

for example, by a highly anisotropic Knight shift in the superconducting state. Since the superconducting ground state in the theory of Bardeen, Cooper, and Schrieffer is a singlet state, it should have no electronic spin susceptibility and hence no Knight shift at all, if this state is separated from states with  $S \neq 0$  by an energy gap. It is conceivable that a theory giving a non-zero Knight shift might also provide an additional source of line width. Alternately, the line width might

simply be increased by clustering of the colloidal particles or some other nonideality of the sample.

#### ACKNOWLEDGMENTS

The author is pleased to acknowledge helpful discussion on the subject of this paper with Professor J. Bardeen, Professor W. D. Knight, Professor F. Reif, and Professor K. Yosida, and with Dr. A. L. Schawlow of the Bell Telephone Laboratories.

## Ferroelectric Polarization Reversal in Rochelle Salt

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(Received November 7, 1957)

An experimental investigation of the polarization reversal process in Rochelle salt shows that besides the slow, lateral motion of *b*- and *c*-domain walls, there is also a fast reversal process characteristic of the nucleation and wall propagation in the orthorhombic *a*-direction. Reversal in this direction is qualitatively analogous to the polarization process in *c*-domain BaTiO<sub>3</sub>.

#### INTRODUCTION

ROCHELLE salt (NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O) is not only the oldest but also one of the best known<sup>1</sup> among ferroelectric crystals. Yet our understanding of ferroelectric phenomena is still rudimentary. In the case of Rochelle salt, the complex arrangement of the atoms forming the space lattice of the unit cell, as well as thermal and mechanical instabilities of the macroscopic crystal, have increased the difficulty of the experimenter intent on showing the relation between the optically-observable domain dynamics and the electrical hysteresis and polarization.

These observations were relatively easy in the case of BaTiO<sub>3</sub>. It was shown<sup>2,3</sup> that, for an electric field applied in an antiparallel direction to the polar axis of a macroscopic "*c*-domain" crystal, there occurs first a nucleation of spike-shaped domains and thereafter a motion and expansion of these domains in the direction of the applied field until the entire crystal volume becomes saturated.

The number of optically visible nuclei increases exponentially with the applied field. For low applied fields, the peak switching current also increases exponentially and the switching time of a crystal decreases logarithmically with the field. Switching at low fields

may be defined in terms of the empirically determined constant  $\alpha$  which represents an "activation field."

At high applied fields, the peak switching current as well as the switching time are linearly dependent upon the field. At high fields, therefore, the crystal behaves more like a resistance during polarization reversal, and no individually moving nuclei may be discerned. The nuclei generated propagate through the crystal with some average mobility  $\mu$ , characteristic of the motion of a single wall. Both  $\alpha$  and  $\mu$  were found to be highly temperature dependent. A rise in temperature towards the Curie temperature brought about a faster polarization reversal because, in spite of the randomizing effect of thermal energy, the increase in symmetry of the crystal unit cell makes it easier for the field to overcome the potential barrier keeping the dipoles in a stable orientation.

Although optical evidence of domain wall motion has not been found yet in guanidinium aluminum sulfate, the electrical behavior<sup>4</sup> of this ferroelectric during polarization reversal closely parallels that of BaTiO<sub>3</sub>. The same observations apply in the case of triglycine sulfate and partly in the case of potassium niobate.

Rochelle salt is, however, unique among ferroelectrics in having not one but two Curie temperatures. The large role played by the hydrogen bonds in Rochelle salt had been established by Hablutzel<sup>5</sup> who succeeded in widening the ferroelectric temperature range by partial chemical replacement of the hydrogen atoms

<sup>1</sup> An exhaustive survey of the literature prior to 1946 is available in the book by W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946). For later publications, see the review article by Shirane, Jona, and Pepinsky, Proc. Inst. Radio Engrs. 43, 1738 (1955).

<sup>2</sup> W. J. Merz, Phys. Rev. 95, 690 (1954).

<sup>3</sup> E. A. Little, Massachusetts Institute of Technology Laboratory for Insulation Research Report No. 87, 1954 (unpublished).

<sup>4</sup> H. H. Wieder, Proc. Inst. Radio Engrs. 45, 1094 (1957).

<sup>5</sup> J. Hablutzel, Helv. Phys. Acta 12, 489 (1939).

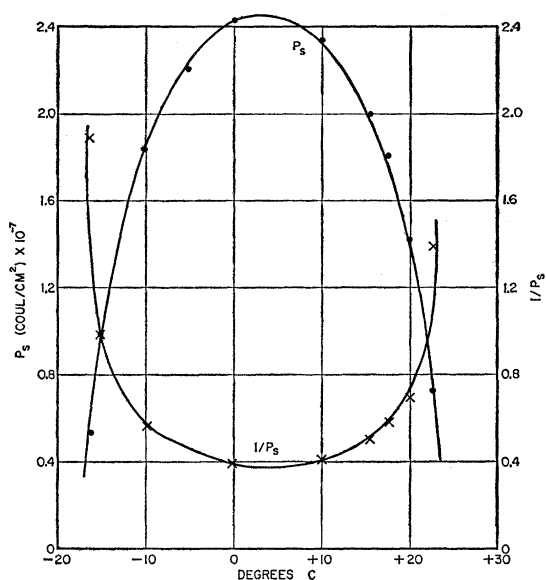


FIG. 1. Spontaneous polarization  $P_s$ , measured from hysteresis-loop data at 60 cps, is shown as a function of temperature. Its reciprocal ( $1/P_s$ ) is also given.

with deuterium. Neutron diffraction studies of Frazer<sup>6</sup> established a large atomic displacement of particular hydrogen atoms in the crystal lattice of Rochelle salt leading to the polar character of this structure and hence playing a large role in ferroelectric behavior of this crystal.

Outside of the ferroelectric temperature range, Rochelle salt is orthorhombic. In the ferroelectric region, this crystal has monoclinic symmetry,<sup>7</sup> the original orthorhombic  $a$ -axis being defined as the polar ferroelectric axis.

Mitsui and Furuichi<sup>8</sup> used the polarizing microscope for a thorough study of domain-wall dynamics in Rochelle salt. The crystals used were of the  $a$ -cut type with domains visible as thin slabs parallel to the orthorhombic  $c$ -direction or  $b$ -direction. They showed that an electric field applied in the direction of the polar axis causes a discontinuous displacement of a particular domain wall, successive positions of the wall producing a hysteresis loop if the field is gradually increased and then decreased. The propagation velocity of the wall was shown to be a linear function of the field.

In another paper, Marutake<sup>9</sup> indicated that wedge-shaped domains exist at the boundaries of large  $c$ -domains as well as at boundaries between  $c$ -domains and  $b$ -domains, probably in order to decrease any induced strains. Upon application of an electric field, wedge-shaped domains appear at the same positions within the Rochelle salt crystal in a similar manner to

the nucleation process in (101) plates of  $\text{BaTiO}_3$ . The possibility that wedge-shaped domain nuclei penetrate the crystal in the direction of the  $a$ -axis was explored by Marutake. His observations of the domain configuration on the opposite sides of an  $a$ -cut specimen of Rochelle salt having various electric fields applied to it indeed supports this idea.

It is of some interest, therefore, to examine experimentally the analogies in electrical behavior between  $c$ -domain  $\text{BaTiO}_3$  and  $a$ -cut Rochelle salt, using the same experimental techniques on Rochelle salt as had been previously employed on  $\text{BaTiO}_3$ , and to explore the inherent similarities between simple, ionic-bonded ferroelectrics such as  $\text{BaTiO}_3$  and complex, hydrogen-bonded crystals such as Rochelle salt.

#### EXPERIMENTAL

Large Rochelle salt crystal blocks grown by the Clevite Research Laboratories were diced into 18 tabular crystal samples having square major surfaces approximately 1 cm per side. The thickness of the samples ran in a graduated range between 0.05 cm and 0.34 cm. In each case the orthorhombic  $a$ -axis was carefully oriented perpendicular to the major faces. Circular silver electrodes of 0.8 cm<sup>2</sup> were vacuum deposited upon the latter.

The crystals were placed in a coaxial sample holder made of brass; light, spring loaded contacts provided electrical connection with the electrodes, and a thermocouple in the immediate vicinity of the crystal served to monitor the ambient temperature. The sample holder, enclosed in a brass jacket for thermal filtering, was placed in a Dewar containing a thermostatically controlled atmosphere of dry nitrogen. Within the sample holder the temperature could be maintained to better than  $\pm 0.5^\circ\text{C}$  and the temperature varied in continuous increments between  $+30^\circ\text{C}$  and  $-25^\circ\text{C}$ .

A bridge similar to that described by Diamant, Drenck and Pepinsky<sup>10</sup> was used to measure the parameters associated with the hysteresis loop of Rochelle salt. For a sinusoidal driving field of 50 cps excellent agreement was obtained between the spontaneous-polarization values  $P_s$  published by Hablutzel<sup>5</sup> and those shown in Fig. 1 for the present crystals. Measured values of coercivity were of the same order of magnitude as those presented by Hablutzel; however, the exact magnitude of the measured coercivity is strongly dependent upon the time rate of change of the driving field, just as was found to be the case in other ferroelectrics. The measured coercivity  $E_c$  depends upon the peak driving field as shown in Fig. 2; and while this variation is perhaps not very great, the coercivity dependence upon the frequency of the driving field is very great indeed.

Provided that the electrothermal and electrocaloric

<sup>6</sup> B. C. Frazer, quoted by Shirane, Jona, and Pepinsky in Proc. Inst. Radio Engrs. **43**, 1775 (1955).

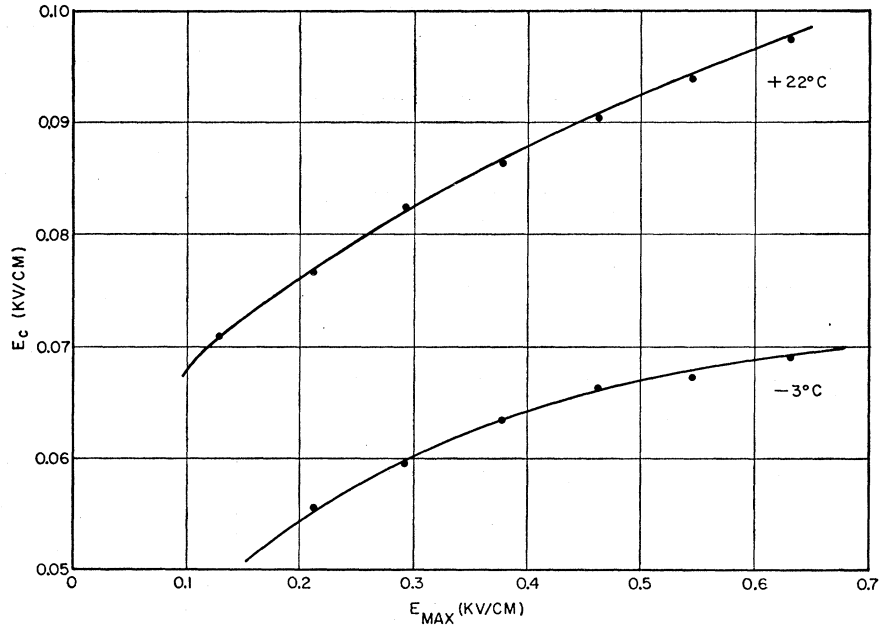
<sup>7</sup> H. Jaffe, Phys. Rev. **51**, 43 (1937).

<sup>8</sup> T. Mitsui and J. Furuichi, Phys. Rev. **90**, 193 (1953).

<sup>9</sup> M. Marutake, J. Phys. Soc. Japan **7**, 25 (1952).

<sup>10</sup> Diamant, Drenck, and Pepinsky, Rev. Sci. Instr. **28**, 30 (1957).

FIG. 2. Measured values of coercivity  $E_c$ , obtained from hysteresis loops are dependent upon the peak field  $E_{max}$  of an applied sine-wave driving field. The same relation holds for other ferroelectric substances.



effects are excluded,  $E_c$  varies as the logarithm of the driving frequency  $\omega$ . The decrease of  $E_c$  with the logarithm of  $\omega$  was ascertainable down to 1 cps, below which dc conductivity problems interfered with the measurements. It seems reasonable to interpret this coercivity dependence upon frequency in the same way as for  $\text{BaTiO}_3$ <sup>11</sup>:

$$\log \omega + (\alpha'/E_c) = k. \quad (1)$$

Here  $\alpha'$  is defined as an activation field and  $k$  is a constant.

While Eq. (1) is based upon the crude assumption that we may consider polarization reversal in a field which varies with time to be essentially the same as reversal in a constant field, it is nevertheless satisfactory for showing the close relation existing between the properties of the hysteresis loop and switching parameters obtained from pulsed polarization-reversal experiments. The latter will be explored in detail subsequently.

From plots of  $E_c$  vs  $\log \omega$  such as Fig. 3, the activation fields may be determined, and a plot of  $\alpha'$  as a function of temperature  $T$  is shown in Fig. 4. The similarity to the curve of  $P_s$  vs  $T$  of Fig. 1 is evident. One might assume that  $\alpha'$  as well as  $P_s$  are structure-sensitive and increase with an increase in crystalline anisotropy. There is as yet no complete crystallographic analysis of the Rochelle salt structure which would corroborate this view. The increase in  $\alpha'$  with anisotropy is clear, however, in the case of  $\text{BaTiO}_3$  in its various ferroelectric crystalline phases.

At higher frequencies, electrothermal effects no longer can be neglected. It is evident from Fig. 3 that as the

frequency increases, the coercivity gradually departs from its logarithmic dependence upon frequency, and

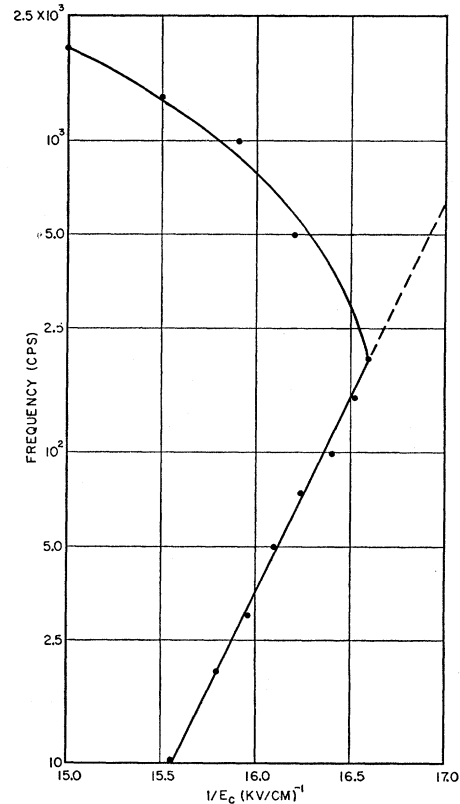


FIG. 3. Reciprocal of the coercivity ( $1/E_c$ ) is dependent upon the logarithm of the frequency of the driving field provided there are no electrothermal effects. The slope of the line ( $1/E_c$ ) vs  $\omega$  defines an activation field  $\alpha'$ .

<sup>11</sup> H. H. Wieder, J. Appl. Phys. 28, 367 (1957).

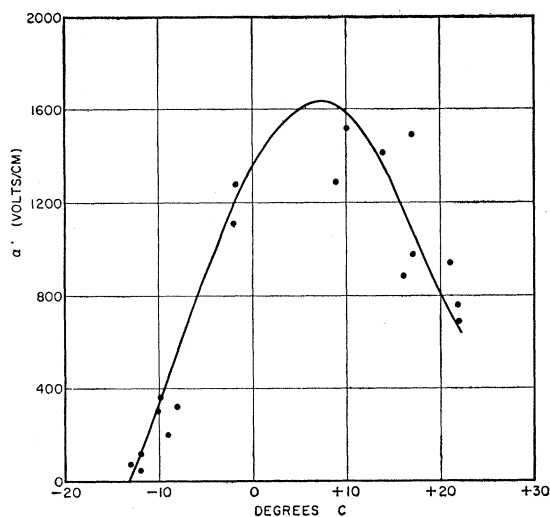


FIG. 4. The activation field  $\alpha'$  calculated from graphs such as Fig. 3, using Eq. (1), is shown to have a temperature dependence proportional to that of  $P_s$  or some power of  $P_s$ .

it has been experimentally ascertained that the particular frequency at which this starts to occur becomes higher as the ambient temperature decreases.

Similar results were obtained in the case of other ferroelectrics. Indeed, in the case of  $\text{BaTiO}_3$ <sup>12</sup> a rise in surface temperature was found to correspond exactly to the decrease in  $E_c$ . This is reasonable if we consider the very low thermal conductivity of Rochelle salt, which is quoted to be smaller than that of quartz.<sup>13</sup> Since polarization reversal is an adiabatic process, it is only to be expected that the temperature of a ferroelectric crystal element would rise with the frequency of the driving field. A simple calculation of the upper frequency limit for which a hysteresis loop may still be obtained, i.e., for which the temperature of the crystal is below the Curie temperature, places it between 50 kc/sec and 100 kc/sec, which is easily verified by experiment.

#### PULSE MEASUREMENTS

Polarization reversal in Rochelle salt under pulse conditions is different from the previously described hysteresis-loop investigations, in that here a step function with a rise time of the order of  $0.01 \mu\text{sec}$  is applied to the crystal and the electric field remains constant throughout the process of reversal. Alternate polarity pulses of selected, variable amplitudes are applied sequentially to the sample under investigation. Pulses of the same polarity may be applied to the crystal in order to differentiate between the transient signal obtained for reversal and nonreversal of polarization.

Representative switching transients obtained from a Rochelle salt sample are shown in Fig. 5. The similarity

to the switching transient obtained from  $\text{BaTiO}_3$  crystals<sup>2</sup> is clearly evident. Of particular significance are the switching time  $\tau_s$ , which is defined here as the time required for approximately  $1.8P_s$  of reversed polarization to be present in the area under the transient 5(a) and the peak current density  $J_{\text{max}}$  obtained from the same figure. The area under the transient of Fig. 5(b) represents simply the charge flowing into the stray capacitance of the cable and the linear capacitance portion of the sample being investigated. Pulses of 600 milliseconds in duration spaced 600 milliseconds apart were applied to the crystals from an electromechanical pulse generator of low impedance. The latter had been described elsewhere.<sup>14</sup> The switching transients were obtained from a 120-ohm resistance in series with the

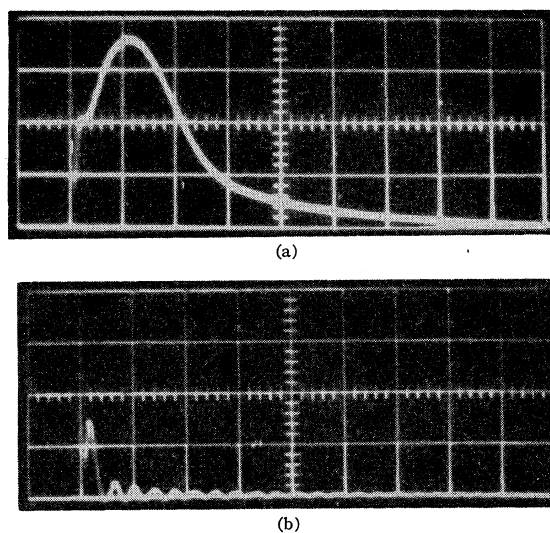


FIG. 5. Representative switching transients of a Rochelle-salt crystal sample obtained at  $+13^\circ\text{C}$ . Abscissa represents time in units of  $20 \mu\text{sec/division}$ ; ordinate is time rate of change of the polarization ( $\partial P/\partial t$ ) in units of  $2.1 \text{ (ma/cm}^2\text{) per division}$ . (a) Reversal of the remanent of polarization with net polarization change of  $2P_s$ . (b) No reversal in remanent polarization. Area under transient is proportional to the linear capacitance of sample and cable.

ferroelectric. The data obtained show the dependence of the switching time and the peak switching current density upon the applied field amplitude as well as the ambient temperature.

As in the case of  $\text{BaTiO}_3$  a dependence of the  $\tau_s$  upon crystal thickness was determined experimentally. No fatigue of polarization reversal was encountered such as described by Mitsui and Furuichi<sup>8</sup> in the case of Rochelle salt, or such as found for  $\text{BaTiO}_3$ . The switching transients did not decay with time for periods of one hour, the longest employed test period. Figure 6 represents the dependence of  $(1/\tau_s)$  upon the applied field  $E$ . Figure 7 shows  $J_{\text{max}}$  as a function of  $E$ . Both

<sup>12</sup> D. S. Campbell, J. Brit. Inst. Radio Engrs. 17, 385 (1957).

<sup>13</sup> H. Jaffe (private communication).

<sup>14</sup> H. H. Wieder and D. A. Collins, Rev. Sci. Instr. 28, 580 (1957).

figures show that the process of polarization reversal in Rochelle salt is analogous to that of other ferroelectrics. The linear part of  $(1/\tau_s)$  vs  $E$  indicates that for high fields we may interpret reversal in terms of the average mobility  $\mu$  of a wall sweeping through the crystal volume in the direction of the applied field. The linear part of  $J_{\max}$  vs  $E$  shows that during reversal the crystal behaves as an energy-consuming device, i.e., a resistance, as postulated by Merz for BaTiO<sub>3</sub>.<sup>2</sup> We take the same empirical expressions:

$$\begin{aligned} \tau_s &= (d/\mu)[E - E_0]^{-1}, \\ J_{\max} &= m(E - E_0); \end{aligned} \quad (2)$$

here  $d$  is thickness of the crystal and  $m$  is the slope of

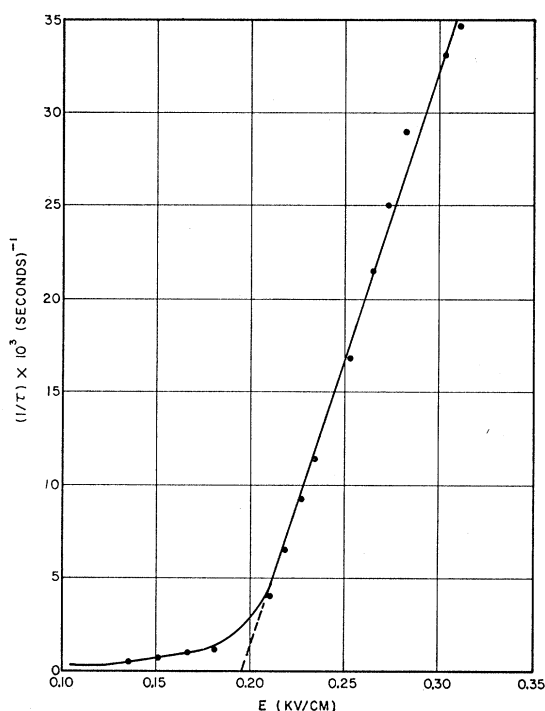


FIG. 6. Reciprocal switching time  $(1/\tau_s)$  shows the exponential and linear dependence upon electric field  $E$  previously found in other ferroelectrics.  $\tau_s$  is determined from transients such as Fig. 5(a).

linear part of the plot of Fig. 7. In each of the two figures,  $E_0$  is taken as the intercept of the linear part of  $(1/\tau_s)$  vs  $E$  and  $J_{\max}$  vs  $E$ , respectively. Since the total amount of reversed polarization during reversal is  $2P_s$ , we may write that

$$2P_s \simeq J_{\max} \tau_s f. \quad (3)$$

The shape factor  $f$  determined from transients such as shown in Fig. 5(a) is approximately 0.8 for Rochelle salt, which contrasts with the value  $f \simeq 2$  found by Merz for BaTiO<sub>3</sub>. A simple substitution of Eq. (3) into (2) shows that:

$$\mu \simeq (1/2P_s) m f d. \quad (4)$$

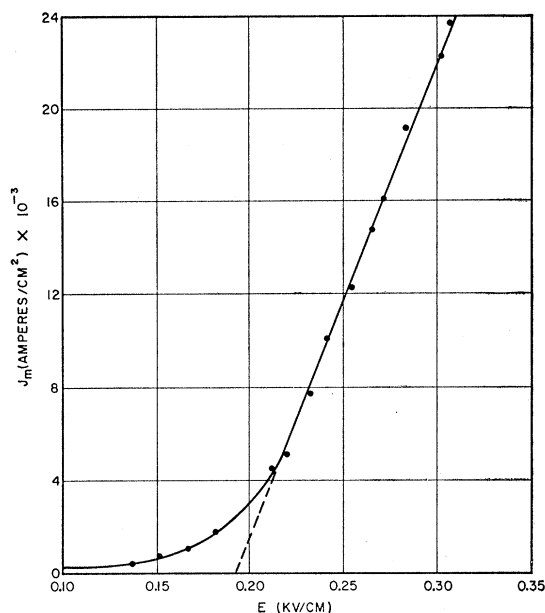


FIG. 7. Peak current density ( $J_{\max}$ ) has the same dependence upon the applied field  $E$  as  $(1/\tau_s)$ . This is also indicated in Eqs. (2) and (3).

The domain wall mobility may therefore be determined either from Eq. (2) or from the  $J_{\max}$  measurements and Eq. (4). From plots such as Figs. 6 and 7, obtained at other temperatures within the ferroelectric range, the mobility as a function of temperature may easily be evaluated. Representative  $\mu$  vs  $T$  plots are shown in Figs. 8 and 9, and are in good agreement with each other. The similarity between these curves and the

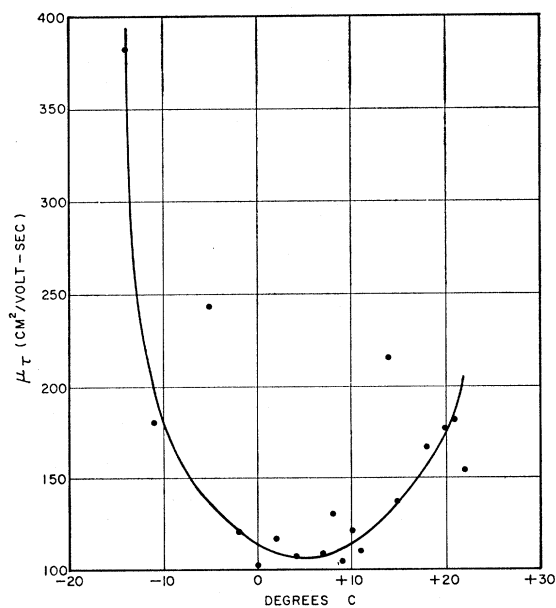


FIG. 8. The mobility  $\mu$  of an average domain wall is calculated from Eq. (2) and graphs such as Fig. 6. Its dependence upon temperature is shown.

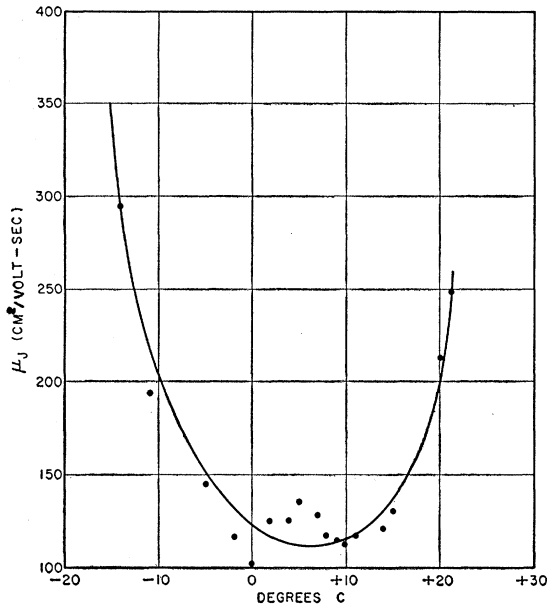


FIG. 9. The mobility  $\mu_J$ , calculated from Eq. (4) and graphs such as Fig. 7, is shown to have the same temperature dependence as  $(1/P_s)$  of Fig. 1.

$(1/P_s)$  curve shown in Fig. 1 is clearly evident, and shows the relation to be expected from Eq. (4). If  $P_s$  or a higher exponent of  $P_s$  is related to the crystalline anisotropy, then an increase in symmetry, *i.e.*, an approach to either of the monoclinic-orthorhombic transitions, should be accompanied by a sharp increase in the experimentally determined mobility.

At lower field amplitudes, an exponential increase of the  $\tau_s$  and  $J_{\max}$  with field is evident from Figs. 6 and 7. This is another property that Rochelle salt has in common with other ferroelectrics.<sup>2,4</sup> Using again the BaTiO<sub>3</sub> analogy, we may write:

$$\begin{aligned} \tau_s &\propto \exp(\alpha/E), \\ J_{\max} &\propto \exp(-\alpha/E). \end{aligned} \quad (5)$$

Therefore the activation field  $\alpha$  may be determined from a plot of  $\alpha_s$  vs  $(1/E)$ , or  $J_{\max}$  vs  $(1/E)$ , a representative plot being shown in Fig. 10. Good agreement within the error of measurement may be obtained between the two plots. For Fig. 10 the value of  $\alpha$  determined from switching-time data is  $\alpha_s \approx 513$  kv/cm, while the corresponding value from  $J_{\max}$  data is  $\alpha_J \approx 599$  kv/cm. A question of interest is whether a threshold field below which no switching may be observed does indeed exist in Rochelle salt. No such threshold field was found at 0°C down to  $E=10$  v/cm for which the area under the switching transient is still essentially  $2P_s$ . It is interesting to note, therefore, that while the number of optically observable nuclei, according to Mitsui and Furuichi,<sup>15</sup> decreases logarithmically with the driving field, nevertheless polar-

ization reversal proceeds to completion unimpeded by any large internal depolarizing fields.

As in the case of BaTiO<sub>3</sub>, the reversal of polarization is retarded by the low mobility of domain walls, but no threshold mechanism seems operative. If a threshold energy does exist, and there must be one because nuclei must obtain a finite energy from the driving field to grow and expand, then it probably is not very much larger than  $kT$ . From plots such as Fig. 10 the magnitude of  $\alpha$  was determined experimentally as a function of temperature. The result is shown in Fig. 11. The similarity to the graph of  $\alpha'$  vs  $T$  shown in Fig. 4 should be noted. Both Figs. 4 and 11 bear a strong resemblance to the plot of  $E_c$  vs  $T$  published by Hablutzel.<sup>5</sup> This is to be expected from similar relations encountered in other ferroelectrics. Thus, for BaTiO<sub>3</sub>,  $(\partial\alpha/\partial T) \approx 10(\partial E_c/\partial T)$ , where  $E_c$  is measured at 60 cps.

#### DISCUSSION

The polarization reversal experiments described in this paper differ basically from the experimental work and the description of domain wall motion in Rochelle salt of Mitsui and Furuichi.<sup>8,15</sup> The work of these authors and their observations refer to the dynamics of  $b$ -domains, *i.e.*, domains parallel to the orthorhombic  $b$ -axis of a Rochelle-salt crystal. No significant difference between  $b$ -domain and  $c$ -domain dynamics was found. The mobility calculated from their experiments yields  $\mu \approx 1.36 \times 10^{-3}$  cm<sup>2</sup> (volt sec)<sup>-1</sup> at +11°C, which is indeed in strong contrast with the data presented here:  $\mu \approx 110$  cm<sup>2</sup> (volt sec)<sup>-1</sup>, at the same temperature. The velocity of a  $b$ -domain wall from their observations, yields, for a field of 200 v/cm at +11°C, a magnitude of  $v \approx 0.14$  cm/sec, while our measurements indicate a velocity at the same field and temperature of  $v \approx 10^8$  cm/

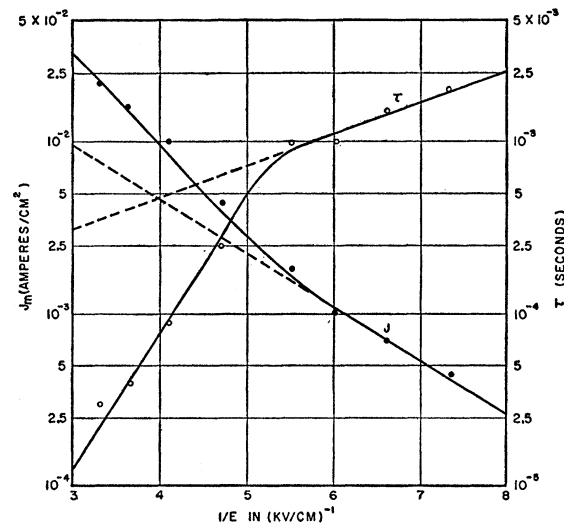


FIG. 10. At low value of  $E$  the switching time and peak current density are related to the applied field by the empirical constant  $\alpha$  representing an activation field as shown by Eq. (5).

<sup>15</sup> T. Mitsui and J. Furuichi, Phys. Rev. **95**, 558 (1954).

sec. Allowing for the differences in experimental method, the discrepancy is much too large to be accounted for in terms either of experimental method or of difference in the quality of the crystals used.

A plausible interpretation is the assumption that the experiments described in this paper are indicative of polarization reversal in the direction of the ferroelectric  $a$ -axis. It had been mentioned earlier that Marutake<sup>9</sup> already presented optical evidence of the motion of nuclei along the direction of the  $a$ -axis. In this respect then, reversal in Rochelle salt along the  $a$ -axis closely corresponds to the reversal in BaTiO<sub>3</sub> in the direction of the  $c$ -axis. On the other hand, the observations of Mitsui and Furuichi might parallel the experiments of Little<sup>3</sup> on the dynamics of  $a$ -domains of BaTiO<sub>3</sub>.

In both cases, polarization reversal in the direction of the ferroelectric axis is inherently faster. Also in contrast to the results of Mitsui and Furuichi, we found that the velocity of the propagation  $v = \mu(E - E_0)$  of an assumed  $a$ -domain wall varies inversely with  $P_s$ , rather than directly as proposed by the above authors in the case of a  $b$ -domain wall.

Rochelle salt is much more anisotropic than BaTiO<sub>3</sub>. Mitsui and Furuichi<sup>8</sup> considered a domain wall to be composed of a relatively large number of unit cells, the polarization vector gradually decreasing and passing through zero and thereafter increasing with a reversal in sign. Upon treating the energy associated with this wall as a continuum they obtained a wall energy of the

order of 0.06 erg/cm<sup>2</sup>. Even though their assumption of the relative insignificance of the first order piezoelectric strain may have been incorrect, this still leaves more than a factor of 100 between the above value and that estimated by Merz<sup>2</sup> for BaTiO<sub>3</sub> walls having only 180° orientations. In the latter case, the wall energy came to 7 ergs/cm<sup>2</sup>.

Sidewise motion of the wall is quite likely caused in Rochelle salt by the relative thickness of the domain walls; energetically, however, motion in the direction of the polar  $a$ -axis is much easier: lower fields are required and the process is accomplished faster as attested by our empirical factor  $\mu$ . This is in contrast to  $c$ -domain BaTiO<sub>3</sub>, where the thin domain walls reduce any but forward coupling of dipoles, and hence no sidewise motion of the walls is experienced when an applied field is directed along the ferroelectric  $c$ -axis.

A fact obvious from the data presented here is that Rochelle salt has the highest mobilities recorded for any ferroelectric. While partly the reason for this is the relative nearness of the transition temperature, and there is of course a sharp increase in the mobility of a ferroelectric crystal as it approaches a phase transition, nevertheless a comparison with BaTiO<sub>3</sub> for equal temperature increments still points out the higher mobility in Rochelle salt. For example: 10 degrees below the paraelectric transition of BaTiO<sub>3</sub>, at +110°C,  $\mu \approx 20$  cm<sup>2</sup> (volt sec)<sup>-1</sup>. For a corresponding temperature increment taken at +13°C, Rochelle salt has a mobility of  $\mu \approx 120$  cm<sup>2</sup> (volt sec)<sup>-1</sup>.

If the process of polarization consists on the atomic scale of a positional displacement of certain hydrogen atoms such as some experimental evidence suggests,<sup>6</sup> then the smaller mass of the hydrogen atom ought to lead to a higher mobility in comparison with the relatively large mass of the titanium ion, on the basis of an admittedly crude comparison. Since little is known about the internal field in Rochelle salt, this remains however only a supposition. Similar tests to those described in this paper if made on deuterated Rochelle salt should provide at least a partial clarification.

Higher fields than those shown in Figs. 6 and 7 were applied to some of the ferroelectric crystals, and the linear relation between  $(1/\tau_s)$  vs  $E$  was shown to hold up to the experimentally attainable  $E = 5$  kv/cm. A reversal time of approximately 10  $\mu$ sec for a crystal 0.33 cm in thickness yields a velocity of the order of  $3 \times 10^4$  cm/sec which is less by a factor of 10 than the velocity of an acoustic wave through Rochelle salt. The latter computed from the compressional frequency constant given by Jaffe and Durana<sup>16</sup> is of the order of  $4 \times 10^5$  cm/sec. As of the present it could not be ascertained whether the acoustic propagation velocity is an upper bound on the speed of polarization reversal in Rochelle salt. Figure 10 shows that at low applied

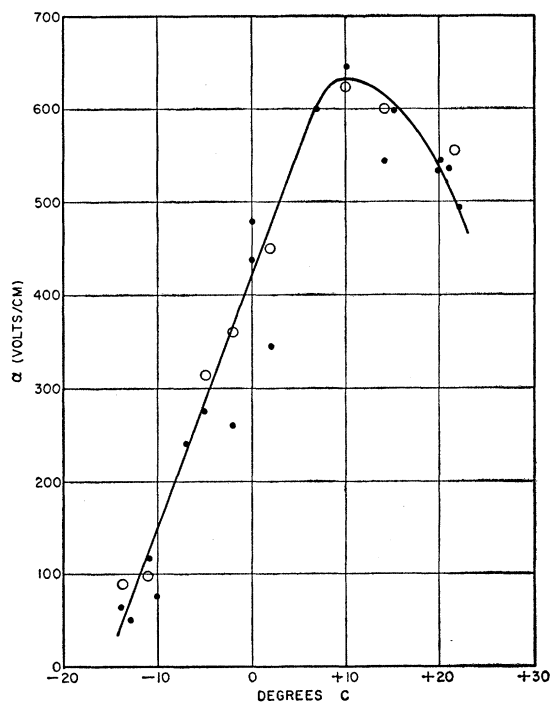


FIG. 11. The activation field  $\alpha$  is shown to depend upon the ambient temperature. Note similarity to curve of  $\alpha'$  vs  $T$  shown in Fig. 4.

<sup>16</sup> H. Jaffe and V. Durana, Clevite Research Center Technical Memorandum (private communication).

fields polarization reversal in Rochelle salt is essentially the same as that in BaTiO<sub>3</sub>. In this respect the results obtained are in agreement with Mitsui and Furuichi,<sup>8</sup> who indicate that the number  $n$  of optically observed nuclei increases with the applied field as  $(\partial n/\partial t) \propto \exp(-\alpha/E)$ . The experimental data of Marutake<sup>9</sup> shows that wedge-shaped domain nuclei propagate in the direction of the  $a$ -axis of Rochelle salt in a manner similar to that encountered for  $c$ -domain BaTiO<sub>3</sub>. Motion and growth of these nuclei occur in discontinuous steps possibly by means of Barkhausen jumps, in a manner similar to that observed in other ferroelectrics. At low fields the effect of domain nucleation should be more important. Yet the polarization-reversal transient has the same characteristic shape at high fields as at low fields. The optical data of domain relaxation shown by Nakamura<sup>17</sup> also show that the rate of increase of observed domain-wall nuclei, as a function of time for a low field of 60 v/cm, has roughly the same shape as our high-field switching transient.

The inference drawn from this is that the switching transient, as in the case of BaTiO<sub>3</sub>, is mainly characteristic of domain-wall displacement rather than nucleation of domains, and that charge flowing into the electrodes is proportional to the volume of reversed polarization with respect to the total volume of the crystal. The extent to which this is indeed related to a nucleation effect cannot yet be ascertained. A comparison of the plot of  $\alpha$  vs  $T$  of Fig. 11 with  $P_s$  vs  $T$  of Fig. 1 indicates a similarity in behavior, which might be explained as a dependence of the activation field upon the crystalline-anisotropy and the spontaneous strain which each vary as  $P_s$ . The same type of relation might hold for the curve of  $\alpha'$  vs  $T$  of Fig. 4. Qualitatively Fig. 4 and Fig. 11 are the same, though the values of  $\alpha'$  are consistently larger than those of  $\alpha$ . Partly this is due to the simplifications in the definition of  $\alpha'$ , and partly to the fact that  $\alpha'$  is determined from hysteresis-loop data, where the periodic increase and decrease of the field does not permit a separation of

nucleation from the process of wall motion and domain growth.

#### SUMMARY AND CONCLUSION

The experiments described in this paper show the analogy between the polarization-reversal process in Rochelle salt and that of other ferroelectrics, irrespective of crystal structure or symmetry. The result and the conclusions to be drawn from them are as follows:

1. The mobility  $\mu$  of Rochelle salt is the highest yet recorded for any ferroelectric, and varies inversely with the spontaneous polarization.

2. The activation field  $\alpha$  is lower by an order of magnitude than that of tetragonal BaTiO<sub>3</sub>, and increases roughly as the spontaneous strain and possibly the crystalline anisotropy.

3. Both  $\alpha$  and  $\mu$  show sharp changes as they approach either of the paraelectric phase transitions, the first decreasing and the latter increasing with temperature.

4. Nucleation and growth occurs in Rochelle salt in directions both perpendicular as well as parallel to an applied field. Nucleation as well as growth is much faster if the field vector is collinear with the  $a$ -axis of the crystal.

5. No threshold field may be found in Rochelle salt down to a field of 10 v/cm. This seems to be a property of most ferroelectric substances studied to date and is probably connected with the very low depolarizing fields<sup>18</sup> present within a ferroelectric.

6. As in the case of other ferroelectric substances, the hysteresis loop may be interpreted in terms of the empirical switching parameters of Rochelle salt, provided that account is taken of electrothermal and electrocaloric effects.

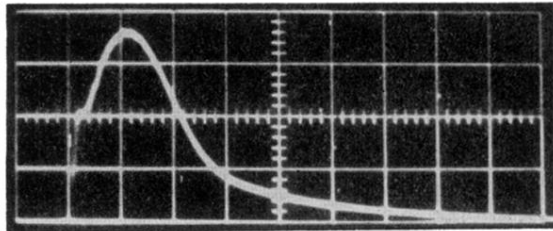
#### ACKNOWLEDGMENTS

The support of the Office of Naval Research is gratefully acknowledged. Mr. D. A. Collins provided expert and valuable assistance in the experimental phase of this work.

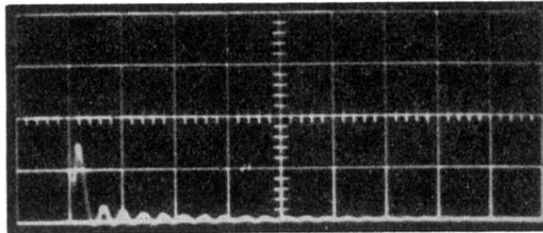
<sup>17</sup> T. Nakamura, Repts, Inst. Sci. Tech. Univ. Tokyo 7, 113 (1953).

<sup>18</sup> R. Landauer, J. Appl. Phys. 28, 227 (1957).





(a)



(b)

FIG. 5. Representative switching transients of a Rochelle-salt crystal sample obtained at  $+13^{\circ}\text{C}$ . Abscissa represents time in units of  $20\ \mu\text{sec/division}$ ; ordinate is time rate of change of the polarization  $(\partial P/\partial t)$  in units of  $2.1\ (\text{ma}/\text{cm}^2)$  per division. (a) Reversal of the remanent of polarization with net polarization change of  $2P_s$ . (b) No reversal in remanent polarization. Area under transient is proportional to the linear capacitance of sample and cable.