# The Inverse Piezoelectric Proyerties of Rochelle Salt at Audiofrequencies

OSCAR NORGORDEN, University of Minnesota (Received March 28, 1936)

Measurements of the inverse piezoelectric dilatation were made as a function of the temperature and of the frequency and. intensity of the applied electric field, It was found to be proportional to the intensity of the electric field from 5 to 47 peak volts/cm for temperatures above the upper Curie point (23.8'C) and from 5 to 40 peak volts/cm for temperatures below the Curie point; also it was found to be practically independent of the frequency from 100 to 4000 cycles/sec. and for temperatures from 13,3'C to 35.4'C. For temperatures below the Curie point the inverse piezoelectric dilatation increased as the frequency was decreased from 100 cycles/sec. This increase

HE similarity of the electrical properties of Rochelle salt to the magnetic properties of ferromagnetic materials was hrst pointed out by Valasek.<sup>1</sup> In recent years numerous measure ments have been made on the electrical properties of Rochelle salt. Cady,<sup>2</sup> however, made the first attempt to develop a theory. Later Kurtschatow' developed a theory analogous to the Weiss theory of ferromagnetism. Mueller' combined the two theories to explain a number of the electrical and optical properties of Rochelle salt.

In this investigation the inverse piezoelectric dilatation was measured as a function of the frequency and intensity of the applied electric field, the temperature being a parameter. An attempt is made to correlate the results with Mueller's theory, which states that the piezoelectric dilatation is proportional to the susceptibility. Thus the measurements of the inverse piezoelectric dilatation can be compared directly with the measurements of the dielectric constant.

#### **THEORY**

If an electric field  $E$  is applied parallel to the a axis on a Rochelle salt crystal, then Voigt's general piezoelectric equations' reduce to

' Valasek, Phys. Rev. 15, 537 (1920); 17, 475 (1921); 19, 478 (1922); 24, 560 (1924). '

was explained in terms of Schulwas-Sorokin and Posnov's theory of relaxation time. For temperatures above the Curie point the inverse piezoelectric dilatation decreased as the frequency was decreased from 100 cycles/sec. Mueller's theory explained the experimental results for frequencies from 100 to 4000 cycles/sec. and temperatures above the upper Curie point. This theory was approximately in agreement with experiment for temperatures from  $13.3^{\circ}$ C to the Curie point and for frequencies from 100 to 4000 cycles/sec. Below 100 cycles/sec. the theory is not in good agreement with the experimental results.

$$
y_z = d_{14}E,\tag{1}
$$

where  $y_z$  is the piezoelectric strain and  $d_{14}$  is the piezoelectric modulus. The piezoelectric dilatation in a direction making an angle of 45° with the b and c axes and  $90^\circ$  with the a axis is a maximum and is a pure translation. The inverse piezoelectric dilatation, the change in length per unit length  $\Delta r/r$ , in this direction is<sup>6</sup>

$$
\Delta r/r = \frac{1}{2}d_{14}E. \tag{2}
$$

The microscopic field F acting upon an electric charge placed in a polarized dielectric is different from the macroscopic field  $E$ . If  $P$  is the polarization per unit volume

$$
F = E + fP, \tag{3}
$$

where  $f$  is a constant which depends upon the arrangement of the molecules and was shown by Lorentz to be  $4\pi/3$  in special cases.

In a medium containing dipoles which are free to rotate, Langevin showed that when a held was applied the thermal motion at a temperature  $T$ brought about an equilibrium condition such that

$$
P = Np(\coth pE/kT - kT/pE) = NpL(pE/kT),
$$

where  $p$  is the moment per dipole,  $N$  is the number of dipoles per  $cc$  and  $k$  is the Boltzmann constant. Expanding the Langevin function  $L(\phi E/kT)$  and taking the first two terms

$$
P = (Np p E/3kT)[1 - (1/15)(p E/kT)^{2}]
$$
  
=  $\alpha' E - \beta' E^{3}$ ,

<sup>5</sup> Bloomenthal, Physics 4, 172 (1933).

<sup>&</sup>lt;sup>2</sup> Cady, Phys. Rev. 33, 278 (1929).

<sup>3</sup> I. 8, Kurtschatow, Seignette-Electricity, Monograph,  $(1933)$ 

Mueller, Phys. Rev. 47, 175 (1935).

 $\frac{1}{2}$  Voigt, Lehrbuch der Kristallphysik (1910), pp. 830, 902.

in which  $\alpha'$  and  $\beta'$  are functions of the temperature.

Guided by the form of this equation Mueller<sup>4</sup> assumed that we may, for the dielectric, write

$$
P = \alpha F - \beta F^3,\tag{4}
$$

in which F replaces E and the linear term  $\alpha$  is the sum of four effects

$$
\alpha = \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4,
$$

where  $\alpha_1$  is the optical polarizability,  $\alpha_2$  is due to the displacement of the ions in the lattice,  $\alpha_3 = e_{14}\delta_{14}$  is due to the piezoelectric backpolarization  $e_{14}y_z$ , and  $\alpha_4$  is the contributions of the dipoles. In a finite crystal,  $\alpha_3$  depends upon the dimensions of the crystal and vanishes if the piezoelectric deformations are prevented.  $\alpha_3$  and  $\alpha_4$  are responsible for the marked temperature dependence of  $\alpha$ .

Mueller<sup>4</sup> also assumed the microscopic field  $F$ should replace  $E$  in Eq. (2)

$$
\Delta r/r = \frac{1}{2}d_{14}F. \tag{5}
$$

If one assumes  $\beta F^3$  to be small, the susceptibility is given by

$$
P/E = \alpha/(1-\alpha f).
$$

Here if we set

$$
\alpha = \theta / f \tag{6}
$$

and assume for the moment that  $\theta$  is a constant. the susceptibility is given by

$$
P/E = C/(T - \theta) \quad \text{where} \quad C = \theta/f
$$

In this expression  $\theta$  appears as a "Curie temperature" when comparison is made with the theory for ferromagnetic materials. In the case of dielectrics with which we are dealing,  $\theta$  may be a function of the temperature. It is to be considered as a quantity entering in the expression for the susceptibility rather than a  $fixed$  transition temperature.

From Eqs. (3), (4) and (6)

$$
E = (1 - \theta/T)F + f\beta F^3. \tag{7}
$$

On solving Eq.  $(7)$  for F to the second approximation

$$
F = TE/(T - \theta) - T^4 \beta f E^3 / (T - \theta)^4.
$$
 (8) edge v

If the cubic term in Eq. (8) is neglected

$$
\Delta r/r = d_{14}TE/2(T-\theta). \tag{9}
$$

Near  $T_c$ , the temperature where the transition from the normal to the "ferro" dielectric state occurs, where  $\theta = T_c$  we may write as an approximation

$$
r/\Delta r = 2(T - T_c)/d_{14}ET_c.
$$
 (10)

This obviously is good only for temperatures near  $T_c$  as we have set  $T - T_c$  for  $T - \theta$  and  $T_c$  in place of T in the denominator. The above applies if  $T > \theta$ .

If  $T<\theta$ , then there is a real solution to Eq. (7) for  $E=0$ 

$$
F_0^2 = 1/f\beta(\theta/T - 1). \tag{11}
$$

This gives the part of the microscopic field which is due to the spontaneous polarization.

The total microscopic field existing when the medium is "permanently" polarized and an external field is applied is

$$
F + F_0 = E + f(P + P_0)
$$
  
= E + f[\alpha(F + F\_0) - \beta(F + F\_0)^3]. (12)

The microscopic field produced by spontaneous polarization is

$$
F_0 = fP_0 = f(\alpha F_0 - \beta F_0^3). \tag{13}
$$

By obtaining a solution for  $F$ , to the second approximation, from Eqs.  $(6)$ ,  $(11)$ ,  $(12)$  and  $(13)$ and substituting this value of  $F$  in Eq. (5)

$$
\frac{r}{\Delta r} = \frac{4(\theta/T - 1)}{d_{14}E[1 - (3E/4)(\beta f/(\theta/T - 1)^3)^{\frac{1}{2}}]}.
$$
 (14)

For the first approximation on Eq.  $(14)$  reduces to

$$
r/\Delta r = 4(T_c - T)/d_{14}T_cE \tag{15}
$$

for temperatures near the Curie point.

Eqs. (10) and (15) can be tested experimentally by variation of  $E$  and  $T$ . Note that the first order approximation Eqs. (10) and (15) for temperatures above and below the Curie point (23.8'C), respectively, are the same except for a factor 2 in the numerator of Eq. (15).

### THE CRYSTALS

Three cubes approximately two cm on an edge were cut by a wet string from a large Rochelle salt crystal obtained from the Brush Development Company. The crystals were polished on a piece of slightly moist plate glass. Two of the surfaces were cut perpendicular to the a axis, and the other four surfaces made an angle of  $45^{\circ}$  with the b and c axes.

The Rochelle salt crystals were annealed in a manner used by Mueller. The crystals were placed in a temperature-controlled oven and heated slowly to 42'C. They were kept at this temperature for seven hours, then allowed to cool slowly to room temperature. This treatment made it possible to get more reproducible results.

Thin metal foil electrodes were fastened to the two surfaces perpendicular to the a axis with a small amount of Canada balsam dissolved in xylol as described by Bush,<sup>7</sup> Mueller<sup>4</sup> and others. These surfaces were completely covered by the foil. This type of electrode has been found to give good results.

A thin sheet of paper was glued with celluloid dissolved in amyl acetate to the surface of the crystal: then alternate sheets of mica and metal foil were glued on as shown in Fig. 1. The lower grounded metal foil acted as an electrostatic shield from the electric field applied to the crystal. These paper and mica sheets glued to the crystal would offer a resistance to the inverse piezoelectric displacement in the horizontal direction, and thus indirectly, to the displacement in the vertical direction. However, for a large number of mountings of this type on the three different crystals, the inverse piezoelectric amplitude was independent of the mounting within the experimental accuracy of the measurements.

The crystals were next placed in an air-tight chamber containing a saturated solution of Rochelle salt. They would absorb a maximum amount of water of crystallization. At the end of four days the crystals were removed and painted with clear glyptal lacquer. Valasek,<sup>1</sup> Vigness<sup>8</sup> and Korner<sup>9</sup> have pointed out the dependence of the electrical properties of Rochelle salt upon the humidity, and this variation of results could be eliminated by the above precaution.

The crystal was glued to a mica insulator and the insulator glued to the brass plate (Fig. 1). A heavy piece of metal was sweat-soldered to the brass plate. Two small blocks of Bakelite were placed against the crystal on adjacent sides and glued in place but not glued to the crystal. These precautions eliminated a large number of extraneous resonance frequencies.

### THEORY OF THE MEASUREMENTS

A brass plate of area 5 was mounted above the crystal and at a distance  $u$  from the top lead foil; cf. Fig. 1. The distance  $u$  could be varied by a calibrated vernier screw. Let the capacitance of the condenser formed by the brass plate and the top foil on the crystal be  $C$ ; then

$$
C = 1.124S/4\pi u \text{ mmf.}
$$
 (16)

The condenser C was connected in series with a high potential  $V$  and a high resistance  $R$ . The condenser  $C$ , the potential  $V$ , the resistance R and the connecting wires had to be very carefully shielded from the alternating voltage applied to the crystal and all stages of the amplifier except the input to the first stage. The input to the first stage was connected across the high resistance  $R$ , but we shall at first neglect the effect of the input admittance of the amplifier upon this simple series circuit. Let  $C_1$ 



Fto. 1. Circuit diagram.<br>
V—including  $V_1$   $R-5\times10^9$  ohm<br>  $-184.2$  volts  $R_1$ —300,000 ohn V—including  $V_1$ <br>
-184.2 volts  $R_1$ <br>  $V_1$   $R_2$   $R_3$   $N_4$   $N_5$   $N_6$  ohms<br>  $V_8$   $N_2$   $N_3$   $N_4$   $N_5$   $N_6$  ohms  $\begin{array}{lll} -184.2 \text{ volts} & R_1 = -300,000 \text{ ohms} \ -1.5 \text{ volts} & R_3 = -1,000,000 \text{ ohms} \ 1.905 \text{ volts} & R_4 = -100,000 \text{ ohms} \ 1.9000 \text{ ohms} & R_5 = -100,000 \text{ ohms} \end{array}$ -10.5 volts<br>-6.0 volts<br>-28.5 volts -28.5 volts T—audiofrequency trans-<br>-150 volts former  $V_4$ —28.5 volts former<br>  $V_5$ —150 volts former<br>
A—microammeter (0–30 : 0–300 microampere

<sup>&</sup>lt;sup>7</sup> Bush, Helv. Phys. Acta **6**, 315 (1933).

<sup>&</sup>lt;sup>3</sup> Vigness, Phys. Rev. **48,** 198 (1935).<br><sup>9</sup> Korner, Zeits. f. Physik **94**, 801 (1935).

be the stray capacitance in mmf in parallel with the condenser  $C$ ; let  $Q$  be the charge on the condensers  $C$  and  $C_1$ ; then

$$
Q = V(C + C_1). \tag{17}
$$

When an alternating voltage is applied to the electrodes perpendicular to the a axis, the crystal vibrates in the vertical direction because of the inverse piezoelectric effect. Let the alternating voltage change from zero to a maximum in a time  $\Delta t$  (one-quarter of a cycle). Then the distance u will change by an amount  $\Delta u$ . If the resistance  $R$  is so large that no appreciable charge can leak from the condensers  $C$  and  $C_1$ in the time  $\Delta t$ ; then

$$
dQ = VdC + (C + C_1)dV = 0.
$$
 (18)

By differentiating Eq. (16) and substituting this value of  $dC$  in Eq. (18)

$$
du = (u/V)(1 + 4\pi uC_1/1.124S)dV.
$$
 (19)

Since  $\Delta u$ , the amplitude of vibration, is very small, then du can be replaced by  $\Delta u$  without an appreciable error. For a fixed position of the upper brass plate,  $r+u$  must be equal to a constant or  $\Delta r + \Delta u = 0$ ; thus

$$
\Delta r = (u/V)(1 + 4\pi u C_1/1.124S)\Delta V. \tag{20}
$$

 $\Delta V$  is the peak alternating voltage across the condenser C and must be equal to the peak alternating voltage drop in R.

## THE AUDIOFREQUENCY AMPLIFIER

The values of all the circuit constants are given in Fig. 1.The input and second stages were resistance-coupled and were operated at a low plate voltage using type 38 tubes, as described plate voltage using type 38 tubes, as describe<br>by Johnson and Neitzert.<sup>10</sup> The input admittano of the input stage to the amplifier was calculated using Chaffee's<sup>11</sup> formula. The input conlated using Chaffee's<sup>11</sup> formula. The input con-<br>ductance was found to be of the order of  $10^{-11}$ mhos and the input susceptance was equivalent to an input capacitance slightly greater than the given input value. Our previous assumption of neglecting the input impedance of the tube is justified if a slightly smaller equivalent value of R is used. This small change in R does not affect

the validity of the assumptions made in deriving Eq. (20). From the calibration curves of the amplifier and the microammeter,  $A$ , (Fig. 1) reading, the input voltage to the amplifier  $\Delta V$ can be calculated.

## THE DETERMINATION OF THE CIRCUIT **CONSTANTS**

The following data are on crystal No. 2. In Eq. (20) the terms u,  $\Delta r$ , V and  $\Delta V$  are variables while  $C_1$  and S are constants for any particular mounted crystal. The stray capacitance  $C_1$  was measured at radio frequencies by a resonance circuit substitution method. The measured value of  $C_1$  was  $9.1 \pm 0.2$  mmf. The area S of the brass plate was 1.995 cm<sup>2</sup>. The value of  $\Delta V$  could be calculated from the microammeter reading, as explained in a previous paragraph. The distance u could be read directly on a vernier except for a small error in the zero reading. If these numerical values are substituted in Eq. (20), one obtains

$$
\Delta r = (u/V)(1+51u)\Delta V. \tag{21}
$$

Consider the special case of Eq. (21) in which  $\Delta r$  and V are constant; u is taken as the independent variable and  $\Delta V$  is the dependent variable. Then Eq. (21) reduces to the form

$$
(1+51u)u\Delta V = \Delta r V = k = \text{constant.} \quad (22)
$$

Experimentally  $u$  was varied, and the values of  $\Delta V$  were calculated from the microammeter readings. The circles in Fig. 2 represent these experimentally obtained points. The theoretical curve obtained from Eq. (22) was matched to the experimental points at the point  $u=0.0457$ cm and is drawn in Fig. 2. The agreement between the theoretical curve and the experimental points is good. Therefore the measured value of the constant  $C_1$  must be reasonably accurate.

Next consider the special case of Eq. (21) in which  $\Delta r$  and u are constant; thus V and  $\Delta V$ are the independent and dependent variables, respectively. Eq. (21) becomes

$$
V = K \Delta V, \tag{23}
$$

where  $K$  is a constant. In Fig. 3 a straight line is drawn through the experimentally obtained

<sup>&</sup>lt;sup>10</sup> Johnson and Neitzert, Rev. Sci. Inst. 5, 196 (1934).

<sup>&</sup>lt;sup>11</sup> Chaffee, Theory of Thermionic Vacuum Tubes, p. 274.



FIG. 2. Comparison of experimental and calculated values of  $\Delta V$  obtained for different values of u. Circles, experimental values; curve, calculated values.

points. The theoretical equation, Eq. (23), is satisfied within the experimental error.

Finally, consider the case in which  $V$  is made equal to the C bias of the input of the 38 type tube. With  $V$  at a very small potential of less than one percent of its original value, the variation of  $\Delta V$  produced by varying  $\Delta r$  and u should also be less than one percent of their original values. This was found to be experimentally true.

The curves in Figs. 2 and 3 show that the values of  $\Delta V$  measured must be due to  $\Delta r$ , the amplitude of vibration of the vibrating crystal, and not from spurious effects such as feed back or extraneous pick up in the input stage.

## STABILITY OF OPERATION

The temperature was kept constant for six hours previous to taking readings in order to insure temperature equilibrium. At a temperature of 35.4'C, a definite alternating voltage was applied to the crystal for four hours and during that time  $\Delta V$  remained constant within  $\frac{1}{4}$  of one



FIG. 3. Check on Eq. (21) and Eq. (23). Values of  $\Delta V$ (measured by A) when  $\Delta r$  and u are constant and V varied.

percent. This showed that the apparatus was stable and also that the inverse piezoelectric dilatation showed no fatigue effect under alternating current conditions.

## SENSITIVITY OF THE EXPERIMENTAL ARRANGEMENT

In making the inverse piezoelectric measurements on crystal No. 2,  $u$  was set at 0.0457  $\pm 0.0009$  cm and the potential V at 184.2 volts. Substituting these values in Eq. (21) gives

$$
\Delta r = (8.2 \pm 0.4) \times 10^{-4} \Delta V. \tag{24}
$$

From the calibration curves of the amplifier and the sensitivity of the microammeter, the sensitivity or the minimum amplitude of vibration that could be easily detected was about  $1.5 \times 10^{-9}$ cm at 1000 cycles/sec., and  $5 \times 10^{-9}$  cm at 30 cycles/sec.

#### RESULTS

The curves given in this paper are from data taken on crystal No. 2. Figs. 4 and 5 give curves for  $\Delta r/r$  as a function of the electric field E for different frequencies at temperatures above and below the Curie point  $(23.8^{\circ}C)$  respectively; E in peak volts/cm is the alternating electric field applied parallel to the a axis. The curves in Fig. 4 are linear except for fields below 5 peak volts/cm. In Fig. 5 the curves deviate from linearity for fields below 5 peak volts/cm and above 40 peak volts/cm.

In Fig. 6,  $\Delta r/r$  is given as a function of the field E for different temperatures at a constant frequency of 700 cycles/sec. The curves are all approximately linear, and the slope of the curves increases as the upper Curie point, 23.8'C, is approached. Similar curves were found for other frequencies in the audio band. This justifies the assumption, made in the theory, in neglecting the cubic term in  $E$  in Eq. (8).

Vigness' measured the inverse piezoelectric displacement as a function of the applied electrostatic field. He obtained a linear relation between  $\Delta r/r$  and the electrostatic field, for fields up to 40 volts/cm.

David<sup>12</sup> measured the dielectric constant,  $K_{11}$ , along the a axis at a frequency of 50 cycles/sec. He observed the dielectric constant  $K_{11}$  to be independent of the applied field for fields up to 50 volts/cm. Because of the close relationship between the dielectric constant  $K_{11}$  and  $\Delta r/r$ , one would expect  $\Delta r/r$  to be linear with respect



FIG. 4. Variation of the inverse piezoelectric dilation with the electric field applied parallel to the  $a$  axis. The temperature is 35.4°C. The zero is shifted for all the curves except the 100 cycles per second curve.

to the applied field up to 50 volts/cm. The measurements of Vigness and David are in agreement with the curves in Figs. 4, 5 and 6.

In Figs. 7 and 8,  $\Delta r/r$  is given as a function of the frequency for various applied fields at temperatures above and below the Curie point, respectively. The curves in Fig. 9 are for an applied field of 18.9 peak volts/cm and for



FIG. 6. Variation of the inverse piezoelectric dilation with the electric field applied parallel to the  $a$  axis at a frequency of 700 cycles per second.

40 30

o 10 20 30<br>Peak Voits / Cm

D

<sup>&</sup>lt;sup>12</sup> David, Helv. Phys. Acta 8, 431 (1935).



FrG. 7. Variation of the inverse piezoelectric dilation with the frequency. The four curves are for different electric field of  $A$ —47.2,  $B$ —37.7,  $C$ —28.3 and  $D$ —18.9 peak volts per cm applied parallel to the a axis. The temperature is 35.4'C.



FIG. 8. Same as Fig. 7. Temperature 17.7°C.

temperatures from 13.3'C to 35.4'C. Similar curves were obtained for other applied fields of 28.3, 37.7 and 47.2 peak volts/cm.

A resonance frequency at about 370 cycles/ sec. was found for all crystals and for different mountings on the brass plate. By gluing the crystal to; the brass plate and by mounting braces to prevent the crystal from vibrating as a rod supported on one end, a large number of resonance frequencies were removed; however that of 370 cycles/sec. remained. Increasing and



Fig. 9. Variation of the inverse piezoelectric dilation with the frequency for an electric field of 18.9 peak volts per cm applied parallel to the  $a$  axis.

decreasing the mass and rigidity of the base plate did not effect this resonance frequency.

Certain conclusions can be drawn from Figs. 7, 8 and 9,  $\Delta r/r$  is approximately independent of the frequency from 100 to 4000 cycles/sec. For temperatures above the Curie point,  $\Delta r/r$  decreases as the frequency is lowered below 100 cycles/sec.; also  $\Delta r/r$  decreases more rapidly with the increasing temperature, for frequencies below 100 cycles/sec. , than above. Below the Curie point  $\Delta r/r$  increases as the frequency is lowered from 100 cycles/sec., and also as the temperature approaches the Curie point. Schulwas-Sorokin and Posnov<sup>13</sup> developed a theory of relaxation time for Rochelle salt that explains the variation of  $\Delta r/r$  for temperatures below the Curie point and for frequencies less than 100 cycles/sec. They assumed that the motion of the dipoles relative to the lattice could be represented by the equation

$$
E = \rho \dot{y}_z + (1/d_{14}) y_z, \tag{25}
$$

where  $\rho$  is the "viscosity" constant,  $d_{14}$  is the piezoelectric modulus and  $E$  is the electric field parallel to the  $a$  axis. This equation assumes that E depends on  $y_z$  in a linear manner and therefore

<sup>&</sup>lt;sup>13</sup> Schulwas-Sorokin and Posnov, Phys. Rev. 47, 166 (1935).

will hold only for fields up to about 45 volts/cm. The solution of Eq. (25) is

$$
y_z = d_{14}E(1 - e^{-t/\rho d_{14}}). \tag{26}
$$

If a field  $E$  is applied to the crystal, the inverse piezoelectric displacement  $\Delta r/r$ , which is proportional to  $y_z$ , does not take place instantaneously; but follows the law given in Eq. (26). The time,  $t_0 = \rho d_{14}$ , is defined as the relaxation time.

Vigness' took oscillograms of the inverse piezoelectric displacement,  $\Delta r/r$ , as a function of the time the electric field was applied. Approximately exponential curves were obtained; these curves appeared to be the sum of three exponential curves. The relaxation times of the three exponential curves were as follows: (1) the order of minutes (2) the order of seconds and (3) too short to . be measured. The second relaxation time was a function of the temperature. It had a maximum at  $4^{\circ}$ C and then decreased to zero at both Curie points.

When the frequency is lowered below 100 cycles/sec. and the temperature is below the upper Curie point, the time for a cycle becomes appreciable compared to the relaxation time  $\rho d_{14}$ . The lower the frequency, the larger  $t$  becomes in this equation; also the closer the temperature approaches the Curie point the smaller the value

of the relaxation time  $\rho d_{14}$ . The larger values of t and the smaller values of  $\rho d_{14}$  will increase  $y_z$  in Eq. (26). This increase in  $\Delta r/r$  from the contribution of Eq. (26) explains the rise in  $\Delta r/r$  at frequencies below 100 cycles/sec. and temperatures below the Curie point in Figs. 8 and 9.

In Fig. 10,  $\Delta r/r$  is given as a function of the temperature for various fields  $E$  and at a frequency of 700 cycles/sec. Because  $\Delta r/r$  is independent of the frequency from 100 to 4000 cycles/sec. , curves practically identical with those in Fig. 10 were obtained for all frequencies in this range. The upper Curie point, as defined by the curve for 6.3 peak volts/cm, is about 23.8 $^{\circ}$ C. The value given by Mueller<sup>4</sup> is 23.7 $^{\circ}$ C.

The data in Fig. 10 are plotted in another way in Figs. 11 and 12; namely,  $r/\Delta r$  is given as a function of the temperature. According to Eqs. (10) and (15), for the first approximation in Mueller's theory,  $r/\Delta r$  is a linear function of the temperature, the intercept on the abscissa axis is the temperature  $t_c$  and  $d_{14}$  can be calculated from the slope of the curves.

In Fig. 11, the value of  $t_c$  is about 23.0°C, and the values of  $d_{14}$  calculated from the four curves for different fields E are shown in Fig. 13 curve A.





FiG. 10. Variation of the inverse piezoelectric dilation with the temperature at a frequency of 700 cycles per second. The five curves are for different electric fields of  $A$ —47.2,  $B$ —37.7,  $C$ —28.3,  $D$ —18.9 and  $E$ —6.3 peak volts per cm applied parallel to the  $a$  axis.

FIG. 11. Variation of the reciprocal of the inverse piezoelectric dilation with the temperature at a frequency of 700 cycles per second. The four curves are for different electric<br>fields of A—47.2, B—37.7, C—28.3 and D—18.9 peak volts per cm applied parallel to the  $a$  axis.



FIG. 12. Same as Fig. 11.

From measurements of the susceptibility above the Curie point, Mueller<sup>4</sup> found  $t_e = 23.0$ °C. This small variation of  $d_{14}$  from its average value is about equal to the probable error. The fact that  $d_{14}$  appears to be a linear function of the applied field could be due to systematic errors.

Next consider the agreement between the experiment and theory for temperatures below, the upper Curie point. The value of  $t_c = 23.5$ °C in Eq. (15) is read from the intercept with the temperature axis of the curves in Fig. 12.  $d_{14}$  can be calculated from the slope of the curves.  $d_{14}$  is not a constant but increases linearly with the field  $E$  as shown in Fig. 13 curve  $B$ . Thus the experimental results are not in good agreement with Eq. (15).

The Eq. (14) made accurate to the second approximation in  $E$  might be expected to give the increase of  $d_{14}$  with E in Eq. (15). Rewriting Eq. (14)

$$
\frac{r}{\Delta r} = \frac{4(t_c - t)}{d_{14}ET_cH'},\tag{27}
$$



FIG. 13. Variation of  $d_{14}$  in Mueller's theory with the electric field. Curves A and B are for temperatures above and below the Curie point, respectively.

where

$$
H = 1 - \frac{3E}{4} \left( \frac{\beta f T^3}{(t_c - t)^3} \right)^{\frac{1}{2}}.
$$
 (28)

However  $H$  decreases with an increase in the field  $E$  instead of increasing. Thus Mueller's theory gives approximately the same value of  $d_{14}$ below the Curie point as above, but  $d_{14}$  is not a constant for temperatures below the Curie point.

At a frequency of 50 cycles/sec., curves similar to those in Figs. 11 and 12 were drawn. The temperature  $t_c$  was found to be about 23.0°C.  $d_{14}$  was not a constant and increased with the field  $E$  for temperatures below and above the upper Curie point. Mueller's theory is not in agreement with experiment for frequencies below 100 cycles/sec.

#### ACKNOWLEDGMENTS

I wish to express my sincere appreciation to Drs. J. Valasek and A. Zeleny for their helpful advice and constructive criticism in this work.