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Electrical Behavior of Barium Titanate Single Crystals at Low Temperatures

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Barium titanate single crystals have electrical characteristics in the orthorhombic and rhombohedral phases which are similar to those observed in the tetragonal region. At a phase transition the coercivity, determined from 60 cps hysteresis loops, decreases sharply from its value at temperatures above the transition. Correspondingly, the polarization reversal time and the spontaneous polarization decrease discontinuously from the values above the transition. All of these phenomena are accompanied by thermal hysteresis. A plot of the dielectric constant as a function of switching time is a straight-line relation and supports the theory of a relaxation-type mechanism for polarization reversal.

I. INTRODUCTION

THE electrical and optical properties of barium titanate single-domain crystals have been the subject of many investigations. Recently published papers have clarified the nature of the transition from the cubic to the tetragonal phase and explored the polarization reversal as a function of various parameters in the tetragonal region. This paper describes the electrical behavior in the orthorhombic and rhombohedral phases of some $BaTiO_3$ crystal plates which contained only parallel or antiparallel domains (*c*-domains) at room temperature.

II. EXPERIMENTAL

A total of ten crystals ranging in thickness from 0.25 to 0.05 mm with electrode areas of 15×10^{-7} m^2 were studied. Optical observation of the electrode areas indicate these to consist of *c*-domains and no attempt was made to distinguish between parallel and antiparallel domain orientation. Electrodes of silver or gold were applied by evaporating the metal through a masking aperture on the selected crystal surfaces. The results described below are characteristic of the crystals in the thickness range of 0.25 to 0.10 mm, but not of the thinner crystals. The spontaneous polarization at plus 25°C is of the order of 26×10^{-6} coulomb/cm^2 and the 60-cps coercivity is approximately 1.2×10^3 volts/cm. The behavior of these crystals (0.25 to 0.10 mm in thickness) appeared to be completely reproducible. The thinner crystals, however, when brought below minus 20°C appeared to develop more or less permanent domain reorientations, i.e., wedge-shaped *a*-domains (in what had previously been a *c*-domain region) which persisted for days or weeks after the crystal had been returned to room temperature.

Figure 1 illustrates the 60-cycle hysteresis loops of a crystal brought from the tetragonal into the orthorhombic and rhombohedral phases. The phase transitions at -5°C and -92°C agree reasonably well with the transition temperatures found by others.[1–3] Temperatures were recorded by means of a thermocouple in contact with the body of the crystal and the circuit employed for the display of the loops is the—by now standard—Sawyer and Tower arrangement.

Figure 2 shows the coercivity as a function of temperature calculated from the hysteresis loops of Fig. 1 and others not shown. Particularly noteworthy is the sharp decrease in coercivity in the vicinity of the phase transitions. Figure 3 shows the spontaneous polarization P_s as a function of temperature obtained from the same hysteresis loops. The agreement with the theoretical curves of Devonshire[4] is reasonably good. All crystals

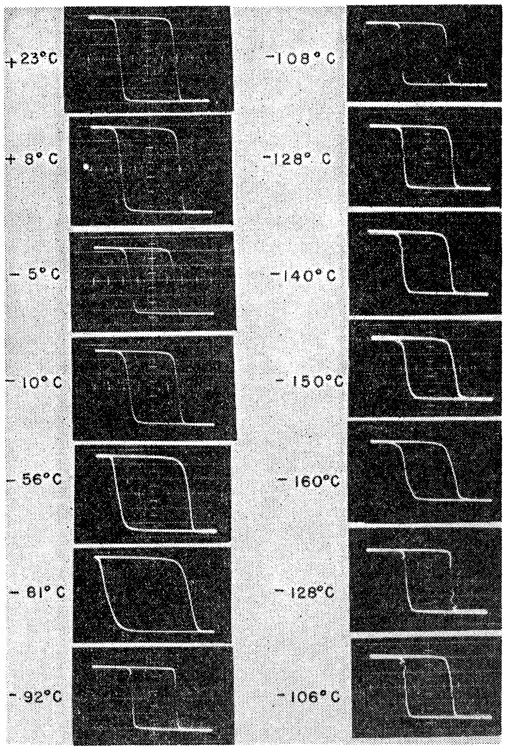

FIG. 1. Hysteresis loops as a function of temperature for the *c*-domain area of a $BaTiO_3$ crystal. For all loops $E=0.63$ kv/cm per horizontal division and $Q=0.11\times10^{-6}$ coulomb per vertical division.

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[1] von Hippel, Breckenridge, Chesley, and Tizza, Ind. Eng. Chem. **38**, 1097 (1946).

[2] H. F. Kay and P. Vousden, Phil Mag. 7, **40**, 1019 (1949).

[3] W. J. Merz, Phys. Rev. **76**, 1221 (1949).

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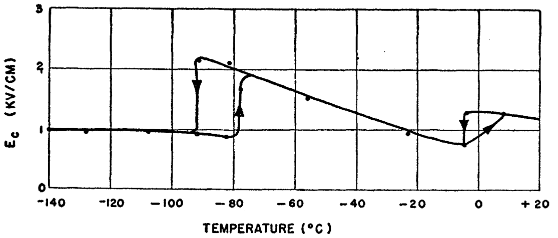

FIG. 2. Coercivity as function of temperature in the orthorhombic and rhombohedral phases.

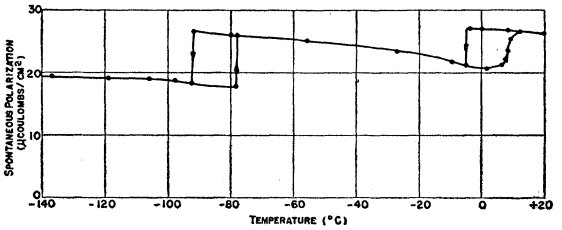

FIG. 3. Spontaneous polarization as a function of temperature.

without exception exhibited the sharp decrease in coercivity following a phase transition. There was a considerable variation, however, in the curves of P_s as a function of temperature between individual crystals.

A determination of the polarization reversal time τ_s as a function of the amplitude of the applied field E was made by using the method described by Merz.[5] Rectangular pulses of approximately 6-μsec duration and 0.04-μsec rise time were applied to the crystal from a 50-ohm impedance source. The crystal was in series with a 25-ohm resistor and the switching transients obtained across the latter allowed the measurement of the peak switching current $i_{\max}$ and the reversal time τ_s. Typical switching signals are shown in Fig. 4.

Figure 5 illustrates the reciprocal switching time $1/\tau_s$ as a function of the applied field E for various temperatures above and below the -5°C (tetragonal to orthorhombic) transition. For values of $E > 5E_c$ the linear relation between $1/\tau_s$ and E was found valid for all crystals and therefore, in this region, τ_s would appear to be related to the propagation of antiparallel domains as described by Merz for the tetragonal region. For values of $E < 5E_c$, considerable variations in the plot of $1/\tau_s$ *versus* E were noted and a report on this behavior will be deferred.

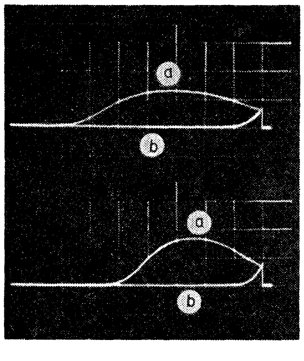

FIG. 4. Representative switching transients obtained by using a rectangular pulse of 6-μsec duration of positive or negative sign and 8.8 kv/cm amplitude: *a* indicates reversal, *b* nonreversal of polarization. Upper photograph taken at +23°C, abscissa = 0.3 μsec/div; lower photograph taken at -18°C, abscissa = 0.1 μsec/div. Ordinate for both is = 0.29 amperes/division.

Figure 6 is a plot of the reciprocal switching time as a function of temperature for a constant field of $E = 8.8$ kv/cm. All crystals gave analogous curves to Fig. 6 and, as was to be expected from the linear relations of $1/\tau_s$ *vs* E, the characteristic shape of the curve is independent of E for $E \gg E_c$.

Figure 7 shows the peak switching current, $i_{\max}$, as a function of E for various temperatures in the orthorhombic and rhombohedral phases. In his investigations of the polarization reversal in the tetragonal phase, Merz[5] derives a switching resistance: $R = \beta d^2/2qAP_s$, where A and d refer to the electrode area and thickness of the crystal, P_s is the value of spontaneous polarization of a single domain, and q is a shape factor determined from the $i(t)$ curves. The slope of the line $1/\tau_s$ *versus* E is proportional to the domain mobility factor β.

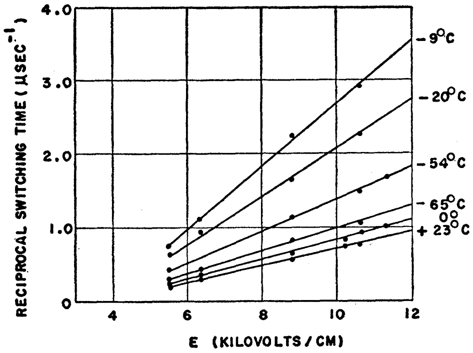

FIG. 5. Reciprocal switching time, $1/\tau_s$, as a function of field E and temperature T in the orthorhombic phase.

Since the crystal used in these experiments had an area of 10^{-2} cm² and thickness of 2×10^{-2} cm, compared to the crystal described by Merz ($A = 10^{-4}$ cm², $d = 5\times10^{-3}$ cm, $R = 500\Omega$), the ratio of the resistances at room temperature should be of the order of 1:6. The value of $R = 290$ ohms obtained from the slope of the $i(t)$ *vs* E curve of Fig. 7 is higher than expected but in view of possible large differences within crystals, not unreasonable.

III. DISCUSSION

The curve of $P_s(T)$ shown in Fig. 3 is in the orthorhombic phase in qualitative agreement with Devonshire's theory[4] and his computations. Based on crystal thermodynamics and the experimentally determined changes in the lattice structure of the $BaTiO_3$ unit cell, this theory accounts for the three phase transitions, the behavior of the initial dielectric constant as a

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[5] W. J. Merz, Phys. Rev. **95**, 690 (1954).

function of temperature, and other experimentally verifiable properties of the single-domain barium titanate crystal. The discontinuous jump in P_s at the ferroelectric transition ($-5°C$) from the tetragonal to the orthorhombic phase is in close agreement with the theory: P_s (orthorhombic)$=\sqrt{2}P_s$ (tetragonal). This agreement is lacking however for the lower ($-92°C$) transition, possibly because the crystal is no longer a *c*-domain. Latter observations made by means of a polarizing microscope indicated complicated twinning effects occurring in the rhombohedral phase.

It should be emphasized that a closer agreement between theory and experiment was obtained by Kay and Vousden[2] for smaller absolute values of spontaneous polarization ($P_s=16\times10^{-6}$ coulomb/cm^2 at room temperature). The crystals used for the experiments described in this paper have higher values ($P_s\simeq26\times10^{-6}$ coulomb/cm^2) in agreement with recent measurements described by Merz.[6] It is expected, nevertheless, that complete agreement with the theory would result if a crystal were to retain a single-domain identity over the entire ferroelectric temperature range.

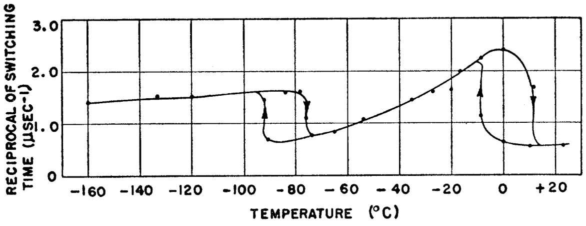

FIG. 6. $1/\tau_s$ as a function of temperature for constant field $E=8.8$ kv/cm.

A qualititative interpretation of the curve $E_c(T)$ shown in Fig. 2 can be obtained by using the graphical representation of the Devonshire equation for the tetragonal phase used by Merz[6] to indicate a theoretical relation between an idealized hysteresis loop and the double hysteresis loop observed above the normal Curie temperature. For convenience, the graph is reproduced in Fig. 8. Note the p and e are a normalized polarization and electric field respectively, and t is a temperature dependent parameter. The sign of t is positive above and negative below the Curie temperature. Points a and a' define a threshold field where the negative going slope and consequent instability causes a jump in polarization to a new, stable value. If this threshold field is tentatively identified with a coercive field, it becomes evident that for negative values of t the coercivity increases. Similar graphs can be obtained for the orthorhombic and rhombohedral phases and it is found that in agreement with the experimental observations shown in Fig. 2, the coercivity decreases for a rise in temperature as the crystal approaches a phase transition.

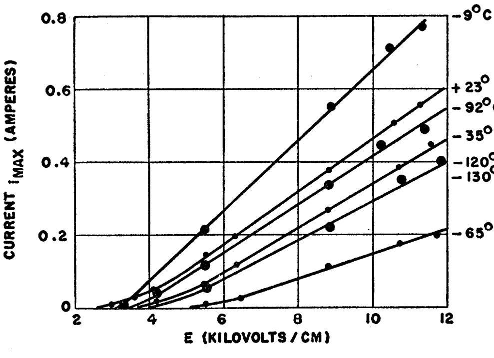

FIG. 7. Peak switching current $i_{\max}$ as a function of field and temperature.

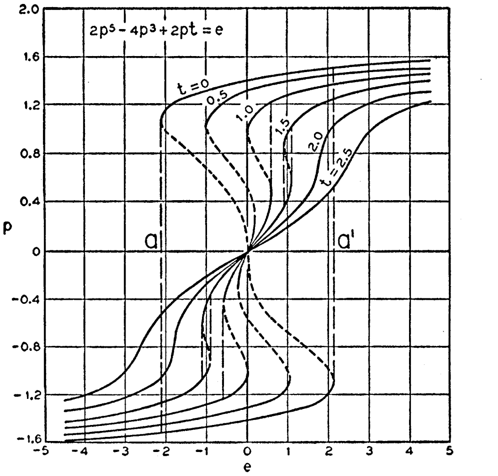

FIG. 8. The plot of a normalized equation in E, P, and T, after W. J. Merz, [Phys. Rev. **91**, 513 (1953)] for temperatures above the normal Curie point.

The data presented in Fig. 5 suggest that for the orthorhombic phase, in analogy to Merz's[5] expression, the switching time is given by

$$\tau_s=\beta d/(E-E''),$$

where β is the reciprocal of the antiparallel domain mobility as defined by Merz and the applied field E is large enough so that only the propagation of the domains has to be taken into consideration, the nucleation time of these domains being negligible in comparison. E'' is the extrapolated value of $1/\tau_s$ for $\tau_s\rightarrow\infty$. Figure 9 illustrates the temperature dependence of β for a constant applied field. It is evident that at a ferroelectric transition the domain mobility $1/\beta$ increases discontinuously from its value above the transition. The mobility gradually decreases as the temperature is lowered and the crystal symmetry is decreased. The behavior of the dielectric constant as a function of temperature for a *c*-domain crystal had been reported by Merz.[3] It is reproduced for convenience in Fig. 10. A comparison with the curve of $1/\tau_s$ as a function of T of Fig. 6 shows strong similarities. If the dielectric constant is plotted as a function of $1/\tau_s$ for the tetragonal phase as reported by Merz, and for

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[6] W. J. Merz, Phys. Rev. **91**, 513 (1953).

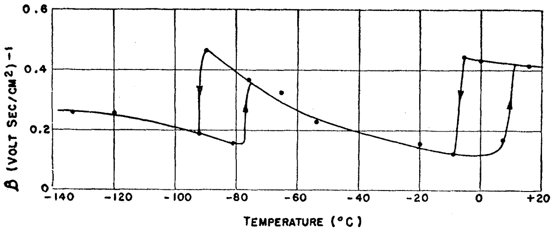

FIG. 9. The reciprocal mobility β, plotted as a function of temperature.

the orthorhombic phase as described in this paper, the straight line relationships indicated in Fig. 11 result.

Young and his co-workers[7] have measured the dielectric constant and dissipation factor of a single crystal of $BaTiO_3$ as a function of frequency. They found that the results thus obtained can be fitted by a Debye relaxation spectrum for the dielectric constant of the type

$$\epsilon^* = \frac{\alpha}{1 + j\omega\tau} + \epsilon_\infty,$$

where ϵ^* is the complex dielectric constant, τ the relaxation time, ϵ_∞ is the extrapolated dielectric constant for very high frequencies, and α the polarizability of a single domain. For applied fields of the order of the coercive field, the calculated value of $\tau \simeq 5.5$ μsec was found to agree well with the observed polarization reversal time of a single domain. Merz had already indicated that antiparallel domain nucleation occurs in $BaTiO_3$ rather than domain wall motion. If the assumption is now made that for a single domain there is a field dependent distribution of relaxation times and that the reversal of polarization is approximated by a rotation, one may write

$$\epsilon' = \epsilon_\infty + \frac{\alpha}{1+\omega^2\tau^2} \quad \epsilon'' = \frac{\alpha}{1+\omega^2\tau^2}\omega\tau.$$

Here, ϵ' and ϵ'' are the real and imaginary components of the complex dielectric constant, ω is related to the frequency at which the dielectric constant is measured and $1/\omega \gg \tau$. Therefore

$$\frac{1}{\tau}\left(\frac{\epsilon''}{\omega}\right) = \epsilon' - \epsilon_\infty.$$

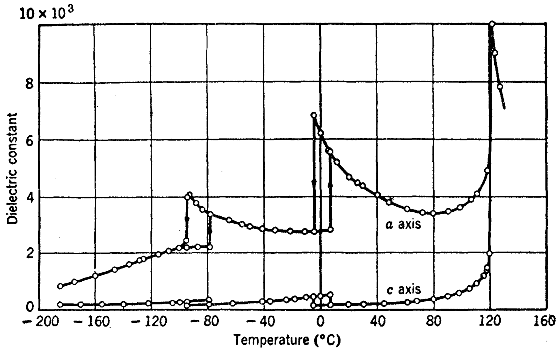

FIG. 10. Initial dielectric constants of barium titanate as a function of temperature [after W. J. Merz, Phys. Rev. **76**, 1221 (1949)].

A plot of ϵ' as a function of $1/\tau_s$ as determined from curves of ϵ *versus* T and $1/\tau_s$ *versus* T should yield a straight line having the intercept $\epsilon' = \epsilon_\infty$. The value of ϵ_∞ determined from Fig. 11 is $\epsilon_\infty \simeq 160$ which compares with a value of $\epsilon_\infty = 210$ to 290 calculated by Young *et al.*[7]

IV. SUMMARY AND CONCLUSIONS

A $BaTiO_3$ crystal which is a c-domain at room temperature will rarely maintain this quality over a wide temperature range in the lower symmetry ferroelectric phases. The measurements described are, therefore, to be considered of a preliminary nature. Certain conclusions, however, may be drawn on the basis of the experimental evidence presented in this paper:

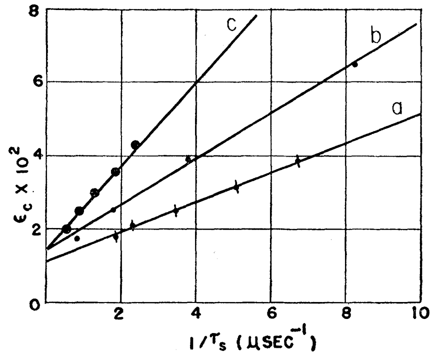

FIG. 11. Real part of complex dielectric constant E, as a function of the reciprocal switching time $1/\tau_s$. Lines a and b are for the tetragonal phase (using $1/\tau_s$ values after W. J. Merz [Phys. Rev. **95**, 691 (1954)]. Line c is for orthorhombic phase (from data presented in this paper). a taken at 4 kv/cm, b at 6 kv/cm, and c at 9.9 kv/cm.

1. Within each ferroelectric phase, the electrical behavior of $BaTiO_3$ crystals shows strong similarities.
2. At a phase transition, from higher to lower crystal symmetry, the spontaneous polarization decreases roughly in accord with the Devonshire theory.
3. For high values of applied field E, the reciprocal of the polarization reversal time increases linearly with E as in the case of the tetragonal phase.
4. The mobility of antiparallel domains jumps discontinuously at a transition to a value higher than that found below the transition.
5. For high values of E, the switching current is a linear function of E over most of the orthorhombic phase. However, since considerable variations were found between crystals, more work will be required in order to define the behavior of the switching resistance in the lower symmetry phases.
6. The coercivity, determined from 60-cps hysteresis loops, drops sharply at a transition only to rise again as

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[7] Drougard, Funk, and Young, J. Appl. Phys. **25**, 1166 (1954).

temperature decreases below the transition. A mathematical model of an idealized hysteresis loop based on the Devonshire equations provides a qualitative interpretation of the relation between coercivity and temperature.

7. The relation between the dielectric constant ϵ_c, and the switching time is shown to be linear for both the tetragonal and the orthorhombic phases. Support is therefore provided for the theory describing polarization reversal as a relaxation mechanism with a field dependent distribution of relaxation times.

V. ACKNOWLEDGMENTS

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Pressure Dependence of de Haas-van Alphen Parameters in Bismuth

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The Hall coefficient, A, of a bismuth single crystal has been measured at 4.2°K, in magnetic fields up to 12 kilogauss, and under liquid helium pressures up to 120 atmospheres. The period (β/E_0) of the oscillations in reciprocal field, the phase, and the monotonic part of the magnetic field dependence of A were found to depend on the pressure with small, but nevertheless easily measurable, pressure coefficients. Only the single-period term observable in bismuth when the magnetic field is parallel to the trigonal axis was studied.

INTRODUCTION

THE low-temperature oscillatory variation of magnetic susceptibility with reciprocal magnetic field, first discovered in bismuth by de Haas and van Alphen,[1] has since been found in about 14 other metals.[2–4] The magnetoresistance and Hall coefficient[5] of several of these metals are known to have similar oscillatory characteristics at low temperatures. Recent experimental studies[6–8] on some of these metals have shown that the period of the oscillations is the same for magnetoresistance and Hall coefficient as for susceptibility. The theory for the behavior of the susceptibility advanced by Peierls,[9] Blackman,[10] and Landau[11] has been found by Shoenberg[12] and others[13] to describe fairly well the observed orientation-dependent susceptibility of several metals. The "effective" electrons, upon which the field dependent susceptibility variations depend, are presumably those whose energy surfaces overlap in **k**-space from one Brillouin zone to another. The energy surfaces are presumed to be approximately hemiellipsoidal in shape where they overlap the zone faces. Since it has been observed for some metals that the periods of oscillations are the same for susceptibility, magnetoresistance, and Hall coefficient, it is believed that the same "effective" overlapping electrons (and/or underlapping holes) participate in all three phenomena, which are described by an equation of the form,

$$y=\sum_j \{f_{yj}+a_{yj}\sin(2\pi E_{0j}/\beta_j H+\theta_j)\}. \quad (1)$$

Here y is either χ (magnetic susceptibility), R (magnetoresistance), or A (Hall coefficient), $\beta=e\hbar/m^*c$ (m^*= the appropriate effective mass), E_{0j} is the energy value of the highest filled overlapping energy surface measured from the energy value at the bottom of the pertinent zone, and θ_j is the phase of the oscillations. The theories provide a fixed value of $\theta_j=\pi/4$ but this is not observed experimentally in general. The periods of the oscillations in Eq. (1) are the β_j/E_{0j} and these periods are determined from experimental measurements since theory does not provide suitable values for β and E_0. For an arbitrary orientation of the crystal with respect to the magnetic field direction one observes beats due to the superposition of the various oscillatory terms in Eq. (1), but for certain special orientations oscillations of a single period are observed.

Many of the metals which exhibit the de Haas-van Alphen effect have high elastic anisotropy so that the application of hydrostatic pressure not only decreases the volume of the crystal, but also changes the c/a ratio. For example, using Bridgman's[14] values for

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[1] W. J. de Haas and P. M. van Alphen, Leiden Comm. No. **212A** (1930).

[2] D. Shoenberg, Physica **19**, 791 (1953).

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[13] T. G. Berlincourt, Phys. Rev. **82**, 242 (1952); Phys. Rev. **94**, 1172 (1954).

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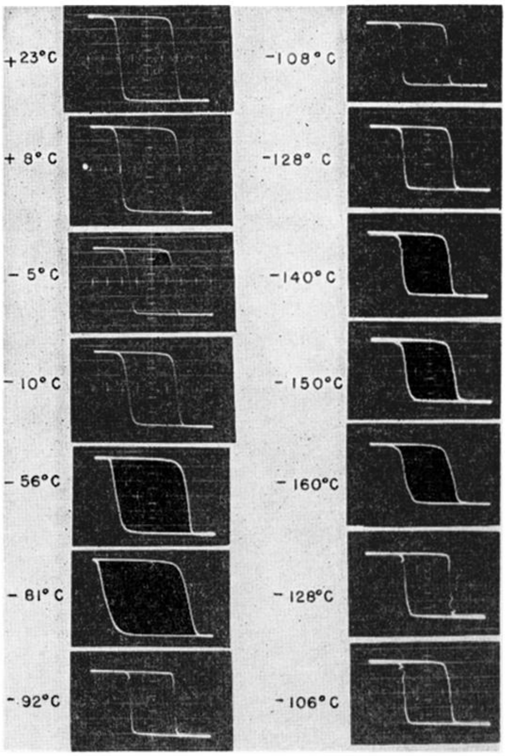

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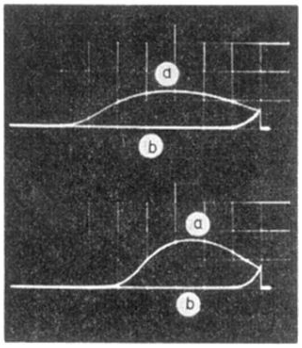

Fig. 4. Representative switching transients obtained by using a rectangular pulse of 6-μsec duration of positive or negative sign and 8.8 kv/cm amplitude: *a* indicates reversal, *b* nonreversal of polarization. Upper photograph taken at +23°C, abscissa$=0.3$ μsec/div; lower photograph taken at −18°C, abscissa$=0.1$ μsec/div. Ordinate for both is $=0.29$ amperes/division.