# The Time of Relaxation in Crystals of Rochelle Salt

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A semiquantitative theory of the action of mechanical and electrical forces is given, using the concept of two relaxtion times. The theory is shown to offer qualitative explanations of numerous features of the experimental results such as the phenomenon of "creep" and the asymmetrical rates of polarization and depolarization observed by Kurchatov and Staub. Experiments on the dielectric constant and power loss have been made over a range from 1 to 1000 hertz, and dispersion curves have been obtained. The theory is applied to explain various features of the results.

## INTRODUCTION

DURING the last few years a number of papers have been published devoted to the study of the anomalous properties of crystals of Rochelle salt, the majority dealing with their electric or mechanical properties. If we try to systematize the results obtained, we may present them in the following form (Table I), in which the principal results of various authors for the polarization ($P$) and deformation ($x$) are given.

## THEORY

From the table it is clear that the deformation and polarization vary similarly. Since Rochelle salt is piezoelectric, it seemed to us that the whole of the polarization in the crystal, irrespective of whether it was obtained by applying electric or mechanical stresses, might be of piezoelectric origin. Both mechanical and electric fields produce deformation in the crystal. The dipole, or ionic group forming part of the molecule is displaced relative to its equilibrium position during the deformation of the lattice. Because of the absence of a center of symmetry in the Rochelle salt crystal, this displacement gives rise to an electric moment. Since the processes in Rochelle salt are reversible, provided the stresses are not too high, we may make use of the method of thermodynamic potential to test the above hypothesis. If we consider isothermal processes, the expression for the thermodynamic potential will be[1]

$$\zeta = \tfrac{1}{2}c_{hk}x_k x_h - e_{ih}\mathcal{E}_i x_h - \tfrac{1}{2}\eta_{il}\mathcal{E}_i\mathcal{E}_l.$$

The polarization is     $P_i = e_{ih}x_h + \eta_{il}\mathcal{E}_l,$     (1)

[1] W. Voigt, Lehrb. d. Kristallphys. pp. 414, 563, 816 (1928).

while the mechanical stress is $M_h = -c_{hk}x_k + e_{ih}\mathcal{E}_i$. In the particular case when the crystal is cut along the axes, the polarization in an electrical field applied along the axis $a$ is

$$P_1 = e_{14}x_4 + \eta_{11}\mathcal{E}_1,     (1')$$

since $e_{11} = e_{12} = e_{13} = e_{15} = e_{16} = 0$ and $\mathcal{E}_2 = \mathcal{E}_3 = 0$. The mechanical stress $M_h = 0$. In order to determine the value of $x_4$ we require only the value of $M_4$: $M_4 = -c_{44}x_4 + e_{14}\mathcal{E}_1 = 0$ since all $c_{4k} = 0$ except $c_{44}$ whence $x_4 = (e_{14}/c_{44})\mathcal{E}_1$. Putting this value of $x_4$ in $(1')$ we get

$$P_1 = (e_{14}^2/c_{44} + \eta_{11})\mathcal{E}_1 = (d_{14}^2 c_{44} + \eta_{11})\mathcal{E}_1 = \eta'_{11}\mathcal{E}_1,$$

where $e_{14} = d_{14}c_{44}$. This expression is true for all crystals of the rhombic system, and it shows that the polarization in an applied electrical field is not only dependent on $\eta_{11}$ but also on the product $d_{14}^2 c_{44}$, whereas one measures experimentally $\eta'_{11} = d_{14}^2 c_{44} + \eta_{11}$. In crystals where $d_{14}$ is of the order $10^{-8}$ e.s.u./dyne, and $c_{44} = 10^{11}$ dyne/cm² the first term will be of the order $10^{-5}$, i.e., negligibly small compared with $\eta_{11}$, which is of the order of unity in most crystals.

In Rochelle salt, $d_{14}$ varies between $4 \cdot 10^{-5}$ e.s.u./dyne and $2.6 \cdot 10^{-4}$ e.s.u./dyne[4] and $c_{44} = 1.64 \cdot 10^{11}$ dyne/cm²,[7] so that the first term is of the order $10^3$, and is very large compared with $\eta_{11}$. Consequently the whole of the polarization in crystals of Rochelle salt is dependent on the first term. This is seen particularly clearly from Staub's[2] work, although his experiments did not show the mechanism of this displacement. For reflections from the surface, (1,0,0), i.e., the plane perpendicular to the axis $a$, Staub did not observe any change in intensity, and it is necessary to conclude that this is a result of the fact

TABLE I. *Summary of previous results.*

| No. | Polarization as function of various factors | Form of function and numerical value | Deformation as function of various factors | Form of function and numerical value |
|---|---|---|---|---|
| 1 | $P = f(\mathcal{E})$ | Saturated $870^3$ e.s.u. $850^9$ e.s.u. | $x = f(\mathcal{E})$ | Saturated $7.5 \cdot 10^{-4\,11}\,5 \cdot 10^{-5}$ calculated from refs. (3) and (4) |
| 2 | $P = f(M)$ | Saturated $940^4$ e.s.u. | $x = f(M)$ | Saturated[6] $4.5 \cdot 10^{-5}$ calculated from refs. (7) and (4) |
| 3 | $P = f(T°)$ | Two Curie points $+22.5°^4$ and $-15°^{10}$ | $x = f(T°)$ | Two Curie points $+23°$ and $-15°;^8$ $+25°^2$ |
| 4 | $P = f(t)$ | "Creep" of charge $t = 3$ min.[4] | $x = f(t)$ | Slow recovery of deformation after removal of field $t = 2$ min.[2] |
| 5 | $t_p = f(T°)$ | Increase of $t_p$ with decrease of temperature[4] | $t_x = f(T°)$ | Increase of $t_x$ with decrease of temperature[2] |

Remarks: $\mathcal{E}$—electric field, $M$—mechanical stress, $T°$—temperature, $t$—time, $t_p$ and $t_x$ relaxation time.

that $d_{11} = 0$ and $x_1 = 0$. Further, Staub did not observe any changes in the position of the interference spots under the action of the electric field, but this can be accounted for by the insufficient accuracy of measurement which, according to the determinations of this author, was equal to 0.3 percent, or $3 \times 10^{-3}$ of the measured magnitude, while the deformation which should give the displacement in the interference spots was of the order $10^{-5}$.

From this point of view we can give a semi-quantitative theory of the behavior of Rochelle salt: under the action of a constant mechanical stress, and also under the action of a constant electric field.

(1) For a *constant applied mechanical stress* in the absence of an electric field we can suppose the motion of a dipole with the lattice to be represented by the equation[12]

$$r\dot{x}_4 + c_{44}x_4 = M_4, \qquad (2)$$

[2] Staub, Helv. Phys. Acta. p. 2 (1933).
[3] Kobeko and Kurchatov, Zeits. f. Physik **66**, 192 (1930).
[4] Schulwas-Sorokin, Zeits. f. Physik **73**, 700 (1932); **77**, 541 (1932).
[5] Isely, Phys. Rev. **24**, 569 (1924).
[6] S. Bloomenthal, Physics **4**, 172 (1933).
[7] Mandell, Proc. Roy. Soc. **A116**, 623 (1927).
[8] R. M. Davies, Nature **120**, 332 (1927).
[9] Oplatka, Helv. Phys. Acta. (1933).
[10] B. Kurchatov and I. Kurchatov, Phys. Zeits. d. Sow. **3**, 321 (1933).
[11] Sawyer and Tower, Phys. Rev. **35**, 269 (1930).
[12] We can neglect the inertial forces because $r$ and $\rho$ are large and the accelerations are consequently small.

where $M_4$ is the applied stress to which the displacement of the dipole is proportional and $r$ is a "viscosity" constant. Solving this equation, we get

$$x_4 = (1 - e^{-t/\theta}) M_4/c_{44}, \qquad (3)$$

where $M_4/c_{44}$ is the final value of the deformation, and $\theta = r/c_{44}$. Since the rotation takes place in a medium with large frictional forces, $\theta$ is large and the approach to this final value of $x_4$ and consequently of the polarization also, occurs very slowly. If we neglect the second term in Eq. (1') because $\mathcal{E}$, = the polarization will be given by

$$P_1 = e_{14}x_4 = (1 - e^{-t/\theta})e_{14}M_4/c_{44}$$
$$= d_{14}M_4(1 - e^{-t/\theta}). \qquad (4)$$

(2) For an applied *electrical field* we can represent the motion of a dipole by the equation

$$\rho\dot{x}_4 + \beta x_4 = \mathcal{E}_1, \qquad (2')$$

from which

$$x_4 = (1 - e^{-t/\tau})\mathcal{E}_1/\beta = d_{14}\mathcal{E}_1(1 - e^{-t/\tau}), \qquad (3')$$

where $\beta = 1/d_{14}$ and $\tau = \rho/\beta = \rho d_{14}$.

From Eq. (1) we get for the polarization if we neglect $\eta_{11}$ in agreement with the preceding argument

$$P_1 = e_{14}x_4 = d_{14}^2 c_{44}\mathcal{E}_1(1 - e^{-t/\tau}), \qquad (4')$$

from which we see that for an applied electrical field also the final value of the polarization is not attained instantaneously.

The final magnitude of polarization obtained with a given deformation should be the same irrespective of whether the deformation was produced by an electric field or a mechanical stress. From Eqs. (4) and (4′), it follows that

$$M_4 = d_{14} c_{44} \mathcal{E}_1, \tag{5}$$

i.e., we get the electrical equivalent of the mechanical stress. From Eq. (5) it is possible to determine the field necessary to produce a given polarization, if the mechanical stress required to produce the same polarization is known. If we take, for example, the polarization $P = 500$ e.s.u., this is obtained with a mechanical stress $M_2'$ $= 12$ kg/cm² applied at an angle of 45° to the axes $b$ and $c$; $M_4 = \frac{1}{2} M_2' = 6$ kg/cm². Corresponding to a load $M_2'$, $d_{14} = 10.8 \cdot 10^{-5}$ e.s.u./dyne.[13] Putting this value in Eq. (5), we get

$$\mathcal{E}_1 = \frac{6 \cdot 10^6 \cdot 300}{1.08 \cdot 10^{-4} \cdot 1.64 \cdot 10''} = 102 \frac{\text{volt}}{\text{cm}}.$$

In Fig. 20 of the monograph of I. V. Kurchatov *Rochelle Electricity*, the curve $P = f(\mathcal{E})$ for a crystal of 1 cm thickness at +14°C is given. From this curve we get a polarization of 500 e.s.u. at $\mathcal{E}_1 = 130$ volt/cm. Similar calculations for a polarization of 300 e.s.u. give $\mathcal{E}_1 = 27$ volt/cm while the value required to produce this polarization experimentally is 50 volt/cm. As we pass to smaller stresses, i.e., into the region of "small polarizibility," the calculated value is considerably less than that actually required to produce the given polarization.

From our point of view, the phenomenon of saturation must be regarded as follows: an increase in the mechanical stress and electric field increases the deformation of the lattice, and consequently the angle formed between the position of the dipole for a given load, and its position before loading. However, there is a certain stress (field) at which the lattice is deformed so much that its smallest dimension is less than or equal to, the greatest dimension of the dipole, so that the latter can no longer rotate. When this limiting deformation of the lattice is reached, the bonds between certain ions in the lattice and the dipoles increase rapidly and the coefficients $c_{44}$ and $\beta = 1/d_{14}$ in Eqs. (2) and (2′)

increase very considerably, producing a decrease in $\theta$ and $\tau$ for large stresses and electric fields. The decrease of $d_{14}$ with increasing mechanical stress was in fact observed by us. The influence of the electric field on $d_{14}$ is described later.

We are thus led to introduce *two* "times of relaxation" $\theta$ and $\tau$. Unfortunately we are not able to predict their theoretical values, as we can say little definitely about the two quantities $r$ and $\rho$. In this respect, therefore, the theory remains qualitative, and must be further investigated to be made completely satisfying. In terms of these concepts we can obtain, however, a fairly complete interpretation of the experimental results.

## EXPERIMENTS WITH STATIC MECHANICAL LOADS

Experiments have previously been made[4] on a crystal 12 mm long along the $a$ axis. The external stress was applied in a direction of 45° to the $b$ and $c$ axis. Fig. 1 gives the experimental results for the polarization as a function of the time elapsed since the application of the load. From these curves one can readily determine the time of relaxation $\theta$ for mechanical deformation of the crystal.* The curve of $\theta$ is given in Fig. 2 (continuous curve).

If we write $\theta = r/c_{44}$ and substitute $r = 10^{13}$ e.s.u. according to Tammann and Hesse[14] and $c_{44} = 3.28 \cdot 10^{11}$ dynes/cm² as measured by Mandell[7] for our experimental arrangement, we obtain a value $\theta = 30$ sec. agreeing well in order of magnitude with our experimental values.

A similar order of magnitude was found by Staub for the time of restoration of intensity of interference spots, after removal of the electric field, when the crystal is left under the influence of the internal mechanical stresses. As both the coefficient of "internal" viscosity and the elastic coefficients are functions of temperature, $\theta$ must be also. In the range from +25°C to −15°C the curve is hyperbolic and $\theta$ varies inversely with the temperature. At −15°C, $r$ becomes very large, so that at lower temperatures the linear dimensions of the lattice are less than the greatest dimension of the dipoles. The latter are then

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* The idea of explaining the phenomenon of "creep" as the time of relaxation belongs to Professor J. Frenkel.

[14] Tammann and Hesse, Zeits. f. an. u. allg. Chemie **156**, 256 (1926).

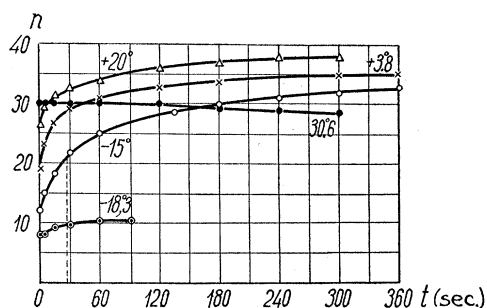[13] Schulwas-Sorokin, Zeits. f. Physik **73**, 700, 704 (1932).

FIG. 1. The "creep" of polarization for an applied me-
chanical stress.



FIG. 2. The relaxation times as functions of temperature.

no longer involved in the deformation and as a consequence there is a considerable decrease in the polarization, as this is now produced only by the ions and electrons.

In general the appearance of "creep" is sharply defined only for small stresses. As the stress is increased the time of relaxation decreases, and at stresses corresponding to saturation[4] the polarization occurs instantaneously. $\theta$ is thus a function of the stress.

## POLARIZATION IN STATIC ELECTRICAL FIELDS

On the basis of the theory given above we can interpret some of the puzzling features of previous experiments on Rochelle salt. The behavior of the crystal is characterized by an "electrical time of relaxation" $\tau$ which is a function of the piezoelectric modulus and of the coefficient $\rho$ which may be called the "coefficient of electrical viscosity," but whose theoretical value is unknown. Since $d_{14}$ is a function of the field, $\tau$ will also be a function of the field.

According to the measurements of I. Kurchatov[15] and of Staub[2] $\tau$ is very small. Both authors also observed an asymmetry in the velocities of the processes of polarization and of depolarization. This asymmetry can be explained from the present point of view if we assume that in the polarization process in an electrical field the appropriate time of relaxation is $\tau$, while the depolarization occurring after removal of the field depends only on the internal mechanical stresses, the rate being determined by the mechanical time of relaxation $\theta$. We can, therefore, also understand the relation between the rate of depolarization and the quantity of elec-

tricity stored in the crystal, which from our point of view is proportional to the mechanical tension in the crystal (cf. Eq. (4)) and $\theta$ is a function of this tension.

## EXPERIMENTS WITH ALTERNATING FIELDS

In 1931 Errera[16] studied the dispersion of the dielectric constant in Rochelle salt. The measurements were made in strong fields and extended over a frequency range of $3.4 \times 10^2$ to $10^6$ $H_z$. Frayne[17] investigated the phenomenon at higher frequencies. It was the aim of the present work to study the behavior of Rochelle salt in weak fields and at lower frequencies than those used by Errera, since the large values of the relaxation time which we obtained with static experiments suggested that the dispersion curve would be anomalous.

### Method of study. Experimental arrangement

The capacity bridge method (Fig. 3) was used for measuring the dielectric constant and the power factor. The arms $C_1$ and $C_2$ consisted of two almost equal, symmetrically mounted condensers of about 1200 cm capacity. Both condensers were placed in a shielded box, and in addition were shielded from one another. The moving plates were connected together, and to the screen at the point $A$. Both condensers were graduated so that it was possible to select a given ratio between the arms of the bridge. The arm $C_3$ contained a precision fixed condenser of 3600 cm capacity. This condenser, when necessary, was connected in parallel with a liquid variable resistance from $0.3 \cdot 10^6 \Omega$ to $300 \cdot 10^6 \Omega$. The arm $C_4$ consisted of a variable air condenser with

[15] I. Kurchatov, Phys. Zeits. d. Sow. **5**, 200 (1934).

[16] J. Errera, Phys. Zeits. **32**, 369 (1931).
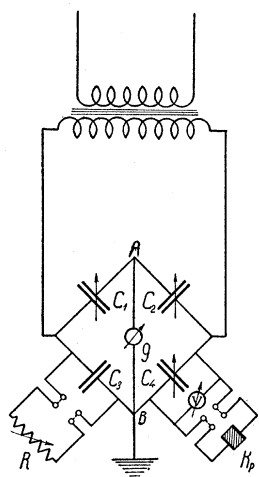[17] J. S. Frayne, Phys. Rev. **20**, 97 (1922); **21**, 348 (1923).

FIG. 3. The capacity bridge which was used for measuring the D.K.

capacity equal to 900 cm, and a condenser of 2550 cm capacity. This condenser was connected in parallel with that containing the crystal. All parts of the bridge were shielded, and the shields earthed. A dynatron generator supplied the alternating potential. The dynatron generator possesses the great advantage over other generators of low frequency in that no inductance coupling is necessary, and the frequency generated is determined by the natural period of the circuit itself. In order to obtain a given frequency it is only necessary to satisfy the condition: $L/CR = R_{in}$, where $R_{in}$ is the internal resistance of the valve, $L$ the self-inductance, $C$ the capacity and $R$ the ohmic resistance of the oscillating circuit.[18] The necessity of obtaining very low frequencies demanded the use of high self-induction, and thus $R$ had also to be large in order to avoid using a generator of very large dimensions. At very low frequencies the quantity $L/CR$ became much less than $R_{in}$ and it was therefore necessary (1) to select valves with low internal resistance, (2) to reduce $R_{in}$ by increasing the positive potential on the control grid. In this way it was possible to adjust the dynatron scheme to obtain frequencies over continual range from 1000 to 0.5. Since the oscillating circuit, in addition to the constant self-induction, contained an adjustable condenser and a variable self-inductance in the form of a multi-layer solenoid with movable core, it was easily possible

to obtain any frequency in the above-mentioned range. The potential from the generator valves reached an amplifier through a potential divider which allowed the magnitude of the potential applied to the transformer to be changed. The transformer windings were divided into sections, so that the voltage applied to the bridge could be regulated. The core of the transformer was earthed.

The measurement of the frequency in different parts of the spectra was made in different ways: from 1000 to 60 hertz the measurements were made with a string frequency meter according to the system of A. I. Belov,[19] by using the fundamental tone for the high frequencies, and the overtones for the low frequencies. Frequencies from 65 to 6 hertz were measured with the frequency meter of Hartmann and Braun with which the region from 14 to 6 hertz was measured by overtones. Finally, the lowest frequencies were measured with a stop watch while listening to the clicks in a telephone, or by watching the vibrations of the pointer of a d.c. voltmeter. On account of the fact that the generator produced a series of overtones in addition to the fundamental tone, it was necessary to filter the current in the bridge in order to make measurements on the fundamental tone, or to use an indicator of the resonance type. The former method presents considerable difficulty because of the large range of frequencies (11 octaves), and consequently we selected the latter. A potential divider connected to an Edelmann string galvanometer was placed in the diagonal of the bridge. With the potential divider it was possible to regulate the potential difference on the galvanometer, and to increase the sensitivity of the indicator according to the balancing of the bridge. The galvanometer could be tuned to any frequency by tightening or slackening the string. Since a platinum wire $2.5\mu$ thick was rapidly destroyed by frequent tightening or loosening, a platinum strip $2\mu$ thick, placed on edge, was used. As the width of the strip was $40\mu$ its strength was many times greater[20] than that of the wire. The use of this strip did not decrease the sensitivity of the apparatus appreciably, since the loss of sensi-

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[18] Colebrook, Exp. Wireless 1931, p. 581.

[19] A. I. Belov, Wireless Telegraphy and Telephony, No. 56, 535 (1929) (in Russian).

[20] N. V. Nickolsky suggested the use of this strip, which he prepared, and we wish to express our gratitude to him.

tivity, as a result of the increased mechanical stress, was compensated by a considerable decrease in the ohmic resistance of the string, which was 108Ω. The sensitivity of the galvanometer for constant potential difference varied from 0.1 volt to $2 \cdot 10^{-5}$ volt, depending on the tension of the string. At resonance the sensitivity was considerably greater.

## Experimental Results

### A. The influence of frequency on the polarization

Following the lines of the theory given in a previous section for the case of harmonically varying mechanical or electrical fields, we replace the right-hand sides in Eqs. (2) and (2') by $M_4$ sin $\omega t$ or $\mathcal{E}_1$ sin $\omega t$, respectively. The particular solutions for the forced vibrations then become for the two cases

$$x_4 = [M_4/c_{44}(1+\omega^2\theta^2)^{\frac{1}{2}}] \sin (\omega t - \delta_1) \quad (6)$$

and $\quad x_4 = [\mathcal{E}_1/\beta(1+\omega^2\tau^2)^{\frac{1}{2}}] \sin (\omega t - \delta), \quad (6')$

where, as previously, $\beta = 1/d_{14}$ and $\mathcal{E} = \rho d_{14}$.

The quantities

$$S = 1/c_{44}(1+\omega^2\theta^2)^{\frac{1}{2}} \text{ and } D = d_{14}/(1+\omega^2\tau^2)^{\frac{1}{2}} \quad (7)$$

will be referred to as the "dynamic modulus of elasticity" and the "dynamic piezo-modulus," respectively. If we assume, in accordance with the above, that the origin of the polarization in Rochelle salt is mainly piezoelectric, we get the mechanical equivalent of the electrical field. The amplitude of the deformation is

$$x_4 = D\mathcal{E}_1 = SM_4, \quad (8)$$

whence $M_4 = D\mathcal{E}_1/S$, i.e., the electric field of amplitude $\mathcal{E}_1$ multiplied by $D/S$ can produce the same effect as an alternating mechanical stress of amplitude $M_4$. The amplitude of the polarization in a crystal acted upon by an alternating electric field of amplitude $\mathcal{E}_1$ will be[21]:

$$P_1 = Ex_4 = (D/S)x_4 = (D^2/S)\mathcal{E}_1.$$

Substituting in this, the values of $D$ and $S$, we get

$$P_1 = d_{14}^2 c_{44} \frac{(1+\theta^2\omega^2)^{\frac{1}{2}}}{1+\tau^2\omega^2} \mathcal{E}_1 = K \frac{(1+\theta^2\omega^2)^{\frac{1}{2}}}{1+\tau^2\omega^2} \mathcal{E}_1. \quad (9)$$

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[21] $E = D/S$ is the dynamic piezo-constant.

The factor multiplying $\mathcal{E}_1$ in the expression for the polarization is the apparent coefficient of polarization, which we shall denote by $\eta_k$. The expression $\eta_k$ at $\omega = \infty$ becomes zero, and when $\omega = 0$ it becomes equal to that obtained for a constant field (see Eq. (4')).

Since $K$ is constant, the expression $(1+\theta^2\omega^2)^{\frac{1}{2}}/(1+\tau^2\omega^2)$ determines the way in which the polarization depends on the frequency, if the measurements at all frequencies are made with a constant amplitude of the field $\mathcal{E}_1$. By taking the first derivative of this equation, and setting it equal to zero, we find the value of $\omega_m$, at which the polarization is a maximum or minimum,

$$\omega_m = (\theta^2 - 2\tau^2)^{\frac{1}{2}}/\tau\theta. \quad (10)$$

The negative sign of the second derivative, if we substitute the value of $\omega_m$ from (10) shows that the function has a maximum. Dropping $2\tau^2$ with respect to $\theta^2$ in the numerator of Eq. (10) (as $\theta \gg \tau$), we find

$$\tau = 1/\omega_{\text{max}}. \quad (11)$$

The experimental curves are given in Fig. 4. Since the amplitude of the field $\mathcal{E}_1$ is the same at all frequencies, the course of $P_1 = f(\omega)$ will also be the same. The two curves in the upper part of the plot refer to two crystals: the curve $\alpha$ refers to a slab, whose thickness in the direction of the axis $a$ was 3.4 mm, while curve $\beta$ is for a crystal of thickness 34 mm. The scale on the right refers to the thin slab, and that on the left to the thick. Further, the curve $\alpha$ was taken at $\mathcal{E}_{\text{eff}} = 26$ volt/cm, and the curve $\beta$ at $\mathcal{E}_{\text{eff}} = 3.5$ volt/cm.

We see that both curves have a sharp maximum. For the thicker crystal $\tau = 4.2 \cdot 10^{-3}$ sec. at 16°C, and for the thinner crystal $\tau = 4.7 \cdot 10^{-2}$ sec. at 15°C.

In order to test the agreement between the experimental curve and the function of Eq. (9), the factor $(1+\theta^2\omega^2)^{\frac{1}{2}}/(1+\tau^2\omega^2)$ was calculated for various frequencies for a crystal whose time of relaxation was also $\tau = 4.2 \cdot 10^{-3}$ sec.

The form of this relation is given in Fig. 4 (dashed curve). The form of both curves is similar. It seems to us that this similarity supports our hypothesis.

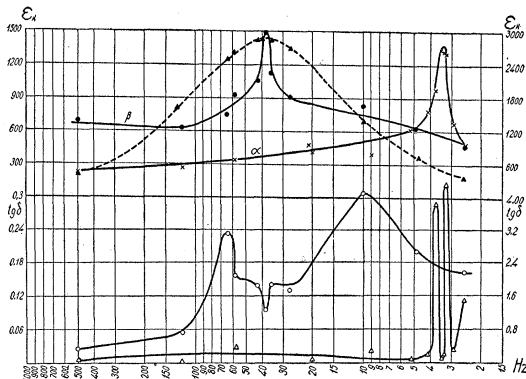Unfortunately, we must be content for the present with a qualitative agreement between

FIG. 4. The apparent dielectric coefficient (upper curves) and the power factor (lower curves) as functions of the frequency.



FIG. 5. The displacement of the position of dispersion maxima with the field.

the experimental and theoretical curves, since the value of the coefficient $d_{14}$ for such small electric fields, and correspondingly small mechanical stresses, is not known. If we use this divergence between the theoretical and experimental magnitudes, we may make an estimate of the value of $d_{14}$ (and possibly also of $s_{44}$) for these small fields, and we find that it must be of the order of $10^{-5}$ to $10^{-6}$ e.s.u./dyne which means that $d_{14} = f(\mathcal{E}_1)$ must pass through a maximum.

## B. The relation between the time of relaxation and the field

In Eq. (6') we saw that $\tau$, the electric time of relaxation, is equal to $\rho d_{14}$, where $d_{14}$ is the piezo-modulus, and $\rho$ is the coefficient of "electric viscosity." The piezo-modulus in its turn is a function of the mechanical stress. The function $d_{14} = f(M_4)$ is approximately hyperbolic[13] and may be written with sufficient accuracy in the form: $d_{14}M_4 = $ const. If we substitute in this expression the equivalent of $M_4$ from Eq. (5), we get $d_{14}{}^2 c_{44}\mathcal{E}_1 = C$. Assuming that $c_{44}$ is independent of the field, we get

$$d_{14} = C_1/\mathcal{E}_1{}^{\frac{1}{2}}. \qquad (12)$$

For the weak fields with which we are determining the time of relaxation, we may suppose that $\rho$ is independent of the field. It then appears that $\tau = Q_1/\mathcal{E}^{\frac{1}{2}}$. It has been actually shown by experiment that the shift of the position of the maximum in the dispersion curve is dependent on the magnitude of the applied field. With an increase of field, the maximum is displaced
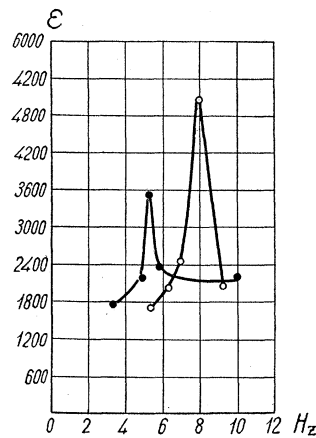
towards higher frequencies. Two maxima in the dispersion curves for one and the same crystal at the same temperature, but with different field strengths, are shown in Fig. 5.

We see from Table II that the value of $Q'$ remains constant for each crystal (column six). The maximum deviation from the mean is 7 percent for the thick crystal, and 2 percent for the thin, when the field is varied from 2 to 7 times.

TABLE II. Values of $\omega_{max}$ and $\tau$ for Rochelle salt crystals.

| $N$ | $\mathcal{E}_1 \dfrac{\text{volt}}{\text{cm}}$ | $\mathcal{E}_1{}^{\frac{1}{2}}$ | $\omega_{max}$ | $\tau \cdot 10^3$ (sec.) | $\tau \times \mathcal{E}_1{}^{\frac{1}{2}} \cdot 10^3$ |
|---|---|---|---|---|---|
| | (a) crystal thickness 18 mm | | | | |
| 1 | 3.6 | 1.9 | 157 | 6.4 | 12.1 |
| 2 | 8.35 | 2.9 | 232 | 4.3 | 12.5 |
| 3 | 11.6 | 3.4 | 301 | 3.3 | 11.2 |
| 4 | 23.9 | 4.9 | 450 | 2.2 | 10.8 |
| | (b) crystal thickness 2.08 mm | | | | |
| 1 | 24 | 4.9 | 14.5 | 70 | 34 |
| 2 | 33.6 | 5.8 | 17.8 | 56 | 33 |
| 3 | 57.8 | 7.6 | 20.3 | 49 | 37 |

## C. The influence of the field on the dielectric constant.

The influence of the field on the dielectric constant was measured by Errera.[16] He found that the dielectric constant increased proportionally to the field. Our first experiments showed that this is not right for our range of frequencies, but here there must be a more complicated relation. Indeed, we have shown that the coefficient of polarization as a function of the field has a sharp maximum for weak fields, the position of
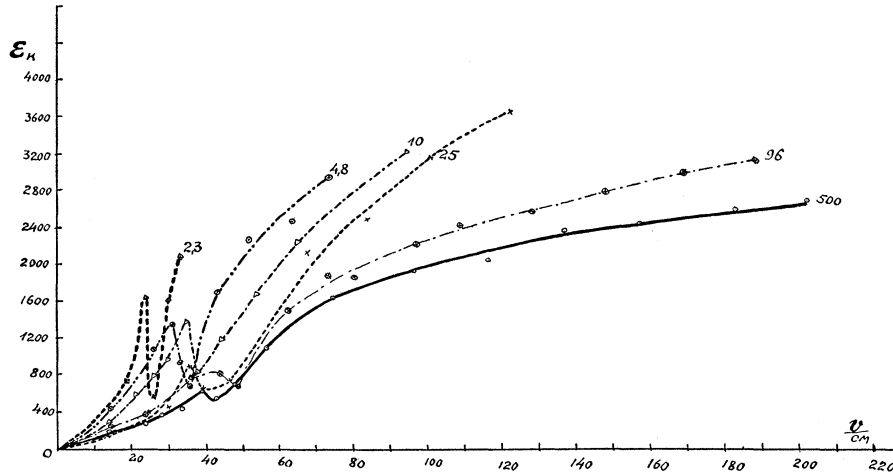
FIG. 6. The apparent dielectric coefficient as a function of the field for various frequencies.

which varies with the frequency (Fig. 6). This maximum decreases with increasing frequency and becomes scarcely perceptible at 500 $H_z$. For the field larger than about 40 volt/cm (depending on the thickness of the crystal) (Fig. 6) the coefficient of polarization increases, but not linearly with the field.

### D. The relation between the time of relaxation $\tau$ and temperature.

Curves similar to those given in Fig. 4 for 16°C were taken at different temperatures. At all temperatures between $-15°$ and $+25°C$, a maximum was obtained. These maxima for certain temperatures are given in Fig. 7 where we see that as the temperature is reduced the maximum shifts towards smaller frequencies, i.e., $\omega_m$ decreases. With temperatures below $-15°C$ and above $+25°C$, no maxima were found in the frequency interval used. (In the figure the curves for the temperatures $-25°$ and $+25.5°C$ are drawn on a greatly enlarged scale.)

The values of $\tau$ calculated from the experimental data according to Eq. (11) are plotted in Fig. 2 (dashed curve), for the crystal the thickness of which was 35 mm and the field $\varepsilon = 3.5$ volt/cm. We see that the variation with temperature is quite similar to the variation of $\theta$ with temperature (Fig. 2).

This similarity for the temperature relation of the mechanical and electrical times of relaxation, obtained by such different methods, appears to support still further our view of the mechanism

of the production of polarization in Rochelle salt. The electric time of relaxation is $\rho d_{14}$. The piezo-modulus $d_{14}$ is known to be a function of the temperature and at $-16°$ and $+25°C$ it becomes very small. The quantity $\rho$ probably depends on the temperature also, but as yet it is difficult to say what will be the character of this relation. It is thus easy to understand why the relation between $\tau$ and temperature is so complex.

### E. The relation between the time of relaxation $\tau$ and the thickness of the crystal.

I. V. Kurchatov studied the effect of crystal thickness on the magnitude of the apparent dielectric constant, and thus of the field necessary to produce saturation. This has been described in his monograph *Rochelle Electricity*. We have studied the effect of crystal thickness on the speed of attaining complete polarization. The
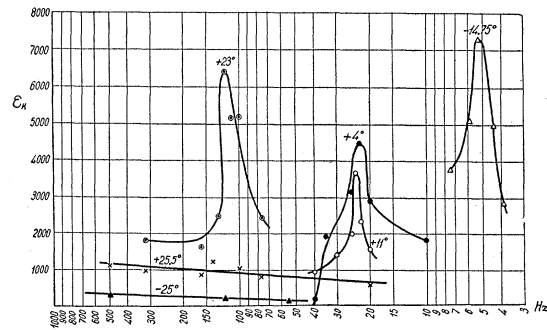


FIG. 7. The displacement of the position of dispersion maxima at different temperatures.
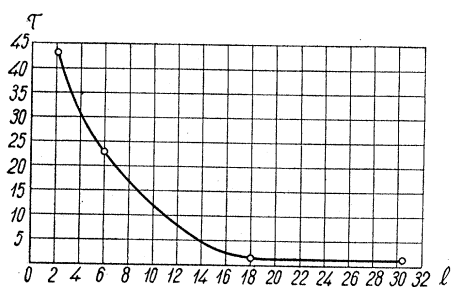
FIG. 8. The time of relaxation as a function of thickness of the crystal.

relation between $\tau$ (expressed in arbitrary units) and the thickness $l$ of the crystal in a field of 25 volt per cm is given in Fig. 8. We see that the time of relaxation decreases as the thickness is increased, but after a certain thickness, which probably depends on the field strength, the time of relaxation does not change. At present it is difficult to explain this effect of crystal thickness. Probably it is necessary to study the question in connection with the effect of field strength on the magnitude of the polarization, and on the time of relaxation in crystals of Rochelle salt.

## LOSSES IN CRYSTALS OF ROCHELLE SALT

According to the hypotheses developed above for the process of polarization in crystals of Rochelle salt, the energy of the electric field must be spent in deforming the crystal. Eq. (2') can be written in the form:

$$e_{14}\rho\dot{x}_4 + (e_{14}/d_{14})x_4 = e_{14}\mathcal{E}_1 \sin \omega t,$$

where we have on the right the magnitude of the force. Multiplying both sides of this equation by $\dot{x}_4$, i.e., by the velocity of deformation, we get on the right side the work done by the field in unit time, while the second term on the left represents a symmetrical oscillation of energy, and the first the amount of energy used up per second.

$$e_{14}\rho\dot{x}_4\dot{x}_4 = e_{14}\rho D^2 \mathcal{E}_1{}^2 \omega^2 \cos^2 (\omega t - \delta)$$

(cf. Eq. (6')). The energy

$$W = e_{14}\rho D^2 \mathcal{E}_1{}^2 \omega^2 / 2 \qquad (13)$$

used up in a period in overcoming the friction should equal the losses.

In the bridge method the losses are determined by measurement of the power factor. From this quantity the losses may be expressed as $W = \omega C \mathcal{E}^2 l^2$ tg $\varphi$, or by substitution of the value $C = Q\eta_k/l$ where $Q$—the area of the electrodes $l$— the thickness of the crystal, and $\eta_k$ from Eq. (13) we get

$$W = (Ql\omega D^2 \mathcal{E}_1{}^2 / S) \text{ tg } \varphi.$$

If we refer this equation to unit volume and equate it to the value of the energy in Eq. (13), we get

$$\text{tg } \varphi = e_{14}\rho\omega S/2 = [d_{14}\rho\omega/2(1 + \theta^2\omega^2)^{\frac{1}{2}}] \qquad (14)$$

since $e_{14} = d_{14}/s_{44}$, and $d_{14}\rho = \tau$. This relation between tg $\varphi$ and the frequency should show a minimum at $\omega_m = 1/\tau$, i.e., at just that frequency at which the dielectric coefficient is a maximum. Our curves for tg $\varphi = f(\omega)$ do in fact pass through a minimum at the relaxation frequency, but on either side of this minimum there are two symmetrically placed maxima, whose appearance we have as yet been unable to explain. The value of tg $\varphi$ at the relaxation frequency, calculated from Eq. (14), after substituting the experimental values of $\omega$ and $\theta$, was 0.002 for the thick crystal, and 0.14 for the thin. The values obtained by measurement were 0.09 and 0.12, respectively. Within the frequency range used, tg $\varphi$ should be practically independent of the frequency, since $(\theta\omega)^2$ is large compared with unity and tg $\varphi$ should depend only on the times of relaxation $\tau$ and $\theta$.

However, we see that there is a very distinct frequency relationship. It seems to us that the cause of this may lie in the fact that in the equation of motion we considered the displacement as proportional to the deformation, instead of equal to the deformation itself.

In conclusion we wish to express our gratitude to Professor J. Frenkel for suggesting this problem, and to Professor W. Fredericks for his interest and critical consideration of our results.