

Velocity of Sidewise 180° Domain-Wall Motion in BaTiO₃ as a Function of the Applied Electric Field

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New techniques are described which permit one to reverse the direction of the spontaneous polarization in liquid-electroded single crystals of BaTiO₃ with one growing domain which nucleates at a predetermined location on the crystal and then expands through sidewise 180° domain-wall motion until the spontaneous polarization in the entire electroded area is reversed. Measurements of the rate of growth of the single domain for a range of applied electric fields give rise to the first quantitative data on the field dependence of the sidewise 180° domain-wall velocity in BaTiO₃. It is found that this wall velocity is given by $v = v_{\infty} e^{-\delta/E}$, where δ is several thousand volts per centimeter and v_{∞} is in general of the order of 10 cm sec⁻¹. The fields employed in these measurements were in the neighborhood of several hundred volts per centimeter and the wall velocities varied from about 10⁻⁶ cm sec⁻¹ to 10⁻² cm sec⁻¹. The measured field dependence of the wall velocity is indicative of a nucleation mechanism for the wall motion, and it is shown that the equation of motion usually employed for domain boundaries does not describe the sidewise 180° wall motion in BaTiO₃. In addition, the well-known $e^{-\alpha/E}$ polarization reversal characteristics of metal-electroded crystals are shown to be consistent with wall motion of the type found in this research.

INTRODUCTION

A FERROELECTRIC domain may grow through (1) forward domain-wall motion in which case the wall moves in the direction of the ferroelectric axis, (2) sidewise domain-wall motion where the wall moves in a direction normal to the ferroelectric axis, or (3) a combination of both. There is some information in the literature on ferroelectric domain growth; however, there is very little quantitative data on the variation of the velocity of ferroelectric domain walls with the applied electric field. It is clear that information of this type is essential to an understanding of the mechanism of polarization reversal in a ferroelectric material.

From optical observations, and a study of the switching transients (dP/dt as a function of time and field) with fields of several thousand volts per centimeter, Merz^{1,2} concluded that the nucleation of reversed domains in single-crystal BaTiO₃ is followed by their growth, through domain-wall motion, which is largely in the forward direction. The velocity of growth v , and therefore the forward velocity of the domain wall, is given by $v = \mu(E - E_0)$, where E is the applied electric field, E_0 the coercive field, and μ the domain-wall mobility. Wieder³ has made electrical measurements on Rochelle salt similar to those of Merz on BaTiO₃, and concluded that the forward domain-wall velocity in Rochelle salt is also related to the applied field by an expression of the type given above.

Mitsui and Furuichi^{4,5} have made direct measurements of the sidewise domain-wall velocity as a function of the electric field in Rochelle salt and they find the sidewise wall velocity is described by $\gamma v = 2P_s(E - E_0)$, in which γ and E_0 are structure sensitive parameters

and P_s is the spontaneous polarization of Rochelle salt. Of the fairly large number of papers which have appeared in the literature on polarization reversal in single-crystal BaTiO₃,⁶ only two of these included experimentation aimed toward a direct observation of sidewise 180° domain-wall motion. Merz^{1,2} concluded that in the field region investigated, several thousand volts per centimeter, there was "practically no sidewise" 180° domain-wall motion. These conclusions were based in part on optical observations of the nucleation and growth of domains in crystals which were under high electrical strain. It was necessary to strain the crystals in order to distinguish between domains of opposite polarization.⁷ In some cases the strains were sufficiently large to fracture the crystal. With a sample geometry such that a component of the applied electric field was perpendicular to the ferroelectric axis, Little⁸ was able to observe the antiparallel domain structure in BaTiO₃ during polarization reversal. Little found no sidewise 180° domain-wall motion for applied fields less than 2.4 kv cm⁻¹, and no nucleations of domains for fields less than 2 kv cm⁻¹. Thus it seems that Little would not expect polarization reversal to occur with fields less than about 2 kv cm⁻¹ which is not consistent with experimental observations of polarization reversal with fields in the neighborhood of several hundred volts per centimeter.^{9,10} Merz and Little measured metal-electroded samples which were subjected to either a high electrical stress, or an applied electric field with a component perpendicular to the polarization direction, both of which lead to results which are difficult to

⁶ For a general discussion of published work on polarization reversal in BaTiO₃ and in other ferroelectrics, the reader is referred to W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4.

⁷ W. J. Merz, *Phys. Rev.* **88**, 421 (1952).

⁸ E. A. Little, *Phys. Rev.* **98**, 978 (1955).

⁹ A. G. Chynoweth, *Phys. Rev.* **110**, 1316 (1958).

¹⁰ R. C. Miller (unpublished data).

¹ W. J. Merz, *Phys. Rev.* **95**, 690 (1954).

² W. J. Merz, *J. Appl. Phys.* **27**, 938 (1956).

³ H. H. Wieder, *Phys. Rev.* **110**, 29 (1958).

⁴ T. Mitsui and J. Furuichi, *Phys. Rev.* **90**, 193 (1953).

⁵ T. Mitsui and J. Furuichi, *Phys. Rev.* **95**, 558 (1954).

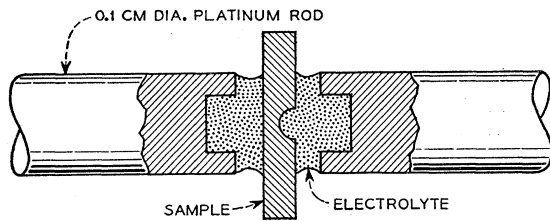


FIG. 1. Schematic drawing showing a portion of the liquid electrode holder with a dimpled sample of BaTiO_3 mounted between the electrodes.

interpret in terms of polarization reversal in the usual sense where the sample is essentially free from any large electrical stress and the electric field applied in the direction of the ferroelectric axis.

Recently it has been shown that with applied fields of several hundred volts per centimeter, polarization reversal with liquid-electroded BaTiO_3 crystals can be accomplished by the expansion of a few switched domains through extensive sidewise 180° domain-wall motion.^{11,12} New techniques have since been developed which permit one to reverse the direction of spontaneous polarization in BaTiO_3 with a single domain which starts out from the center of the electroded area and then expands sidewise through 180° domain-wall motion until the entire electroded region is switched. These techniques, the measurement of the sidewise 180° wall velocity as a function of the applied electric field, and conclusions based on the measured field dependence of the wall velocity, are described in this paper.

THE METHOD

Very clear crystal plates with extremely good smooth surfaces are selected from material grown by the Remeika method.¹³ The selected samples are mounted in a jig and dimples 2.5×10^{-2} cm in diameter are sand blasted in a large area surface of the crystal plates. The depth of the dimple is made equal to about one third of the sample thickness. Following this, the samples are etched in concentrated H_3PO_4 at 155°C for 10 to 20 min, rinsed in distilled water, alcohol, and dc-poled in water. The crystals which then appear free of a domains and imperfections (other than the dimple)

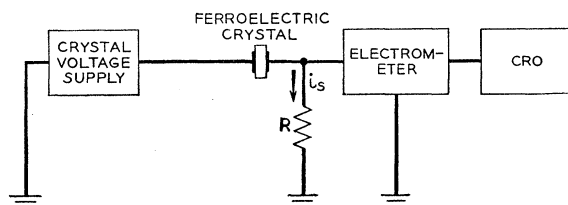


FIG. 2. Block diagram of the circuit used to measure the BaTiO_3 switching current, dP/dt , as a function of time.

¹¹ R. C. Miller, Phys. Rev. **111**, 736 (1958).

¹² R. C. Miller, Bull. Am. Phys. Soc. Ser. II, **3**, 99 (1958).

¹³ J. P. Remeika, J. Am. Chem. Soc. **76**, 940 (1954).

over an area somewhat larger than the electrode area employed, 0.1 cm in diameter, are selected for experimentation. The sample to be measured is mounted in a liquid electrode holder¹¹ so that the resultant configuration is as shown schematically in Fig. 1. The electrolyte used in these experiments was a saturated aqueous solution of LiCl at room temperature.

With the arrangement shown in Fig. 1, the dimpled area is a region of high electric field compared with the surrounding region, and hence the dimpled area would be expected to switch more easily than other regions. Provided no domains nucleate outside the dimpled area, and sidewise 180° wall motion occurs more easily than nucleation of new domains, the crystal should switch by the expansion of a single domain growing out from the dimpled area. Observations of the switching

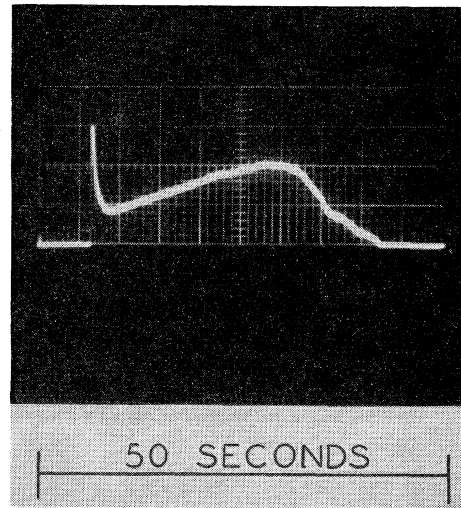


FIG. 3. Typical switching transient, i_s versus t , for a dimpled sample of BaTiO_3 which undergoes polarization reversal with a single domain that grows out from the dimple through sidewise 180° domain-wall motion. The constant voltage is applied at the start of the cathode-ray oscilloscope sweep. However, polarization reversal does not start until a few seconds later.

current and the c -domain configuration on partially switched samples show that the crystals do indeed switch in the manner just described.

A block diagram of the circuit used to measure the switching current, i.e., dP/dt , as a function of time is shown in Fig. 2. The crystal voltage supply can be cycled plus and minus automatically, or it can be used as a voltage source of variable magnitude and length. The signal across the resistor R is fed into an electrometer whose output is observed on a cathode-ray oscilloscope which is equipped with a camera for recording the switching current i_s as a function of time. Figure 3 shows the type of switching transient obtained with a dimpled sample which undergoes complete polarization reversal with one domain expanding out from the dimpled area. The constant voltage to switch the crystal was applied at the time the cathode-ray oscil-

lescope sweep began but polarization reversal did not start immediately. This delay is observed with many crystals and is termed a "time lag." The time lag may be many minutes long after which the crystal will switch completely in a time which is characteristic of the magnitude of the applied field. When polarization reversal begins, the dimpled region switches rapidly and gives rise to the initial peak in i_s after which the current decreases as the wall expands out to the thicker portion of the crystal. Then i_s increases linearly with time (the switched area enlarges proportional to t^2) as the domain expands in two directions with uniform velocities in each direction. When the domain grows out to the electrode periphery, the switching current

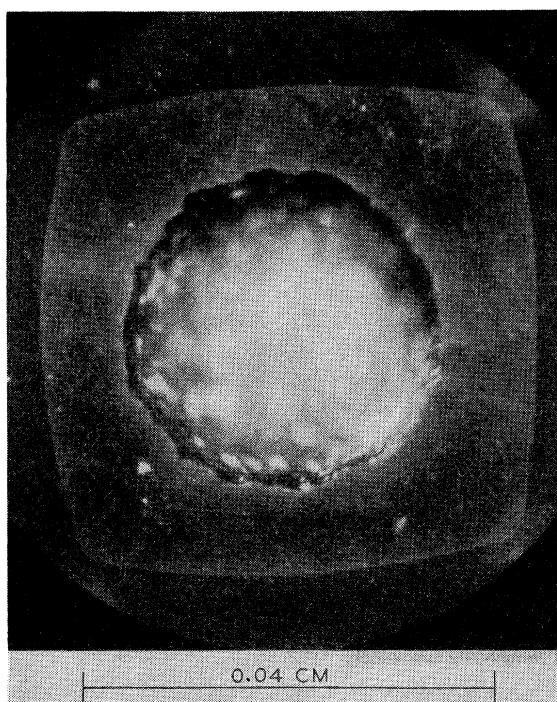


FIG. 4. Photomicrograph of the single switched domain observed on a partially switched dimpled sample of BaTiO₃. The sand blasted dimple is clearly visible in the center of the domain.

decreases and finally goes to zero as the entire liquid-electroded region is switched.

Figure 4 shows a photomicrograph of the c -domain configuration of a sample which switched in the above fashion and which had the applied field of 320 v cm^{-1} removed before the growing domain reached the circular electrode periphery. To observe the c -domain pattern, the sample is removed from the electrode holder and etched in a 0.5% HF aqueous solution for 15 to 20 sec,¹⁴ after which, the c -domain pattern can be observed with a microscope by reflected light. Throughout this paper the term "HF-etched" will be used for the etching operation just described. The acid etch tech-

¹⁴ G. L. Pearson and W. L. Feldmann (to be published).

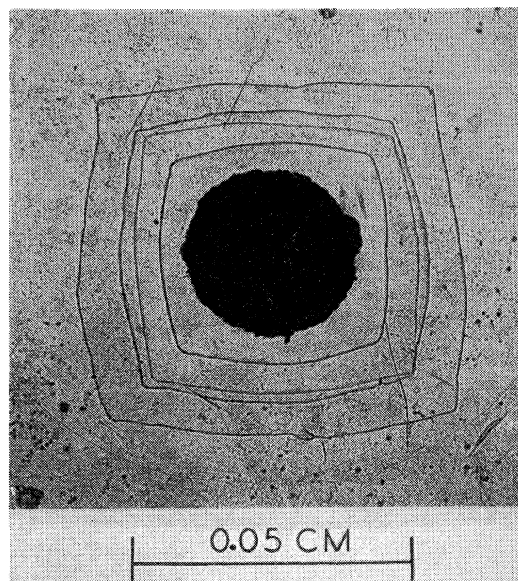


FIG. 5. Photomicrograph of a dimpled BaTiO₃ sample which has been partially switched and etched, four times. The four concentric squares demonstrate that the single domain grows as an expanding square. Different lighting conditions are responsible for the different appearance of the domains shown in Figs. 4 and 5.

nique for delineating c -domain configurations has been used by others,¹⁵⁻¹⁸ but different etchants were employed. One advantage of the present etchant over others is that the samples can be re-etched in H₃PO₄ at 155°C to remove most of the HF pattern and then used again. The dimple is visible in Fig. 4 and is in the center of the domain which is roughly square in shape but has blunted corners. The long sides of the domain make an angle of approximately 45° with the crystalline a axes. Figure 5 shows a photomicrograph of a dimpled sample which was partially switched, and HF-etched, four times. Outlines of the four domains, concentric squares, are clearly visible. The lighting used to take the photomicrograph shown in Fig. 5 was different from that used in Fig. 4, and hence the different appearance of the domains in the two figures.

Every dimpled sample does not undergo polarization reversal in the manner just described. In some instances, a dimpled crystal will switch by the expansion of single domain which nucleates outside the dimpled area. This behavior is easy to detect electrically for the switching transient will have a peak in it as the domain wall passes rapidly through the dimpled area. An example of this behavior is shown in Fig. 6.

DETERMINATION OF THE WALL VELOCITY

In the following analysis it will be assumed that the expanding domain is always square once it has grown

¹⁵ J. A. Hooton and W. J. Merz, *Phys. Rev.* **98**, 409 (1955).

¹⁶ D. Kontoleon and J. Tomlinson, *Metal Progr.* **69**, 98 (1956).

¹⁷ D. P. Cameron, *IBM J. Research Develop.* **1**, 2 (1957).

¹⁸ R. C. DeVries and J. E. Burke, *J. Am. Ceram. Soc.* **40**, 200 (1957).

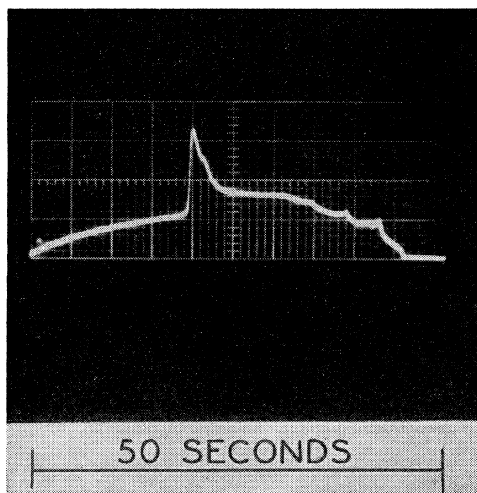


Fig. 6. A plot of i_s versus t for a dimpled sample of BaTiO_3 which undergoes polarization reversal with a single domain that nucleates outside the dimpled area. The peak in i_s occurs as the wall moves into the dimpled region which then switches rapidly.

to a size somewhat larger than the dimpled area. If it is assumed the domain is circular rather than square, the calculated wall velocities will be changed by a constant factor, namely 10%, so that the shape is not critical. It is important only that the shape remain constant during the measured portion of its growth, which is a condition easy to attain as can be seen from Fig. 5. In the region where i_s versus t is linear, i.e., the domain is square in shape, the wall velocity v is related to the switching current by

$$v = i_s / 16P_s x. \quad (1)$$

In this expression, P_s is the spontaneous polarization of BaTiO_3 (2.6×10^{-5} coulomb cm^{-2}),¹⁹ and $2x$ is the length of one side of the square domain. The quantity x is calculated from the integrated switching current,

$$x = \left[\frac{1}{8P_s} \int_0^t i_s dt \right]^{\frac{1}{2}}. \quad (2)$$

Therefore, the measurement of i_s during all the time that an electric field is on the sample enables one to calculate v . It is assumed that the conditions of the experiment are such that the ratio of the rate at which electrical energy is required to move the domain walls, to the rate at which energy is required to increase the amount of domain wall present, is large. If this condition is not satisfied, Eqs. (1) and (2) will still be valid, but the wall velocity will depend on x as well as on the electric field. This ratio is $2EP_s x / \sigma_w$, where σ_w is the wall energy per unit area. If one uses the largest theoretical estimate of the wall energy,¹ 10 ergs cm^{-2} , and assumes conditions similar to those encountered

in these experiments, i.e., $E = 300$ v cm^{-1} and $x = 2 \times 10^{-2}$ cm, this ratio turns out to be about 300, so the condition is satisfied.

To obtain the wall velocity as a function of the applied field, the initial field which starts the crystal switching is removed early in the linear portion of i_s versus t . Then i_s is measured for different fields which are applied to the sample in the form of voltage pulses a few seconds long. After the data are taken, the sample is removed from the liquid electrode holder, HF-etched and the c -domain configuration observed to make certain the crystal had been switching in the desired manner. If the crystal was well behaved, Eqs. (1) and (2) are then used to calculate v as a function of the applied field.

Measurements are not usually attempted for fields larger than about 350 v cm^{-1} since it is found that one may introduce additional domains if the applied field becomes too large. Data for fields higher than about 350 v cm^{-1} are obtained using different techniques and will be presented in a future paper. Data on the low-field side are limited to fields somewhat higher than those for which conduction currents through the sample and through the liquid electrode holder structure become comparable to the current which arises from the wall motion.

RESULTS AND DISCUSSION

Data for samples 1(II), 6(II), and 7(I) are shown in Fig. 7 in which $\log v$ is plotted versus the reciprocal of the applied electric field. Sample 1(II) was grown from a melt which contained 0.1 mole % AgNO_3 , while samples 6(II) and 7(I) were grown from a melt which contained 0.02 mole % Fe_2O_3 . These crystal lots were not grown explicitly for this research, but came from a large number of existing lots some of which had a good number of high-quality specimens suitable for these experiments. As can be seen from Fig. 7, there is some evidence that impurities affect the domain-wall motion, though information of this type is very meager. Most of the data are fitted by an expression of the type

$$v = v_\infty \exp(-\delta/E), \quad (3)$$

in which v_∞ and δ are independent of the applied electric field E over a large fraction of the range measured. The measurements have been extended to over three decades of wall velocity. With the exception of lowest field points, the data shown in Fig. 7 are described by an expression of the type given in Eq. (3). The lowest field point, or points, frequently lie above a straight line extended from the higher field data. The uncertainties connected with the very low-field measurements are in general sufficiently large to bring many of these points into agreement with the other data; however, since these very low-field points always lie on or above the extrapolated data, they appear to represent a deviation from Eq. (3).

¹⁹ W. J. Merz, Phys. Rev. **91**, 513 (1953).

Table I gives values of δ and v_∞ obtained for a number of samples. In cases where the sample was measured more than once, the operations involved between measurements are indicated. The HF etch used to delineate the c -domain configuration seems to have little, or perhaps no, effect on the results. There is no indication in the data shown that there is a marked thickness dependence of the wall velocity. The impurity content of the material seems to influence the wall motion as there appears to be a meaningful difference between the results for the two lots of material used. No chemical analyses were performed on the materials under consideration, so that only the impurity content added to the melt is known.

It might be thought that sample and/or electrode holder conductivity are responsible for the deviation of the low-field results from Eq. (3); however, experimental attempts to measure the conductivity of the holder and sample ensemble indicate a conductivity about one order of magnitude too small to account for the observed deviations. The measured areas of the single domains observed on partially switched samples

TABLE I. A summary of some of the experimental results on 180° domain-wall velocity, v , in BaTiO₃ as a function of the applied electric field, E . The experimental data for $v \geq 10^{-6}$ cm sec⁻¹ have been fitted by an equation $v = v_\infty e^{-\delta/E}$. Values of v_∞ and δ obtained in this fashion for a number of samples are given in the table.

Sample	10 ³ × thickness cm	v_∞ cm sec ⁻¹	10 ⁻³ × δ v cm ⁻¹
1(I) ^a	1.4	2.0	2.2
1(II) ^{a,b}	1.4	0.7	1.9
1(III) ^{a,b}	1.4	1.3	2.0
2(I) ^a	1.6	3.0	2.4
2(II) ^{a,b}	1.6	4.5	2.6
2(III) ^{a,c}	1.1	3.6	2.7
2(IV) ^{a,b}	1.1	4.5	2.8
3 ^a	1.1	9.1	2.8
4 ^d	2.2	7.8	3.2
5 ^d	1.9	18	3.5
6(I) ^d	2.0	30	3.6
6(II) ^{d,e}	1.9	68	3.9
7(I) ^d	2.0	55	3.9
7(II) ^{d,e}	1.9	35	3.8

^a Crystals grown from melt which contained 0.1 mole % AgNO₃.

^b Same sample as the one listed above it except for HF etch employed after previous partial switch.

^c Same sample etched in H₃PO₄ at 155°C and measured at a new location.

^d Crystals grown from melt which contained 0.02 mole % Fe₂O₃.

^e Same sample as the one listed above it, but etched in H₃PO₄ at 155°C and measured at same location.

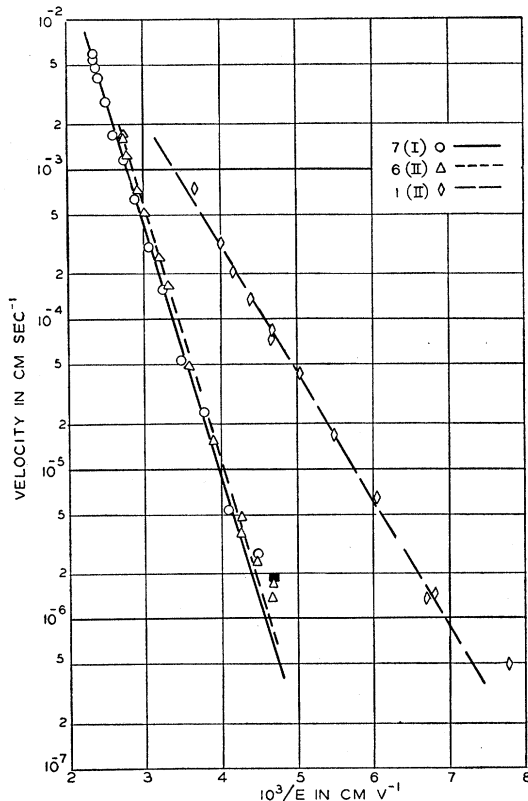


FIG. 7. A plot of the logarithm of the sidewise 180° wall velocity versus the reciprocal of the electric field for three BaTiO₃ samples. Samples 7(I) and 6(II) were grown from a melt which contained 0.02 mole % Fe₂O₃, while the melt from which sample 1(II) was grown contained 0.1 mole % AgNO₃. The point indicated by a solid black square is a single wall-velocity measurement on sample 6(II) which was determined by a different method than the other experimental points shown.

agree to within the experimental uncertainties, $\pm 3\%$, with the area calculated from $(2P_s)^{-1} \int_0^t i_s dt$, where t includes all the time during which polarization reversal takes place. However, in the usual experiment, the contribution to the switched area of $\int i_s dt$ due to low-field polarization reversal is very small so that agreement of the two areas under consideration cannot be interpreted as evidence that the very low-field electrical data give rise to meaningful wall velocities.

In order to check the low wall velocity data, another measurement technique was used in the case of sample 6(II). First, the normal type of data were taken, i.e., i_s was measured as a function of the electric field. Following the last measurement of i_s , a field of 214 v cm⁻¹ was left on the sample for one hour, after which the sample was removed from the holder and HF-etched. From the difference between the size of the single domain measured on the etched sample, and that calculated with Eq. (2) from the i_s measured prior to the application of the field for one hour, a wall velocity was obtained. The point determined in this manner, along with the values of v calculated from the i_s versus E data, are shown in Fig. 7. These results show that wall velocities obtained by the two different methods agree to within the experimental uncertainties involved. Additional measurements of the two types just described are in progress in a still lower field region than that considered above, a region where the data obtained in the usual fashion are suspect due to conductivity effects mentioned before.

Problems connected with liquid electrode stability make measurements of the wall velocity as a function of temperature somewhat difficult so that very little

data at temperatures other than room temperature have been obtained. In the case of one sample, the wall velocity was measured for a single value of E at 30°C above room temperature and it was found that the high temperature velocity was two orders of magnitude larger than that measured with the same field at room temperature. Hence, on the basis of this one experiment there seems to be a pronounced temperature dependence of the wall velocity.

As mentioned earlier, there are very few data in the literature with which the present results can be compared. All other experimental investigations, two of forward wall motion¹⁻³ and one of sidewise wall motion,^{4,5} indicate that the measured wall velocity $v \propto E - E_0$ where E_0 is a coercive field. The sidewise wall motion was measured on Rochelle salt by Mitsui and Furuichi (hereinafter referred to as MF), who found that the sidewise wall velocity is described by

$$\gamma v = 2P_s(E - E_0), \quad (4)$$

in which γ and E_0 are structure sensitive parameters. As an example of the magnitude of MF's results, with E equal to 80 v cm⁻¹, v is about 10⁻¹ cm sec⁻¹ at 18°C. The present data will not fit an expression like Eq. (4) unless γ and E_0 vary with E in some drastic manner. It should also be noted that in some cases the motion of magnetic domain walls is described by the analogous magnetic expression equivalent to Eq. (4).²⁰ MF determined their wall velocities from measurements of the position of the domain wall as a function of time as the wall moved from one trapped position to another. This domain-wall motion is characterized by a large velocity as the wall breaks away from its trapped position which then decreases uniformly as it approaches the new trapped position at which point $v=0$. These wall jumps correspond to volumes of 5×10^{-6} cm³ to 10^{-4} cm³ which reverse polarization in times equal to a few tens of milliseconds. The wall velocities reported by MF were those calculated for the wall as it breaks away from its initial trapped position where the velocity is large, and not an average velocity for the wall as it moves between trapped positions. In the present data, it is clear that the measured quantity is an average wall velocity. There is no indication that the 180° BaTiO₃ domain-wall motion is discontinuous on the same scale as in the case of Rochelle salt. In fact, with the aid of observations with Barkhausen pulse measuring equipment^{9,11} it can be stated that discontinuous wall jumps in times of the order of 10⁻² sec or less, involving volumes 10⁻¹¹ cm³ or larger, do not occur in the present experiments. This limit is set by the characteristics of the measuring equipment. Also, there is no direct experimental evidence in the present work of a coercive field E_0 for

the sidewise wall motion. If it is assumed that a coercive field would enter the experimentally determined wall velocity expression as $v = v_\infty \exp\{-[\delta/(E - E_0)]\}$ and that this expression is valid in the lowest field range measured, then E_0 , if it exists, is probably less than something like 40 v cm⁻¹. Therefore, all the evidence indicates that 180° domain-wall motion in BaTiO₃ is quite different from that observed in Rochelle salt. This is perhaps not too surprising since many characteristics of the two materials under consideration are known to be different.⁶

Kittel²¹ has proposed an equation of motion for the 180° domain wall in BaTiO₃ which is similar to that used for a ferromagnetic domain wall,²⁰ namely

$$m_w \ddot{x} = 2P_s E - \beta \dot{x} - \eta x, \quad (5)$$

in which m_w is the effective mass of a unit area of the wall, $\beta \dot{x}$ is a viscous damping term, and ηx is the restoring force which acts on the wall due to its location in some local potential minimum. Kittel has pointed out that high-frequency dielectric constant measurements on polycrystalline BaTiO₃ do not show a resonance behavior as would be expected from Eq. (5), but this may have been absent due to "a combination of frictional effects and spread in domain widths." In any event, Kittel does not confirm nor disprove the validity of Eq. (5) for small amplitude 180° wall motion.

For large amplitude motion in which $m_w \ddot{x}$ is negligible, ηx can be replaced by a term which is related to the height of the potential minimum and independent of x ; such a term would serve to reduce the effect of the applied field, that is,

$$\beta \dot{x} = 2P_s(E - E_0), \quad (6)$$

in which E_0 is a coercive field. The Rochelle salt wall-velocity data^{4,5} are described by an expression of this type. The present results show that Eqs. (5) and (6) with β and E_0 field independent, do not correctly describe the large-amplitude BaTiO₃ 180° wall motion; and therefore, it is not evident that any resonance effects in the dielectric measurements due to wall oscillation should be expected.

Landauer, Young, and Drougard²² have suggested that the well-known $e^{-\alpha/B}$ dependence of the switching of BaTiO₃ may be due to domain expansion rather than nucleation as originally proposed by Merz.¹ It will be shown that at least part of the $e^{-\alpha/B}$ dependence can be explained by the field dependence of the wall velocity given in this paper. The $e^{-\alpha/B}$ dependence of the switching of BaTiO₃ refers to the manner in which the maximum value of the switching current, i_{\max} , and the time, τ_s , for all but a small fraction of the electroded

²⁰ For a general discussion of magnetic domain-wall motion, the reader is referred to the following review article: C. Kittel and J. K. Galt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 3.

²¹ C. Kittel, *Phys. Rev.* **83**, 458 (1951).

²² Landauer, Young, and Drougard, *J. Appl. Phys.* **27**, 752 (1956).

area to switch, vary with the applied field. Experimentally it has been shown² that i_{\max} and τ_s vary with E in the following manner:

$$i_{\max} = i_{\infty} e^{-\alpha/E} \quad (7)$$

and

$$\tau_s = \tau_{\infty} e^{\alpha/E}. \quad (8)$$

The above relations are obeyed in the lowest field range measured by Merz which is in the neighborhood of several thousand volts per centimeter. Making use of arguments presented in detail by Chynoweth,⁹ it can be shown that with random nucleation and rapid forward growth through the thickness direction, followed by sidewise domain-wall motion in two directions, one has

$$i_{\max} \propto v k^3 \quad (9)$$

and

$$\tau_s^{-1} \propto v k^3. \quad (10)$$

In these expressions v is the sidewise domain-wall velocity and k is the nucleation probability which is defined by

$$dN/dt = k(N_0 - N), \quad (11)$$

where N is the number of nucleated sites and N_0 is the total number of nucleation sites. As will be discussed in more detail later, the nucleation probability is usually assumed to have the form $k \propto e^{-\kappa/E}$. Therefore, since $v \propto e^{-\delta/E}$, the theoretical expressions for i_{\max} and τ_s^{-1} are proportional to $\exp[-(\delta + 3\kappa/2)/E]$, which is in agreement with the electrical studies of Merz. In the absence of data on the field dependence of the sidewise wall motion, Chynoweth⁹ assumed $v \propto E$ and did not obtain theoretical expressions for both i_{\max} and τ_s like those given in Eqs. (7) and (8). The values of δ found in the present work are approximately one third the value of α given by Merz, so that $\kappa \approx \alpha/2$. It has been assumed in the analysis which leads to Eqs. (9) and (10) that kt is large compared with unity, which means that the nucleations are essentially over before the time at which i reaches its maximum value. If kt is assumed to be small compared with unity for times as long as τ_s , that is, for only a small fraction of the N_0 sites nucleated, then one finds that the right-hand sides of Eqs. (9) and (10) become $v^3 k^3$. Thus for $kt \ll 1$, i_{\max} and $\tau_s^{-1} \propto \exp[-(2\delta + 4\kappa)/3E]$ which also agrees with the work of Merz; and now for $\delta \approx \alpha/3$, α is approximately equal to κ . It should be emphasized that δ is determined from low-field wall velocity measurement on liquid-electroded crystals whereas α was obtained from high-field switching studies on metal-electroded crystals. In any event, it seems reasonable that some power of $e^{-\delta/E}$ will appear in the theoretical expression for i_{\max} and τ_s^{-1} due to the observed field dependence of the sidewise wall motion. More experimentation is

required to determine just what fraction of the Merz α comes from the field dependence of the 180° wall velocity.

It has been shown^{1,9} that a nucleation probability k of the form

$$k \propto e^{-\kappa/E} \quad (12)$$

would be expected for a nucleus of such a shape that the depolarizing field can be neglected in the expression for the change in free energy on the formation of a nucleus. The question arises as to whether the sidewise domain-wall motion investigated in this research, $v \propto e^{-\delta/E}$, is due to motion of the wall parallel to itself, or to nucleations adjacent to the wall which govern the rate of domain growth and which have nucleation probabilities per unit length of domain wall of the form given in Eq. (12). If the wall motion is indeed controlled by nucleations adjacent to an existing wall, one might ask why nucleations should be favored close to a wall. There are several reasons why nucleation may be easier very close to an existing wall over points far removed from a wall. It might be possible for nucleations to take place adjacent to a wall in such a way that less new domain wall has to be created than for nucleations in completely unswitched environments, which if true, would favor nucleations close to an existing wall. Also, there is quite a bit of evidence^{1,8,11,17} that the 180° domain walls are not parallel to the c axis but at some angle θ to the c axis. Even though a slanted wall probably has a larger energy per unit area than a wall parallel to the c axis due to an additional electrostatic field energy term in the former, a slanted wall might be easier to move through a nucleation mechanism than a wall which is parallel to the c axis. For example, on the unswitched side of a slanted wall, a field which arises from the divergence of the polarization at the wall, $2P_s \sin\theta$, will have a component in the direction of the applied electric field. This enhanced field if sufficiently large should favor nucleation at points adjacent to a slanted wall over nucleations in regions beyond the influence of this additional field. At this time, it is not possible to say whether the wall moves as a unit parallel to itself or in an irregular fashion due to many nucleations at points very close to the wall.

SUMMARY

It has been shown that polarization reversal in single-crystal BaTiO₃ can be accomplished with liquid-electroded samples by the nucleation and subsequent growth through 180° domain-wall motion of a single domain. The single domain can be made to nucleate at a predetermined location on the crystal. The rate of expansion of the single domain has been measured as a function of applied electric fields in the range of several hundred volts per centimeter and it is found that the 180° domain-wall velocity is described by $v = v_{\infty} e^{-\delta/E}$

for over three decades of velocity. The measured dependence of the wall velocity on the electric field can be shown under certain conditions to be consistent with the well-known $e^{-\alpha/E}$ switching dependence of BaTiO₃. A nucleation mechanism for the wall motion is suggested by its field dependence, and the field dependence rules out the equation of motion usually applied to domain boundaries.

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Surface Transport Theory

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A theory is presented for the dependence of the galvanomagnetic parameters on the surface potential of a semiconductor. The expression for the conductivity reduces to that given by Schrieffer when the magnetic field is zero. Formal equations for the magnetoconductivity and Hall coefficient are derived. By using a constant relaxation time, and a linear space charge region potential, one can obtain closed-form expressions for the conductivity effective mobility and the Hall effective mobility. The Hall mobility is found to be 13% smaller than the conductivity mobility for large values of the surface potential.

INTRODUCTION

IN a recent paper, Petritz¹ derived a set of expressions for the Hall coefficient and magnetoresistance which depend on the surface potential of a semiconductor. His derivation was based on an unbounded solution of the Boltzmann equation. As a result, the expressions do not explicitly describe the surface potential dependence. In an earlier paper, Schrieffer² derived a formal expression for an effective conductivity mobility from a diffuse-scattering boundary condition on the solution of the Boltzmann equation. In this paper, we extend the problem to include the presence of a magnetic field. Formal expressions are found for the magnetoconductivity and Hall coefficient as functions of surface-dependent terms. By using a linear potential in the space-charge region we can evaluate the appropriate integrals for these terms when the relaxation time is independent of energy. The conductivity and Hall effective mobilities are compared with each other.

GENERAL THEORY

We shall follow the general procedure used by Schrieffer. The Boltzmann equation is assumed to have a relaxation time τ in the collision term³ so that

$$\mathbf{v} \cdot \text{grad}_v f + \mathbf{a} \cdot \text{grad}_v f = (f_0 - f)/\tau, \quad (1)$$

where f is the distribution function for the electrons

in the specimen and f_0 is their equilibrium distribution. We let

$$f = f_0 + f_1, \quad (2)$$

where f_1 is the perturbation function. Spherical energy surfaces are assumed so that the equilibrium distribution function is given by

$$f_0 = C \exp \left\{ -\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT} + \frac{q\psi(z)}{kT} \right\}. \quad (3)$$

The accelerations in the various directions are

$$\begin{aligned} a_x &= -q(E_x + v_y H)/m, \\ a_y &= -q(E_y - v_x H)/m, \\ a_z &= -qE_z(z)/m. \end{aligned} \quad (4)$$

We assume that the magnetic field is in the z direction and is constant in magnitude. Introducing Eqs. (2), (3), and (4) into Eq. (1) and neglecting products of $f_1 E_x$ and $f_1 E_y$, we obtain

$$\begin{aligned} v_z \frac{\partial f_1}{\partial z} - \frac{qE_z}{m} \frac{\partial f_1}{\partial v_z} - \frac{qH}{m} \left(v_y \frac{\partial f_1}{\partial v_x} - v_x \frac{\partial f_1}{\partial v_y} \right) \\ + \frac{f_1}{\tau} = -\frac{qf_0}{kT} (E_x v_x + E_y v_y). \end{aligned} \quad (5)$$

By Lagrange's method, we obtain a particular solution of Eq. (5):

$$\epsilon = \frac{1}{2} m v_z^2 - q\psi(z). \quad (6)$$

¹ R. L. Petritz, *Phys. Rev.* **110**, 1254 (1958).

² J. R. Schrieffer, *Phys. Rev.* **97**, 641 (1955).

³ A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London, 1953).

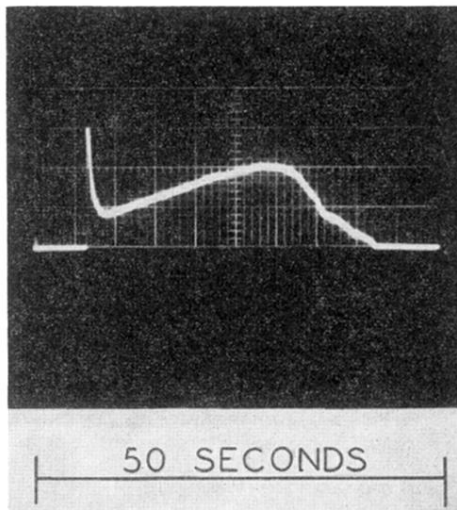


FIG. 3. Typical switching transient, i_s versus t , for a dimpled sample of BaTiO_3 which undergoes polarization reversal with a single domain that grows out from the dimple through sidewise 180° domain-wall motion. The constant voltage is applied at the start of the cathode-ray oscilloscope sweep. However, polarization reversal does not start until a few seconds later.

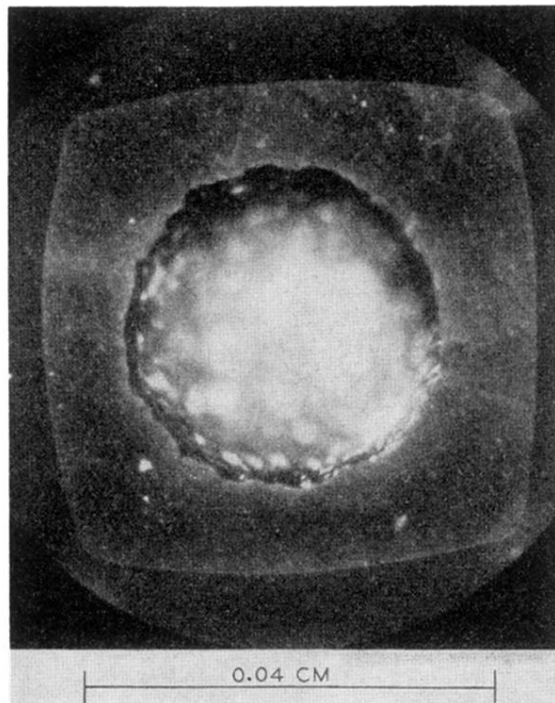


FIG. 4. Photomicrograph of the single switched domain observed on a partially switched dimpled sample of BaTiO_3 . The sand blasted dimple is clearly visible in the center of the domain.

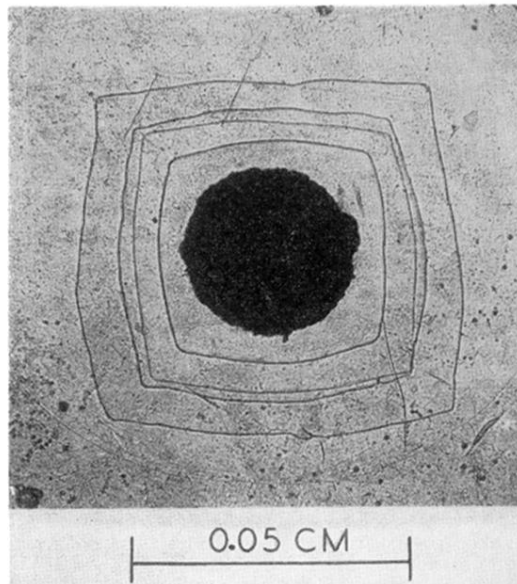


FIG. 5. Photomicrograph of a dimpled BaTiO₃ sample which has been partially switched and etched, four times. The four concentric squares demonstrate that the single domain grows as an expanding square. Different lighting conditions are responsible for the different appearance of the domains shown in Figs. 4 and 5.

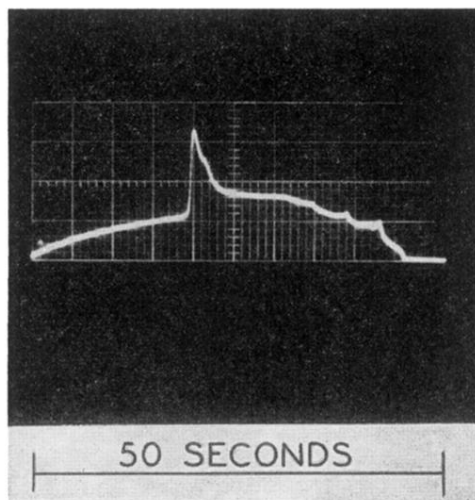


FIG. 6. A plot of i_s versus t for a dimpled sample of BaTiO_3 which undergoes polarization reversal with a single domain that nucleates outside the dimpled area. The peak in i_s occurs as the wall moves into the dimpled region which then switches rapidly.