Dynamic Behavior of Domain Walls in Barium Titanate*

ELIZABETH A. LITTLE
Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received January 26, 1955)

The nucleation and growth of 90° and 180° domains in barium titanate single crystals have been measured with optical techniques. Both types of domains nucleate as long thin wedges with an initial velocity of the order of 10^4 cm/sec for a driving field of 5 kv/cm. For 90° domains, detailed measurements of the nucleation rate as a function of time and field strength are given. After domains have been introduced into a crystal, their growth may be described in terms of wall motion. The 90° wall displacement depends strongly on strains and clamping of the crystal; wall motion appears to cease for frequencies in the megacycle range, where the piezoelectric resonances of the crystal set in. The sideways growth of 180° wedges is affected by the availability of neutralizing electric charges. Interaction of 180° and 90° domains may lead to 90° wall configurations with head-to-head or tail-to-tail orientation of the polar axes.

THE investigation of ferroelectricity in barium titanate and its derivatives, is one of the long-range projects of the Laboratory for Insulation Research.[1] In the course of this work, a number of facts have been established concerning the existence and formation of domains in $BaTiO_3$ single crystals,[2] and a detailed domain analysis has been made by birefringence studies.[3] These investigations have been carried out mainly with static fields. To arrive at a better understanding of hysteresis loops, frequency response and aging characteristics of ferroelectrics requires dynamic studies with movie cameras, and transient or ac voltages. The present paper is a first contribution to the subject of "domain dynamics."

CRYSTALS AND METHODS OF INVESTIGATION

Crystals were grown from ternary melts according to the method developed by Matthias *et al.*[4] and the best "*a*" crystal plates (where the polar axis lies in the plane of the plate) were selected. These crystals, *ca* 10 μ thick, had an area of *ca* 400×400 μ^2. Electrodes were painted on two opposite edges by laying the crystal flat on a microscope slide and applying silver paint (Dupont 4548) with the help of a micromanipulator.

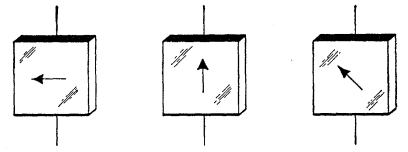


FIG. 1. Three different types of "*a*" crystals, distinguished by the edges to which electrodes are attached.

Depending on whether the electrodes were applied to the [100], [001], or [101] edges, i.e., parallel, perpendicular, or at 45° to the polar axis, we shall refer to them as [100], [001] or [101] "*a*" crystals (Fig. 1).

A polarizing microscope equipped with a micrometer eyepiece and a Land camera sufficed for most observations. Fast processes were photographed with a 16-mm movie camera (Cine-Kodak, 64 frames per sec). The wall displacements could be measured with a microfilm viewer to $\frac{1}{2}$ μ. The linear magnification in our birefringence studies ranged up to 1100×.

Electric fields applied to the crystals included short rectangular single pulses from $\frac{1}{4}$ to 200 μsec duration, sinusoidal signals from 20 to 3×10^5 cps, and dc fields. Voltages up to 500 v proved adequate for most experiments.

90° DOMAINS

A 90° wall is a {101} twin plane and readily visible in transmitted light as a dark line approximately 0.4 μ thick (Fig. 2). Ghosts appear at the edges of the line by optical diffraction and are also observed at the edges of the crystals at high magnification. At room temperature, the 90° wall stands at an angle of 44°15′ to the polar axis; this angle corresponds to the *a/c* ratio of the unit cell [Fig. 3(a)]. A 90° wall is therefore actually an 88°30′ wall, a concept of importance for the study of wall dynamics. The 1°30′ difference in orientation between the crystal axes across a 90° twin plane implies a slip of one domain with respect to its neighbor as the 90° wall moves [Fig. 3(b)]. In conse-

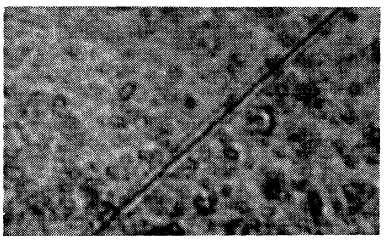


FIG. 2. A 90° wall (1000×).

* Sponsored by the Office of Naval Research, the Army Signal Corps, and the Air Force; it is based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics at the Massachusetts Institute of Technology.

[1] See A. von Hippel, Revs. Modern Phys. **22**, 221 (1950).
[2] B. Matthias and A. von Hippel, Phys. Rev. **73**, 1378 (1948).
[3] P. W. Forsbergh, Jr., Phys. Rev. **76**, 1187 (1949).
[4] Blattner, Matthias, and Merz, Helv. Phys. Acta **20**, 225 (1947); Blattner, Matthias, Merz, and Scherrer, Experientia **3**, 148 (1947).

quence, it is not astonishing that mechanical pressure can introduce and move 90° walls.

Figure 4 shows a group of wedge-shaped 90° domains as sometimes found in a crystal after cooling through the Curie point. Both the narrowness of the wedges and the fact that many wedges terminate along the same line, can be attributed to the mechanical distortions caused by 90° wedges.

Nucleation of 90° Domains

To study 90° domains without interference by 180° domains, we selected a [100] crystal with the polar axis parallel to the electrodes. A good crystal of this kind is initially a single-domain crystal. A dc field exercises a strong torque tending to rotate the polar axis by 90°. If the field is increased slowly, 90° wedges are nucleated at the crystal boundaries [Fig. 5(a)] at

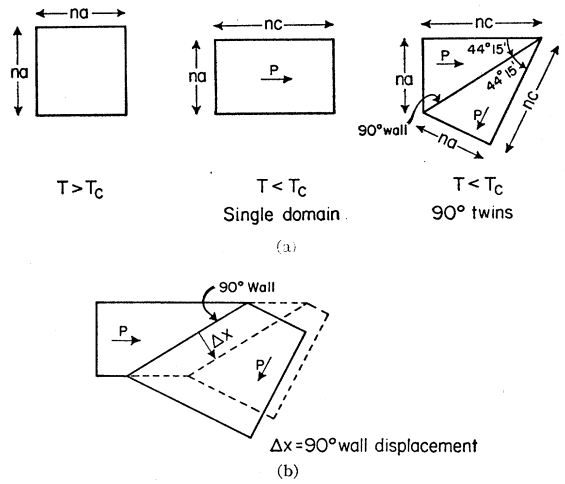


FIG. 3. 90° twinning: (a) distortion of square crystal due to phase change at Curie point (T_c) and 90° twinning (exaggerated); (b) change in shape of twinned crystal due to displacement of 90° wall by Δx (exaggerated).

a critical field strength E_c and extend, 2 to 10 μ wide, across the crystal (*ca* 0.05 cm) in less than 1/100 sec. When the field is removed, the stresses caused in the crystal by the presence of 90° domains frequently force the wedges out of the crystal. They shrink slowly at first, then disappear suddenly.

In a field of opposite polarity [Fig. 5(b)], 90° wedges will enter from the opposite side of the crystal, that is, they start normally at the cathode side. However, there are exceptions, particularly at high temperatures.

A special [100] crystal (crystal "A") was chosen for the following experiments because 90° wedges were always forced out of it by stresses when the field was removed. The field required to maintain wedges in the crystal (about 1 kv/cm) serves as a measure of the magnitude of the mechanical stresses involved. The critical dc field strength E_c of nucleation for crystal "A" is plotted against temperature in Fig. 6. The

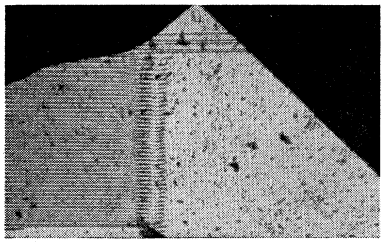


FIG. 4. A group of 90° wedges in an "a" crystal.

similarity of this curve with that of the spontaneous polarization and strain in a single-domain crystal[5] confirms that these quantities are related.

To determine the initial growth of 90° wedges as a function of time and field strength, a square pulse was applied to the single-domain crystal "A" and the number of wedges in the crystal immediately afterwards recorded. After a few minutes of rest, strain had forced the domains out and restored the single domain crystal. The number of wedges N was measured as a function of pulse height E and pulse time t (Fig. 7). Each measurement at a given E and t was repeated several times; the estimated accuracy is indicated. Above 10 kv/cm, N depends somewhat on prehistory.

No wedges were observed for $\frac{1}{4}$ μsec pulses and $E \leq 11$ kv/cm; for pulse times longer than 1 μsec, every observed domain extended across the crystal; for shorter times, some wedges did not reach the opposite side. Pulses longer than 10 μsec widen the wedges slightly after they have traversed the crystal. However, no wedges were wider than 20 μ for pulses of 200 μsec or less. The expansion normal to the wedge axis proceeds with a velocity of *ca* 100 cm/sec at 7.4 kv/cm.

Figure 7 shows that N increases with E and t. A threshold pulse length t_0 exists for a given field strength

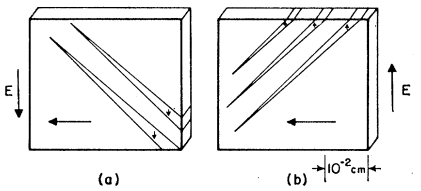


FIG. 5. 90° wedge nucleation in a [100] crystal: (a) positive field, and (b) negative field.

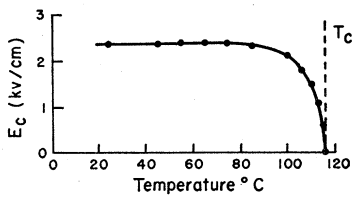


FIG. 6. Critical field for 90° wedge nucleation in crystal "A" as a function of temperature.

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

below which no wedges are formed. It appears (Fig. 8) that $t_0(E-E_c)^2$ is nearly a constant for low fields, while at high fields

$$t_0=t_s e^{B/E}, \tag{1}$$

where $B=25$ kv/cm and $t_s=0.05$ μsec. If t_0 is interpreted as the minimum time required for 90° wedges to grow large enough to be observed, i.e., to about 500 μ the limiting velocity of a wedge at high fields would be *ca* 10^6 cm/sec, or of the order of sound velocity.

N proves for a given field strength to be about proportional to $\ln(t/t_0)$ as

$$N=0.28e^{\gamma E}\ln(t/t_0), \tag{2}$$

$$dN/dt=0.28e^{\gamma E}/t \quad (t\geq t_0), \tag{3}$$

where $\gamma=0.36\times10^{-5}$ $(\text{v/m})^{-1}$. Thus the nucleation rate decreases with time and increases with E. This time dependence appears reasonable from the standpoint that, after nucleation has started, less material is available for new domains.

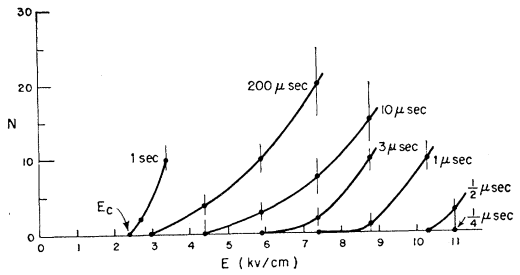


FIG. 7. Number N of 90° wedges nucleated by a square pulse as a function of pulse length and pulse height.

90° Wall Motion

After 90° wedges have been introduced into a crystal, domain growth can be described in terms of wall motion. Once a wedge has grown across a crystal, the two now-parallel walls separate and move sideways with decreasing velocity and some irregularity. We investigated this situation in a [100] crystal "B", which retained its domains when the field is removed. In other words, the mechanical restoring force in this crystal was small.

Application of a small field to this crystal made the parallel walls of a 90° domain oscillate. Since the wall velocity is zero at both extremes of an ac oscillation, the wall appeared to split in two at high frequencies. The distance $|x|$ between the two lines is designated as "wall amplitude" (Fig. 9) and plotted as a function of E and of frequency. At 20 cps the critical field for the onset of motion is small and the wall amplitude at low field strengths is approximately proportional to E^2. The minimum field strength for wall motion increases with frequency, hence the wall amplitude at constant field decreases.

At 300 kcps and fields above 3.5 kv/cm, crystal "B" heated up beyond the Curie point. Since temperature change affects the wall amplitude, measurements at high frequency and high field strength must be viewed with caution.

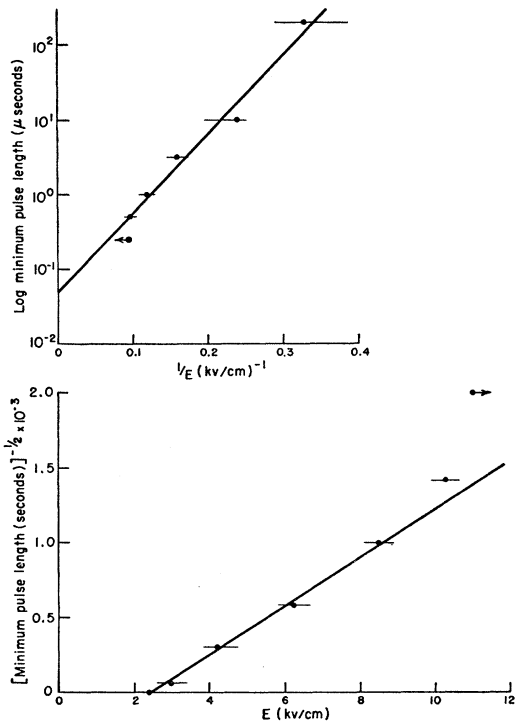


FIG. 8. Minimum pulse length t_0 for nucleation of 90° wedges as a function of pulse height E.

No significant difference was found between the amplitude of oscillation at the edge and in the middle of a crystal.

A 90° wall seems to be thick and its motion not a process of discrete molecular steps. Significant is the low critical field strength at low-frequency oscillations. The trend of the critical field as a function of frequency, neglecting heating effects, suggests that the wall should

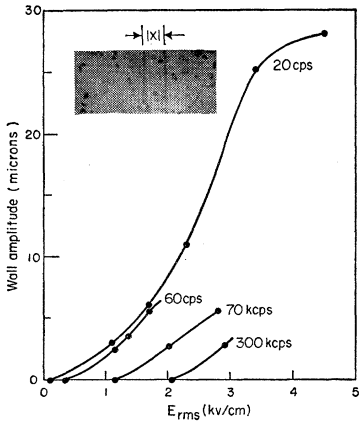


FIG. 9. 90° wall amplitude in ac fields as a function of frequency and field strength.

not be able to move at finite field strengths for frequencies much above about 3 Mc/sec. The lowest piezoelectric resonance of our crystals was about 5 Mc/sec. Since 90° wall motion is strongly affected by macroscopic mechanical distortions, it is not surprising to find that the wall motion is damped out as the acoustic resonance frequency is approached.

180° DOMAINS

Antiparallel domains are difficult to observe. Merz[6] first made 180° domains visible by applying an electric field normal to the c axis. The polar axes in adjacent domains are thus rotated in opposite directions and have different extinction positions (Fig. 10). For an optical study of the dynamic behavior of 180° walls, thin "a" crystals with {101} edges are therefore well suited. One component of the field makes the domains visible, the other forces them to grow. If not very large fields are applied, the formation of 90° domains can be avoided. Figure 11 shows such a [101] crystal with its antiparallel domains; the domains of one polarity are placed in extinction (black), those of opposite polarity

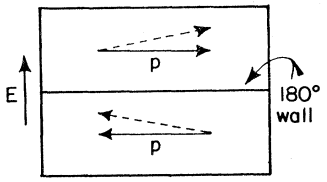


FIG. 10. Rotation of polar axes near a 180° wall in a field perpendicular to the wall.

transmit light. A transition region of about $\frac{1}{2}$ μ width at the wall does not rotate in the field.

Nucleation and Initial Motion

To study the initial growth of 180° domains, short rectangular pulses were applied to a single-domain [101] crystal. A negative[7] pulse of 7.5 kv/cm (10 μsec or longer) applied to a single-domain crystal orientated at extinction causes occasionally some thin spikes ($\frac{1}{2}$ to 5 μ at the widest part) to appear, extending from several edges nearly across the crystal (0.05 cm); they remain visible for as long as a second after pulsing. For as many as 50 subsequent pulses the same wedges have been observed; they do not appear to grow.

In an inverse experiment, some large (20 μ wide and 500 μ long) 180° wedges were introduced into the crystal by a dc field, and short positive pulses ($E=7.5$ kv/cm), spaced several seconds apart, applied to remove them. Each pulse makes the domains still present visible for about a second. With pulses of 10 μsec or longer, some domains are removed entirely by the first pulse; a bright region is left behind which fades out in

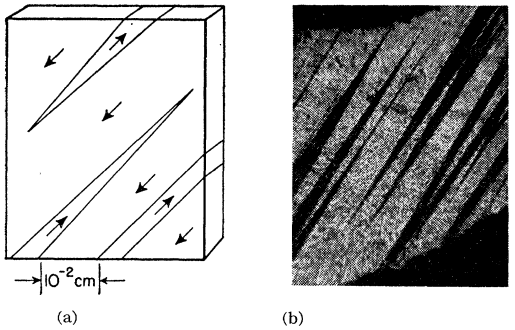


FIG. 11. 180° domains in a [101] crystal.

about a second. For pulses shorter than 1 μsec, each pulse narrows the domains significantly, and the wedge tip retreats slightly.

Two tentative conclusions can be drawn from these experiments: (1) an antiparallel domain is formed as a spike at the edge of the crystal and extends along the polar axis with a velocity between 5×10^3 and 5×10^4 cm/sec at 7.5 kv/cm; (2) space-charge effects associated with the wedges may cause the bright region; their relaxation time in our crystals is of the order of a second.

This second conclusion, based on the visible aftereffects of pulses, requires closer scrutiny. If a 180° domain is wedge-shaped with a wedge angle θ, the spontaneous polarization P_s produces a large electric field ca $(P_s/\epsilon_0)\sin\theta$ at the walls. The spontaneous polarization[8] at room temperature is about 0.26 coul/m^2; hence $E\simeq10^5\sin\theta$ kv/cm. Such a field must create a large lattice distortion near the 180° wall, but quasi-stationary domains (wedge angle of 20° or more) do not show such distortions. This suggests that a compensating electric charge accumulates and neutralizes the ends of the dipole chains.

These experiments are in line with the concept of von Hippel[9] that the conductivity of $BaTiO_3$ crystals is of great importance for the dynamics of domain formation, and with observations by Mitsui and Furuichi[10] on the effect of charges on the domains in Rochelle salt crystals.

Growth of 180° Domains

The manner in which spikes grow in a negative dc field until the crystal polarization is reversed, is illustrated schematically in Fig. 12. The last domains to

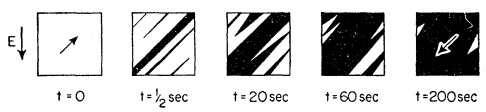


FIG. 12. Schematic diagram of 180° domain switching process in a [101] crystal.

[6] W. J. Merz, Phys. Rev. **88**, 421 (1952).
[7] The field strength will be designated as negative when opposite to the initial polarization.
[8] W. J. Merz, Phys. Rev. **91**, 513 (1953).
[9] A. von Hippel, Z. Physik **133**, 158 (1952).
[10] T. Mitsui and J. Furuichi, Phys. Rev. **90**, 193 (1953).

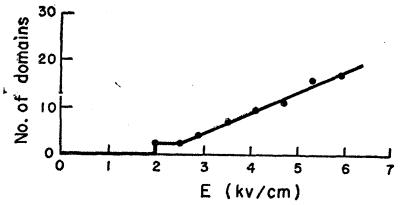


FIG. 13. Number of 180° domains nucleated in a dc field as a function of field strength.

leave are wide wedges at the edges of the crystal, often difficult to remove completely even with a high field.

To study these processes without interference by 90° wedges, the negative field is applied gradually, reaching its peak value in about $\frac{1}{2}$ sec. Typical thin spikes starting from both directions extend across the crystal before this peak field is reached. The spikes tend to nucleate at identical places at the edge of the crystal when the experiment is repeated. Their number increases with E (Fig. 13) as well as with the time derivative of the field. For low field strengths, few new spikes appear after E is reached; for fields greater than 6 kv/cm, spikes tend to grow from existing walls and N continues to increase during the experiment. The times required to reach approximately 50 percent (a) or 90 percent reversal (b) were measured as a function of the peak field strength (areas of opposite polarity were estimated visually). Since $1/t$ describes the velocity of reversal, this parameter has been plotted in Fig. 14 in its dependence on E.

A minimum field strength of about 2 kv/cm is required for the nucleation of 180° wedges. For E smaller than about 2.4 kv/cm, the wedges did not grow for observation times as long as 12 hours. Both the number of domains and the growth velocity increases with E;

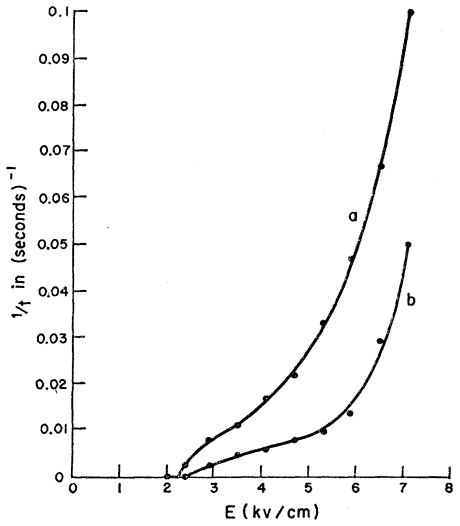


FIG. 14. Reciprocal of time required for 180° domains to reverse the polarization of a [101] crystal: (a) by 50 percent and (b) by 90 percent.

the growth is slowed down appreciably in the last stages of reversal.

This experiment leads again to the interpretation that, while the forward advance of spikes is initially fast, the sideways growth rate of 180° wedges is limited by the electrostatic energy of the depolarizing field. The large wedge angles observed towards the end of the process appear to require the accumulation of neutralizing charges on the domain walls. Since the walls of adjacent domains merge as growth proceeds, the velocity of polarization reversal decreases with time as the number of domains decreases.

The 180° walls are probably quite thin (possibly only one lattice distance) and the activation energy for motion perpendicular to the polar axis correspondingly very high. Such motion however is observed, and must therefore be explained by a sequence of dipole flips which propagate along the polar axis (Fig. 15). The fact that about the same limiting field is observed for nucleation and growth is in line with this observation, for both processes involve the reversal of individual dipole moments.

If one breathes on the crystal, the 180° domains move faster. This supports the idea that the con-

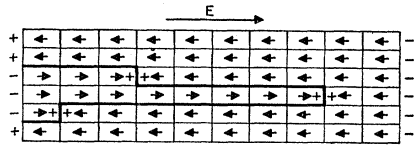


FIG. 15. Model for a 180° wedge.

ductivity of the crystals is of importance and that we have to consider surface as well as volume conductivity.

While the results reported (high initial forward velocity, slow sideways growth leading to saturation) are qualitatively the same for all crystals studied, there are quantitative differences from crystal to crystal, as would be expected when imperfections and conductivity vary from sample to sample. 180° domains in [001] "a" crystals appear to behave similarly to those in [101] "a" crystals.

Dielectric Measurements

Figure 16 shows the equivalent susceptibility[11] χ_{eq}' as a function of measuring field strength for a [001] "a" crystal with frequency as a parameter. χ_{eq}' approaches about 300 for low fields. The critical field for domain motion for the [001] crystal appears to be somewhat lower than observed visually for a [101] crystal, even when the different geometry is taken into account. This might imply that very thin and therefore

[11] $\chi_{eq}=A_1/\epsilon_0 E_0$, when A_1 is the coefficient of the first Fourier term, $E=E_0 \sin\omega t$ is the applied field and $P=\sum_{k=1}^{\infty} A_k \sin k\omega t$ is the polarization.

invisible spikes move at low fields. That the wall motion damps out at around 10^4 cps is consistent with our optical results. That χ_{eq}' increases rapidly with decreasing frequency is electrical evidence of the slow switching process. Hyde,[12] in this laboratory, found by tracing hysteresis loops that the slope $\Delta P/\Delta E$ continues to increase for frequencies as low as 10^{-1} cps. This would be expected from our domain observations with dc fields.

After this study was completed, the author received a prepublication copy of work by Merz[13] on the switching of 180° domains, observed electrically. The initial spike velocity determined from the switching time agrees well with our values measured optically. A significant difference is that we actually observed the 180° walls moving perpendicularly to the polar axis, an effect not perceived in Merz's electrical measurements.

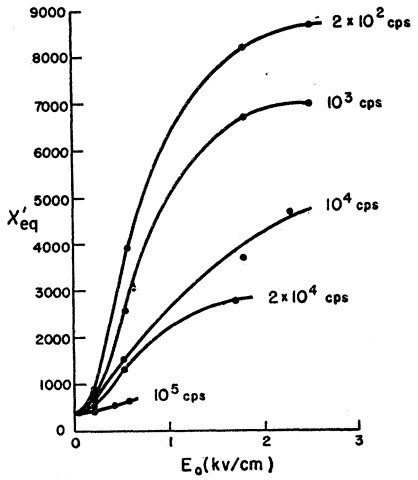


FIG. 16. Dependence of "equivalent" susceptibility on field strength and frequency in an [001] "a" crystal.

INTERACTIONS OF 90° AND 180° DOMAINS

When 90° and 180° domains are simultaneously active in a crystal, complicated interaction effects occur. The general behavior, however, may be predicted from a few rules which can be best demonstrated in a [101] crystal (Fig. 17). This is the type in which we studied the 180° domains, but now we make no effort to suppress 90° domains. Beginning the experiment with a single-domain crystal (a), we suddenly apply a negative dc field, and both 90° and 180° wedges form and grow (b). After a short time a 90° wall is in contact with 180° wedges and the motion is impeded (c). The antiparallel wedges penetrate into the adjacent area with a 90° turn (d), because otherwise the electric field concentration at the 90° wall becomes excessive. Finally, the antiparallel domains disappear and a

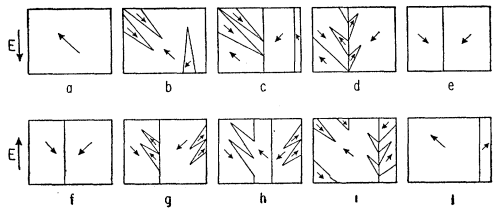


FIG. 17. Schematic diagram of 180° and 90° wall interactions in a [101] crystal.

head-to-head (or tail-to-tail) configuration of the 90° walls remains (e). This can be verified by measuring the rotation of the extinction axes of adjacent domains; these axes rotate in opposite directions. As the field gets larger, a region nearly 5 μ wide near the wall rotates so far that it appears bright yellow when the rest of the crystal is at extinction.

There is no observable optical difference between a head-to-head, tail-to-tail or head-to-tail 90° wall at magnifications up to 1100×. Obviously free charges at the 90° wall have neutralized the interfacial polarization that would otherwise produce a large field.

A domain configuration, as discussed above, may be called pseudo-saturated because, even though there exist 90° domains, they cannot be removed by a field as long as the energy barrier for rotation is too high.

If the field direction is now reversed [Fig. 17(*f*)], no net force acts on the 90° wall when the field is first applied. If the field is just greater than the critical field for nucleation of 180° domains (2 kv/cm), such domains will nucleate in spikes from the 90° wall and from the crystal edges and proceed slowly to invert the 90° domains (g). After 180° domains have nucleated at a 90° wall, a force acts through them on the 90° wall, and this wall may break away from its initial position and its space charge (h). It moves now freely and rapidly as a head-to-tail wall until running into another set of 180° domains (i). Where the 90° wall comes to a stop, depends on the growth rate of the 180° domains and on field strength. Strain may play a part in determining the final equilibrium configuration in the field, but the end result is again complete pseudo-saturation (j).

In order to measure these domain interactions, a negative square pulse with a rise time of <0.01 sec

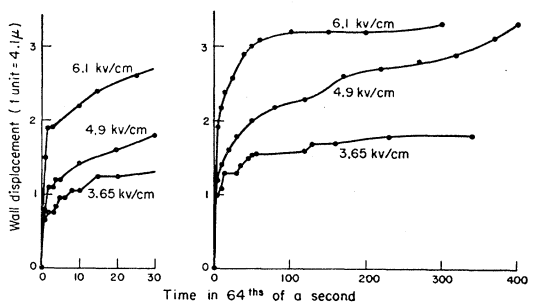


FIG. 18. 90° wall displacement in a [101] crystal as a function of time (two time scales) for several field strengths.

[12] J. Hyde, thesis, Massachusetts Institute of Technology, June, 1954 (unpublished).

[13] W. J. Merz (private communication, June, 1954); Phys. Rev. **95**, 690 (1954).

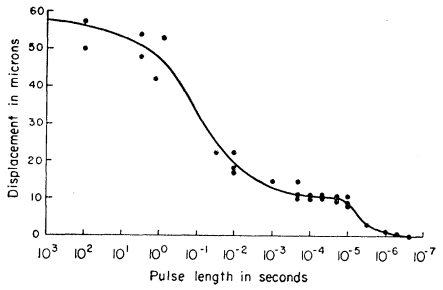


FIG. 19. 90° wall displacement in a [101] crystal caused by a square pulse of height 6.8 kv/cm as a function of pulse length.

and a duration of *ca* 6 sec was applied to the [101] crystal. A large positive field was applied previously for several minutes to insure that the crystal was initially pseudo-saturated. The motion of a typical 90° wall, as recorded by its position on movie film, is plotted for two different time scales in Fig. 18 with the pulse height as parameter.

The characteristics of typical 90° wall motion are here clearly evident. For the initial free motion the velocity is very high; next the wall velocity abruptly decreases as the wall collides with 180° domains. The slow process approximately fits an exponential relation with a time constant of about $\frac{1}{2}$ sec. There may be some additional motion for times as long as several minutes. Irregularities in the motion of the 90° wall reflect changes in the 180° domains affecting its progress. These jerky steps are prominently displayed in slow motion pictures and give rise to a ferroelectric Barkhausen effect.

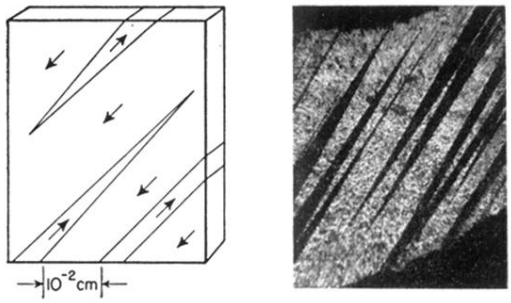
Figure 19 shows the 90° wall displacement caused by a negative square pulse (height 6.8 kv/cm) as a function of pulse length. As the pulse shortens below 10 μsec, the wall displacement drops rapidly to zero. The free motion of the 90° wall takes place with a velocity of about 50 cm/sec. After intersecting the 180° domains it continues with much slower speed until the crystal is pseudo-saturated.

Naturally, there are many variations of the case here discussed. New 90° wedges may enter from an edge and extend rapidly across the crystal. After meeting 180° wedges, the 90° walls are slowed down, as shown previously. Since 180° domains can nucleate from any 90° wall on one or both sides of it, more complicated interactions are bound to arise.

ACKNOWLEDGMENTS

The author is greatly indebted to Professor A. R. von Hippel for suggesting the problem and for his advice and encouragement during the course of this research. She wishes to thank Dr. P. W. Forsbergh, Jr., for an introduction to the intricacies of domain patterns in barium titanate and many illuminating discussions; Professor F. R. Kotter for the use of his rectangular-pulse generator; Professor H. E. Edgerton for a stroboscopic light source; W. B. Westphal for assistance in obtaining the dielectric measurements; and L. E. Johnson, B. Frackiewicz, and Professor D. J. Epstein for help in the electrical instrumentation.

The author wishes to express her gratitude to the International Business Machines Corporation for support in the form of a fellowship, and to Dr. D. R. Young of I.B.M. for informative discussions.



(a) (b)

FIG. 11. 180° domains in a [101] crystal.

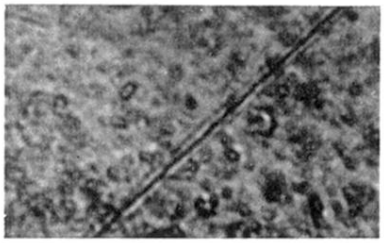


FIG. 2. A 90° wall (1000×).

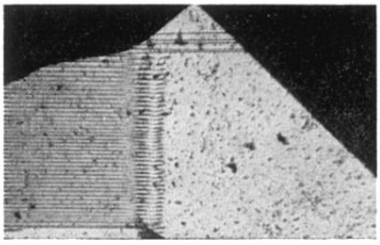


FIG. 4. A group of 90° wedges in an "*a*" crystal.

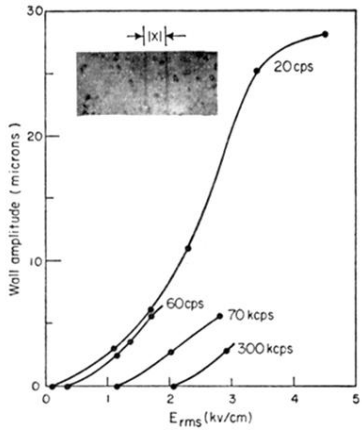


FIG. 9. 90° wall amplitude in ac fields as a function of frequency and field strength.