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Triple Hysteresis Loops and the Free-Energy Function in the Vicinity of the 5°C Transition in $BaTiO_3$

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The effect of an electric field on the transition between the orthorhombic and tetragonal states in single crystals of $BaTiO_3$ has been investigated. With zero bias the tetragonal to orthorhombic transition occurs near 5°C and the inverse transition at 11°C, exhibiting a temperature hysteresis of about 6°C. As expected, an external field in the direction of the polarization in the tetragonal state lowers both transition temperatures. Measurements show that the temperature depression varies linearly with the field. A strong field (>20 kv/cm) can lower both transition temperatures below the 5°C transition at zero field. Thus at a constant temperature, in a small temperature range below 5°C, the crystal can be switched reversibly between the two states by means of an electric field. Since the spontaneous polarization is smaller in the orthorhombic state, this phenomenon can be displayed as a "triple loop" in the familiar polarization *vs* electric field hysteresis plot. The dielectric constant has been measured as a function of temperature, and as a function of field at fixed temperatures. Transitions between states are sharp whether the transition is produced by varying the temperature or the electric field, provided the faces are completely electroded.

Numerical coefficients for various terms in the free-energy expansion for $BaTiO_3$, have been determined from certain of the experimental measurements. Calculations for various physical properties based upon the free-energy expansion agree reasonably well with these properties determined experimentally.

INTRODUCTION

THE general properties of barium titanate are quite well known. Transitions between different states occur near the three temperatures 120°C, 5°C, and −80°C. Above 120°C, the material is a paraelectric solid possessing cubic symmetry. In the temperature range 5°C to 120°C, barium titanate is spontaneously polarized along a 100 direction and the structure is strained into tetragonal symmetry, having the c parameter approximately 1% greater than the a. The polarization direction is parallel to the longer axis. At 5°C a transition to orthombic crystal structure accompanied with a change in direction of the spontaneous polarization to the pseudo-cubic 110 direction takes place. At −80°C, a further transition finds the polarization directed along the body diagonal (111 direction), with rhombohedral symmetry. Each of the three transitions exhibits a temperature hysteresis.[1,2] A series of investigations has been made of the effect of an electric field on the dielectric constant, and hysteresis loops at the 5°C transition (tetragonal to orthorhombic), and a report of the experimental procedures and results is presented. To save repeated writing, the symbols ($T\rightarrow O$) and ($O\rightarrow T$) will be used to designate transitions from the tetragonal state to the orthorhombic state, and vice versa, respectively.

EXPERIMENTS

The $BaTiO_3$ crystals used in these investigations were carefully chosen flat plates, grown in our laboratory, which were single domain "c plates," characterized by a low dielectric constant (~ 170) at room temperature. Thin platinum electrodes were evaporated on the large area surfaces after the crystals had been etched and cleaned. A typical crystal was about 0.1 mm thick, and had an area of 3 to 5 square mm. The flat faces of the crystal were wholly electroded. Results on partially electroded samples are unsatisfactory, because the nonelectroded portion of the crystal is not subjected to the applied electric field, and consequently, transitions which are field-dependent do not occur uniformly over the crystal plate. This means that the two regions will, at times, be in two different crystal states, and the mechanical strains at the boundary are severe. The nonelectroded portion of the crystal amounts to an effective mechanical clamp, prohibiting the crystal to behave as a free crystal.

The measurements which were of primary interest to us were the variations of (1) the dielectric constant, and (2) the P_z *vs* E_z (polarization-field) hysteresis loop, as functions of temperature and electric field. A voltage proportional to the dielectric constant was applied to the Y axis of an X-Y recorder and the desired independent variable (temperature or electric field strength) was fed to the X terminals. The essential features of the automatic dielectric constant plotter have been described by Drougard and Young.[3] The hysteresis loops were observed on an oscilloscope using the conventional circuitry.

The prepared sample was placed in the copper furnace of a cryostat. The furnace was filled with an atmosphere of dried N_2 gas at 40 psi which insured better heat contact between the crystal and a massive copper block which held the recording thermocouple. Using a temperature control circuit similar to that described by Drougard *et al.*[4] a temperature regulation of better than ±0.1°C was attained in the range −30°C

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[1] A. von Hippel, Revs. Modern Phys. **22**, 221 (1950).

[2] W. Känzig and N. Maikoff, Helv. Phys. Acta **24**, 343 (1951).

[3] M. E. Drougard and D. R. Young, Phys. Rev. **94**, 1561–1564 (1954).

[4] Drougard, Landauer, and Young, Phys. Rev. **98**, 1010 (1955).

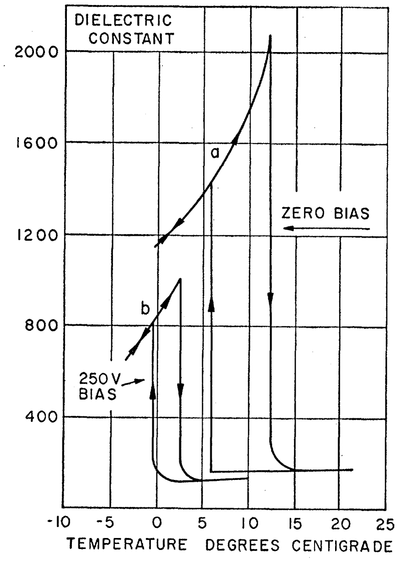

FIG. 1. Plot of dielectric constant *versus* temperature for the tetragonal to orthorhombic transition in $BaTiO_3$, curve *a*; zero field. Curve *b*; 250 volts bias. ($E=2.6\times10^4$ volts/cm.)

to room temperature. The furnace of the cryostat was placed above a free surface of liquid N_2 in a Dewar flask, and the desired temperature resulted from the proper current through the heater windings. Copper-constantan thermocouples were used for the regulation and measurement of temperature.

RESULTS

(a) Dielectric Constant *versus* Temperature

The typical behavior of the dielectric constant in the transition region plotted against temperature is shown in Fig. 1 for two values of biasing fields. The sample, completely electroded, having a dielectric constant at room temperature near 170 shows a discontinuity in dielectric constant, upon cooling, at 6°C, to a value approximately seven times larger (curve *a*). Below 6°C the dielectric constant decreases rapidly with decreasing temperature. As the crystal is warmed the reverse transition ($O\rightarrow T$) occurs near 12°C exhibiting a temperature hysteresis of about 6 degrees. A similar run with a dc bias (curve *b*) shows clearly that both transition temperatures are lowered by a field and that the temperature hysteresis has decreased. The lowering of the transition temperatures is to be expected since the applied field is in the direction which favors the tetragonal state. In case *b*, where the dc bias is 250 volts ($E=2.6\times10^4$ volt/cm) the ($O\rightarrow T$) transition occurs at a lower temperature than does the ($T\rightarrow O$) for zero field. This result suggests the possibility that at an appropriate temperature below 6°C it is possible to "switch" reversibly between the two states by changing the field applied to the crystal. This phenomenon is displayed in two experiments to be described.

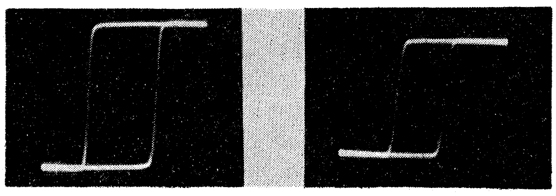
Tetragonal Orthorhombic

FIG. 2. Photographs of 60-cps hysteresis loops in the tetragonal state and orthorhombic state in $BaTiO_3$. (P_z *vs* E_z.)

(b) Hysteresis Loops

Photographs of 60-cps hysteresis loops are shown in Fig. 2 for a crystal in both the tetragonal and orthorhombic states. A comparison of the loops shows that the coercive field of the tetragonal state is 1.6 times larger than that of the orthorhombic, and the spontaneous polarization in the tetragonal is ~1.25 times larger than in the orthorhombic state. These observations agree with the results of Wieder[5] who has made similar measurements. Both pictures were taken with the crystal within 2° of the transition temperature.

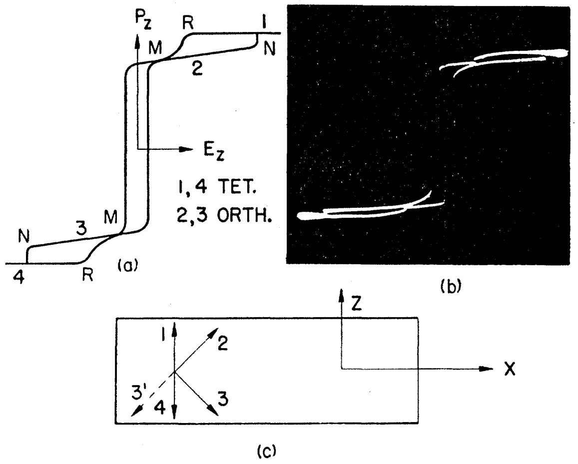

FIG. 3. Triple hysteresis loops in $BaTiO_3$. (a) Ideal triple loop; (b) an actual photograph of a triple loop; (c) orientation of axis pertaining to the discussion section.

Since the *z* component of the polarization in the two states differs, the transition between states by varying the field at a constant temperature can be displayed on a triple hysteresis loop, (P_z *vs* E_z). The repeated transitions ($T\leftrightarrows O$) produce severe mechanical shocks on the crystal, and all crystals shattered when attempts were made to observe such transitions at 60 cps. By using a 5-cps "looper," with a maximum peak-to-peak amplitude of 1000 volts, hysteresis loops were obtained without damage to the crystal. A photograph of the hysteresis loop is shown in Fig. 3. Accompanying the photograph is a drawing of a typical triple loop. The crystal, at a temperature near, but below, the ($T\rightarrow O$) transition at zero bias, is in the orthorhombic state at zero and low fields exhibiting orthorhombic coercivity

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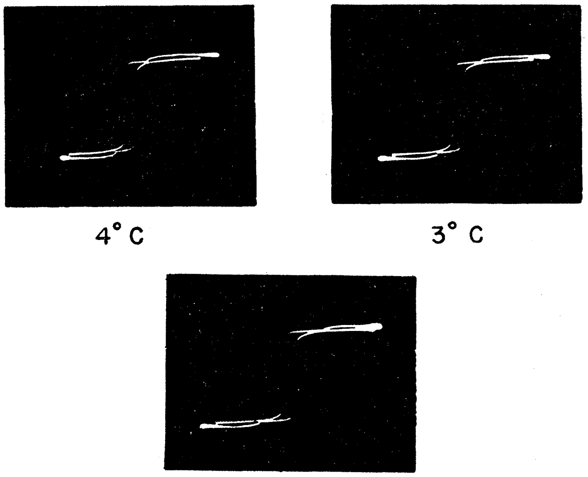
[5] H. H. Wieder, Phys. Rev. 99, 1161 (1955).

and polarization (region near M in Fig. 3). At a larger field (point N), the crystal "switches" to the tetragonal state with a larger polarization. As the field diminishes from the maximum, the transition hysteresis (in field) is exhibited so that the $(T \rightarrow O)$ transition occurs at a lower field (point R) than the $(O \rightarrow T)$ transition. Thus, this cycle of events gives rise to a "triple-loop" which is analagous to the "double-loop" exhibited at the tetragonal-cubic (120°C) transition.[6]

Photographs of triple loops of a crystal as a function of temperature are as shown in Fig. 4. It is clear that as the temperature decreases, the field required to drive the crystal into a triple-loop increases, so that the tetragonal portions of the loop move out toward higher fields. The $(O \rightarrow T)$ transition occurs at a very rapid rate, since it appears only as a discontinuity in the oscilloscope trace. This observation will be discussed when the loop is compared with theoretical considerations.



4° C

3° C

2° C

FIG. 4. Triple loops in $BaTiO_3$ *vs* temperature, showing that the tetragonal portions of the loop move out to higher fields as the temperature decreases.

(c) Clamping Experiment

Drougard and Young[3] have described a domain-clamping effect, which they observed on $BaTiO_3$ crystals in the tetragonal state as the direction of polarization was slowly reversed. The experiments were repeated on a crystal in the orthorhombic state with similar results. Figure 5 shows the dielectric constant ϵ_z, in the orthorhombic state plotted against electric field. The field was varied by means of a slowly driven helipot which took 20 minutes for a full voltage excursion. The dielectric constant decreases to less than $\frac{3}{4}$ of its initial value during the polarization reversal showing the dielectric constant of a mechanically clamped crystal. Using the expression relating the dielectric constant for the free, ϵ_f, and clamped crystal, ϵ_c, $\epsilon_c = \epsilon_f(1-k^2)$ the value of the electromechanical coupling coefficient, k, for this state is 0.56. For the tetragonal state at room temperature, Drougard and Young[3] report $k=0.48$. The coercive voltage measured in this dc manner on a particular sample is 675 volts/cm for the tetragonal state, and 435 volts/cm in the orthorhombic. The ratio of coercivities, measured in this manner, is 1.55, and agrees well with the 1.6 value obtained from the comparison of the hysteresis loops.

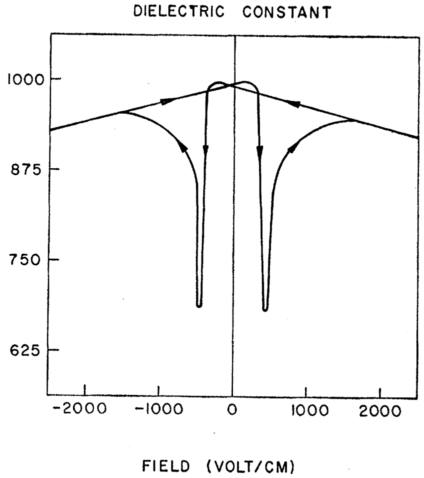


FIG. 5. Dielectric constant (ϵ_z) of the orthorhombic state as a function of small fields.

(d) Dielectric Constant *vs* Field

The reversible transition $(T \rightleftarrows O)$ produced by a field at a constant temperature can be demonstrated more vividly by plotting the dielectric constant rather than the spontaneous polarization (triple loop) against the electric field. This is true because the dielectric constants in the two states differ by a larger factor than do the respective polarizations. The equipment used in the clamping experiment was adapted to produce fields up to 60 000 volts/cm, and using this equipment, a plot of the dielectric constant *versus* field shown in Fig. 6 is obtained. With a completely electroded crystal near 4°C (slightly below the transition temperature) and with zero field, the crystal is in the orthorhombic state at A. As the field increases, the dielectric constant decreases toward B, goes through a minimum, and increases. At C, the field E_{cT} is sufficient to drive the crystal from the orthorhombic state to the tetragonal state (and into a single-domain because of the large field) with the corresponding large decrease in dielectric constant C to D. In the tetragonal state, the dielectric constant decreases slowly with additional field D to E. Upon decreasing the field from point E, the dielectric constant behaves as shown, E to F. The field E_{cO} is insufficient to hold the crystal in the tetragonal state, therefore, the crystal spontaneously reverts to the

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

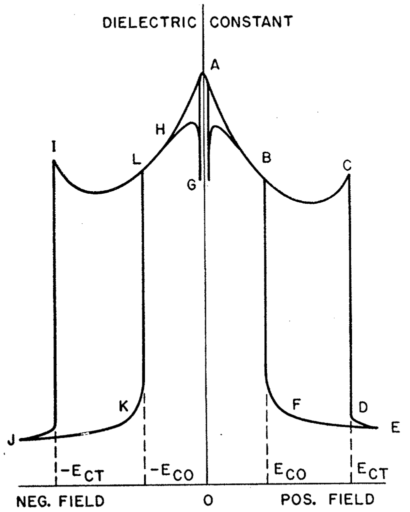

FIG. 6. Dielectric constant (ϵ_z) plotted against a large field, showing the transition between states produced by the field.

orthorhombic state at point B. The dielectric constant repeats through A, and at a small negative value of the field the polarization changes sign, the crystal switches, and the clamping effect is exhibited by the sharp decrease at G. Then, increasing the field in the negative direction produces the same effects described for the positive field as shown with the dielectric constant following the pattern given by the successive letters H through L. Good crystals give very symmetrical patterns as displayed in Fig. 6.

The critical fields E_{cO} and E_{cT} are functions of temperature as shown in Fig. 7, which is a composite of such runs (Fig. 6) at various temperatures. It is readily noted that both E_{cO} and E_{cT} increase with decreasing temperature; an obvious result since the crystal becomes more strongly orthorhombic with decreasing temperature. The critical field values, E_{cT} and E_{cO}, are plotted against temperature in Fig. 8. The dependences of each are seen to be linear with temperature and to have approximately the same slope. Similar plots made for other crystals yielded parallel lines within experimental accuracy. This condition implies that the temperature hysteresis is independent of the field, a fact which does not agree with the results of the constant-field variable-temperature experiment associated with Fig. 1. This discrepancy between the two experiments is most likely explained by a space-charge buildup, which can be quite different in the two cases due to the rates at which the experiments were done. On the average, two hours elapsed between the two transitions shown in Fig. 1, but for the experiment shown in Fig. 6 less than three minutes elapsed between transitions. Since other experiments, involving dc fields on barium titanate, done in our laboratory have been affected by space charge buildup, necessitating the use of ac fields to obtain reliable results, it is certain that the varying-field data are better than those taken with steady dc fields.

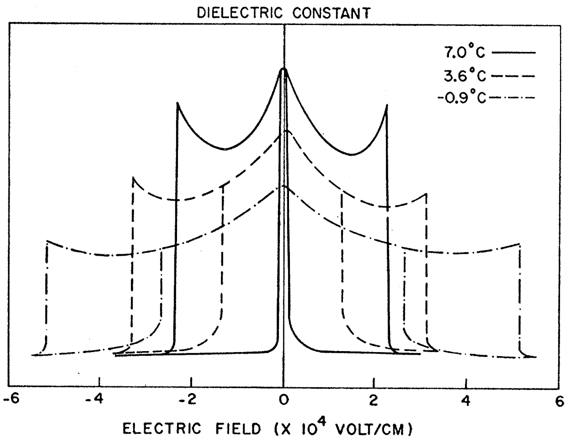

FIG. 7. The temperature dependence of plots such as those shown in Fig. 6.

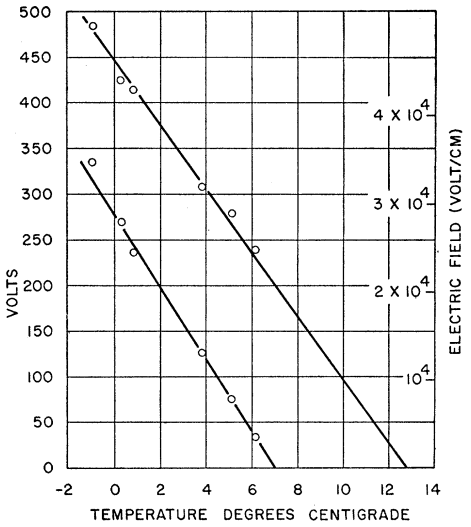

FIG. 8. The two critical fields, E_{cO} and E_{cT}, as functions of temperature.

DISCUSSION

We will attempt to correlate the experimental results with a mathematical expansion proposed by Devonshire[7] on the theory of barium titanate. Devonshire has expressed the Helmholtz free energy per unit volume of the stress-free crystal, F, in terms of even powers of polarization, P, The expansion applicable to both the tetragonal and orthorhombic states, as usually written, is

$$F=F_0+A(P_x^2+P_z^2)+B(P_x^4+P_z^4)+C(P_x^6+P_z^6)+D(P_x^2P_z^2). \quad (1)$$

F_0 is the free energy of the crystal for zero polarization. In Eq. (1) it is assumed that the polarization has no component in the y direction ($P_y=0$). To obtain a satisfactory explanation of the observations on the

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[7] A. F. Devonshire, Phil. Mag. 40, 1941 (1949), and Advances in Phys. 3, 85 (1954).

tetragonal-orthorhombic transition, it has been found necessary to add to (1) a cross term of the sixth order of the form $G(P_x^2P_z^4+P_x^4P_z^2)$.

The orientation of the axes is shown in Fig. 3(c). The axis parallel to the direction of the applied field is chosen as the z axis. Hence, E_x must be zero. The tetragonal polarization lies in the z direction [vectors labeled 1 and 4 in Fig. 3(c)]. We assume that the polarization in the orthorhombic state lies entirely in the x-z plane (i.e., there are no domains having the polarization in the x-y or y-z planes). The vectors labeled 2, 3, and 3′ in Fig. 3(c) represent possible orthorhombic directions.

Numerical values for the five coefficients A, B, C, D, and G are needed to make quantitative use of Eq. (1). In his calculations Devonshire assumed that all, but A, were temperature-independent, but as will be shown shortly, this is hardly justified. We begin with the fact that at some temperature within the temperature hysteresis region the free energy for the two states must have equal minima. The midpoint, 8°C, is arbitrarily chosen; hence the coefficients will first be determined for 8°C. Later, small adjustments will be made to the coefficients for other temperatures.

The coefficient A is obtained from an extrapolation of the Curie-Weiss law from measurements taken in the cubic state. Merz[6] showed that $A=3.7\times10^{-5}\times(T-T_0)$, where T_0 is the Curie-Weiss temperature. Measurements made in our laboratory on our crystals confirm this relationship, with T_0 being equal to 108°C. At 8°C, $A_8=-3.7\times10^{-3}$ cgs units. (The subscript has been added to indicate the temperature.) Measurements taken of the spontaneous polarization P_z, and the dielectric constant ϵ_z, in the tetragonal state at 8°C give us information to calculate B_8 and C_8. The coefficients B and C at any temperature are obtained from the following expressions:

$$B=\frac{\pi/\epsilon_z+2A}{2P_z^2}\quad\text{and}\quad C=\frac{\pi/\epsilon_z+A}{3P_z^4}. \tag{2}$$

Using the values $P_z=8\times10^4$ cgs units, $A_8=-3.7\times10^{-3}$, and $\epsilon_z=160$ cgs units (corresponding to 170 at room temperature) we obtain $B_8=-9\times10^{-13}$ cps units and $C_8=12\times10^{-23}$ cgs units. Merz[6] reported values for B and C which he obtained from observations on double hysteresis loops above the Curie temperature. His reported values, in the neighborhood of 120°C, are $B=-1.7\times10^{-13}$ cgs units and $C=3.8\times10^{-23}$ cgs units and are substantially smaller than the ones quoted here. Recently Drougard *et al.*[4] reported on the B coefficient obtained from dielectric constant measurements *versus* polarization in the temperature range 120°C to 150°C. Drougard's results are; at 120°C, $B=-2.6\times10^{-13}$ cgs units and at 150°C, $B=-1.3\times10^{-13}$ cgs units with points taken at intermediary temperatures lying on a straight line. Figure 9 contains a plot of B *vs* temperature. The values above the Curie temperature are those of Drougard,[4] and the value at 8°C is that reported here. Since the 8°C result lies quite close to the extrapolated values of Drougard, it seems quite certain that B depends on temperature in a linear manner. The equation of the line in Fig. 9 is $B(T)\cong5\times10^{-15}(T-T_1)$, $T_1=180$°C. The C value reported here ($C=12\times10^{-23}$ cgs units) is considerably larger than Merz's value of 3.8×10^{-23}, which probably means that it, also, is temperature-dependent.

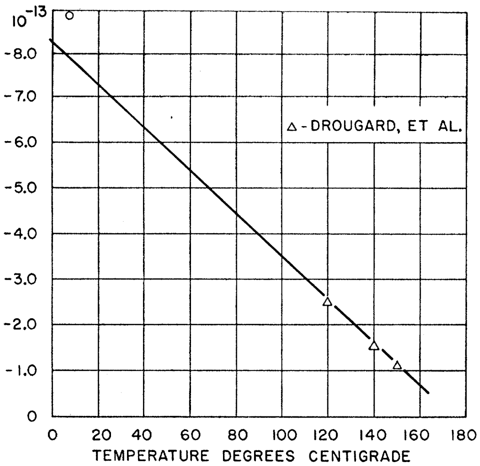

FIG. 9. The B coefficient as a function of temperature.

The coefficients D and G are obtained from measurements in the orthorhombic state at 8°C. The z component of the spontaneous polarization (P_O) at $E_z=0$ provides one relationship, and the other results from equating the free energy in the two states, $F(ORTH)=F(TET)$. Solving these two relationships simultaneously for D and G, one obtains the following expressions:

$$\begin{aligned}D&=\frac{1}{P_O^2}[A(3\alpha^2-4)+B(3\alpha^2P_T^2-2P_O^2)+C(3\alpha^2P_T^4)],\\ G&=\frac{1}{P_O^4}[A(\alpha^2-1)+B(\alpha^2P_T^2)+C(\alpha^2P_T^4+P_O^4)],\end{aligned} \tag{3}$$

in which $P_T=$ tetragonal polarization $=8\times10^4$ cgs units, $P_O=$ orthorhombic polarization $=6.5\times10^4$ cgs units, and $\alpha=P_T/P_O=1.23$. From these equations and the numerical values of the various components, one obtains values for D and G: $D=4\times10^{-13}$ cgs units, and $G=6\times10^{-23}$ cgs units. These are of the same order as B and C, which, presumably, justifies their inclusion in the expression for the free energy.

The triple hysteresis loop is a plot of the z component of the polarization, P_z, *vs* the applied electric field, E_z. Since the temperature must be below the transition temperature of 5°C in order to observe a triple loop, the values obtained at 8°C for the coefficients are not quite correct. Slightly adjusted values [using Eqs. (2)] for 0°C are listed below:

$$A_0=-4.0\times10^{-3},\quad B_0=-9.2\times10^{-13},$$

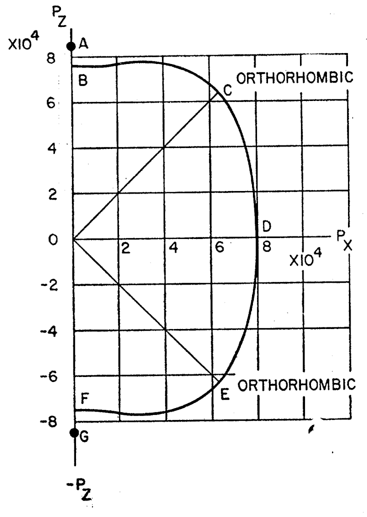

FIG. 10. A plot showing the manner in which P_x and P_z vary while traversing a triple loop, consistent with Devonshire's free-energy equation.

and

$$C_0 = 12.2 \times 10^{-23}.$$

Corrections to D and G using the above formula are rather uncertain, and we consider them constant.

The triple loop as observed on our oscilloscope is an experimental plot of P_z *vs* E_z. From the Devonshire equation we are able to draw a theoretical curve of P_z *vs* E_z in the temperature range near 0°C. The field E_z is obtained from the free-energy function

$$E_z = \partial F/\partial P_z = 2AP_z + 4BP_z^3 + 6CP_z^5 + 2DP_x^2P_z + G(2P_x^4P_z + 4P_x^2P_z^3). \quad (4)$$

In this form it is not possible to plot E_z *vs* P_z because of the P_x appearing in the last three terms. To eliminate P_x, we use the fact that $E_x = 0$, which gives us an additional relationship between P_x and P_z. We form an equation for E_x;

$$E_x = \partial F/\partial P_x = 0 = A + 2BP_x^2 + 3CP_x^4 + DP_z^2 + G(2P_x^2P_z^2 + P_z^4). \quad (5)$$

This relationship between P_x and P_z is plotted in Fig. 10. This curve gives the successive values of polarization permissible for a continuous change in the direction of polarization from position A to position G, (Fig. 10) (or from position 1 to position 4 in Fig. 3). In actual operation it is doubtful whether the polarization reversal in the orthorhombic state goes from state 2 to 3 as shown (Fig. 3), but rather goes from 2 to 3′ because of the mechanical constraints produced by neighboring domains which reverse the direction of polarization at slightly different times.

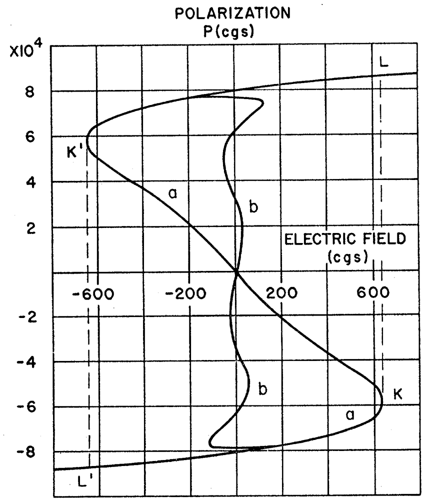

FIG. 11. A plot of the polarization, P_z, *vs* field E_z derived from the free-energy equation at 0°C. Curve *a* is for the case $P_x = 0$, and curve *b* is obtained when P_x is eliminated through the plot of Fig. 10.

Theoretically, two paths would be permissible for the state to reverse from A to G, Fig. 10. One is down the $P_x = 0$ axis, but this is ruled out because the triple loop shows that the crystal goes through 2 opposite states in the orthorhombic state, which is the curved path through the points B, C, D, E, and F.

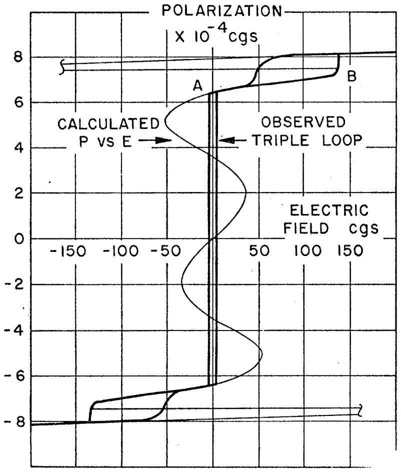

FIG. 12. Comparison of the theoretical P_z *vs* E_z with an observed triple loop.

We now have the necessary information to plot a P_z *vs* E_z curve from Eq. (4). Equation (4), with P_x eliminated through Eq. (5), is plotted in Fig. 11. Two curves are shown; the large sweeping curve *a* in which $P_x = 0$, and curve *b* which results when P_x is eliminated (curved path of Fig. 10). Curve *b* is the one of interest that we wish to compare with the triple loop. To assist us, we have redrawn curve *b* on an expanded scale in Fig. 12. Superposed on the curve is a triple loop as observed.

The features of the agreement between the calculated curve and observed loop will be delayed while we insert brief mention of the theoretical switching process. According to the Devonshire picture, the polarization follows the field along the P_z *vs* E_z curve in regions where the slope $(\partial P_z/\partial E_z)$ is positive. At fields where the slope becomes infinite (such as at points K and K' in Fig. 11), the polarization instantly changes to a point on the curve where $\partial P_z/\partial E_z$ is again positive (points L, and L' Fig. 11). Hence the loop, according to theory, consists of the two dotted lines K to L and K' to L', plus the parts of the curve where $\partial P/\partial E>0$. The loop thus formed, which would not be greatly different from that drawn for room temperature, has critical fields (the term critical field will refer to fields at which $\partial P/\partial E=\infty$) of about 600 cgs units (180 000 volts/cm), compared to observed coercivities near 1000 volts/cm.[8] A discrepancy of more than two orders of magnitude exists between the two results. In comparing theoretical curves with observed loops, there is special interest in the agreement or disagreement between calculated critical fields and observed coercive fields. The nature of the polarization reversal (switching behavior) in cases where a large discrepancy exists between theory and experiment (such as the room-temperature case cited above) has been discussed by Merz[9] and Landauer, Young, and Drougard.[8] The work of Merz shows that the process is governed not by the Devonshire theory but rather by the rate of nucleation of oppositely oriented domains. Therefore this discrepancy is not too surprising.

Now we return to a comparison of the triple loop and P_z *vs* E_z curve of Fig. 12. The observed triple loop is drawn in broad lines; the calculated curve in a light line. There are regions where the two agree well. At point B, the $(O\rightarrow T)$ transition field as measured agrees quite well with the calculated critical field. It is interesting that this transition occurs so rapidly that no vertical trace of this transition has been observed on the oscilloscope. There is more evidence, to be presented later, which further indicates that the observed field for this transition agrees with the calculated critical field. The observed coercive field in the orthorhombic state is near 2 cgs whereas the calculated critical value is approximately 50 cgs. The $T\rightarrow O$ transition is far from agreeing with theory, and it is obviously a slow transition. It seems apparent that the rate of the transition is rapid if the observed field is reasonably close to the calculated critical field for the transition, and slow if a large discrepancy exists.

Other features of the picture agree quite well. The slope of the curve in the P_z *vs* E_z plots (Figs. 11 and 12) is proportional to the dielectric constant. The dielectric constant in the orthorhombic state is 5 to 10 times larger than in the tetragonal state, and the respective slopes in Fig. 12 bear this out quite well. A consequence of this fact is that the two small loops between the orthorhombic and tetragonal state should decrease in height as the temperature decreases and the fields increase. This is observed in the photographs of Fig. 4.

In following the curve from A to B in Fig. 12 (orthorhombic state), the slope first decreases and then increases, and obviously passes through an inflection point. Since this slope is proportional to the dielectric constant, the dielectric constant should decrease with increasing field, go through a minimum, and then increase before the transition occurs. The results shown in Fig. 6 bear out this behavior of dielectric constant *vs* field. The fact that the dielectric constant does go through a minimum, and increases before the transition is a further indication that the observed $(O\rightarrow T)$ transition field at point B takes place according to the process proposed by Devonshire and not by a nucleation process.

Data contained in Fig. 8 enable one to calculate the latent heat, L, of the orthorhombic to tetragonal transition. The Clausius-Clapeyron relation applicable to this transition is given by the following equation:

$$\partial E/\partial T=L/T(P_{zO}-P_{zT}). \qquad (6)$$

$\partial E/\partial T$ (the slope of the lines in Fig. 8) is -3.6×10^3 cgs units/deg K. Substituting the values given for the z components of the polarization in each state ($P_{zT}=8.0\times10^4$ cgs units, and $P_{zO}=6.5\times10^4$ cgs units), and for $T=280°\mathrm{K}$, we obtain: $L=46$ cal/mole. This result is essentially three times greater than the results presented by Volger[10] (16 cal/mole) and Blattner, Känzig, and Merz[11] (16 cal/mole). Each of two latter results was determined by integrating the specific heat curve over the transition range. Volger's result was obtained on sintered polycrystalline materials; Blattner's *et al.* on powdered $BaTiO_3$.

The Devonshire free energy equation permits a calculation of the dielectric constant perpendicular to the direction of the polarization in the tetragonal state. This has been measured to be approximately 4000 cgs units. The dielectric constant in the a direction can be calculated from the free energy function as follows:

$$\left.\frac{\partial^2 F}{\partial P_x^2}\right|_{P_x=0}=\frac{4\pi}{\epsilon_x}=2(A+DP_z^2+GP_z^4). \qquad (7)$$

At 25°C, $A=-3.07\times10^{-3}$ and $P_z=7.8\times10^4$ cgs units. Inserting these into Eq. (7) with the values of D and G given earlier, we obtain $\epsilon_x=3950$. This agreement with the measured dielectric constant further substantiates the use of the Devonshire function and the value of the coefficients.

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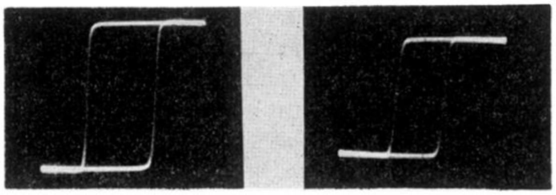


Tetragonal Orthorhombic

FIG. 2. Photographs of 60-cps hysteresis loops in the tetragonal state and orthorhombic state in $BaTiO_3$. (P_z *vs* E_z.)

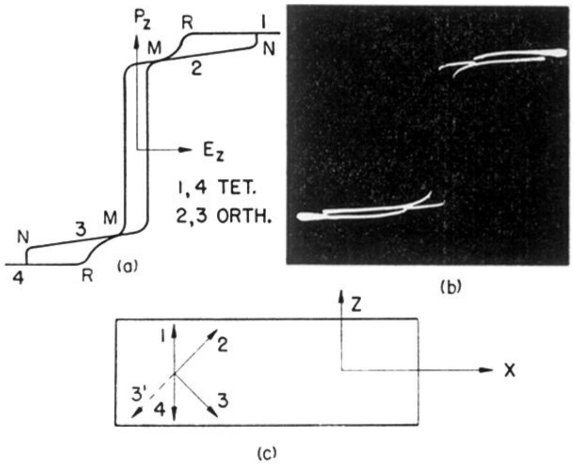
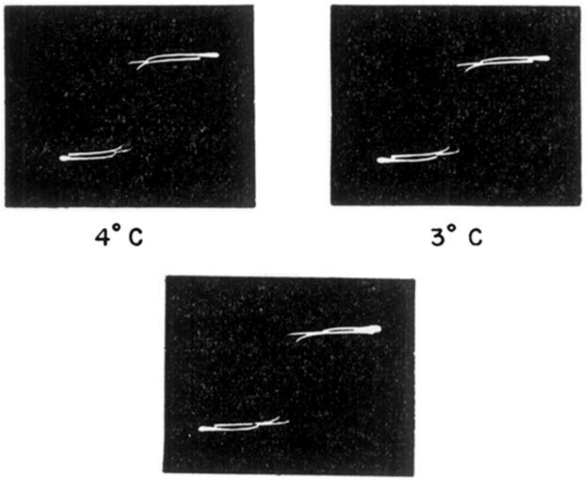


FIG. 3. Triple hysteresis loops in $BaTiO_3$. (a) Ideal triple loop; (b) an actual photograph of a triple loop; (c) orientation of axis pertaining to the discussion section.



4° C

3° C

2° C

FIG. 4. Triple loops in $BaTiO_3$ *vs* temperature, showing that the tetragonal portions of the loop move out to higher fields as the temperature decreases.