or inhomogeneities of the electric field may be responsible for the transition's occurring at smaller field intensities.

DIELECTRIC DISPERSION IN ROCHELLE SALT

Schulwas-Sorokin and Posnov[19] and Goedecke,[20] among others, have reported results which are assumed to arise from relaxation phenomena in Rochelle salt. The first two authors ascribe the relaxation to viscous resistance against mechanical deformations, the latter to the retardation time of the dipole orientation. It should, however, be noted that the measurements were carried out in the ferroelectric temperature range and that the interpretations are based on the erroneous assumption that the dielectric and elastic properties of Rochelle salt follow the laws which hold for ordinary solids. A closer inspection reveals that the observed phenomena are due to the interaction, saturation and hysteresis effects, and that the existence of a relaxation time longer than 10^{-6} sec. is not justified by any experiment. It seems rather obvious that power factor data and voltage decay curves cannot be interpreted in terms of a relaxation time when most of the power loss is due to hysteresis and when the polarization is not proportional to the electric field. The fact that at the resonance frequency of a foiled plate the impedance minimum is unusually broad in Rochelle salt, can be explained without assuming strong viscous damping. Since an electric field changes the elastic compliance s_{44} the resonance frequency is modulated by the exciting a.c. field and the resonance peak is broadened. It is sharp only when a large steady field is applied across the electrodes. In this case, it follows from the data in Fig. 2 that a small variation of the field has little effect, and our experiments show indeed a considerably sharper resonance point when a strong steady field is acting.

The strongest point in favor of the dipolar relaxation theory seems to be the fact that at high frequencies the dielectric constant in the a

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[17] W. Bantle and P. Scherrer, Nature **143**, 980 (1939); J. G. Hooley and C. C. Stevenson, Phys. Rev. **56**, 121 (1939); J. Mendelsohn and K. Mendelsohn, Nature **144**, 595 (1939).

[18] S. Bloomenthal, Physics **4**, 172 (1933).

[19] R. D. Schulwas-Sorokin and M. V. Posnov, Phys. Rev. **47**, 166 (1935).

[20] H. Goedecke, Zeits. f. Physik **94**, 574 (1935).

direction has considerably smaller values than at audiofrequencies. But also this effect can be explained by the interaction theory by using the discussion in the appendix of paper II. There it was shown, for the special case of a plate, 1 cm long, in the state of longitudinal vibration in the direction at 45° to the b and c axes, that the polarization of a volume element at the distance y' from the center of the plate is

$$P_x=E_x[\kappa_1-\{1-\cos(y'\omega/v)/\times\cos(\omega/2v)\}d_{12}'^2/s_{22}'].$$

The dielectric measurements record the average polarization

$$P_{\mathrm{Av}}=\int_{-\frac{1}{2}}^{+\frac{1}{2}}P_x dy'$$

and give therefore a susceptibility

$$\kappa_{\mathrm{Av}}=\kappa_1-\left(1-\frac{2v}{\omega}\tan\omega/2v\right)d_{12}'^2/s_{22}'.$$

For low frequencies $\tan\omega/2v=\omega/2v$, and hence $\kappa_{\mathrm{Av}}=\kappa_1$, but for a high frequency, which is not near a resonance point of the plate, $2v/\omega\tan\omega/2v=0$, whence

$$\kappa_H=\kappa_1-d_{12}'^2/s_{22}'.$$

Since $d_{12}'^2/s_{22}'=\epsilon_F k^2/4\pi$, (Eq. (13), II), where k is Mason's electromechanical coupling coefficient, we obtain for the dielectric constant of a free crystal at high frequencies

$$\epsilon_H=\epsilon_F(1-k^2). \tag{19}$$

This relation was given by Mason, but his statement, that ϵ_H is the dielectric constant of the clamped crystal, is not correct. A high frequency field creates a strain distribution in the crystal. The average value of these strains is zero, but this fact does not imply that ϵ_H is identical with ϵ_{cl}. Above the Curie point ϵ_H is larger than ϵ_{cl}, but is much smaller than ϵ_F, the dielectric constant at low frequencies. Between the Curie points Eq. (19) is also valid, but here ϵ_H is much smaller than ϵ_{cl} or ϵ_F^0, however, it is slightly larger than ϵ_{cl}^0, the dielectric constant of the spontaneously deformed clamped crystal. A simple calculation leads, for temperatures above the Curie point, to the relation

$$(\chi_1-1/\kappa_1)/(1/\kappa_H-1/\kappa_1)=c_{44}(s_{22}+s_{33}+2s_{23})+1=1.46. \tag{20}$$

For the ferroelectric temperature range an analogous relation holds

$$(\chi_1^0-1/\kappa_1^0)/(1/\kappa_H-1/\kappa_1^0)=1.46. \tag{20$'$}$$

From Eqs. (20′) and (16) it follows that the susceptibility of Rochelle salt at high frequencies reaches at the Curie points its largest value $(\kappa_H)_{\max}=1.46\ c_{44}/f_{14}^2$. This corresponds to a maximum dielectric constant of about 400. At the transition temperature near 5°C κ_H has a minimum. Eqs. (20′) and (9c) furnish $(\kappa_H)_{\min}=(\kappa_1^0)_{\min}/(1+\frac{1}{2}\cdot 1.46)$ which gives, approximately, $(\epsilon_H)_{\min}=0.6(\epsilon_F^0)_{\min}\cong 100$. According to Eq. (19) this relation implies that k has a minimum value of 0.65. Mason measured a minimum $k=0.60$, but since his values of ϵ_1^0 are rather large, he finds also a large value of $(\epsilon_H)_{\min}=160$. Direct measurements of the dielectric constant at high frequencies have been carried out by Mikhailov.[13] He checks the theoretical value $(\epsilon_H)_{\min}=95$, and finds at the upper Curie point a maximum of about 250. Also the measurements of Busch[21] and Doborzynski[22] are in fair agreement with the theory. The above calculations hold, of course, only if the crystal vibrates in the assumed manner. For other modes of vibration the dielectric constant at high frequencies is different, but in general κ_H will differ only slightly from the dielectric susceptibility of the clamped crystal (above the Curie point) or of the spontaneously deformed clamped crystal (between the Curie points). The existence of relaxation effects can be accepted only if future measurements should lead to still smaller values.

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[21] G. Busch, Helv. Phys. Acta **6**, 315 (1933).

[22] D. Doborzynski, Acad. Polonaise Sci. et lettres, Bull. (1938) p. 37.