HIGH FIELD POLARIZATION REVERSALS IN LIQUID ELECTRODED BARIUM TITANATE CRYSTALS

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Summary

The study of the polarization reversal in liquid electroded crystals of barium titanate has previously been mainly restricted to switching fields less than $1 \cdot 2$ kV/cm. This paper studies the reversal in the field range $1 \cdot 5$–6 kV/cm. For these higher fields, it is concluded, from switching current transients and " static " domain patterns, that the reversal is achieved by a small number of parallel-sided domains expanding radially sidewise at a constant velocity. All the domains appear to begin growing when the field is first applied. The cross-sectional shape of the domains varies from circular at fields greater than 3 kV/cm to square at fields less than 3 kV/cm. The number and distribution of the domain centres is determined by the surface conditions of the crystal, where the electrodes are situated, and not by the applied field.

By the use of a specially developed algebraic analysis it is found possible to calculate directly from certain types of current transients the number of domains involved in the reversal, their cross-sectional shape, and their sidewise velocity. The calculated results show that the velocity v has a field E dependence of the form $v \sim \exp(-\delta/E)$. This confirms earlier low field measurements and indicates that some type of nucleation mechanism is involved in the wall movement. If the E dependence of the switching time, t_s, is measured simultaneously with v, it is found that $t_s \sim \exp(\alpha/E)$ with α having a numerical value approximately equal to δ.

To allow further study of the reversal a computer program was developed for calculating the current transients resulting from any specified arrangement of domain centres within the electrode boundary. The computed results show the large effect the domain configuration can have on the transient shape. In those cases where the computed and the experimentally obtained transients can be related, a further method is available for calculating the domain wall velocity.

I. INTRODUCTION

Initially it was thought (Merz 1954; Little 1955) that the polarization reversal in single crystals of barium titanate was achieved by the growth through the thickness of the crystal of a very large number of surface-nucleated spike domains of reversed phase. More recently, Miller and Savage (1958, 1959, 1960), using liquid and semitransparent metal electrodes, have demonstrated most conclusively that for switching fields in the range $0 \cdot 1$–$1 \cdot 2$ kV/cm, the polarization reversal is accomplished by the extensive 180° sidewise expansion of a few domains. Also from their measurements they have been able to deduce that the velocity v of the domain wall has a field E dependence of the form, $v = v_\infty \exp(-\delta/E)$, where the constants v_∞ and δ are only slightly field dependent.

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The work described in this paper is concerned with a study of the polarization reversal in barium titanate, using liquid electrodes and high switching fields (1·5–6 kV/cm). It forms an extension of the low field observations made by Miller and Savage. Because the domain wall velocity increases rapidly with field, Miller and Savage's technique of directly viewing the motion of the anti-parallel domains during a reversal is, unfortunately, limited to switching fields of less than about 1 kV/cm. In this work, the domain motion under high fields was observed by means of a series of " static " domain patterns obtained after partially switching the crystal by varying amounts. By studying these patterns in conjunction with the switching current transients, a clear picture of the mechanism of the polarization reversal was obtained. Based on this mechanism, a simple algebraic analysis was derived for calculating directly from certain types of current transients some of the properties of the switching domains. To permit a more complete analysis of the reversal, the algebraic model was extended by means of a computer program. Finally, the experimentally observed and the calculated results were used to determine the most probable mechanism for the movement of the domain walls.

II. METHOD

The experimental arrangement was similar to that used by Miller (1958). The liquid electrodes were formed by two drops of aqueous lithium chloride solution positioned between the crystal and 1 mm diameter platinum rods.

The switching current transients were measured by the conventional technique (Merz 1956, and others) of photographing on an oscilloscope screen the voltage developed across a small resistance in series with the switching crystal. The switching field was applied in the form of a single positive voltage pulse obtained from a variable amplitude, variable width pulse generator. For obtaining complete switching transients, the pulse width was kept constant at 180 μs, i.e. a time greater than the switching times for the 1·5–6 kV/cm field range. Because the switching transients in opposite directions were usually slightly different, a series of measurements were always made in the one direction. In between measurements, the direction of polarization was reversed by a field of −5 kV/cm being applied for 5 s.

The " static " domain patterns were obtained at various stages of the switching process. The partial switching was achieved simply by applying to the crystal a pulse, whose width was a fraction of that required for complete switching at the field under consideration. Both the acid etching (Hooton and Merz 1955) and the charged powder (Pearson and Feldmann 1959) techniques were used for producing the " static " domain patterns. It was found that, whilst the acid etching produced a sharp delineation of the domain boundary, the charged powder technique did not destroy the surface conditions of the crystal. Thus, the charged powder technique has the important advantage that, after obtaining one domain pattern, it is possible to reapply the liquid electrodes and continue the switching a further stage by means of the partly grown domains. In this way the growth of an individual domain can be studied.

III. Experimental Results

With evaporated metal electrodes the switching current transient always has a characteristic smooth-humped shape. By comparison, it was found that with liquid electrodes there was no one distinctive shape for the current transient. Furthermore, it was observed that, instead of a smooth curve, the current
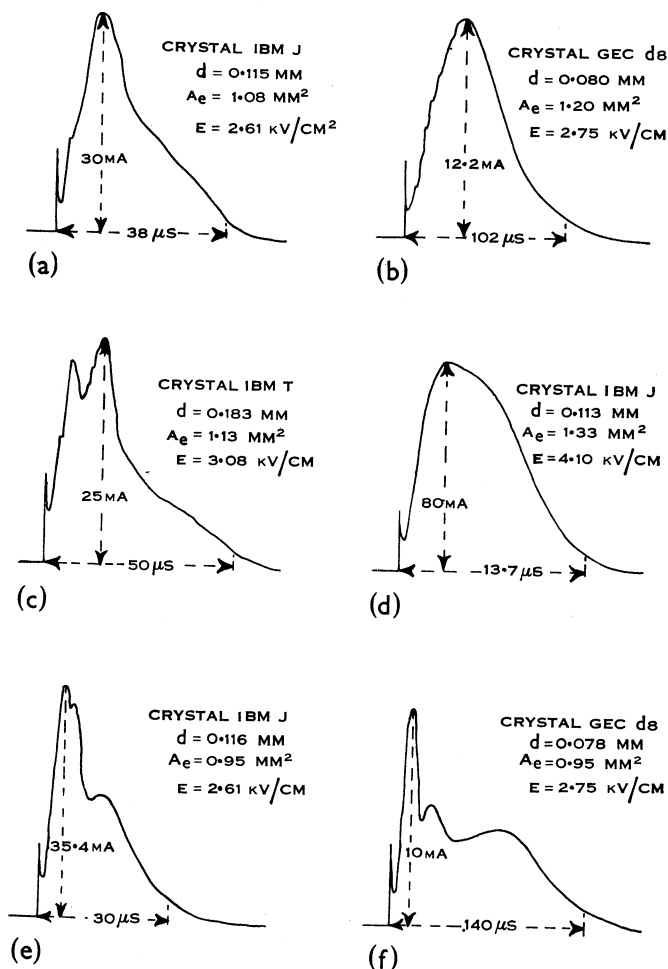

Fig. 1.—Some representative switching current transients obtained with liquid electrodes and high fields. For each of the photographed transients the following details are specified : the current and time dimensions, the crystal from which the transient was obtained, the thickness d of the crystal where the electrodes were located, the electrode area A_e, and the switching field E used.

transient was characterized by discontinuities of varying size, shape, and number. Figures 1 and 2 are tracings of some photographed current transients obtained with liquid electrodes and switching fields in the range 1·5–6 kV/cm. It was observed that the shape of the transient, in addition to varying from crystal to crystal, also varied when the electrodes were placed on different parts of the

same crystal. However, it was found that with the electrodes in any one particular position, the switching transients, due to fields ranging from 1·5 to 6 kV/cm, if scaled to unit height and length, were very nearly identical. The only observed difference, and even this did not apply to all crystals, was that as the field decreased additional minor " bumps " or discontinuities appeared in the transient.

Within the field range investigated, the switching time, t_s (defined as the time for the current transient to fall to 0·1 of its maximum value) was found to vary with the field E according to the empirical expression, $t_s = t_\infty \exp (\alpha/E)$. Merz (1954) and Peacock (1959) have shown that the same relation applies for metal electroded crystals. However, it was observed that under similar con-conditions and with the same applied E, t_s with liquid electrodes was anything from 4 to 30 times greater than with metal (evaporated silver) electrodes.
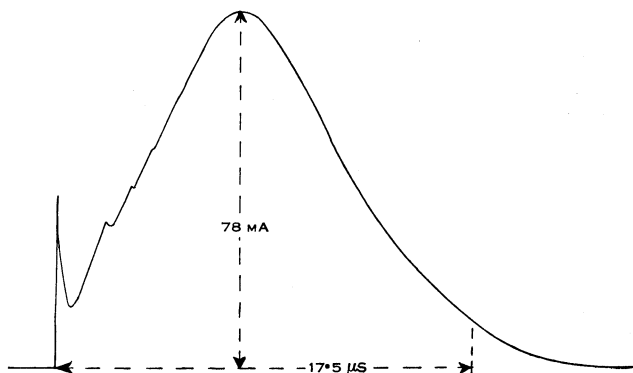

Fig. 2.—A switching current transient obtained from crystal IBM B using liquid electrodes and a field of 3·39 kV/cm. The area of the electrodes was 1·33 mm² and the thickness of the crystal where the electrodes were located was 0·090 mm.

Also, with liquid electrodes, it was not unusual to find a 15% variation in the switching transients in opposite directions with the same field. By comparison, with metal electrodes these differences were usually limited to less than 5%.

Similar to metal electroded switching, it was found with liquid electrodes that both the switching and the non-switching transients always commenced with a small " spike ". Peacock (1959) has shown that the size and shape of this spike corresponds to the charging of the circuit capacities. Since this explanation appears to be correct (Burfoot 1959), this " spike " is neglected in the algebraic and numerical treatments of the polarization reversal given below.

The " static " domain patterns revealed that for high field switching with liquid electrodes the polarization reversal is accomplished by a relatively small number of domains of reversed phase expanding radially sidewise until the complete electroded area is covered.

From acid etch patterns of the type shown in Figure 3, it can be calculated that the walls of the expanding domains are no more than 0·25° out of parallel

with the c axis of the crystal.   Peacock (1959) by comparison has observed that for domains of diameter less than 7×10^{-4} cm, the domain walls can diverge by as much as $1 \cdot 5°$ from the vertical.   These two results are, however, not incompatible, since by the time Peacock's small slightly conical domains have grown by sidewise expansion to the size of those shown in Figure 3, the domain walls will be very nearly parallel.

A major difference between switching with liquid and metal electrodes is that with metal electrodes a large number of domains take part in the reversal (Merz 1954).   This explains why longer switching times were observed with liquid electrodes.
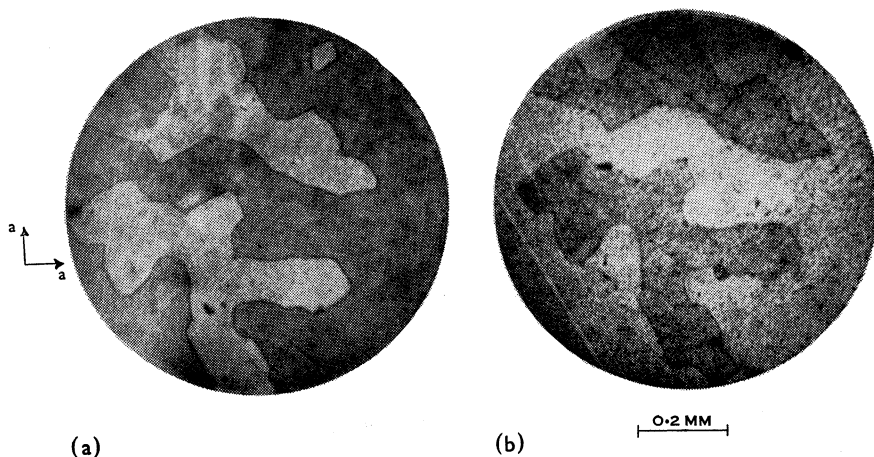

(a)   (b)

Fig. 3.—Domain etch patterns of the upper (a) and lower (b) surfaces of portion of an electroded area, which has been approximately 50% partially switched by a field of $1 \cdot 60$ kV/cm applied through liquid electrodes.   On the upper surface the growing domains are represented by the lighter areas, whilst on the lower surface they are represented by the darker areas.   There is very good correspondence between the two surfaces.   The hydrochloric acid etch patterns were obtained on crystal GEC d8, which had a thickness of $0 \cdot 079$ mm where the electrodes were located.   The total electroded area was $1 \cdot 13$ mm². The orientation of the crystalline a axes is marked alongside the upper surface.   It is thought that the lined pattern visible on the lower surface may represent collision boundaries between the growing domains.

For any particular electrode position on the crystal surface, the charged powder technique showed that for all values of field, in the range $1 \cdot 5$–6 kV/cm, the same domains take part in the switching process.   Furthermore, it was generally found that most of the growing domains were approximately the same size.   This would suggest that the majority of domains begin to grow when the field is first applied.

The discontinuities in the switching transients were found to be due to the coalescences of single domains (or groups of domains) with each other or with the electrode boundary.   By comparison, with metal electrodes, because of the large number of growing domains, coalescences between a few domains have no visible effect upon the shape of the switching transient.

It was observed that the cross-sectional shape of the expanding domains is dependent on the value of switching field used.   For fields in the range 3–6 kV/cm,

the domain shape is approximately circular (see Fig. 4). However, as the field is lowered from 3 to 1·5 kV/cm, the domains tend to become squares. From Figure 3, it can be seen that these squares are orientated in two or possibly three major directions with respect to the crystalline *a* axes. This change in the shape of the domain cross section would seem to be the explanation for the
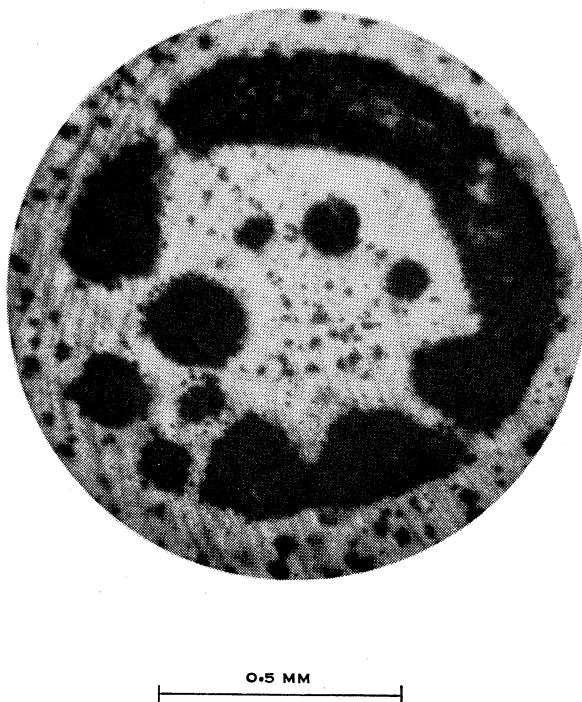

0·5 MM

Fig. 4.—A domain powder pattern of a complete electroded area, which has been approximately 50% partially switched by a field of 4·02 kV/cm applied through liquid electrodes. The darker areas, i.e. those areas indicated by the absence of sulphur, are the growing or reversing domains. The electrode boundary is clearly defined by the nearly complete dark ring just inside the edge of the photomicrograph. The pattern was obtained on crystal IBM T, which had a thickness of 0·180 mm where the electrodes were located. The total electroded area was 0·84 mm².

additional minor discontinuities that were sometimes observed in the current transient as the field was decreased. Miller and Savage (1958, 1959) have also observed, for a lower range of field, that the domain shape varies with the switching field.

IV. THE MECHANISM OF THE POLARIZATION REVERSAL

The experimental results obtained with liquid electrodes and high switching fields (1·5–6 kV/cm) confirm Miller and Savage's (1958, 1959) low field (0·1–1·2 kV/cm) observations that the polarization reversal in single crystals of barium titanate is achieved by the 180° sidewise expansion of a small number

of approximately parallel-sided domains.   Furthermore, for the high field range investigated, it was observed that, whilst the cross-sectional shape of the domains varied with the switching field used, the number and position of the domains taking part in the reversal remained constant.

Peacock (1959) has suggested that the " hair-line " nuclei from which the sidewise expansions take place are small remnant cylindrical domains from the previous switching.   Another explanation is that the application of the field causes a small number of domains to nucleate at or near the surface.   These domains then grow rapidly through the crystal forming small cylinders or truncated cones capable of subsequent radial expansion.   Although there is no direct evidence to support either theory, the results obtained with liquid electrodes indicate that the conditions of the surface where the electrodes are situated largely determine the number and location of the growing domains.   A possible reason for this is that, wherever there are surface indentations, there will be local increases in the field which will favour the nucleation and/or growth of domains. In this respect, it is interesting to note that Miller and Savage (1958), by artificially creating such " dimples ", have been able to nucleate domains in pre-determined positions.

The large differences in the shape of the current switching transients which were found to occur with liquid electrodes, can be explained in terms of the different domain configurations which result from the varying electrode surface conditions.   This effect is well evidenced in Figure 8.   There need be, for example, only a small difference in the surface conditions on the two faces of the crystal to cause the observed 15% variation between the current transients measured in opposite directions.

Miller and Savage's (1958, 1959) low field, liquid electrode measurements showed that, under a constant applied field, the sidewise domain wall motion proceeds at a constant velocity.   It seems reasonable to assume that the same type of motion occurs for liquid electrode, high field switching.   Such an assumption is verified by the fact that the partial switching transients that can be obtained with liquid electrode, high field switching can be placed together to form a " patchwork " transient which is very nearly identical with the equivalent complete switching transient.   It is interesting to note that in some recent work dealing with surface layer properties Miller and Savage (1961) have observed that initially the average domain wall velocity decreases with increasing wall displacement.   However, they observed that after the wall has moved a distance of about 2000 Å the wall velocity becomes constant.   Since the wall velocity measurements described below were made after the wall had moved distances greatly in excess of 2000 Å, the basic assumption of a constant wall velocity can still be considered valid.

As pointed out in the introduction, the original work done with metal electrodes failed to reveal any sidewise domain wall motion.   However, Burfoot and Peacock (1959) have concluded theoretically from certain experimental data that a limited amount of sidewise expansion does, in fact, occur.   This, together with Miller and Savage's (1960) low field observations with semi-

transparent metal electrodes, suggests that, although with metal electrodes the sidewise motion is restricted (probably because of non-uniformities in the electrical contact), the mechanism for the reversal is basically the same as with liquid electrodes.

V. ALGEBRAIC TREATMENT OF THE POLARIZATION REVERSAL

The mechanism for the polarization reversal discussed above allows an algebraic analysis to be made of those current transients which have clearly defined discontinuities in the initial ascending part of the transient, e.g. Figure 1 (b) and Figure 2. For such transients, it is possible to determine by the analysis given below the number of domains taking part in the switching, their sidewise velocity, and their cross-sectional shape.

(a) Method of Analysis

As a first example, consider N cylindrical domains which start growing simultaneously, when the field is first applied at time $t=0$, from hair-line nuclei distributed randomly under the electrode area.

If these cylinders are expanding radially with velocity v, and if the first two to coalesce have their centres b_1 apart and the second two, their centres b_2 apart, and if t_{c1} and t_{c2} are the times at which the first and second coalescences take place, then for $0 < t \leqslant t_{c1}$ the area of the electrode which is covered by the growing domains is given by the equation

$$A = N\pi v^2 t^2. \tag{1}$$

Landauer (1957) has shown that the current i which flows through the electrodes of a crystal of thickness d is related to the volume of reversed ferro-electric material, V_r, and the saturation polarization P_s by the expression

$$i = (2P_s/d)(dV_r/dt). \tag{2}$$

For sidewise expansion of parallel-sided domains, which extend from one face of the crystal to the other, equation (2) can be reduced to

$$i = 2P_s \cdot dA/dt. \tag{3}$$

Hence, by differentiating equation (1), it can be deduced that for $0 < t \leqslant t_{c1}$

$$i = 4N\pi P_s v^2 t. \tag{4}$$

Similarly, for $t_{c1} \leqslant t \leqslant t_{c2}$, by calculating the area and then differentiating with respect to time, it can be shown that

$$i = 4P_s v^2 t \{N\pi + \sin \theta_1 - \theta_1 + [t_{c1}/(t^2 - t_{c1}^2)^{\frac{1}{2}}][\cos \theta_1 - 1]\}, \tag{5}$$

where $\theta_1 = 2 \cos^{-1}(t_{c1}/t)$ and $t_{c1} = b_1/2v$.

Similarly for $t_{c2} \leqslant t \leqslant t_{c3}$ it can be shown that

$$i = 4P_s v^2 t \{N\pi + \sin \theta_1 - \theta_1 + \sin \theta_2 - \theta_2 + [t_{c1}/(t^2 - t_{c1}^2)^{\frac{1}{2}}][\cos \theta_1 - 1] + [t_{c2}/(t^2 - t_{c2}^2)^{\frac{1}{2}}][\cos \theta_2 - 1]\}, \tag{6}$$

where $\theta_2 = 2 \cos^{-1}(t_{c2}/t)$ and $t_{c2} = b_2/2v$.

Equations (4), (5), and (6), which represent the initial part of the current transient obtained with circular domains, are plotted in Figure 5. From these equations, it can be deduced that:

(i) The maximum dip at the first discontinuity occurs at

$$t = 1 \cdot 05 t_{c1}. \tag{7}$$

(ii) The value of the current at this dip

$$I_{c12} = [1 - 0 \cdot 121/N] I_{c11}. \tag{8}$$

(iii) The ratio of the current peaks at the first and second discontinuities

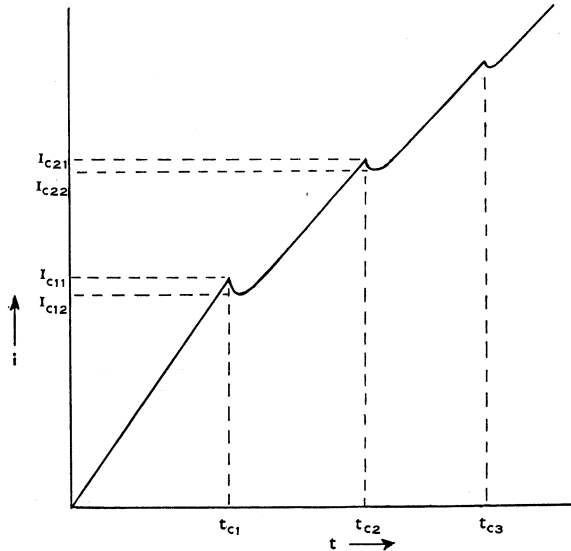$$I_{c21}/I_{c11} \simeq (N-1) t_{c2}/N t_{c1}. \tag{9}$$

Fig. 5.—The initial part of the current transient resulting from the sidewise expansion of circular domains.

(iv) di/dt for $0 < t \leqslant t_{c1}$, defined as slope 1, is $\sim$ to N, and the value to which di/dt tends for $t_{c1} \leqslant t \leqslant t_{c2}$, defined as slope 2, is $\sim$ to $N-1$, and the value to which di/dt tends for $t_{c2} \leqslant t \leqslant t_{c3}$, defined as slope 3, is $\sim$ to $N-2$. Hence

$$N = 1/(1 - \text{slope } 2/\text{slope } 1) = 2/(1 - \text{slope } 3/\text{slope } 1). \tag{10}$$

(v) The velocity of the sidewise motion

$$v = (I_{c11}/4\pi P_s N t_{c1})^{\frac{1}{2}}. \tag{11}$$

For square domains, the etch patterns of the type shown in Figure 3 reveal that the expanding domains are rotated in several directions with respect to the crystalline a axes. However, to allow a simplified analysis the N square domains are assumed to be orientated in one direction only.

If as before, b_1 and b_2 are the lengths of the lines joining the centres of the first and second pairs of square domains to coalesce, and if in addition φ_1 and φ_2 are the angles these lines make with the domain walls which are normal to the collision boundaries, then, by differentiating with respect to time the expressions for the areas covered by the growing domains, it is possible to derive three equations for the initial part of the current transient. (These equations are
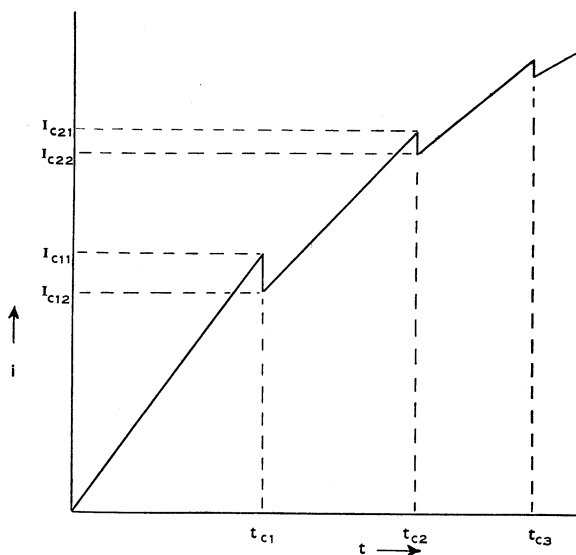

Fig. 6.—The initial part of the current transient resulting from the sidewise expansion of square domains.

analogous to equations (4), (5), and (6).) From the three equations, the form of which is plotted in Figure 6, the following information can be determined about the current transient:

(i) $$I_{c12}=[(N-0\cdot5)/N+\tan \varphi_1/2N]I_{c11}. \tag{12}$$

From this equation it can be seen that the ratio of I_{c12} to I_{c11} can vary from a maximum of 1, when $\varphi_1=45°$, to a minimum of $0\cdot75$ when $\varphi_1=0°$ and $N=2$.

(ii) $$I_{c21}/I_{c11}=(N-1)t_{c2}/Nt_{c1}+(1+\tan \varphi_1)/2N. \tag{13}$$

(iii) Similar to circular domains

$$N=1/(1-\text{slope } 2/\text{slope } 1)=2/(1-\text{slope } 3/\text{slope } 1). \tag{14}$$

(iv) $$v=(I_{c11}/16P_sNt_{c1})^{\frac{1}{2}}. \tag{15}$$

The discontinuities in the current transient, in addition to being due to domains coalescing with each other, can also be caused by domains growing out to the circular electrode boundary. The two types of coalescences are, however, distinguishable, since in one case two walls are moving at the collision boundary and hence the ratio of the slopes of the transient before and after the discontinuity, is $N/(N-1)$; whilst in the other case only one wall is moving, and hence the

ratio of the slopes is $N/(N-0\cdot5)$. Furthermore, with only one domain wall moving, the decrease in the current at the discontinuity is smaller and also for square domains instead of an instantaneous drop, there is a rounding-off effect. For the group of transients analysed below, it was found that the first discontinuity was due to two domains colliding with each other, rather than one domain with the boundary.

The technique which was developed for analysing the current transients was as follows :

(i) The shape of the discontinuities was used to determine whether the domains were circular or square.

(ii) If circular, the number of domains was calculated from either equation (8), (9), or (10). If square, the number was calculated from equation (14). A further check on the number of square domains was given by the simultaneous solution of equations (12) and (13). This procedure also gave a value for φ_1.

(iii) The velocity of sidewise motion was then calculated for circular domains from equation (11) and for square domains from equation (15).

(b) Results

With the liquid electrodes on a particular part of crystal IBM B (thickness $0\cdot090$ mm) a series of current transients were photographed at different switching fields in the range $2\cdot5$–6 kV/cm. One of these transients is shown in Figure 2. Because the same discontinuities were visible on each transient, it was possible by using the analytical method of Section V (a), to determine the field dependence of the domain wall velocity.

The results are shown plotted as small crosses in Figure 7. At each value of the field, five separate current transients were photographed, and it was found that the total variation in the calculated velocities from these transients was less than 6%.

Figure 7 shows that the velocity-field relationship has the form

$$v = v_\infty \exp\left(-\delta/E\right), \tag{16}$$

where $\delta = 7\cdot8$ kV/cm and $v_\infty = 2\cdot8 \times 10^4$ cm/s.

Measurements over the same field range showed that the switching time-field relationship was of the form

$$t_s \sim \exp\left(\alpha/E\right), \tag{17}$$

where $\alpha = 8\cdot2$ kV/cm.

Calculations made at the first and higher discontinuities of the current transient showed that the number of domains taking part in the switching remained constant at $5 \pm \frac{1}{2}$ domain, for the field range considered. However, at the lowest field measured, $2\cdot55$ kV/cm, it was found that the circular domains had changed to squares. This agrees with the results of the static domain patterns described in Section III.

Liquid electrode measurements made on other crystals in the field range $1\cdot5$–6 kV/cm, in addition to confirming equations (16) and (17), also showed that the ratio of δ to α is always between $0\cdot9$ and $1\cdot0$.

VI. Numerical Treatment of the Polarization Reversal

The method described in Section V (*a*), for calculating the initial part of the current transient in terms of the sidewise expansion of a small number of domains, is limited by the complexity of the algebra to about the first two coalescences of domains with each other or with the electrode boundary. In order to study the remainder of the current transient it is necessary to obtain a numerical solution. A convenient method of doing this is by using a digital computer program. A brief description of the program developed for the Ferranti " Mercury " Computer is given in the Appendix.
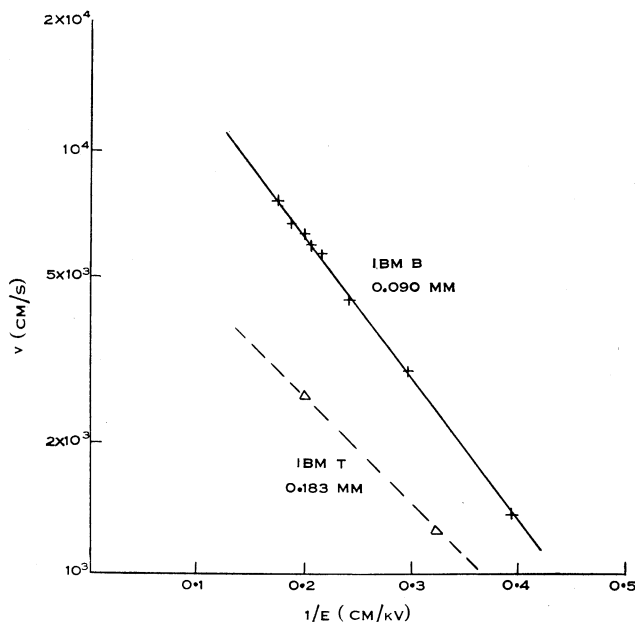

Fig. 7.—Logarithm of the sidewise 180° domain wall velocity versus the reciprocal of the applied field for two samples. The results for crystal IBM B, shown as a full line, were calculated by the method described in Section V (*b*). The results for crystal IBM T, shown as a dotted line, were obtained by the method described in Section VI.

The data required for this program consist of specifying :

(i) the number of domains,

(ii) the position of the domains within a circular electrode of radius 1 and centre 1,1,

(iii) the time at which each domain begins to expand—this facility was provided to allow for nucleation rate studies,

(iv) whether the domains, which expand at unit velocity, are circular or square.

Once the data have been stored, the program proceeds to compute the rate of growth of domain area as a function of time. For sidewise expansion see equation (3) ; this represents the form of the switching transient.

Some of the transients, which were obtained for circular domains in this way, are shown plotted in Figure 8. Because the circular electrode used in the computer program has a radius of 1, the area under each of these transients is equal to π. To simulate the liquid electrode, high field switching behaviour described in Section III, the domains used for obtaining the transients of Figure 8 were arranged to begin growing simultaneously when the field was first applied at $t=0$.

Figure 8 (a) shows the transient resulting from the radial expansion of two centrally situated circular domains. As is to be expected, the shape of the discontinuity due to the coalescence of these two domains has the same form as Figure 5. Furthermore, the tail of the transient is quite smooth and in this respect is similar to the experimentally obtained transients of Figure 1 (b) and Figure 2.

It is interesting to compare Figures 8 (b), 8 (c), and 8 (d), since in each case there are five domains taking part in the switching. The large differences in the resultant transients indicate that, with a small number of domains, the shape of the transient is critically dependent upon where the domain centres are located within the electrode boundary.

A domain configuration of particular interest is that of Figure 8 (e). The transient resulting from this configuration has the same shape as the experimentally obtained Figure 1 (c).

An inspection of the domain configuration of Figure 8 (e) reveals that the domain centres are mostly spaced at two critical distances, within the electrode boundary. The smaller of these L_1 is given by measuring either:

    (i) half the distance between any two adjacent domain centres of the five inner domains,

  (ii) half the distance between the centres of any pair of the three outer pairs of domains,

 (iii) the distance the six extreme outer domain centres are away from the circular boundary.

The other critical distance L_2 is given by measuring either

    (i) half the distance between several of the adjacent outer domain centres, or

  (ii) half the distance most of the outer domain centres are away from the nearest of the inner domain centres.

The two peaks in the transient of Figure 8 (e) are due to the two series of coalescences which occur after the domains have expanded distances L_1 and L_2. From the domain configuration of Figure 8 (e), it can be calculated that L_1 and L_2 are respectively $0 \cdot 06$ and $0 \cdot 15$ of the electrode diameter.* Knowing the diameter of the liquid electrodes used in obtaining Figure 1 (c), the actual values of L_1 and L_2 can be calculated.

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  * Although the transient of Figure 8 (e) can be obtained with many other different domain configurations, the two critical distances, L_1 and L_2, will always remain the same.

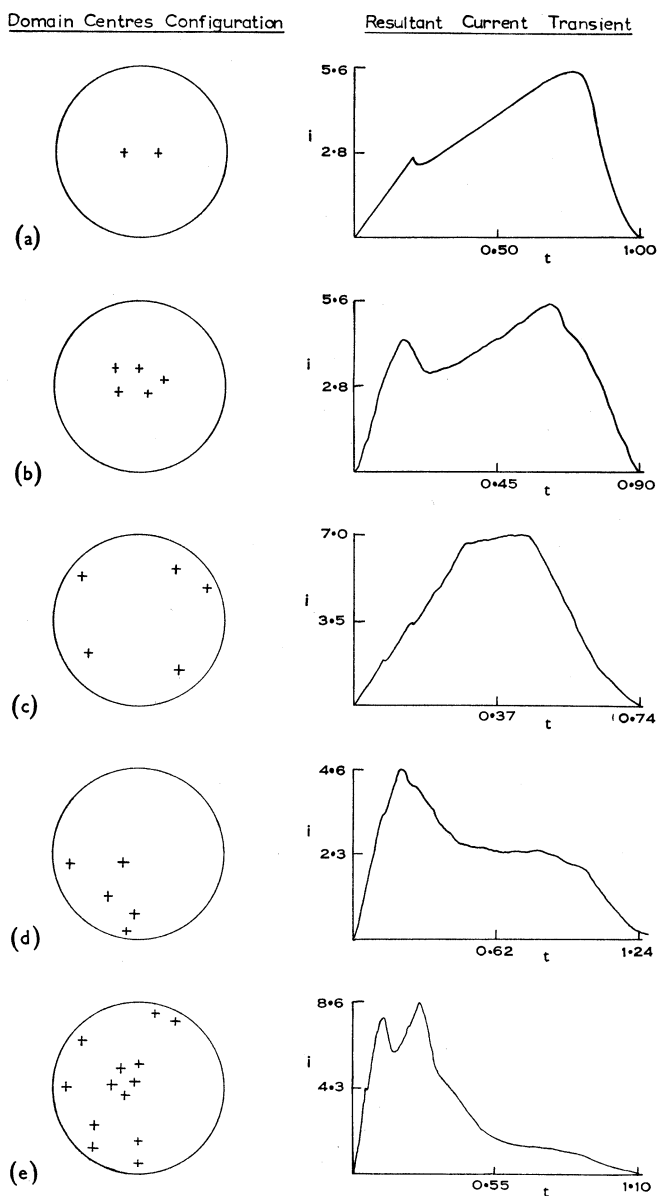Domain Centres Configuration   Resultant   Current   Transient

Fig. 8.—Computed current transients resulting from specified domain centre configurations. The five cases shown are for circular domains, which begin to grow simultaneously when the field is first applied at $t=0$.

Since, for Figure 1 (c), the times t_1 and t_2 at which the peaks occur can be measured, the velocity can be deduced from either

$$v = L_1/t_1 \quad \text{or} \quad v = L_2/t_2. \tag{18}$$

Unfortunately, when the current transients were first measured, it was not realized that the velocity could be calculated in this way. Consequently, the transient shown in Figure 1 (c) was only measured at two values of the field. The corresponding velocities for these fields, as calculated from equation (18), are shown plotted as small triangles in Figure 7. The vertical heights of the triangles represent the variation in the velocity depending on which of the two peaks was used for the calculation.

If it is assumed that a straight line joins the two triangles plotted in Figure 7, then it can be calculated that for crystal IBM T, that δ, the exponential coefficient in equation (16), has a value of $5 \cdot 8$ kV/cm. A comparison between this δ and the δ calculated for crystal IBM B in Section V (b) suggests that the thicker the crystal the smaller the value of δ. This is in agreement with some liquid electrode, low field measurements made by Miller and Savage (1960).

VII. DOMAIN WALL MOTION

The liquid electrode, high field measurements have shown that both the sidewise domain wall velocity and the switching time have an exponential field dependence. Furthermore, δ and α, the two exponential coefficients, are approximately equal.

Miller and Savage's (1958, 1959) low field, liquid electrode measurements have also shown that $v \sim \exp(-\delta/E)$. By comparing their results with Merz's (1956) measurements, they deduced that δ was equal to about $0 \cdot 3\alpha$. In order to account for the remainder of α they postulated a nucleation probability constant R_1, whose field dependence was assumed proportional to $\exp(-\beta/E)$.

The liquid electrode, high field measurements described in Section III have shown that the same number of domains take part in the reversal irrespective of the magnitude of the applied switching field. Consequently, the field dependence of the nucleation probability constant is very small, if not non-existent; and hence it is to be expected that δ will be approximately equal to α.

In order to obtain a ratio between α and δ, Miller and Savage were forced to compare their low field, liquid electrode measurements of δ with Merz's high field, metal electrode measurements of α. Such a comparison also introduces the difficulty of relating measurements made on different crystals grown from different melts. As illustrated in Figure 7 of Miller and Savage's own paper (1958) and in other places (Remika 1954), the values of α and δ for a particular crystal are critically dependent upon the type and percentage of impurities in the melt from which the crystal is grown. By comparison, the measurements of α and δ reported in Section V (b) were made simultaneously on the same crystal, within the same field range and with the same electrodes. Hence, it would seem more probable that δ is nearly equal to α rather than to $0 \cdot 3\alpha$.

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However, the significant correlation between Miller and Savage's work and that reported in this paper is that with liquid electrodes, at both low and high fields, the polarization reversal is accomplished by a small number of domains expanding sidewise at a constant velocity, the field dependence of this velocity being proportional to $\exp(-\delta/E)$.

Various explanations have been offered for the mechanism of the 180° wall motion. Peacock (1959) has suggested that once the domains have exceeded a critical size the walls expand sidewise at a velocity which is largely controlled by a " viscosity " factor. For cylindrical domains, it has been calculated that this sidewise velocity has a field E dependence of the form

$$v = \eta(E - E_c), \tag{19}$$

where η is the viscosity coefficient and E_c is the coercive field, which, in turn, can be defined by the expression $E_c = r_c E/r$, where r is the radius of the growing domain at a particular time t and r_c is the critical radius of a cylindrical domain. Peacock has calculated that for a crystal of thickness $0 \cdot 1$ mm and with a field of 1 kV/cm, r_c is 5×10^{-6} cm.

Since a liquid electrode, high field reversal is achieved by a small number of domains expanding to a relatively large size, the radii of the growing domains will be, during most of the switching, greatly in excess of the critical radius quoted above. Hence, it can be deduced that the value of E_c in equation (19) is negligible with respect to E.

The experimentally derived equation (16) can, at very high fields (i.e. above 3 kV/cm), be approximated to equation (19). If this approximation is made, E_c has a value of about $1 \cdot 5$ kV/cm, i.e. a value comparable with the range of E investigated. Because of this, together with wall energy considerations, it can be concluded that the 180° domain walls do not move as units parallel to themselves in the way suggested by Peacock.

Landauer (1957) has pointed out that the 180° domain walls may expand sidewise by a process involving the multiple nucleation of new domains adjacent to the existing walls. The exponential field dependence of the velocity obtained in Section V (b) would certainly suggest a nucleation mechanism. Furthermore, it seems likely that domains will nucleate preferentially near existing walls. In a recent paper, Miller and Weinreich (1960) have concluded theoretically that multiple nucleations, in the form of small triangular steps on existing walls, will satisfy most of the experimental data available about sidewise motion. Nevertheless, it is considered that more experimental evidence, especially in the form of temperature measurements, is required before a complete understanding is obtained of the sidewise 180° domain wall motion in barium titanate.

VIII. CONCLUSIONS

The experimental evidence obtained with liquid electrodes at high fields has shown that, under a constant applied field, the polarization reversal in single crystals of barium titanate is achieved by a small number of parallel-sided domains expanding sidewise at a constant velocity. These domains, which

extend from one face of the crystal to the other, generally begin expanding simultaneously when the field is first applied. The origin of the hair-line nuclei (or domain centres) from which the expansions take place is yet to be explained. However, it would appear that the number and distribution of these nuclei is dependent not upon the magnitude of the applied switching field but upon the surface conditions of the crystal where the electrodes are situated. One field effect which was noted, however, was that the cross-sectional shape of the domains changed from circular at high fields to square at low fields. This transition was found to occur at a switching field of about 3 kV/cm.

The current transients obtained with liquid electrodes are characterized by discontinuities of varying size, shape, and number. If these discontinuities are of a particular form, it is possible by an algebraic analysis to determine from the current transient the number of growing domains, their sidewise velocity, and their cross-sectional shape. By using this method of analysis it was found that, within the field range $1 \cdot 5$–6 kV/cm, the velocity field relationship was of the form $v = v_\infty \exp(-\delta/E)$. Such an expression, in addition to indicating the absence of a coercive field, also suggests that the movement of the domain walls is controlled by some type of nucleation mechanism.

The results obtained from the computer program show that with a small number of domains, i.e. liquid electrode switching, the shape of the current transient is critically dependent upon where the domains are located within the electrode boundary. Occasionally it was found possible to identify photographed transients with transients calculated by the computer. In such cases, since the domain configuration is known, the actual domain wall velocity can be calculated.

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APPENDIX

The computer program described below was designed to calculate the current transient resulting from a number of domains expanding sidewise at a constant velocity of 1. The sites* from which these domains expand can be positioned anywhere within a circular electrode boundary of radius 1 and centre 1,1. In addition to specifying the time at which each domain begins to expand, it is also possible to specify whether the domains are to grow as circles or squares. Similar to the simplification used in the algebraic analysis of Section V (*a*),
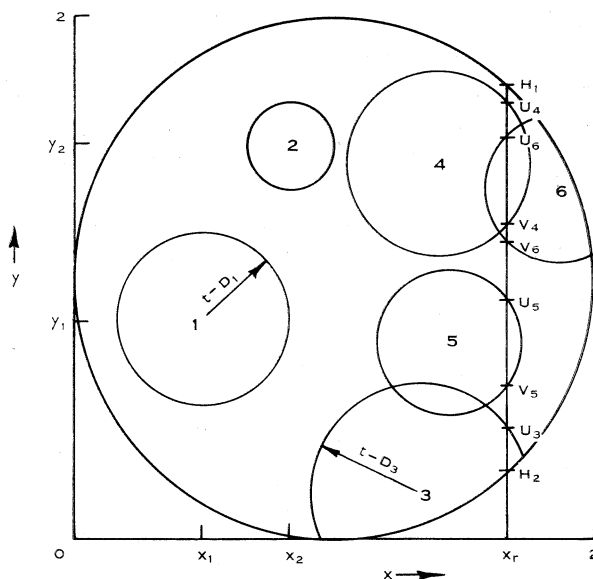

Fig. 9.—Method of computing the area of the electrode covered at time *t* by the growing domains.

the orientation of the square domains was limited to one direction with respect to the crystalline *a* axes. For convenience in programing, this direction was chosen to be parallel with the *x* and *y* axes of Figure 9.

The best method of explaining how the computer calculates the current transient is by reference to the simple example shown in Figure 9. In this diagram six circular domains are specified. The centres of these domains are located at x_1y_1, x_2y_2, . . ., x_6y_6. Since the domains are expanding with unit

* Up to a maximum of 80 sites can be specified.

velocity, at the particular time t for which the diagram is drawn, the radii of the domains are $t-D_1, t-D_2, \ldots, t-D_6$, where $D_1, D_2, \ldots, D_6$ are the specified times at which the various domains begin to grow.

Initially the computer must calculate the area of the electrode which is covered at time t by the growing domains. The method which was adopted for doing this was to determine the total contribution C made by the various domains along the vertical line drawn through successive values of x from $x=0$ to $x=2$. For example, at $x=x_r$, it can be seen from Figure 9 that C is equal to $(U_4-V_6)+(U_5-V_5)+(U_3-H_2)$: where U_k and V_k are the upper and lower points of intersection the kth domain makes with the vertical line through x_r and H_1 and H_2 are the upper and lower points of intersection the circular boundary makes with the vertical line through x_r.

Once the C's have been calculated at successive values of x, the area A covered at time t by the domains can be determined by numerical integration using Simpson's rule.

By repeating this procedure for various values of time, from $t=0$ to the time at which the domains have completely covered the electrode, the growth of domain area as a function of time can be calculated. If this expression is then numerically differentiated with respect to time, the rate of growth of domain area as a function of time is obtained. As indicated by equation (3), for sidewise expansion, this is directly proportional to the current transient.

Based on the numerical method given above, a program was written in Autocode for the University of London's " Mercury " Computer. In order to obtain a comparable accuracy to the algebraic treatment given in Section V (a), it was found necessary to specify 200 increments in time and to apply Simpson's rule over 200 ordinates. The computing time needed to calculate a typical current transient, due to the expansion of six domains, was approximately 10 minutes.