

Domain Formation and Domain Wall Motions in Ferroelectric BaTiO₃ Single Crystals

WALTER J. MERZ

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received April 19, 1954)

The nucleation and growth of ferroelectric domains in barium titanate have been studied as a function of applied electric field and temperature. The optical and electrical measurements were made on thin single-crystal plates normal to c , the polar direction. When the electric field applied along this direction is reversed, new domains with opposite polarization are formed. The manner of growth of these domains is very different from that of domain growth in ferromagnetic materials. The sidewise motion of the 180° side walls (walls between domains with antiparallel polarization) which is common in ferromagnetic crystals is almost never found in barium titanate. Instead its polarization is changed by the formation of very many new antiparallel domains which are extremely thin (10^{-4} cm) and appear to grow only in the forward direction. The explanation of this behavior is found in the weak coupling between the dipoles perpendicular to the dipole direction. The wall thickness is small, of the order of one to a few lattice constants; the wall energy in BaTiO₃ is of the order of 10 erg/cm². Electrical pulsing experiments substantiate the optical observations very clearly. Pulsing the samples at different temperatures shows that the nucleation rate of new domains is accelerated at elevated temperatures. Furthermore, the growth of the new domains is faster at higher temperatures. Experimental results are presented showing how the switching current and the switching time depend on applied electrical field, on temperature, and on the size of the sample.

I. INTRODUCTION

THE ferroelectric domains in BaTiO₃ single crystals have been studied by a number of authors, especially by Forsbergh.¹ All these investigations showed that the sometimes very complex domain arrangements can be explained by twinning of crystals along {011} planes. However, the formation and movement of antiparallel domains (domains with opposite polarization) have not been discussed extensively up to now. One difficulty is that without special means one cannot see the antiparallel domains very easily. We became interested in these antiparallel domains because they are very important in the process of reversing the dipoles with an electric field. Questions such as how long it takes to reverse the polarization, how fast the domain walls move, how large the current is which flows, and how these properties depend on the applied electrical field, temperature, and size of the sample can be answered by the study of the formation of the antiparallel domains and the movement of the walls between them. Besides the theoretical interest in the switching mechanism of electrical dipoles, all the above-mentioned questions are of prime importance when BaTiO₃ single crystals are used as memory devices.

II. OPTICAL OBSERVATIONS ON DOMAINS

We can distinguish among three types of domain boundaries (walls) in BaTiO₃. The first one is the boundary between a domain in which all the dipoles are aligned perpendicular to the crystal plate under investigation (c domain) and a domain in which all the dipoles are aligned in a direction parallel to the crystal plate surface (a domain). Since the c axis of the tetragonal crystal is the optic axis, the c domain looks dark through a microscope between crossed nicols. The

a domain is bright when viewed between crossed nicols except in two special positions where the direction of electric polarization is parallel or perpendicular to the direction of polarization of the light. We call this type of boundary a 90° wall because the two domains are polarized at 90° to each other. The 90° wall goes through the crystal at an angle of 45° to the major surfaces (Fig. 1), so that no surface charges can build up on the wall, as will be discussed later.

In the second case, the boundary is also a 90° wall, but the polarization on both sides of the wall lies parallel to the major surfaces of the crystal plate (a domains). In contrast to the first case these walls go straight through the crystal at 90° to the major surfaces. Because of total reflection of the light at the boundary, one can see this type of 90° wall very easily (Fig. 2). The direction of polarization of the two domains can be determined with a quarter-wave plate.

The third type of boundary is the 180° wall, that is, a boundary between domains with antiparallel polarization. As shown in a previous paper,² we can see these antiparallel domains only when the crystal is strained (by external or internal stresses or by an external electrical dc field). In Fig. 3 an edge of a c domain crystal is shown. The dark and bright lines represent the domains with parallel and antiparallel polarization. In other words the c domain, usually thought of as a single domain, consists of very many domains with antiparallel polarization. The width of these domains is of the order of 10^{-4} cm. In Fig. 4 a similar case is shown. The 45° lines are 90° walls, as shown before in Fig. 2. However, when the crystal is strained we can see that every supposedly single domain splits up into many domains with antiparallel polarization. They arrange themselves in such a way that no surface charges are

¹ P. W. Forsbergh, Jr., Phys. Rev. **76**, 1187 (1949).

² W. J. Merz, Phys. Rev. **88**, 421 (1952).

built up on the 90° walls: head-to-tail zig-zag arrangement, as shown in Fig. 4.

When an electrical field is applied to the crystal, we can, of course, move the domain walls and align the domains.³ The most interesting experiment, however, is the one in which we can observe the formation of new domains with opposite polarization. If one applies an ac voltage to a c -domain crystal and watches the edge of it, using a stroboscopic light source whose frequency is close to the ac frequency, it is possible to see how the new domains with opposite polarization are formed and how they grow. The new domains are created at the surface and at imperfections in the form of needles which then grow in the forward direction through the crystal. Two important conclusions are drawn from these observations. First there are very many new domains, and second there is practically no sidewise growth of the new domains. In other words the nuclei which have the shape of needles grow only in the forward direction. This behavior is quite different from the ferromagnetics and will be discussed later. Figure 5 shows a few of the needles as observed with stroboscopic light. In order to facilitate the observations of this

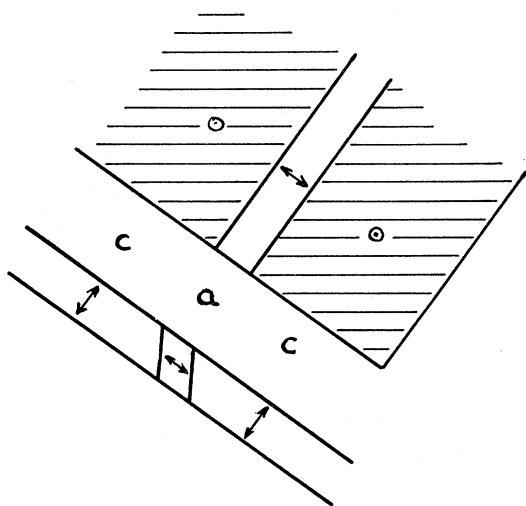
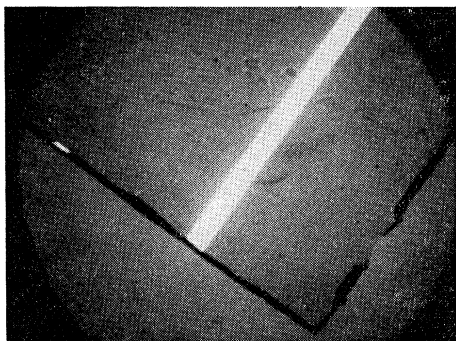


FIG. 1. Photo and schematic sketch of 90° walls between an a domain and two c domains in BaTiO_3 . ($\times 50$).

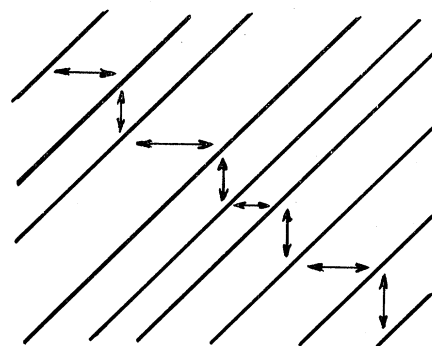
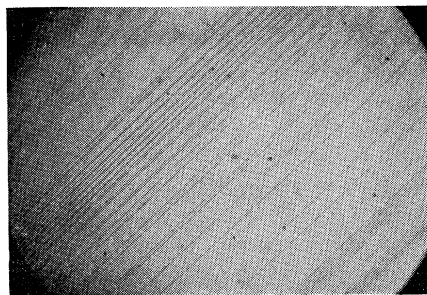


FIG. 2. 90° walls between a domains in BaTiO_3 . ($\times 50$).

effect, the crystal was highly strained. In some cases where this strain was excessive small cracks and thus a domains and 90° walls were produced (see the 45° lines in Fig. 5). The width of the new domains is also of the order of 10^{-4} cm, like the antiparallel domains in Figs. 3 and 4.

III. ELECTRICAL PULSING EXPERIMENTS

Both optical and electrical investigations were performed on single crystals grown by Remeika³ of this laboratory. Experiments showed that reproducible results can only be obtained if one uses very strain-free crystals with extremely clean surfaces and electrodes which adhere to the crystal very uniformly without straining it. Since the dielectric constant of BaTiO_3 is very high (10^5 to 10^6 for the steep part of the hysteresis loop⁴), one has to be sure that no impurities are between the crystal and the electrode. Evaporated films of noble metals on extremely clean crystal surfaces gave good results. A photograph of the ferroelectric 60-cycle hysteresis loop of a BaTiO_3 single crystal is shown in Fig. 6. Some characteristic data of this loop were given in a previous paper.⁴ ($E_c \sim 500$ volts/cm; $P_s = 26 \times 10^{-6}$ coulomb/cm²; ratio of two slopes $\sim 10^3$.)

The domain formation and domain wall motions as described in Chapter II were also investigated electrically by the following pulsing experiments. Square pulses are applied to a crystal (thickness $d = 5 \times 10^{-3}$ cm;

³ J. P. Remeika, J. Am. Chem. Soc. **76**, 940 (1954).

⁴ W. J. Merz, Phys. Rev. **91**, 513 (1953).

electrode area $A = 10^{-4}$ cm²) in series with a resistance. The rise time of the pulses has to be short compared to the time required for the field to reverse the polarization of the sample. Furthermore, the length of the pulses has to be longer than the time required to reverse the polarization. We applied pulses of 1 to 10 μ sec length with a rise time of about 0.02 μ sec. If repeated square pulses of just one sign are applied to the crystal, one observes just a small current flowing through the series resistance for a very short time. The change in polarization is small as long as we just travel along the flat part of the hysteresis loop. On the other hand, if positive and negative square pulses are applied alternately to the crystal, one observes a much larger current flow (through the series resistance) for a much longer time. The reason is that traversing the hysteresis loop causes large changes in polarization. In Fig. 7 the two cases are shown and named "0" and "1" because they represent the reading out of a binary zero and of a binary one when the crystal is used as a memory device. The initial peak of "1" is mostly due to lead capacity, whereas the wide region of "1" is due to switching of domains.

In Fig. 8 we plot the measured peak current i_{\max} (shown in Fig. 7) versus the applied field E of the pulse. Figure 9 is a plot of switching time t_s versus applied

field E . The higher the applied field E , the faster the dipoles switch and thus the larger the peak current i_{\max} .

Figure 8 shows that the plot of switching current versus applied field can be divided into two parts, a curved low-field strength part and a linear high-field strength part. At high fields the crystal thus behaves like an ohmic resistance in series with a voltage bias. We can calculate this switching resistance R in the following way. From Fig. 9 we know that the switching time t_s is proportional to $1/(E-E'')$, where E'' is a kind of coercive field strength. Since the new domains have to grow from one side of the crystal to the other side (Fig. 5), t_s must also be proportional to the thickness d of the sample; thus

$$t_s \cong \beta d / (E - E''), \tag{1}$$

with $\beta = \text{constant}$. Furthermore,

$$i_{\max} \cdot t_s = \text{constant (total charge)} = 2 \cdot P_s \cdot A \cdot q \tag{2}$$

with $P_s = \text{spontaneous polarization (coulombs/cm}^2\text{)}$; $A = \text{area of the crystal (cm}^2\text{)}$; and $q = \text{constant of order of about 2 which takes care of the shape of the } i(t) \text{ curve (Fig. 7)}$. We then get

$$R = \frac{\Delta V}{\Delta i} = \frac{d(E - E'') \cdot \beta d}{2 \cdot P_s \cdot A \cdot q(E - E'')} \cong \frac{\beta d^2}{2 \cdot q \cdot A \cdot P_s}, \tag{3}$$

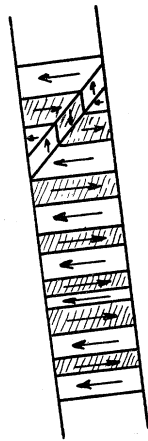
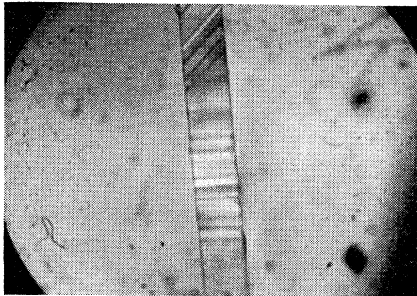


FIG. 3. 180° walls (antiparallel domains) at the edge of a crystal. ($\times 50$).

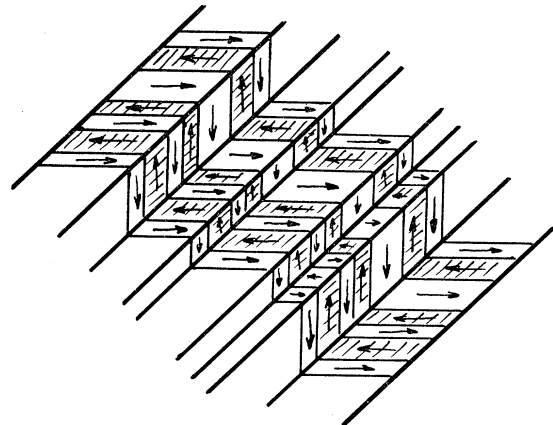
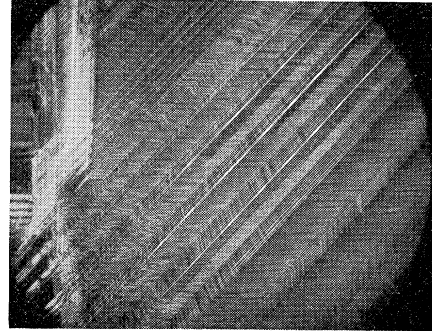


FIG. 4. 180° and 90° walls in a BaTiO₃ crystal surface. ($\times 50$).

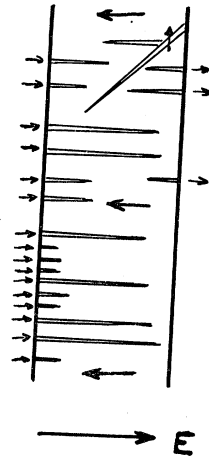
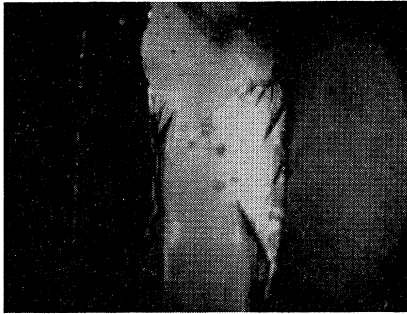


FIG. 5. New antiparallel domains observed with stroboscopic light. ($\times 50$).

if E' is close to E'' ; that is, the switching resistance R of the linear part in Fig. 8 is proportional to the square of the thickness d of the sample and inversely propor-

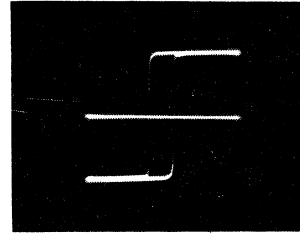


FIG. 6. 60-cycle hysteresis loop of BaTiO_3 .

tional to the electrode area A of the sample. This has experimentally been found to be true. The resistance of the electrodes has of course to be subtracted from the measured resistance. All the curves shown in this paper were obtained on samples with the following dimensions: thickness $d = 5 \times 10^{-3}$ cm, electrode area $A = 10^{-4}$ cm².

The low field strength part of Fig. 8 can be expressed best in the following way:

$$i_{\max} \sim e^{-\alpha E}, \tag{4}$$

with $\alpha = \text{constant}$. In Fig. 10 a logarithmic plot of i_{\max} versus $1/E$ is shown. We get a straight line over 5 decades. One very interesting result of this is that even at field strengths below the 60-cycle coercive force we get switching if we wait long enough. The apparent coercive force increases when the frequency of the applied field is increased.

Measurements at different temperatures show that at higher temperatures the switching time becomes shorter and thus the switching current increases considerably. But the general shape of the curves $i(E)$ (Fig. 7) stays the same. Figure 11 shows the plots of current i versus field E for different temperatures. It can be seen that

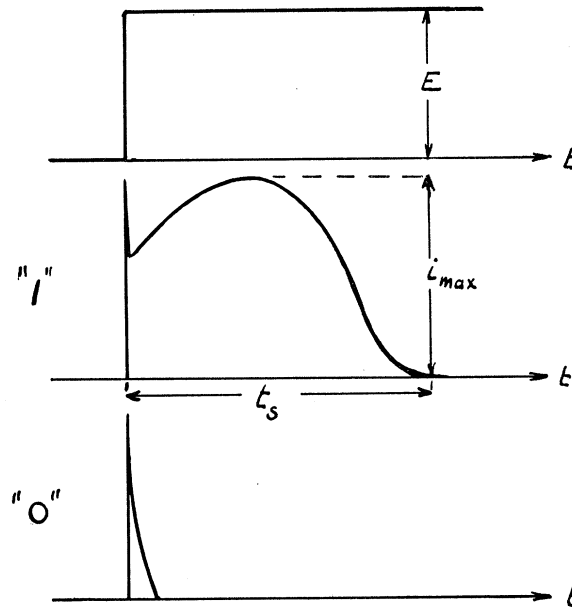
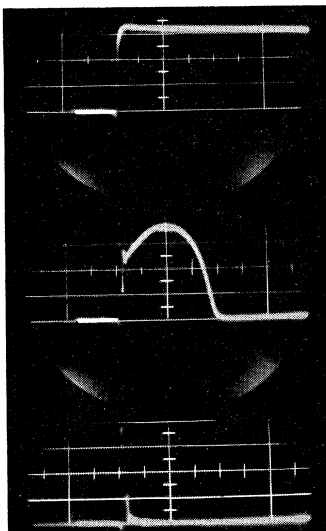


FIG. 7. Pulsing current and pulsing field versus time.

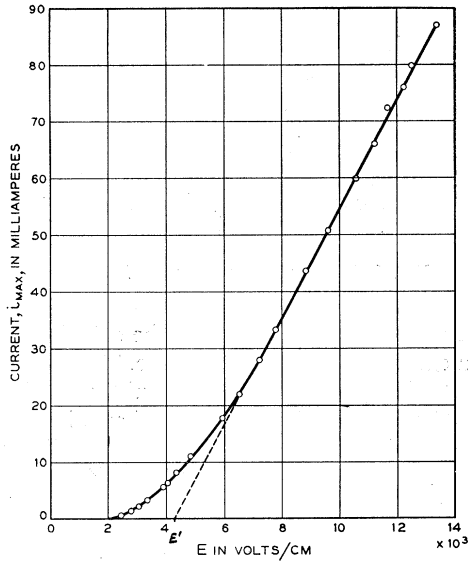


FIG. 8. Pulsing current i_{max} versus applied field E .

the resistance R (inverse slope of the linear part) decreases with increasing temperature as shown in Fig. 12. In a similar way, the switching time t_s drops with increasing temperature for the same applied field strength as shown in Fig. 13. The constant β from Eq. (1), which is proportional to the slope of the lines in Fig. 13, is plotted as a function of temperature in Fig. 14. The behavior is very similar to $R(T)$ (Fig. 12), as is to be expected since R is proportional to β [Eq. (3)] and the only other temperature dependent quantity, P_s , does not change rapidly with temperature.

The low field strength part is shown in Fig. 15. At all temperatures we can represent the curves best by

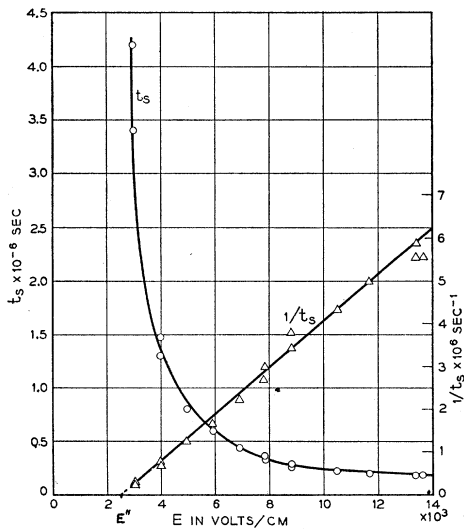


FIG. 9. Switching time t_s and $1/t_s$ versus applied field E .

writing

$$i_{max} \sim e^{-\alpha(T)/E}. \tag{5}$$

The value of the coefficient $\alpha(T)$ is plotted versus temperature in Fig. 16. We will discuss these experiments in the next chapter.

IV. DISCUSSION

The most interesting result obtained from our domain observations is that by reversing the applied electric field very many new domains are created. Furthermore, the polarization in $BaTiO_3$ does not change by a side-

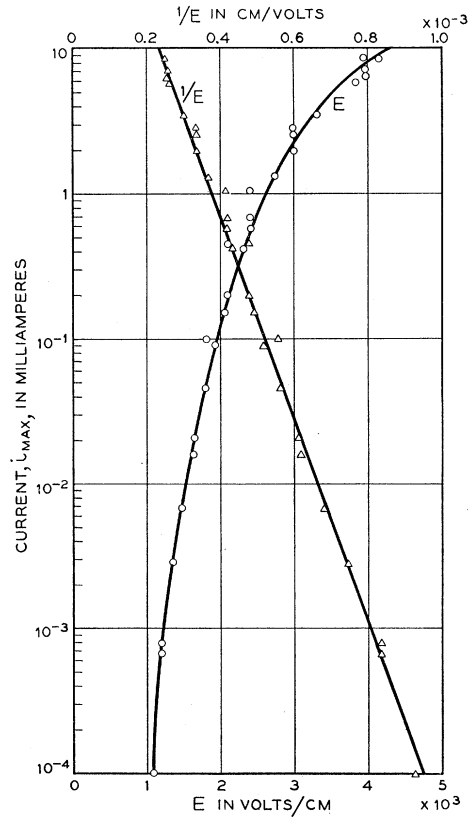


FIG. 10. Switching current versus applied field E and versus $1/E$.

wise motion of the side walls of those domains which are already polarized in the right direction. $BaTiO_3$ prefers to create many new small domains instead of making an existing properly polarized domain grow. This is in contrast to ferromagnetics, where from the work of Williams and Shockley⁵ we know that in good single crystals of iron we can observe only a few domain walls and that these move sidewise when a magnetic field is applied. Figures 3 and 4 illustrate the case of crystals where about half of the domains have a polarization pointing in one direction whereas the other half have a polarization pointing in the opposite direction. In Fig. 5 we have shown the situation where the

⁵ H. J. Williams and W. Shockley, Phys. Rev. 75, 178 (1949).

domains are in the process of reversing and only a few of them have the direction of the reversed electric field. The boundaries of the antiparallel domains are not as sharp as the 90° walls because what we see are only changes in birefringence due to strains. However, we get a good idea of the size and shape of the domains with antiparallel polarization. The question is "why do the 180° side walls not move sidewise in contrast to the magnetic case?"

We think the explanation is as follows. The forward coupling of the electric dipoles is large so that the growth of the nuclei in the forward direction is fast. The coupling sidewise, however, is very small. In other words, an electric dipole does not care too much whether the neighboring dipoles on the side are parallel or antiparallel. Of course, the parallel alignment is usually

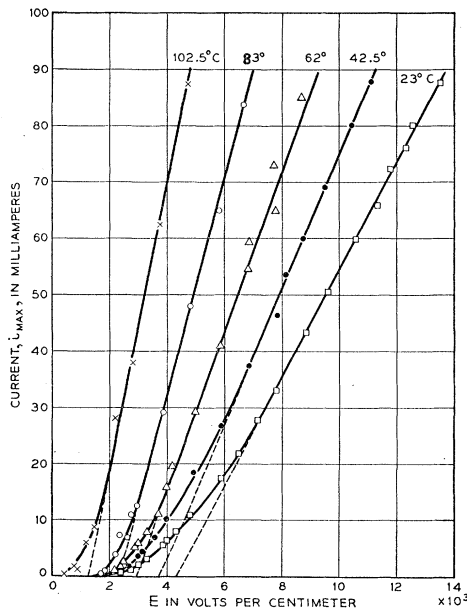


FIG. 11. Switching current *versus* applied field at different temperatures.

preferred because the crystal is ferroelectric. On the other hand, we know from the work of Kittel⁶ that an antiferroelectric arrangement is energetically almost as likely as a ferroelectric one. Furthermore, crystals similar to BaTiO₃ are known where the antiparallel arrangement is preferred (PbZrO₃, for example).⁷

Furthermore, we can also explain this behavior by investigating the wall thickness and the wall energy. The energy of the wall per cm² can be represented as

$$\sigma_w = \sigma_{dip} + \sigma_{anis}, \tag{6}$$

where σ_{dip} is the contribution from dipole-dipole interaction and σ_{anis} is the contribution from anisotropy.

⁶ C. Kittel, Phys. Rev. **82**, 729 (1951).

⁷ Shirane, Sawaguchi, and Takagi, Phys. Rev. **84**, 476 (1951).

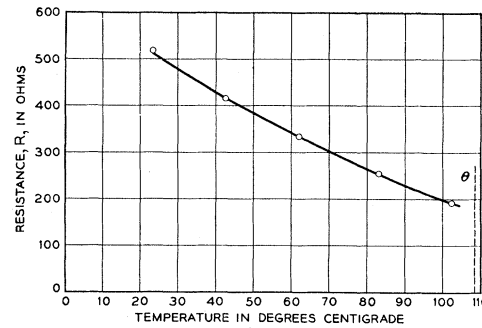


FIG. 12. Switching resistance R *versus* temperature.

In the ferromagnetic case one replaces σ_{dip} by $\sigma_{exchange}$ because the exchange interaction is much larger than the dipole-dipole interaction. Here the dipole energy is the important one and may be estimated from calculations of dipolar interactions.⁸ The result is roughly

$$\sigma_{dip} \cong 10^{-14} / N a^2 \text{ erg/cm}^2, \tag{7}$$

where N is the thickness of the wall in atomic separations and a is the lattice constant. The energy due to anisotropy we can calculate in the following way. The elastic energy per cm³ which is stored when we deform the unit cell from tetragonal to cubic is of the order of

$$\epsilon_{elast} \cong \frac{1}{2} c_{33} z_z^2 \text{ erg/cm}^3, \tag{8}$$

where c_{33} is an elastic constant and z_z is the spontaneous strain in BaTiO₃ at room temperature because of elec-

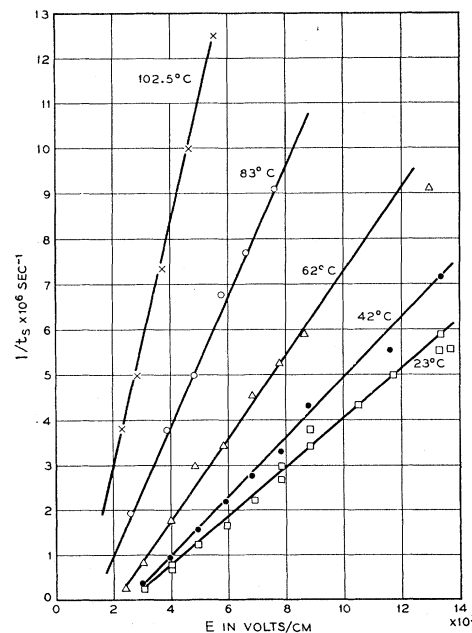


FIG. 13. Reciprocal switching time *versus* field at different temperatures.

⁸ P. W. Anderson (private communication); see also W. Kinase, Busseiron Kenkyu **69**, 145 (1953).

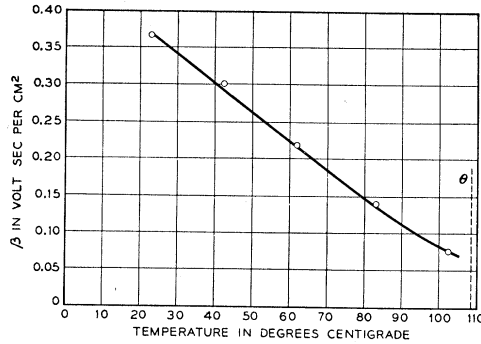


FIG. 14. β (reciprocal mobility) versus temperature.

tromechanical effects. Thus, the wall energy per cm^2 due to anisotropy becomes

$$\sigma_{\text{anis}} \cong \frac{1}{2} c_{33} z_z^2 N a \text{ erg/cm}^2. \quad (9)$$

From (7) and (9) we get for the total wall energy density

$$\sigma_w \cong (10^{-14}/N a^2) + \frac{1}{2} c_{33} z_z^2 N a \text{ erg/cm}^2. \quad (10)$$

The minimum wall energy is obtained when

$$\partial \sigma_w / \partial N = 0 = - (10^{-14}/N^2 a^2) + \frac{1}{2} c_{33} z_z^2 a, \quad (11)$$

or when

$$N \cong (2 \times 10^{-14} / c_{33} z_z^2 a^3)^{\frac{1}{2}}. \quad (12)$$

It is clear that N (wall thickness expressed in atomic separations) must be small in BaTiO_3 because the dipole-dipole interaction is small and the anisotropy large. We obtain for N at room temperature with $c_{33} = 2.0 \times 10^{12}$ dynes/cm²,⁹ $z_z = 7 \times 10^{-3}$,¹⁰ $a = 4.0 \times 10^{-8}$ cm¹¹:

$$N \sim 1. \quad (13)$$

This indicates that in contrast to a ferromagnetic material such as iron, where N is of the order of 10^2 to 10^3 , the wall thickness in BaTiO_3 is extremely small, of the order of 1 to very few lattice constants.

The total wall energy we can obtain by substituting Eq. (12) into Eq. (10),

$$\sigma_w \cong (2 \times 10^{-14} c_{33} z_z^2 / a)^{\frac{1}{2}}. \quad (14)$$

For BaTiO_3 we then obtain

$$\sigma_w \cong 7 \text{ erg/cm}^2, \quad (15)$$

which is higher than in iron by a factor of about 5.

Can we explain the very slow sidewise motion of the side walls of the domains if there is any at all? According to Anderson¹² it can be expected that if the wall is only one or a few lattice constants thick, it has a definite position of equilibrium in the lattice, and to move it over by one unit cell requires an energy of the order of magnitude of the total wall energy itself (~ 10

erg/cm²). In the magnetic case, however, where the wall is a few hundred lattice constants thick, the energy required to move the wall one lattice constant is very small because the total wall energy is spread out over a much larger region. Since the energy gained by moving the wall one lattice constant to the side is only about

$$EP = 1/10 \text{ erg/cm}^2, \quad (16)$$

with $E \sim 10^4$ volts/cm, which is much smaller than the wall energy [Eq. (15)], it is obvious that it is very unlikely that the side walls can move sidewise. The crystal thus prefers to create many new nuclei with the reversed polarization as we can see optically so clearly.

Both the optical and the electrical pulsing experiments show that the reversing of the polarization in BaTiO_3 occurs in two steps, first the nucleation of new domains and second the linear growth of these nuclei in the forward direction. At low field strengths the switching current is mainly determined by the number n of nuclei which are formed per unit time. The pulsing experiments showed [Eq. (5)] that the current increases exponentially with $-1/E$. Thus we can write that

$$i \sim dn/dt \sim e^{-\alpha(T)/E}. \quad (17)$$

The question is whether we can explain this $1/E$ dependence with a nucleation theory. We can write for the free energy of formation of a nucleus with anti-parallel polarization¹³:

$$\Delta F = -2EP_s V + \sigma_w A + \frac{1}{2} NP_s^2 V, \quad (18)$$

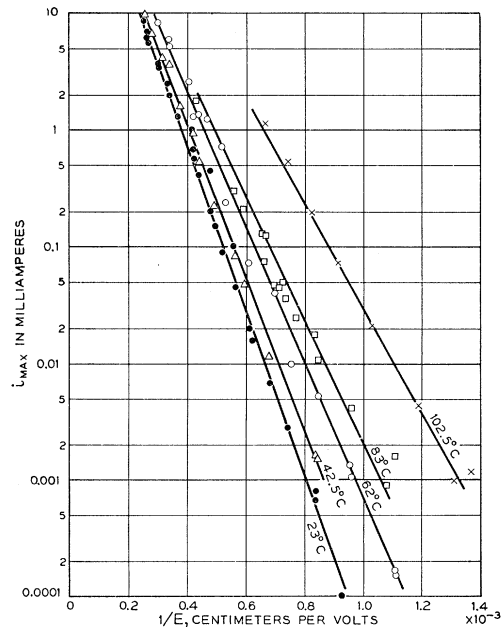


FIG. 15. Switching current versus reciprocal field at different temperatures.

⁹ Bond, Mason, and McSkimin, Phys. Rev. **82**, 442 (1951).

¹⁰ W. J. Merz, Phys. Rev. **76**, 1221 (1949).

¹¹ Helen B. Megaw, Proc. Roy. Soc. (London) **A189**, 261 (1947).

¹² P. W. Anderson (private communication).

¹³ R. Becker and W. Doering, *Ferromagnetismus* (Springer, Berlin, 1939).

where the first term represents the electrostatic energy, which is gained by the formation of a nucleus, the second term represents the surface energy, and the third term the field energy of the depolarizing field. In Eq. (18), V is the volume and A is wall area of the nucleus; σ_w is the wall energy/cm² and N is the depolarizing factor; P_s is the spontaneous polarization and E is the applied electric field.

If we assume for the shape of the nucleus something like a thin long cone or ellipsoid as optical observations indicate, we can write

$$V = a \cdot r^2 l, \quad A = brl, \quad N = cr^2/l^2, \quad (19)$$

where r is the radius of the base, l is the length of the nucleus, and a, b, c are constants. The minimum of ΔF can be found by differentiating Eq. (18) with respect to r and l and equating to zero. We then find for the critical dimensions:

$$r^* \sim 1/EP, \quad l^* \sim 1/E^{3/2}P^{1/2}, \quad (20)$$

and thus

$$\Delta F^* \sim 1/E^{5/2}P^{3/2}. \quad (21)$$

We obtain then for the rate of nucleation of new domains

$$\frac{dn}{dt} \sim \exp\left(-\frac{\Delta F^*}{kT}\right) \sim \exp\left(-\frac{\text{constant}}{E^{5/2}P^{3/2}kT}\right), \quad (22)$$

which does not agree with the experimentally found $e^{-1/E}$ dependence.

There is a way to get the $e^{-1/E}$ dependence of the current as suggested by Wannier.¹⁴ We assume that the depolarizing field can be neglected because the nucleus is very long and thin. Furthermore, we assume that the nucleus has the shape of a long flat dagger with a length l (in the direction of the field) and a cross dimension $l \times w$, where $l \gg w > t$. We then get

$$\Delta F = -2EPlwt + \sigma_w'(wl + tl) + \sigma_w''wt, \quad (23)$$

and, since $w > t$,

$$\Delta F = -2EPlwt + \sigma_w'wl + \sigma_w''wt, \quad (24)$$

where the width w can be considered as a constant but still $w \ll l$ and $w > t$. We then find for the critical dimen-

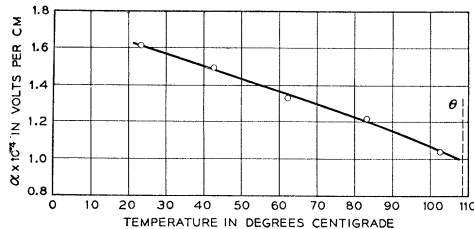


FIG. 16. Activation energy α versus temperature.

¹⁴ G. H. Wannier (private communication).

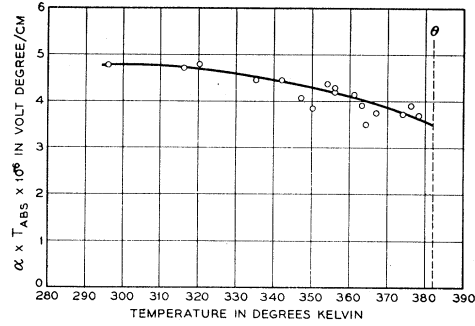


FIG. 17. Activation energy α times temperature T versus temperature.

sions:

$$l^* \sim \sigma_w'/EP, \quad t^* \sim \sigma_w''/EP, \quad (25)$$

and thus

$$\Delta F^* \sim \sigma_w' \sigma_w''/EP; \quad (26)$$

$$dn/dt \sim \exp(-\sigma_w' \sigma_w''/EPkT),$$

which gives the experimentally observed $e^{-1/E}$ dependence of the current. Since $l^* \gg t^*$, Eq. (25) says that $\sigma_w'' \gg \sigma_w'$, which means that the wall energy/cm² of the front wall is much higher than the wall energy/cm² of the side walls of the nucleus. This is to be expected because on the front wall we find an electric charge.

However, we have no direct proof for the fact that w should be larger than t . The strain patterns we see in Figs. 3, 4, and 5 indicate a value of about 10^{-4} cm for the width w of the antiparallel domains so that t would not be observable if the above-mentioned assumption is correct. By comparing Eqs. (17) and (26), we find that the experimentally measured $\alpha(T)$ (Fig. 16) must be

$$\alpha(T) \sim \sigma_w' \sigma_w''/PkT. \quad (27)$$

If we plot $\alpha(T) \times T$ (Fig. 17), we notice that this curve looks very similar to the spontaneous polarization P_s versus T curve⁴ or a higher power of P_s versus T . We are therefore led to the conclusion that

$$\sigma_w' \cdot \sigma_w'' \sim P^n \quad \text{with } n \sim 2 \text{ to } 4, \quad (28)$$

which in turn is proportional to the spontaneous lattice deformation $x_z^{n/2}$ or $z_z^{n/2}$ or some similar expression, since x_z and z_z are proportional to $P_s^{2,4}$. Therefore, the wall energies depend strongly on the spontaneous lattice deformations, as also can be seen in Eq. (14). Whether the nuclei are dagger-shaped, as assumed above, or whether they are needle- or cone-like, as optical observations might indicate, cannot yet be determined.

At high field strengths the current i_{\max} varies linearly with the applied field E (Fig. 8). Since at these high fields the nucleation is extremely fast, we can assume that the peak current is determined only by the velocity v with which the nuclei grow in the forward direction.

$$i_{\max} \sim v = d/t_s = \mu(E - E''), \quad (29)$$

where d is the thickness of the sample, t_s the switching time, and μ a mobility. Experimentally we know d and t_s for different fields E (Fig. 9), so that we can calculate the mobility μ . We obtain at room temperature

$$\mu \cong 2.5 \text{ cm}^2/\text{volt sec}, \quad (30)$$

so that we obtain for the velocity v values of the order of

$$v = 0.5 \times 10^4 \text{ cm/sec} \\ \text{for an applied field of } 2000 \text{ v/cm}, \\ \text{or} \quad (31)$$

$$v = 3.5 \times 10^4 \text{ cm/sec} \\ \text{for an applied field of } 14\,000 \text{ v/cm}.$$

These are average values because they were obtained from the total switching time t_s of the whole crystal. It is quite possible that the velocity with which one single domain grows is larger because the nucleation time, though small, is finite. However, it is reasonable to assume that the average velocity of one domain at applied field strengths of the order of 10^4 volts/cm is of the order of 10^4 to 5×10^4 cm/sec, which is comparable to the wall velocity in ferromagnetic crystals. However, it is interesting to note that it is smaller than the velocity of sound in BaTiO₃. An accurate direct measurement of v by measuring the velocity with which the end point of a new antiparallel domain (Fig. 5) moves through the crystal, was not possible because of stability problems.

Since the mobility μ is equal to $1/\beta$ as defined in Eq. (1), we can see from Fig. 14 that μ increases strongly with temperature. This is to be expected because the switching certainly is easier to perform when the crystal is less anisotropic. (The ratio c/a approaches 1 when we approach the Curie point.)

V. CONCLUSIONS AND SUMMARY

Though we do not understand all the details of the switching mechanism in ferroelectric BaTiO₃, we can observe quite clearly the following fundamental differ-

ences between the switching in a ferromagnetic crystal such as iron and a ferroelectric crystal such as BaTiO₃. The wall thickness in BaTiO₃ is very much smaller than in iron; probably just one or very few lattice constants thick. A similar result was obtained for ferroelectric rochelle salt by Mitsui and Furuichi¹⁵ and for ferroelectric KH₂PO₄ by Kaenzig and Sommerhalder.¹⁶ The wall energy per cm² seems to be somewhat larger than in iron. BaTiO₃ reverses its polarization by forming very many new domains whereas in iron the magnetization is reversed mostly by wall motion. The nucleation problem thus becomes very important in BaTiO₃. This can be seen very clearly in Figs. 8 and 11 where one observes a very large curved part in the plot of the switching current *versus* applied electric field. In the magnetic case, on the other hand, a linear behavior is found between magnetic flux change and magnetic field even at very low field strengths.¹⁷ Since there is practically no sidewise motion of the side walls, there is no interference (crosstalk) between one set of electrodes to another on the same crystal plate even when they are very closely spaced (10^{-2} cm or less). This is, of course, of great importance when BaTiO₃ crystals are used in a matrix-type memory.

Further studies on the nucleation time, the dielectric relaxation time, and the switching losses especially near the transitions are under way and will be reported later.

VI. ACKNOWLEDGMENT

I would like to thank many of my colleagues without whose help the present work would not have been possible. In particular I would like to thank J. P. Remeika for the preparation of the very excellent crystals; P. W. Anderson, J. R. Anderson, G. H. Wannier, and J. K. Galt for very many helpful discussions; R. Nelson for helping with some experiments; and E. M. Kelly and J. Andrus for help in the preparation of samples.

¹⁵ T. Mitsui and J. Furuichi, Phys. Rev. **90**, 193 (1953).

¹⁶ W. Kaenzig and R. Sommerhalder, Helv. Phys. Acta **26**, 603 (1953).

¹⁷ Galt, Andrus, and Hopper, Revs. Modern Phys. **25**, 93 (1953).

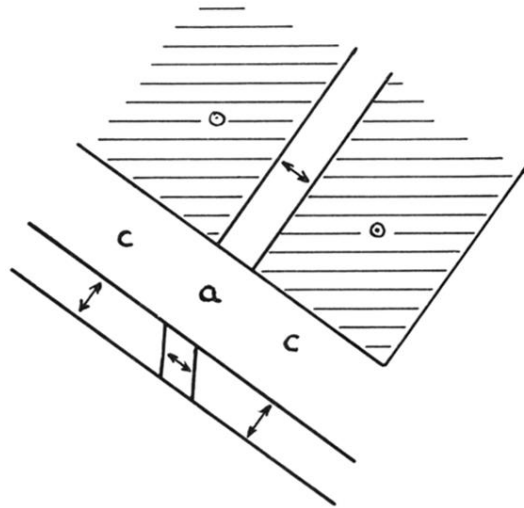
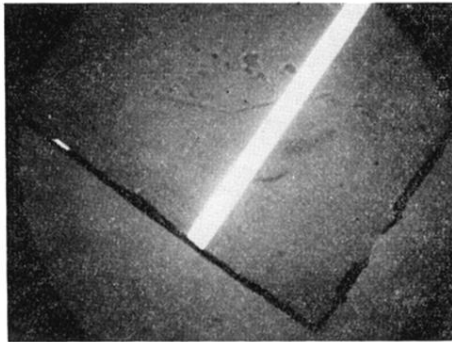


FIG. 1. Photo and schematic sketch of 90° walls between an *a* domain and two *c* domains in BaTiO_3 . ($\times 50$).

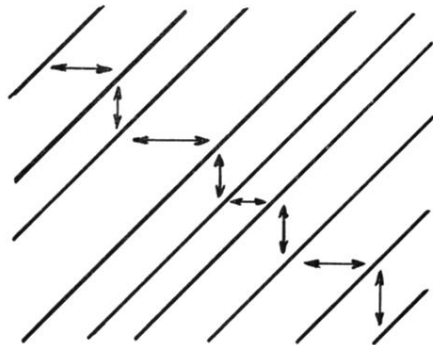
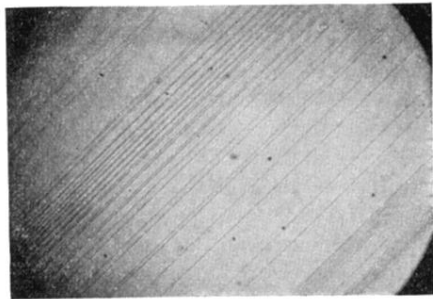


FIG. 2. 90° walls between a domains in BaTiO₃.
($\times 50$).

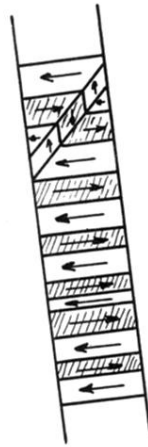
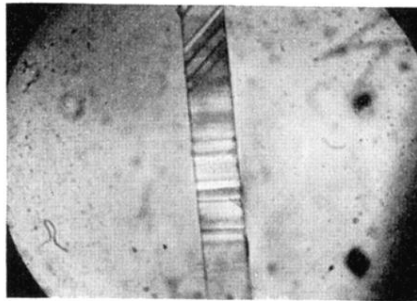


FIG. 3. 180° walls (antiparallel domains) at the edge of a crystal.
($\times 50$).

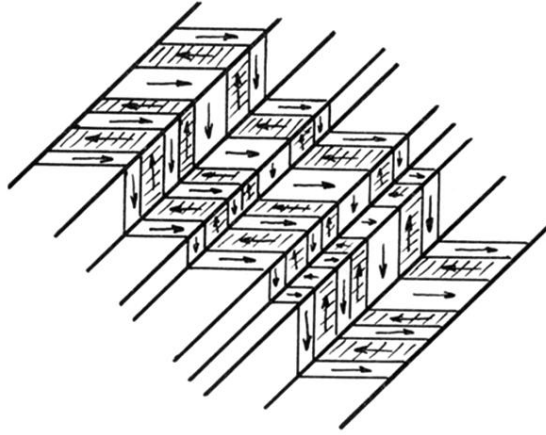
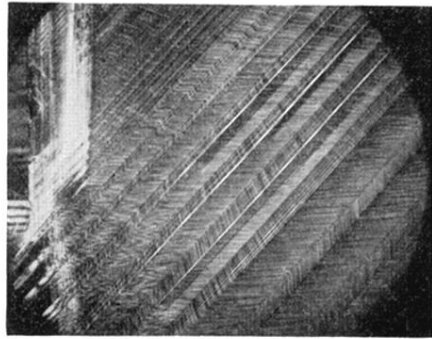


FIG. 4. 180° and 90° walls in a BaTiO_3 crystal surface.
($\times 50$).

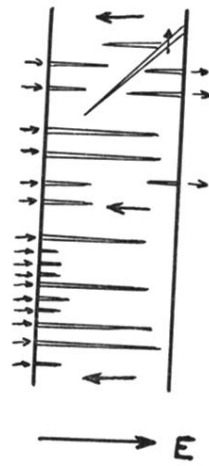
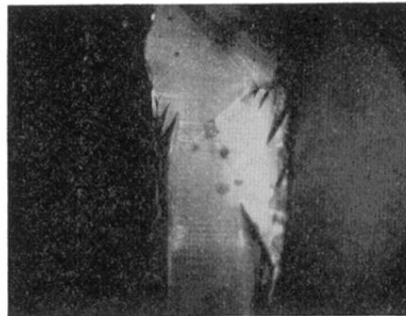


FIG. 5. New antiparallel domains observed with stroboscopic light.
($\times 50$).

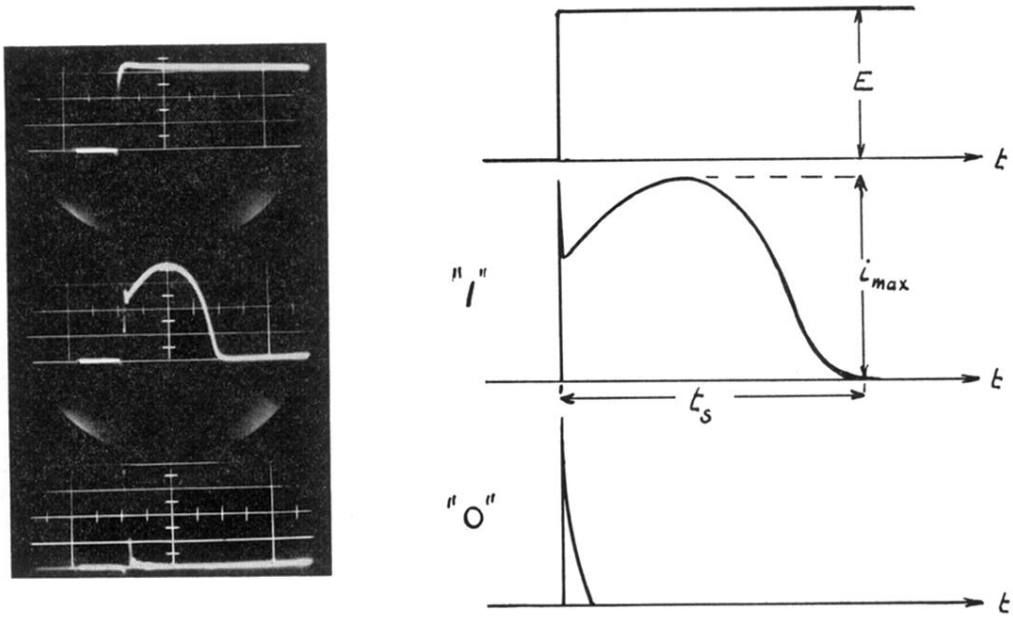


FIG. 7. Pulsing current and pulsing field *versus* time.