

pressional viscosity is a steep function of average chain length. As nearly as can be judged from the relative slopes of the viscosities measured by longitudinal and shear waves, the activation energy of the compressional viscosity is equal to that of the second shear viscosity.

Some measurements were also made for a poly- $\alpha$ -methyl styrene liquid and the results are shown by Fig. 18 for three frequencies over a temperature range. One interesting difference is at once obvious, namely, that any hysteresis effects are small, since at low temperatures the ratio of reactance to resistance becomes greater than 50, whereas it did not exceed 8 for polyisobutylene. This correlates also with the fact that the high frequency losses of solid polystyrene are much less than those of high molecular weight polyisobutylene at ordinary temperatures. Analyzing the data of Fig. 18, using the solid curves of Fig. 4, one obtains the shear elasticity  $\mu_2$  and the shear viscosity  $\eta_2$  shown by Fig. 19.

The shear elasticity is somewhat higher than that for a 5560 molecular weight polyisobutylene but has about the same change with temperature. The variation of  $\eta_2$ , however, is much larger for poly- $\alpha$ -methyl styrene than for polyisobutylene, and corresponds to an activation energy of 23.6 kilocalories.

Some measurements were also made of very light liquids such as water and cyclohexane. By observing the fifth and seventh reflection for both amplitude and phase changes, measurable results were obtained. For both cases within the experimental error, the values agreed with the steady flow measurements. Hence in agreement with Eq. (1), they are considerably below their relaxation frequencies, and indicate that no configurational type elasticities exist for these liquids. These measurements show that the enhanced losses for longitudinal waves for these liquids must be due to compressional viscosities.

## Ultrasonic Measurements on Rochelle Salt Crystals\*

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A pulse technique at 10 Mc/sec. has been used to study the anomalous elastic properties of rochelle salt single crystals at temperature around the upper Curie temperature. The temperature dependence of foiled crystal constant  $S_{44}^E$  and of the attenuation of waves which contain a component of shear strain in the  $X$  crystallographic plane is reported. The attenuation measurements are formulated in terms of the interaction theory.

The dependence of the velocity in  $45^\circ X$  cut crystals of rochelle salt on a d.c. field in the  $X$  crystallographic direction shows a marked unipolarity. This change in velocity which is caused by the bias field arises from the two following sources: one is the usual saturation on effect which produces a change in velocity that is independent of the polarity; the other is the morphic effect which results from the induced monoclinic constants, and which produces a velocity change, the sign of which is dependent on the polarity.

### I. INTRODUCTION

IT is well known that rochelle salt exhibits extraordinary elastic, dielectric, and piezoelectric properties: Several experimental and theoretical studies of these properties have been made.<sup>1</sup>

In the past the data on the elastic properties have been obtained principally by the self-resonance method. Recently Huntington<sup>2</sup> has used a pulsed ultrasonic technique for determining a com-

plete set of elastic moduli for rochelle salt at room temperature. The present paper reports the use of the ultrasonic method to study further certain interesting aspects of rochelle salt.

In the self-resonance experiments the wavelength of the sound waves in the specimen is of the order of the specimen dimensions, while in the pulsed ultrasonic method the frequency is sufficiently high that the specimens are essentially infinite compared to the wave-length of the sound. The boundary conditions for the two cases lead to expression for the velocity in terms of the elastic compliance coefficients  $S_{ij}$  and of the elastic moduli  $C_{ij}$ , respectively.

The interesting elastic phenomena in Rochelle salt center around the anomalous temperature dependence and the saturation effects (both

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<sup>1</sup> For a review of the investigations of rochelle salt, see W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946).

<sup>2</sup> H. B. Huntington, *Phys. Rev.* **72**, 321 (1947).

mechanical and electrical) of the shear compliance  $S_{44}^E$  of the foiled crystal. In the self-resonance experiments  $S_{44}^E$  appears in the velocity equations either alone or in a sum with other coefficients  $S_{ij}$ . In the pulsed method the quantity  $C_{44}^*$ , where<sup>2</sup>

$$C_{44}^* = 1/S_{44}^E = C_{44} - f_{14}^2/\chi_1$$

appears in the velocity equation alone or in a sum with the moduli  $C_{ij}$ . However, for the former case  $S_{44}^E$  approaches infinity at the Curie points and therefore is the dominant term while for the latter case  $C_{44}^*$  approaches zero and other terms become important.

In this work the pulsed method has the following advantages: first, the induced monoclinic elastic constants which are produced by a bias field can be observed since they are not masked by the term  $C_{44}^*$ ; second, it is possible to make measurement on  $45^\circ X$  cut bars right at the Curie temperature where  $S_{44}^E$  approaches infinity.

## II. EXPERIMENTAL PROCEDURE

The pulsed method at 10 Mc/sec. has already been described.<sup>2</sup> With it velocities could be measured with an accuracy of about 0.5 percent.

The rochelle salt specimens which were studied in this investigation were obtained from the Brush Development Company. The crystals were rectangular parallelepipeds with dimensions of the order of one inch. The two following cuts were principally used:

1.  $45^\circ X$  cut specimens.  $X$  cut quartz transducers were used for transmission in either of the two  $45^\circ$  directions. The  $X$  faces of the specimens were foiled.
2.  $90^\circ Z$  cut specimens. The  $Z$  dimension, which was the direction of a transmission, was one-quarter inch. The  $Y$  cut quartz transducer was oriented so that the transverse mode which was generated was polarized in the  $Y$  crystallographic direction. The  $X$  faces were foiled.

The temperature of the specimens was controlled to  $0.02^\circ\text{C}$  by means of a water bath thermostated by a mercury-tuolene regulator.

When an electrical bias field was required, the field was produced by applying a potential between the foils on the specimen faces. In order to insure a uniform bias field at right angles to the direction of propagation, the quartz transducer (which had metallic electrodes) was isolated from the rochelle salt specimen by a two-inch length of an ammonium dihydrogen phosphate single crystal.

## III. THE TEMPERATURE DEPENDENCE OF $S_{44}^E$

For the  $Z$  cut specimen with the  $Y$  cut transducer oriented as described above, the velocity  $v$  is

$$\rho v^2 = C_{44}^* = 1/S_{44}^E,$$

where  $\rho$  is the density. The plotted points on Fig. 1

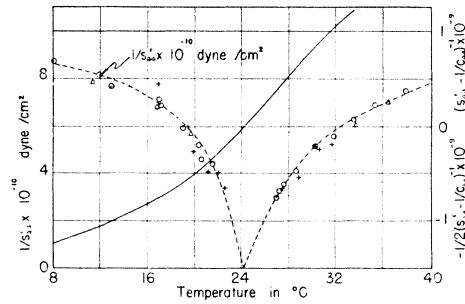


FIG. 1. Temperature dependence of  $1/S_{44}^E$ , the elastic compliance for a foiled crystal, for rochelle salt. Dotted curve is computed from data in Fig. 2. Plotted points are from velocity measurements of a transverse mode in the  $Z$  direction. Solid curve shows the Curie-Weiss law for  $S_{44}^E$ .

give the results of the measurements of this quantity through temperature ranges on either side of the upper Curie point. Velocity measurements were not possible between  $22.7^\circ\text{C}$  and  $26.8^\circ\text{C}$  because of the high attenuation.

For propagation along a  $45^\circ$  direction of a  $45^\circ X$  cut specimen, a quasi-compressional mode with velocity  $v_b$  and a quasi-transverse mode with velocity  $v_d$  are coupled together. These velocities are related by the equation<sup>2</sup>

$$C_b + C_d = (C_{22} + C_{33})/2 + C_{44}^*, \quad (1)$$

where  $C_b = \rho v_b^2$  and  $C_d = \rho v_d^2$ . The temperature variation of the quantity  $C_b$  is given by Fig. 2. The quantity  $C_d - (C_{22} + C_{33})/2$  varies slowly with temperature having a temperature coefficient of  $-0.001/^\circ\text{C}$ .<sup>3</sup> The minimum value of  $C_{44}^*$  occurs with minimum value of  $C_b$  at the temperature of  $24.2^\circ\text{C}$ .

These measurements result in a value of  $24.2^\circ\text{C} \pm 0.1$  for the upper Curie temperature. Values have been reported in the literature from  $22.25^\circ\text{C}$  to  $24.5^\circ\text{C}$ , the most widely accepted value being  $23.7^\circ\text{C}$ .<sup>4</sup> This wide spread in the results seems more likely to be due to the method in which the quantity is measured than to a difference in specimens.

If one assumes that  $C_{44}^*$  vanishes at the Curie temperature, one has

$$C_d - (C_{22} + C_{33})/2 = -C_{b(\min.)} = -2.64 \times 10^{11}.^5$$

If one computes  $C_{44}^*$  from  $C_b$  making use of the above values for the magnitude and temperature coefficient of  $C_d - (C_{22} + C_{33})/2$ , one obtains the dotted curve in Fig. 1. Also, the quantities  $(1/C_{44}^* - 1/C_{44})^{-1}$  and  $-1/2(1/C_{44}^* - 1/C_{44})^{-1}$  are plotted for temperatures above and below  $24.2^\circ\text{C}$ ,

<sup>3</sup> This temperature coefficient was computed from temperature coefficients of the elastic compliances given by Mason (see reference 1, p. 132).

<sup>4</sup> H. Mueller, Phys. Rev. **57**, 829 (1940).

<sup>5</sup> Huntington's values (see reference 2) give  $-2.58 \times 10^{11}$  for  $C_d - (C_{22} + C_{33})/2$ ; this value equals  $2.64 \times 10^{11}$  within the combined errors.

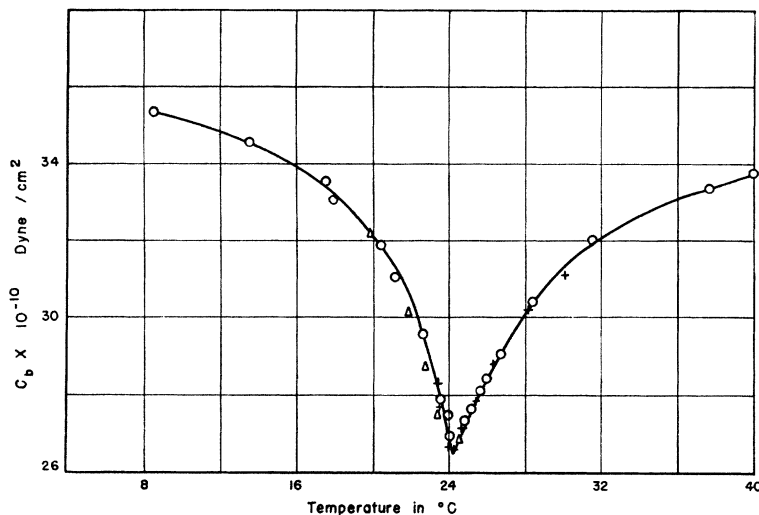


FIG. 2. Temperature dependence of the velocity  $v$  of a compression mode in  $45^\circ X$  cut crystals of rochelle salt.  $C_b = \rho v^2$ .

respectively. Through a limited temperature range around  $24.2^\circ\text{C}$ , a straight line results as predicted by the interaction theory.<sup>4</sup> The slope of the line leads to a value of  $67.3 \times 10^{-12}$  for  $\sigma$ , the Curie constant. Mason's data for  $S_{44}^E$  gives a value for  $\sigma$  of  $66.7 \times 10^{-12}$ .<sup>4</sup>

#### IV. THE TEMPERATURE DEPENDENCE OF ATTENUATION

The temperature dependence of the attenuation of 10 Mc/sec. ultrasonic pulses in rochelle salt is given in Fig. 3. Curves  $a$ ,  $b$ , and  $c$  give the attenuation in db/cm for the quasi-compression mode which travels in the  $45^\circ$  direction of the  $45^\circ X$  cut specimens, for the transverse mode in the  $90^\circ Z$  cut specimens, and for the compression mode propagated along the crystallographic axes, respectively.

Both of the modes which have a maximum in the attenuation at the Curie temperature contain a component of shear strain in the  $X$  plane and the expressions for their velocities contain  $C_{44}^*$ . Therefore, this anomalous temperature dependence of the attenuation apparently has the same origin as the

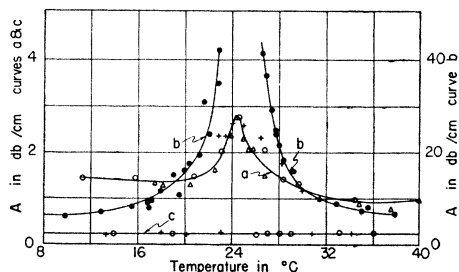


FIG. 3. Temperature dependence of  $A$ , the attenuation in decibels per cm of travel, for 10 Mc/sec. ultrasonics in rochelle salt single crystals. Curve  $a$ —compression mode in  $45^\circ X$  cut crystals. Curve  $b$ —transverse mode travelling in  $Z$  direction. Curve  $c$ —compression mode propagated along crystallographic axes.  $\circ$   $Z$  direction +  $Y$  direction. Correction for curve  $c$ , one-half  $A$  is plotted.

other well-known anomalies in the properties of rochelle salt and can be formulated in terms of the interaction theory.

Mason has shown<sup>6</sup> that the low values of " $Q$ " which were observed by him in the foiled  $45^\circ X$  cut bars of rochelle salt vibrating at their resonant frequencies were principally a result of dielectric loss rather than mechanical loss. Mason introduced this loss into his analysis by use of a complex inverse dielectric susceptibility  $\chi_{e1}$  for the  $X$  crystallographic direction. The wave equation for the  $90^\circ Z$  cut specimens becomes

$$\rho(\partial^2 u_2 / \partial t^2) = C_{44}^{**}(\partial^2 u_2 / \partial x_3^2), \quad (2)$$

where

$$C_{44}^{**} = C_{44} - f_{14}^2 / \chi_{e1}. \quad (3)$$

$u_2$  is the displacement along the  $Y$  crystallographic axis, and  $x_3$  is the position coordinate along the  $Z$  direction.

The solution of this equation is

$$u_2 = u_{20} \exp(-i\omega t) \exp[-(\alpha_2 - i\beta)x_3],$$

where

$$\alpha_2 - i\beta = -i\omega(C_{44}^{**} / \rho)^{-1/2}. \quad (4)$$

Combining Eqs. (3) and (4), one obtains

$$\alpha_2 - i\beta = -i\omega \rho^{1/2} \left\{ \frac{\chi_1 D_{14} + \chi_1'^2 C_{44} - i\chi_1' f_{14}^2}{D_{14}^2 + (C_{44} \chi_1')^2} \right\}^{1/2}, \quad (5)$$

where  $\chi_{e1}$  has been written as

$$\chi_{e1} = \chi_1 - i\chi_1', \quad \text{and} \quad D_{14} = \chi_1 C_{44} - f_{14}^2. \quad (5)$$

Mueller has pointed out<sup>4</sup> that  $f_{14}$  and  $C_{44}$  are nearly independent of temperature, but that  $\chi_1$  varies with temperature in such a manner as to cause  $D_{14}$  to vanish at two temperatures. This

<sup>6</sup> W. P. Mason, Phys. Rev. **58**, 744 (1940).

vanishing of  $D_{14}$  in the interaction theory is the origin of the Curie points.

Except very near the Curie temperatures, where  $D_{14}$  vanishes, the second degree terms in  $\chi_1'$  can be neglected, and

$$\beta = \omega/v = \omega(c_{44}^*/\rho)^{-\frac{1}{2}}, \quad (6)$$

while

$$\alpha_2 = -\rho v(\chi_1' f_{14}^2 \omega)/2D_{14}^2. \quad (7)$$

Since  $D_{14}$  tends toward zero,  $\alpha_2$  tends to very large values. For small values of  $D_{14}$  the exact expression, Eq. (5), must be used; it predicts finite values of attenuation and non-vanishing values of velocity. However, in the temperature range, where the attenuation is sufficiently small to allow measurements to be made (see Fig. 3), Eqs. (6) and (7), the approximate expressions hold.

The attenuation due to the electrical loss also can be formulated for the  $45^\circ X$  cut specimens. The attenuation coefficient  $\alpha_2'$  is

$$\alpha_2' = \frac{-\rho V' \chi_1' f_{14}^2 \omega}{2[D_{14} + (C_{22} + C_{33} + 2C_{23})/4]^2}, \quad (8)$$

where  $v'$  is the velocity. This attenuation is also seen to pass through a maximum at the temperature for which  $D_{14}$  vanishes.

The compression modes along the crystallographic axes involve no electromechanical coupling. Therefore, the losses shown by Fig. 3, curve  $c$ , include no dielectric loss; instead these losses are made up of apparent attenuation inherent in the pulsed method and of true mechanical absorption. The apparent absorption arises from beam spreading, pulse distortion, and scattering of the ultrasonic energy. If one assumes that both the modes with and without electromechanical coupling experience the same attenuation due to causes other than dielectric losses, one can obtain values of  $\alpha_2'$  and  $\alpha_2$  by subtracting Fig. 3, curve  $c$  from Fig. 3, curve  $a$  and curve  $b$ , respectively. The results are shown in Fig. 4, curves  $b$  and  $c$ .

By combining Eqs. (7) and (8), one obtains a relationship between  $\alpha_2$  and  $\alpha_2'$ . If one computes  $\alpha_2$  by using  $\alpha_2'$  from Fig. 4, curve  $c$  and Mueller's data<sup>7</sup> on the temperature variation for  $\chi_1$ , one obtains Fig. 4, curve  $a$ . The temperature scale on the data for  $\chi_1$ , was shifted so that the minimum of  $\chi_1$  occurred at  $24.2^\circ\text{C}$ , our Curie temperature. The constant  $f_{14}$  was taken as  $7.8 \times 10^4$  c.g.s. units.<sup>8</sup> A value of  $C_{44} = 11.97 \times 10^{10}$  dyne/cm<sup>2</sup> then was chosen so that  $D_{14}$  vanished at  $24.2^\circ\text{C}$ .

Values of  $\chi_1'$ , the complex part of the dielectric susceptibility, have been computed from Eq. (8). The temperature variation of this quantity is given by the 10 Mc/sec. curve on Fig. 5. The quantity

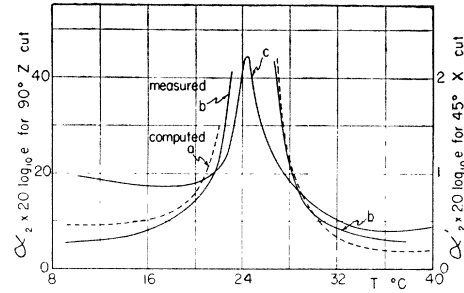


FIG. 4. Temperature dependence of the part of the attenuation as a result of dielectric loss for 10 Mc/sec. ultrasonics in single crystals of rochelle salt. Curve  $a$  is  $\alpha_2$  for transverse mode travelling in  $Z$  direction computed by Eqs. (7) and (8). Curve  $b$  is measured values of  $\alpha_2$  for the same mode. Curve  $c$  is the measured value of  $\alpha_2'$  for the compression mode in  $45^\circ X$  cut crystals.

$-\chi_1'$  can be shown to be equal to  $\omega R$ , where  $\omega$  is the angular frequency and  $R$  is the series resistivity of the dielectric. In Fig. 5, values of  $\omega R$  given by Mason<sup>6</sup> at three frequencies are compared with  $\chi_1'$ .

The quantity  $-\chi_1'$  is proportional to the energy loss per cycle. If the dielectric loss is a hysteresis type, one would expect the loss per cycle and therefore  $\chi_1'$  to be independent of frequency. On the other hand, if the dissipation is a conduction type,  $\chi_1'$  will be proportional to frequency. The results shown in Fig. 5 indicate that below the Curie temperature  $\chi_1'$  is essentially constant for the three dielectric measurements indicating a hysteresis type loss; however,  $-\chi_1'$ , measured by the pulsed method at 10 Mc/sec., is considerably lower. This result is believed to arise from the much lower amplitude of polarization in the pulsed measurements than in the dielectric measurements. Above the Curie temperature  $\chi_1'$  is seen to increase with frequency although less rapidly than  $\omega$ . Therefore, for that temperature range the dissipation of the conduction type is the predominant term.

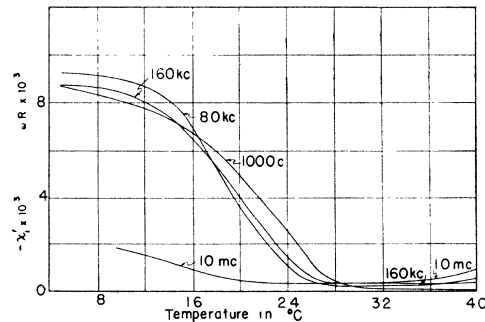


FIG. 5. Comparison of the temperature dependence of the dielectric resistivity  $R$  with  $\chi_1'$ , the imaginary part of the complex inverse susceptibility of rochelle salt crystals. The resistivity  $R$  was taken from dielectric measurements by Mason (6) at 1000 c/sec., 80 kc/sec. and 160 kc/sec. The quantity  $\chi_1'$  was measured by the pulsed ultrasonic method at 10 Mc/sec.

<sup>7</sup> See reference 1, p. 620.

<sup>8</sup> W. P. Mason, Phys. Rev. 55, 775 (1939).

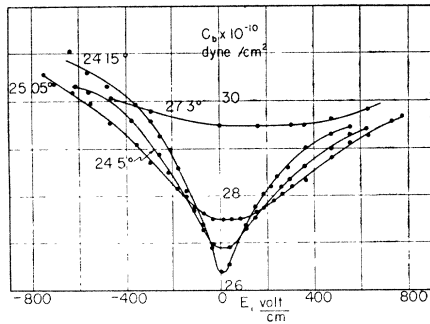


FIG. 6. Dependence of the velocity  $v$  of a compression mode in 45°  $X$  cut rochelle salt crystals on  $E_1$ , the electric field strength in the  $X$  direction for temperatures above the Curie temperature. The quantity  $C_b$  is equal to  $\rho v^2$ .

V. THE ELECTRIC FIELD EFFECT

When a d.c. bias field is applied along the  $X$  crystallographic axis of a rochelle salt crystal at a temperature near the Curie temperature, a marked increase in the velocity occurs in all modes which contain the elastic compliance  $S_{44}^E$  (or the elastic moduli  $C_{44}^*$ ) as a major term in the velocity equation. The dependence of  $S_{44}^E$  on field strength  $E_1$ , is adequately predicted by the following formula from the interaction theory.<sup>9</sup>

$$1/S_{44}^E = C_{44} - f_{14}^2 / (\chi_1 + 3BP_1^2), \quad (9)$$

where the polarization  $P_1$  is a function of  $E_1$ .  $B$  is the coefficient of the fourth degree term in  $P_1$  introduced in the stress-strain energy functions to account for saturation effects. Mueller<sup>10</sup> and Matthias<sup>11</sup> used the self-resonance method to study the dependence of the velocity in 45°  $X$  cut bars on field strength and their results were consistent with Eq. (9).

When the pulse technique was applied to study the dependence of velocity in rochelle salt on  $E_1$ ,

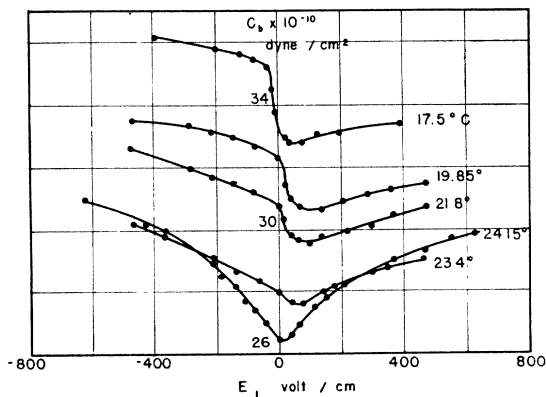


FIG. 7. The quantity  $C_b = \rho v^2$  as a function of electric field strength  $E_1$ . Same as Fig. 6, except temperatures are below the Curie temperature.

<sup>9</sup> H. Mueller, Phys. Rev. 58, 565 (1940).

<sup>10</sup> H. Mueller, Phys. Rev. 57, 842 (1940).

<sup>11</sup> B. Matthias, Helv. Phys. Acta 16, 99 (1940).

the polarity of the bias field was observed to have a large effect. This unipolarity was not observed by the self-resonance method and is not predicted by Eq. (9). The dependence of the velocity on the electric field strength in 45°  $X$  cut specimens is given for several different temperatures in Figs. 6, 7, and 8. For each of these curves the direction of propagation was along one of the two 45° directions and the electric field was applied along the  $X$  axis, perpendicular to the direction of travel. The temperature was held constant by thermostating the specimen and the electric field strength was varied.

Figures 6 and 7 show the variation of  $C_b$  with field strength for a series of temperatures above and below the Curie temperature, respectively. These curves contain data on several specimens. However, in all cases the 45° direction along which an expansion occurred upon the application of a positive voltage was chosen as the direction of propagation. In a 45°  $X$  cut rochelle salt crystal an electric field applied in the  $X$  crystallographic direction causes an expansion along one 45° direction and a contraction along the other. It is apparent that there is a large asymmetry in the field effect with respect to the polarity of the bias field. Below the Curie temperature even the sign of the initial change in  $C_b$  is reversed upon the reversal of the polarity.

Figure 8 gives the results of two sets of measurements which were made on the same specimen. Curve  $a$  was taken for propagation along the 45° direction which expanded upon the application of the positive voltage while curve  $b$  was taken along the other 45° direction.

In all cases the asymmetry was such that the velocity was larger for the polarity of the field that caused a contraction of the crystal along the direction of propagation.

VI. DISCUSSION OF THE MEASUREMENTS OF THE ELECTRIC FIELD EFFECT

Rochelle salt is normally assigned to the rhombic hemihedral class, No. 6. However, it has been pointed

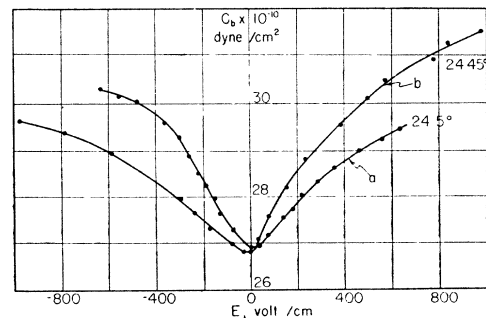


FIG. 8. The quantity  $C_b = \rho v^2$  as a function of electric field strength  $E_1$  for the two perpendicular 45° directions in a 45°  $X$  cut rochelle salt crystal. Curve  $a$ —propagation along 45° direction which elongates with positive field strength; curve  $b$ —propagation along other 45° direction.

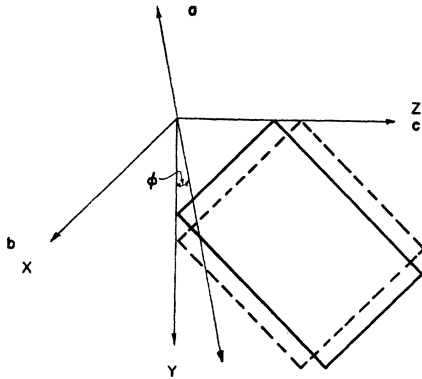


FIG. 9. Convention for assigning crystallographic axes to rochelle salt with monoclinic structure.

out by Jaffe<sup>12</sup> that when the crystal lattice is sheared the symmetry of the crystal is reduced. The reduction in symmetry occurs spontaneously in the ferroelectric temperature range even in the absence of an electric field and artificially in any temperature range when a d.c. bias field is applied in the  $X$  crystallographic direction. Jaffe has shown that in the sheared condition the crystal should be assigned to the monoclinic hemimorphic class, No. 3. As a result of the deformation, new physical constants come into being in the crystal. Mueller has given the name "morphic effects" to the effects that arise with the new constants.

The author believes that the asymmetry observed in these measurements is a morphic effect arising from the new elastic constants introduced when the crystal is sheared by the electric field. To test this theory one must see how the new constants enter into the velocity equation.

When the crystal lattice is sheared in the  $X$  plane through the angle  $\phi$  as shown in Fig. 9, the monoclinic crystallographic axes  $a$ ,  $b$ , and  $c$  are assigned as indicated. By the convention chosen for the case of rochelle salt the  $X$  axis coincides with the polar axis  $b$ , the  $Z$  axis coincides with the  $c$  axis, and the  $Y$  axis is chosen to complete a right-handed system.

The change from the rhombic crystal structure to the monoclinic structure adds the elastic constants  $C_{14}$ ,  $C_{24}$ ,  $C_{34}$ ,  $C_{56}$ , and the piezoelectric constant  $f_{26}$  to the constants necessary to describe the system. If one computes the transformed elastic constant  $C_{22}'$  in the monoclinic crystal for a system of axes rotated  $45^\circ$  around the  $X$  axis, one obtains

$$C_{22}' = \frac{C_{22} + C_{33} + 2C_{23} + 4C_{44}}{4} \pm (C_{24} + C_{34}), \quad (10)$$

the minus and plus signs holding for a rotation from the positive  $Y$  direction toward the positive and negative  $Z$  axes, respectively. Therefore, by

<sup>12</sup> H. Jaffe, Phys. Rev. 51, 43 (1937).

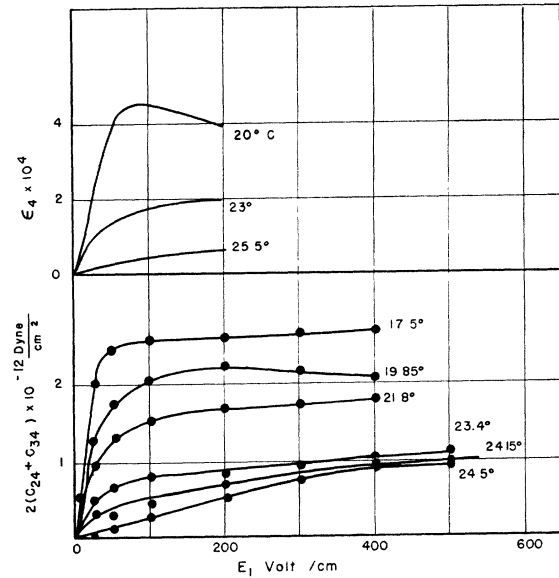


FIG. 10. Lower curves—the dependence of the sum of the induced monoclinic elastic constants  $C_{24}$  and  $C_{34}$  on the electric field strength  $E_1$  for rochelle salt crystals. Upper curves—dependence of strain on static fields, from Vigness (see reference 13).

use of Fig. 9 showing the expansion and contraction of the  $45^\circ X$  cut crystal when the crystal lattice is sheared, it is seen that the positive and negative signs hold for the contracted and expanded dimensions, respectively.

The velocity in the  $45^\circ$  direction is given by

$$\rho v^2 = C_b \cong C_{22}' - f_{14}^2 / \chi_1. \quad (11)$$

The induced piezoelectric constant  $f_{26}$  can be neglected in the piezoelectric term.

From Eq. (11) it follows that the difference in the quantity  $C_b$  for positive and negative fields of the same magnitude is  $2(C_{24} + C_{34})$ . The dependence of this difference on field strength is given in Fig. 10 for several different temperatures. On the same figure static measurements made by Vigness<sup>13</sup> of the piezoelectric strain as a function of field strength are shown. The striking similarity between the two sets of curves indicates a very definite correlation between the observed asymmetry and the distortion of the crystal lattice and helps to verify the hypothesis that this is a morphic effect.

Neither the elastic nor the piezoelectric data are sufficiently complete to allow one to determine an exact relationship between  $(C_{24} + C_{34})$  and the strain  $\epsilon_4$ . However, if one assumes that the two quantities are proportional, one has

$$C_{24} + C_{34} = k \epsilon_4,$$

where

$$k \sim 3 \times 10^{13} \text{ dyne/cm}^2/\text{radian}.$$

<sup>13</sup> I. Vigness, Phys. Rev. 46, 255 (1934).

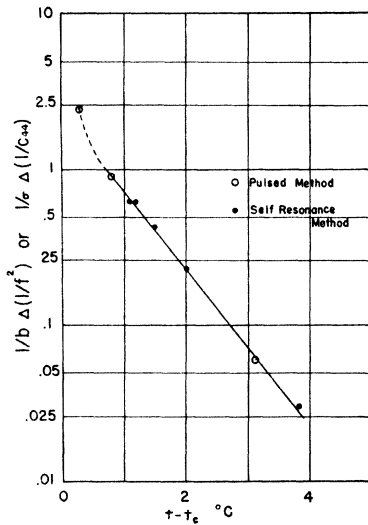


FIG. 11. The temperature dependence of  $1/\sigma \Delta(1/C_{44})$  on rochelle salt crystals. The applied field strength was 300 volt/cm. The quantity  $t_c$  is the upper Curie temperature. Self-resonance data is from Mueller (see reference 9).

The question arises as to why this unipolarity was not observed by the investigators who studied the field effect by the self-resonance method. The resonant frequency is proportional to the reciprocal of Young's modulus  $Y$  which for the  $45^\circ X$  cut bar in the monoclinic state is given by

$$1/Y = 1/4[S_{22} + S_{33} + 2S_{23} + S_{44}^E \pm (S_{24} + S_{34})],$$

where the sign to be taken again depends on the polarity of the bias field.

By computing  $(S_{24} + S_{34})$  from the value of the elastic moduli of rochelle salt one obtains

$$S_{24} + S_{34} = [-1.86 \times (C_{24} + C_{34}) + 1.89 \times C_{14}] \times 10^{-23}. \quad (12)$$

The value of  $C_{14}$  is unknown, but one can say that the effect of  $S_{24} + S_{34}$  could be at the most 5 percent of the total change with field. Therefore, it is not surprising that the morphic effect has not been reported previously, since the self-resonance method is considerably less sensitive to the effect than is the pulsed method.

The relationship between the change in the resonant frequency  $f$  of the  $45^\circ X$  cut bar and in the elastic moduli  $S_{44}^E$  (or  $1/C_{44}^*$ ) is<sup>9</sup>

$$1/\sigma \Delta(1/C_{44}^*) = 1/\sigma \Delta S_{44}^E = 1/b \Delta(1/f^2),$$

where  $b$  is a constant depending on the mode of the bar. The changes which were produced in these two quantities by the application of a field of 300 volt/cm are shown in Fig. 11 for several values of  $(t - t_c)$ , where  $t$  is the temperature of the crystal and  $t_c$  is the Curie temperature. The values of  $1/b \Delta(1/f^2)$  were taken from Mueller's data;<sup>9</sup> for those experiments  $t_c$  was  $23^\circ\text{C}$ . The data for  $1/\sigma \Delta(1/C_{44}^*)$  were obtained from Fig. 6 by computing the average value of the change in  $C_b$  for values of  $E_1$  of  $+300$  and  $-300$  volt/cm; the temperature  $t_c$  of course was  $24.2^\circ\text{C}$ . Since all these points lie on a single curve, it follows that the same dependence of  $S_{44}^E$  (or  $1/C_{44}^*$ ) on field strength  $E_1$  has been found by the self resonance and pulsed methods.

#### VII. ACKNOWLEDGMENT

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