M. E. Drougard
E. J. Huibregtse

The Effect of an Electric Field on the Transitions of Barium Titanate

Abstract: A review is presented of the effects of electric fields on the ferroelectric phase transitions of barium titanate at 120°C and 5°C. The double hysteresis loop observed at the Curie point and the triple hysteresis loop and dielectric constant measured at the 5°C transition are examined in the light of Devonshire's thermodynamic theory of ferroelectricity in barium titanate. The data and various published experimental results are shown to agree with calculations based on the Devonshire free-energy function. The discrepancy between the coercive fields predicted by the theory and those actually observed is discussed.

Introduction

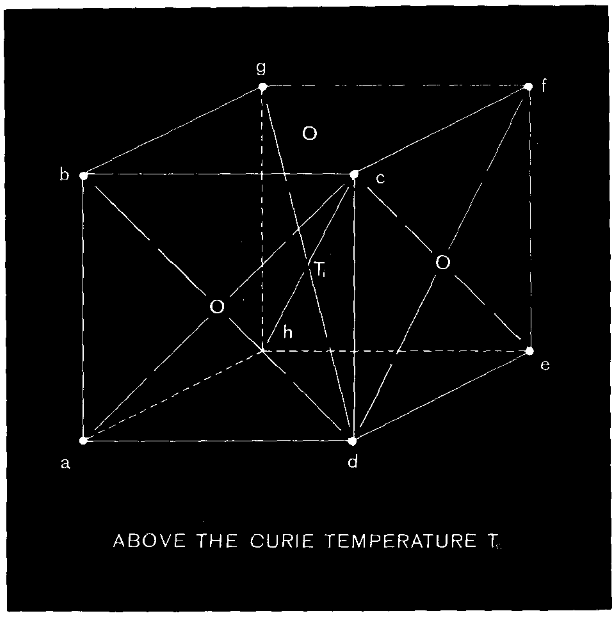
The ferroelectric phase transitions can be affected by mechanical or electrostatic forces. When a crystal is not subjected to any mechanical stress, the only parameters in the equation of state are temperature and electric field. The effects of the field are most pronounced in the immediate vicinity of the transitions, and a number of experiments have been made on these effects by the authors and other workers. The results have been analyzed in this paper in the light of the phenomenological theory of ferroelectricity in perovskite structures originally proposed by Devonshire.[1] A brief summary of the pertinent properties of barium titanate will be presented first, together with the basic features of the theory.

The crystalline form of $BaTiO_3$ which exhibits ferroelectric properties has the perovskite structure with cubic symmetry at high temperatures. Upon cooling through 120°C, a spontaneous polarization appears parallel to one of the cubic axes, and simultaneously a slight deformation of the unit cell occurs. The cell elongates along the direction of polarization by about 0.7% and contracts by about 0.3% in the perpendicular directions. The crystal retains the tetragonal symmetry down to 5°C, where the polarization becomes parallel to a diagonal of a face of the unit cell. Simultaneously, a slight shear appears in this face, which assumes the shape of a rhombus. The third edge of the former cubic cell remains perpendicular to this face. Finally, around −90°C, the unit cell becomes further distorted into an isosceles rhombohedron, with the polarization vector now lying along its longest diagonal.* These deformations are illustrated in Fig. 1.

*Jona and Pepinsky, Phys. Rev. **105**, 861 (1957), have indicated that the symmetry of the lowest temperature phase might not be rhombohedral.

Figure 1 **The unit cell of barium titanate at different temperatures.**
a) Cubic structure above the Curie temperature T_c. b) Tetragonal structure in the range of temperature from 5°C to T_c. c) Orthorhombic structure showing the shear in the face of the pseudo-cube. The plane ab'c'd' is the same as abcd and contains P_s. The edges of the orthorhombic unit cell are parallel to ac', b'd', and d'e'.

Figure 1a



Although the magnitude of the spontaneous polarization is quite large (26 μcoul/cm^2 at room temperature), the longitudinal and angular deformation strains are very small (1% or less, and 12′, respectively). This led Devonshire to consider the crystal to be a strained cubic material at temperatures below 120°C. If no stresses are applied, the three components of the polarization vector $P_xP_yP_z$ are sufficient, together with the temperature T, to describe the free energy of the material. Asymmetry considerations lead to an expansion (limited to terms of the 6th power in polarization):*

$$\begin{aligned}\mathcal{A} = \mathcal{A}_0(T) &+ A(P_x^2+P_y^2+P_z^2) + B(P_x^4+P_y^4+P_z^4)\\ &+ D(P_x^2P_y^2+P_y^2P_z^2+P_z^2P_x^2)\\ &+ C(P_x^6+P_y^6+P_z^6)\\ &+ G(P_x^2P_y^4+P_x^4P_y^2+\ldots). \qquad (1)\end{aligned}$$

The last term, which was not included by Devonshire, has been added to obtain a better fit in the neighborhood of the 5°C transition.

Since the inverse dielectric constant† is known to be proportional to the temperature in a wide range above the Curie point, A is taken to be a linear function of the temperature:

$$A=\alpha(T-T_0). \qquad (\alpha>0) \qquad (2)$$

In the absence of any evidence to the contrary, B, D, C and G are assumed to be constants. Devonshire showed that these constants can be chosen so that the minimum of the free energy occurs for $P_x = P_y = P_z = 0$ above 120°C; for $P_x = P_y = 0$, $P_z \neq 0$ between 120°C and 5°C; for $P_y = 0$, $P_x = P_z \neq 0$ between 5°C and −90°C; and for $P_x = P_y = P_z \neq 0$ for temperatures lower than −90°C. In each state the dielectric constant and the saturation polarization computed from this polynomial approximation are in satisfactory agreement with the available data.

*In the remainder of this paper, at least one component of P will be zero. Hence the term in $P_x^2P_y^2P_z^2$ has been omitted.

†If the dielectric constant is large,

$$\left(\frac{\partial^2 A}{\partial P^2}\right)_T = \frac{\partial E}{\partial P} \cong 4\pi\frac{\partial E}{\partial D} \cong \frac{4\pi}{\varepsilon} \text{ (cgs units)}$$

The 120°C transition

The transition at 120°C between ferroelectric and non-ferroelectric states is known as the *ferroelectric Curie point*. The experimental plot of dielectric constant as a function of temperature, shown in Fig. 2, reveals an apparently discontinuous transition between the two states, accompanied by a temperature hysteresis; i.e., the transition from the ferroelectric to the non-ferroelectric state occurs at a higher temperature than the reverse transition. It is interesting to note that these peculiarities can be predicted from the theory developed in the preceding paragraphs, using the values computed by Devonshire, as corrected by Merz[2]. Since only one component of the polarization is different from zero between 120°C and 5°C, the series expansion (1) for the case of a free crystal reduces to:

$$\mathcal{A}(T)-\mathcal{A}_0(T)=AP^2+BP^4+CP^6 \qquad (3)$$

From the properties of the free-energy function, it is known that, at constant temperature, the electric field E is given by

$$E = \frac{\partial\mathcal{A}}{\partial P} = 2AP + 4BP^3 + 6CP^5. \qquad (4)$$

Figure 1b

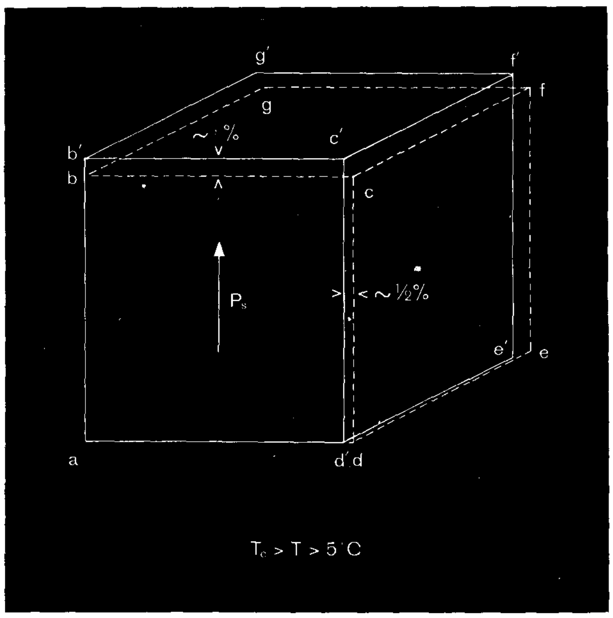
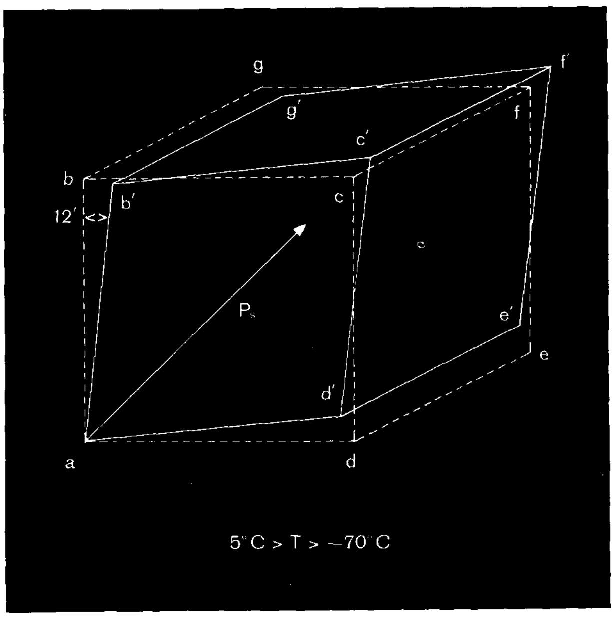


Figure 1c



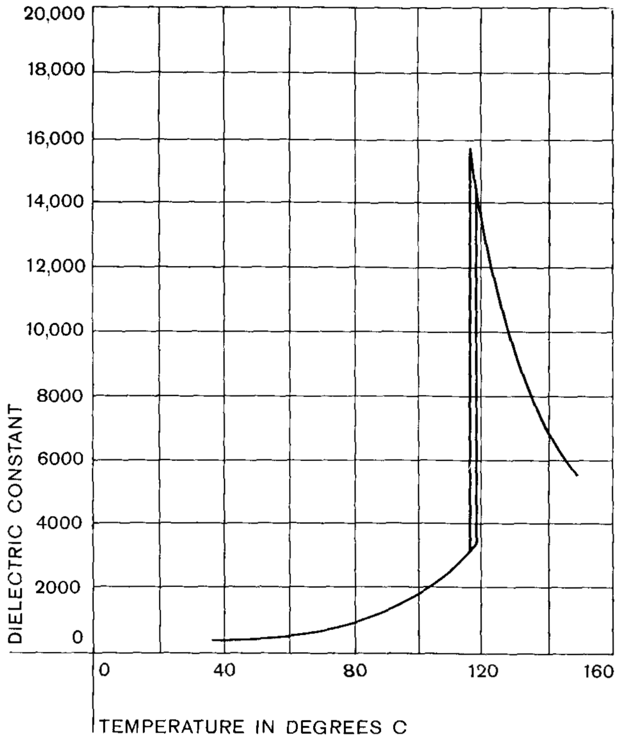


Figure 2 **The dielectric constant versus temperature through the transition at the Curie point.** *The temperature hysteresis is 2 degrees C, and the maximum dielectric constant is about 16,000.*

In the absence of a field, a non-zero polarization can exist if

$$A + 2BP^2 + 3CP^4 = 0. \qquad (5)$$

The constants B and C have been found by experiment to be respectively negative and positive, and the only necessary condition for a positive (real) solution in P^2 to exist is then:

$$B^2 - 3AC > 0. \qquad (6)$$

At high temperatures, A is positive and very large, and this condition is not satisfied. However, as the temperature is lowered, A becomes smaller in accordance with Eq. (2) and relation (6) is satisfied from a certain temperature T_1 down. From T_1 to T_0, since $A/3C$ is positive, there are two positive values of P^2 that satisfy Eq. (5). From T_0 down, there is only one such value. In all cases, one of the solutions is larger, and the other one smaller, than $-B/3C$. Let the larger solution be P_1^2 and the smaller one P_2^2.

If we are looking for stable states of the material, the only acceptable value of P^2 is one that minimizes the free energy; that is, makes the dielectric constant positive. The condition is $(dE/dP > 0)$:

$$A + 6BP^2 + 15CP^4 > 0. \qquad (7)$$

Elimination of the term in BP^2 between (7) and (5) shows that we must have:

$$3CP^4 > A. \qquad (8)$$

Condition (8) is satisfied only by the larger value of P^2 and not by the smaller one; since $P_1^2 P_2^2 = A/3C$, the solution $P = 0$ is seen to be acceptable as long as it represents a free-energy minimum, that is, as long as A is positive. Hence, in the whole range of temperatures T_0 to T_1, limited by the conditions

$$A > 0, \qquad A < \frac{B^2}{3C},$$

there are three free-energy minima, one for $P = 0$ and two for $P = \pm P_1$.

If the height of the energy barrier between two adjacent minima were small enough compared to the thermal energy available for nucleation of the new phase, the transition between the ferroelectric and paraelectric states would occur at the temperature at which the two minima of the free energy are equal, i.e., for a value of spontaneous polarization given by

$$A + BP^2 + CP^4 = 0. \qquad (9)$$

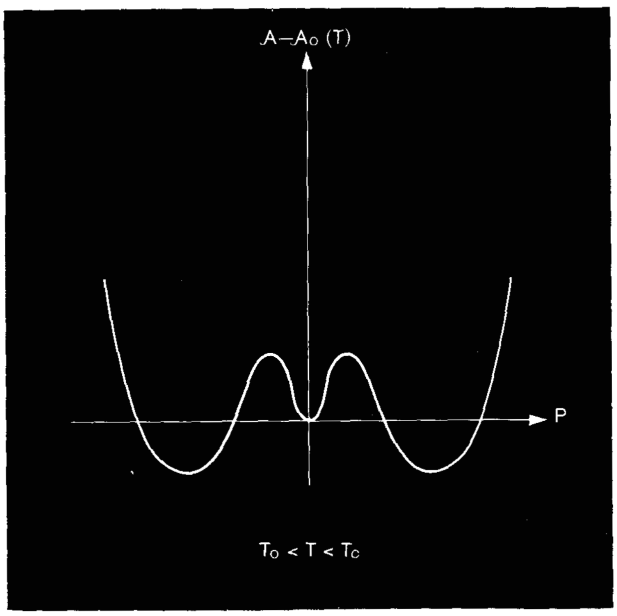
This equation, together with condition (5), yields

$$P_c^2 = -\frac{2A}{B}, \qquad B^2 = 4AC. \qquad (10)$$

The last equality determines a temperature T_c, called by Devonshire the critical temperature, at which the polarized and unpolarized states have the same free

Figure 3 **The free-energy function, A, plotted against the polarization for three different temperatures.**

Figure 3a *Below the Curie temperature.*



energy. From T_0 to T_c the ferroelectric state is stable, and the unpolarized state is metastable; the reverse is true from T_c to T_1. The situation is illustrated in Fig. 3. Due to the non-negligible height of the free-energy peak between the two minima, the transition from ferroelectric to non-ferroelectric state upon heating occurs at a temperature slightly above T_c, the reverse transition (upon cooling) slightly below T_c. Since there is a thermal hysteresis, the transitions may be expected to be discontinuous, as observed.

Since the dielectric constant of the material in the vicinity of the Curie point is extremely large, the polarization induced by a large field is not small compared to P_c. It is then to be expected that the application of a static electric field should have a measurable effect on the transition temperatures. More specifically, the transition temperatures should be slightly displaced upward, since the application of a field favors the polarized state. Unless special precautions are taken, however, the experimental results are quite disconcerting and disagree from sample to sample. One important difficulty, which will be elaborated upon in the following paragraphs, arises from the fact that the sample has to be free of mechanical constraints. This difficulty can be obviated, but there remains another problem: the slow time change of the voltage gradient across the crystal. Immediately upon application of a d-c voltage, the field across the sample is presumably homogeneous. However, there are many indications that with prolonged application, the field in the bulk of the sample decreases, resulting in poorly defined transitions.

This last difficulty, too, can be eliminated quite easily by resorting to an a-c field and keeping the temperature constant. The experiment was first performed by Merz,[2] who observed well defined double hysteresis loops and showed how the existence of such loops could be explained by the theory presented above.

The appearance of double hysteresis loops can be discussed most simply with the help of a plot of the relation between E and P, given by Eq. (4). First we note that the origin is always a point of the curve and a center of symmetry. The slope of the tangent at the origin is positive if $T > T_0$, negative when $T < T_0$. Also, if $T < T_0$, it was deduced from Eq. (6) that the curve intersects the P axis at two points, and if $T_0 < T < T_1$, the curve intersects this axis at four points.

Next, it is readily seen that the slope dE/dP may be zero when

$$A + 6BP^2 + 15CP^4 = 0. \qquad (11)$$

This equation has two roots in P^2 if

$$3B^2 - 5AC > 0. \qquad (12)$$

If $A > 0$, both roots are positive, if $A < 0$, there is only one positive root. Condition (12) determines a temperature θ, above which Eq. (11) has no real solution.

This discussion is illustrated by Fig. 4. Below the temperature T_0 $(A<0)$ in Fig. 4a, the PE plot has roughly the shape of an S. Starting from point A, for instance, and increasing the field, we come to point B, where $dE/dP = 0$, that is, the dielectric constant is infinite; hence the polarization jumps to point C. When the field is increased further, the polarization changes but little. Upon decrease and reversal of the field, point E is attained, where again the polarization jumps discontinuously to point F, et cetera. One obtains, then, the well known hysteresis loop.

When the temperature is made very slightly larger than T_0 (Fig. 4b), two relative maxima of E appear for a small value of P^2, very close to the origin. These max-

Figure 3b Equal to the Curie temperature.

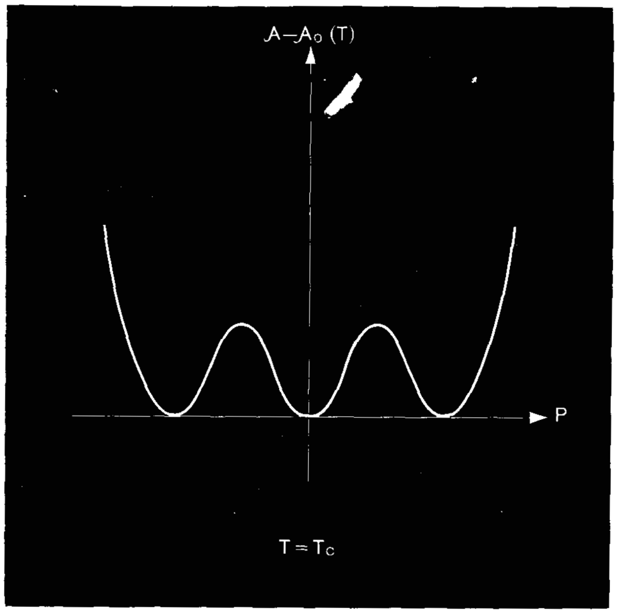
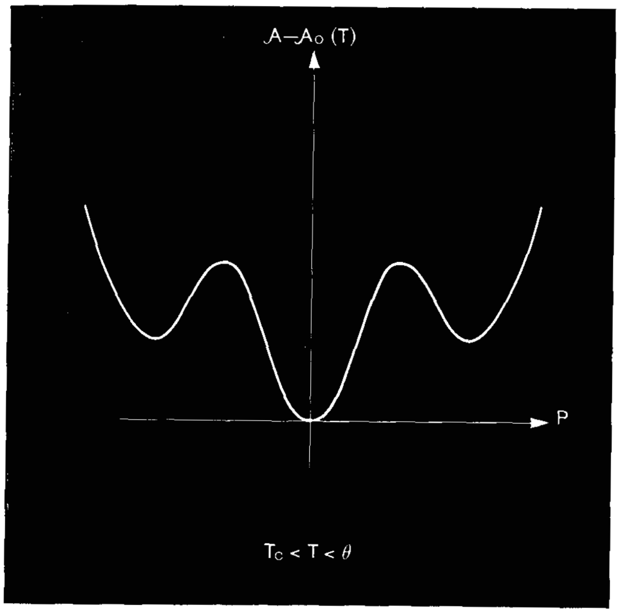


Figure 3c Above the Curie temperature.



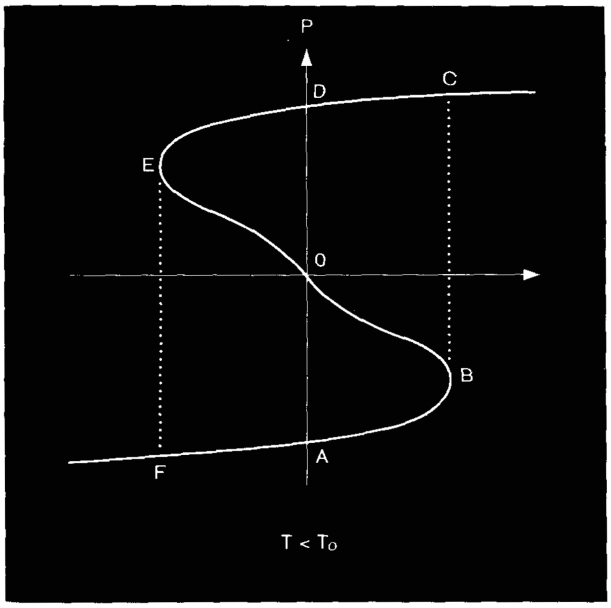


Figure 4a

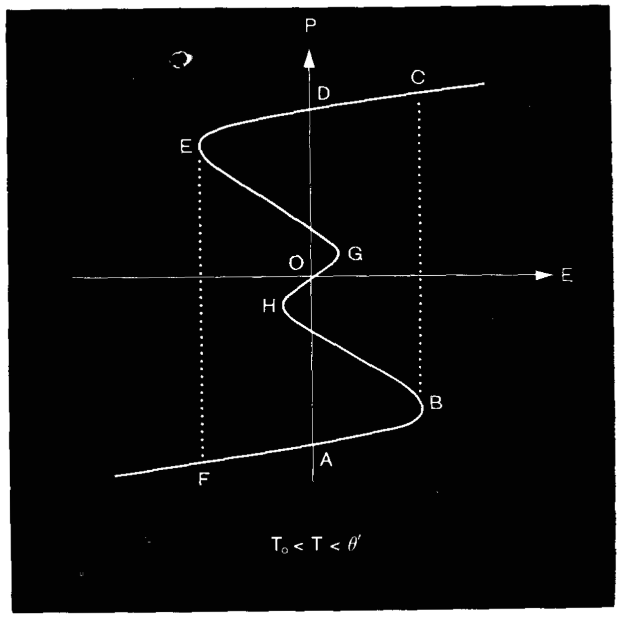


Figure 4b

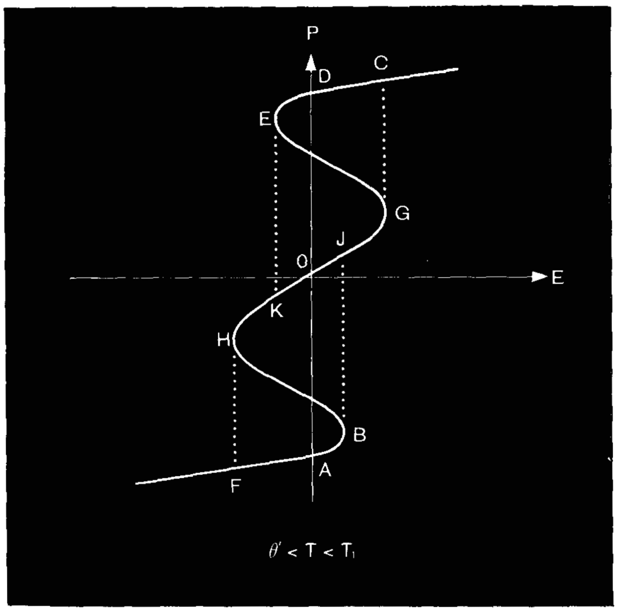


Figure 4c

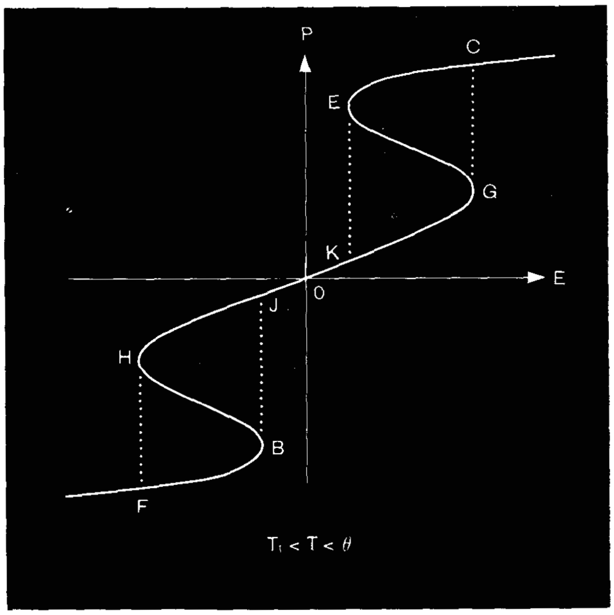


Figure 4d

Figure 4 **The polarization versus the electric field for a temperature with each of four temperature ranges:** *a) for T less than T_0. b) for $T_0<T<\theta'$. c) for $\theta'<T<T_1$, characterized by a broken loop, but not two distinct loops. d) $T_1<T<\theta$, the temperature region in which the two loops are separated by a region in the paraelectric state. The double loops disappear above the temperature.*

ima move away from the origin as the temperature is increased, and at a certain temperature θ', the extrema at G and B occur for the same value of the field. In this range of temperature, the loop has its normal ferroelectric aspect.

Above temperature θ', however, (Fig. 4c) the loop begins to have a different aspect. The maximum at E still occurs for a negative value of field, but the magnitude of this field is smaller than that for which the maximum at H occurs. A broken loop is then obtained, the paths being *ABJGC* and *CDEKHF*.

The double loops appear when the temperature is made larger than T_1, as shown in Fig. 4d. They move away from the origin and shrink in size when the temperature is raised, and disappear when the sample is heated beyond θ.

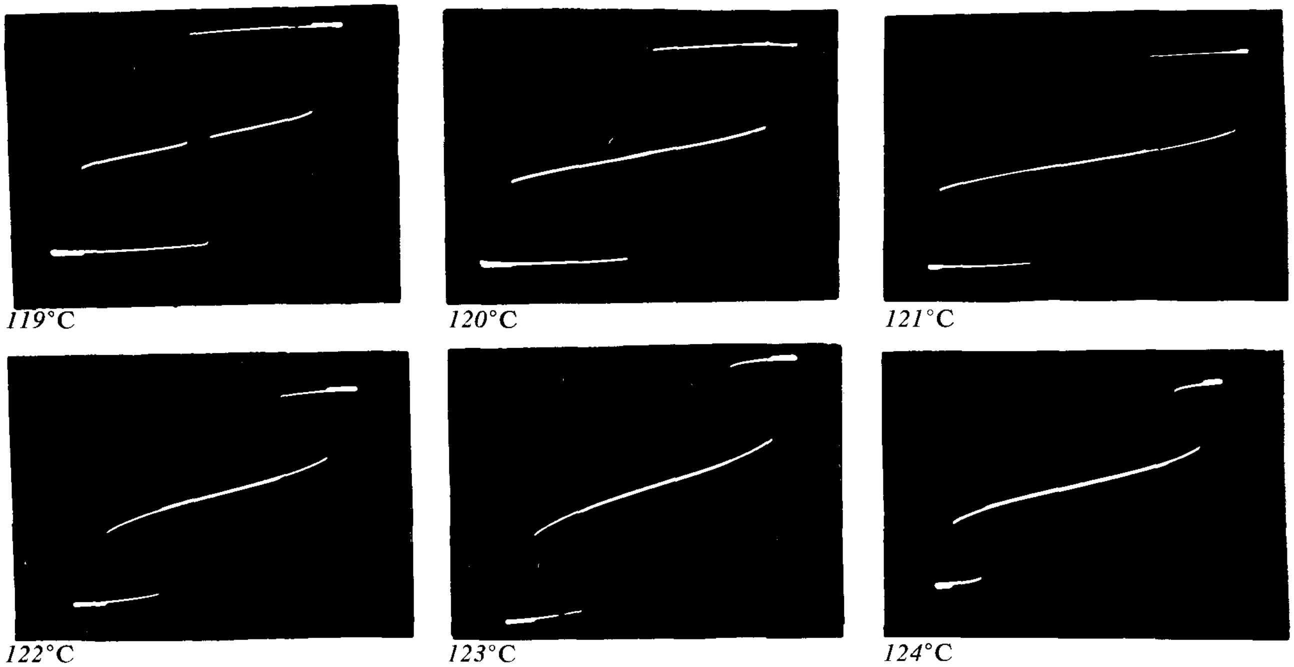


Figure 5 **Photographs of double hysteresis loops, showing the discontinuity between states when the crystal is completely electroded.**

From the considerations above, one would expect the ferroelectric loop to be characterized by discontinuous jumps of the polarization and a very well-defined transition field. Unfortunately, though, these conditions are not satisfied by actual loops. One of the reasons for this departure from the theory is that two domains of opposite polarization can well coexist in a crystal; hence the sample, instead of switching as one block, can reverse its polarization by small domains, and there are many indications that this process actually takes place[3].

Above temperature T_1, however, the situation is quite different because of the strains that take place when a barium titanate crystal becomes polarized. It has been mentioned in the Introduction that the onset of polarization is accompanied by a distortion of the lattice cell from perfectly cubic to slightly tetragonal. Similar distortions take place when a crystal is polarized by an applied field above the Curie point, and the corresponding strains have been shown to be proportional to the square of the polarization.

It is then apparent that these distortions should make it very difficult for a gradual transition to take place in Fig. 4d from the state of low polarization (G) to that of high polarization (C). We should expect such transitions to be discontinuous. However, this reasoning is valid only if the sample is really free to distort under the application of a field. If the sample, for instance, has electrodes on only two small, directly opposing regions on two opposing faces, it is not completely free of mechanical stresses, because the applied field tends to distort the material between the electrodes while the rest of the crystal tends to stay cubic. The two regions then mutually clamp each other, and poorly defined transitions result. If care is taken, however, to avoid this effect by covering two opposite faces entirely with electrodes, very discontinuous transitions result (Fig. 5). From the arguments developed above, these transitions are expected to become less discontinuous when the difference in dimensions between the two states becomes very small, and this type of transition is actually observed in a range of less than a degree below the temperature θ at which the double loops disappear.

It would seem at first that such well-defined transitions should permit a very accurate calculation of the constants involved, and therefore a check on the initial hypothesis that B and C do not vary with temperature. However, two difficulties arise which impair the accuracy of such calculations. The first one is the hysteresis heating, which takes place just as it does around an ordinary ferroelectric loop. The temperature of the crystal then changes discontinuously during the transition. In addition, the temperature of the crystal when it goes from the state of lower polarization to that of higher polarization is not the same as when the reverse transition takes place. The second difficulty arises from the possibility of thermal nucleation of the new phase before the field has attained the value for which the dielectric constant becomes infinite.

Actually, the best determination of the coefficients A and B in the vicinity of the Curie point results from measurements of the dielectric constant. The coefficient A can be obtained simply by measuring the zero-field

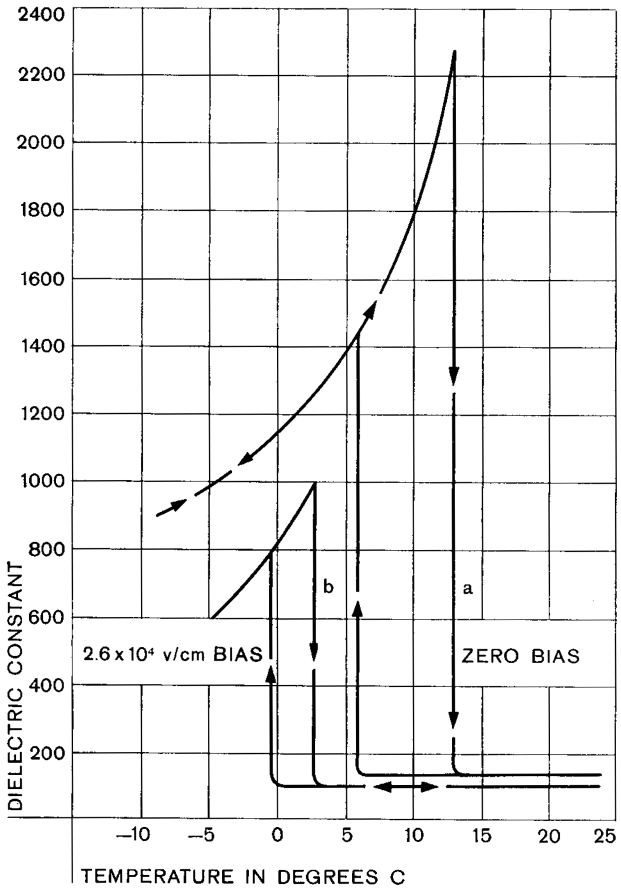


Figure 6 **The dielectric constant ε_{zz}, plotted experimentally against temperature through the region of the 5°C transition.**
Curve A is that observed with zero bias; curve B with a bias of 2.6 × 10⁴ volts/cm.

dielectric constant. The coefficient B can be determined from a study of the field dependence of the dielectric constant[4]. This coefficient goes to zero at about 175°C and then decreases linearly down to the Curie point, where its value is 2.5×10^{-3} cgs. Unfortunately, the method used to measure the coefficient B does not lend itself to a very accurate determination of C, because the very high fields required would damage the samples. The best determination of C is obtained from the double loops, and this is not accurate at all for the reasons explained above.

It should be noted on Fig. 5 that the field-induced transitions between states of low and high polarization occur before the field has attained the value for which the dielectric constant (proportional to the slope of the loops in their continuous portions) has become infinite. This point will be discussed at the end of this paper.

The 5°C transition

We mentioned in the Introduction that, at 5°C, a transition occurs in which the direction of the spontaneous polarization shifts abruptly from that along the pseudocube edge to that along the pseudocube face diagonal. An angular deformation of 12′ in the plane of the polarization shift distorts the crystal structure from tetragonal to orthorhombic. Cameron presented an optical study of the orientation of domains in the orthorhombic state[5]. In this section we propose to discuss experiments which have been performed in this transition region as functions of temperature and electric field and to correlate experimental results with predictions obtained from the free-energy function of Devonshire. For brevity, this will be referred to as the *5°C transition.* The similarities and the difference between the transitions at the Curie point and at 5°C are to be emphasized. Perhaps the most fundamental difference between them is that at 5°C the transition exists between two states, each of which is ferroelectric, in contrast to the case at the Curie point, where one of the two states is paraelectric. A consequence of this fact is an added complexity to the Devonshire free-energy function which describes the observed results. In the tetragonal state one component of the polarization is sufficient to express the free-energy function; but two components are required to describe the polarization along the face diagonal of the unit pseudocube in the orthorhombic state. We have chosen these to be P_x and P_z, where the latter lies in the direction parallel to the applied electric field. It is assumed that no polarization component lies in the y-direction. Equation (1) for the orthorhombic state becomes

$$\mathfrak{A}(T)-\mathfrak{A}_0(T)=A(P_x^2+P_z^2)+B(P_x^4+P_z^4)+C(P_x^6+P_z^6)+DP_x^2P_z^2+G(P_x^2P_z^4+P_x^4P_z^2). \quad (13)$$

Figure 6 shows the dielectric-constant behavior as the sample was subjected to a temperature cycle through the transition region. The curve labeled A is a typical plot obtained for a crystal not subjected to an electrical field. The dielectric constant decreases slowly with decreasing temperature down to 5°C, where a discontinuous increase occurs, corresponding to the change to the orthorhombic state. Upon further cooling, the dielectric constant decreases quite rapidly until it eventually levels off at about −35°C. When the crystal is then warmed, the dielectric constant increases until the change back to the tetragonal state occurs, at around 11 to 12°C, or about 6°C higher than the reverse transition upon cooling.

Curve B in Fig. 6 is typical of the behavior of the dielectric constant versus temperature if a large d-c electric field is impressed across the sample. As before, the field is applied in the z-direction. The external field "strengthens" the tetragonal state, thereby requiring that the crystal be cooled to a temperature below 5°C before the transition to the orthorhombic state occurs. For the particular case shown in Fig. 6, a d-c bias of 2.6×10^4 volts/cm reduced the transition temperature from 6° to about 0°C. If the effect of temperature depression be linear with the field, it appears that a field of 4×10^3 volts/cm would depress the transition temperature by one degree. This relationship has been verified reasonably well for many crystals of different thicknesses.

The orthorhombic-to-tetragonal transition in the presence of a field occurs (for the particular case cited in Fig. 6) at 3°C, showing a temperature hysteresis of 3 degrees, compared with 6 degrees obtained with zero bias. This would suggest that the temperature hysteresis decreases with increasing biasing field. However, another experiment (to be described later) shows that if the transitions are repeated rapidly enough the temperature hysteresis is essentially independent of the field. We ascribe the narrowing of the hysteresis to a slow build-up of space charge near the surfaces, which increases the field near the electrodes and decreases the field through the bulk of the crystal.

It is apparent from Fig. 6 that the orthorhombic-to-tetragonal transition with bias can occur at a lower temperature than the tetragonal-to-orthorhombic transition with zero bias. This behavior is the basis for the experiments to be described in which the transition was observed as a function of the applied field. If the crystal, which yielded the data in Fig. 6, is kept at some temperature between 3 and 5°C the crystal is in the orthorhombic state for zero and low fields, and in the tetragonal state above some critical value of field. Thus, we can induce the transition between the two states by means of a field.

For the 5°C transition, the Devonshire free-energy function is able, again, to predict reasonably well these experimental results. The free-energy function (13) consists of five terms, each having an undetermined coefficient. The procedure for determining suitable values for these coefficients is described elsewhere.[6] It is sufficient here to say that A is obtained from the Curie-Weiss law (Eq. 2); B and C are computed from the measured dielectric constant and spontaneous polarization in the tetragonal state; and D and G from the orthorhombic polarization, and by equating the free energies calculated separately for the tetragonal and orthorhombic states at the midpoint of the temperature hysteresis range. Temperature dependencies of A and B are known, but C, D and G are considered to be constants, at least over the few degrees of interest for this 5°C transition. The values for the coefficients are:

$$A = 3.7 \times 10^{-5}(T-T_0) \text{ cgs}, \quad \text{where } T_0 = 110°\text{C}$$

$$B = 4.5 \times 10^{-15}(T-T_2), \quad \text{where } T_2 = 175°\text{C}$$

$$C = 9 \times 10^{-23}$$

$$D = 6 \times 10^{-13}$$

$$E = 4 \times 10^{-23}$$

Since the temperature T is much less than both T_2 and T_0 in the region of 5°C, A and B are negative; whereas C, D and G are positive constants.

The free-energy equation (13) can be differentiated with respect to P_x and P_z, yielding the two components of the electric field,

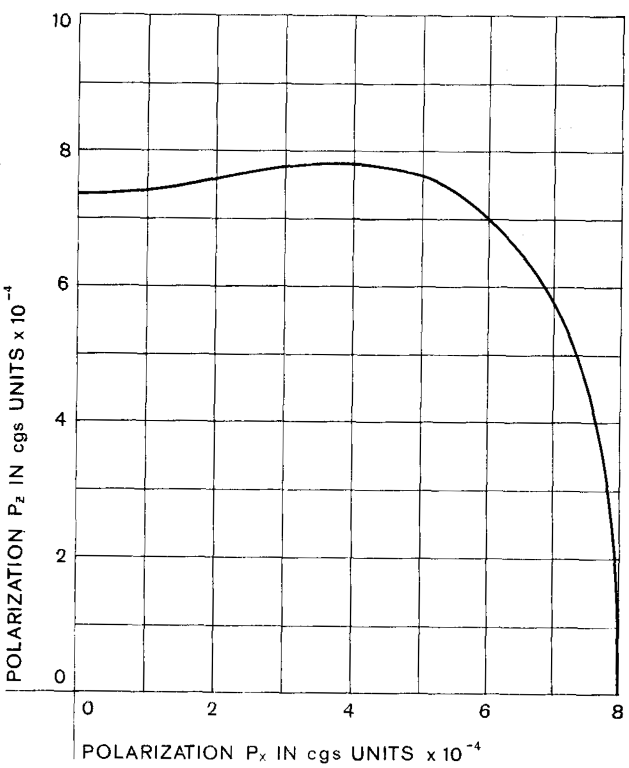
$$E_x = \frac{\partial \mathfrak{A}}{\partial P_x} = 2AP_x + 4BP_x^3 + 6CP_x^5 + 2DP_xP_z^2 + 2GP_xP_z^4 + 4GP_x^3P_z^2; \qquad (14)$$

$$E_z = \frac{\partial \mathfrak{A}}{\partial_z} = 2AP_z + 4BP_z^3 + 6CP_z^5 + 2DP_x^2P_z + 2GP_x^4P_z + 4GP_x^2P_z^3. \qquad (15)$$

In order to compare theoretical predictions and experimental results, we need a plot of E_z vs P_z. This plot cannot be obtained from Eq. (15) as it stands, because of the terms including P_x. An independent relationship between P_x and P_z, by which P_x can be eliminated from (15) is that expressed in Eq. (14), if E_x is equated to zero. The relation P_x vs P_z from Eq. (14) is plotted in Fig. 7. The condition $E_x = 0$ is reasonable because the electrodes in the plane are equipotential surfaces and the samples are extremely thin. However, since an x-component of the polarization appears or disappears when a crystal goes through the transition, the requirement $E_x = 0$ implies that the crystal must break up into domains having opposite polarization in the x-direction. The surface conductivity of the material is sufficient that such a process would prevent the buildup of a field in the x-direction. There is experimental evidence that this process actually takes place.[4]

Having eliminated P_x from Eq. (15) we are now able to plot the desired P_z vs E_z behavior, and this is shown in Fig. 8. Since A and B are temperature-dependent,

Figure 7 **The relationship existing between P_x and P_z obtained from Eq. (14) by letting $E_x = 0$.** *The curve describes the manner in which the two components of polarization may vary theoretically as a triple loop is being traversed.*



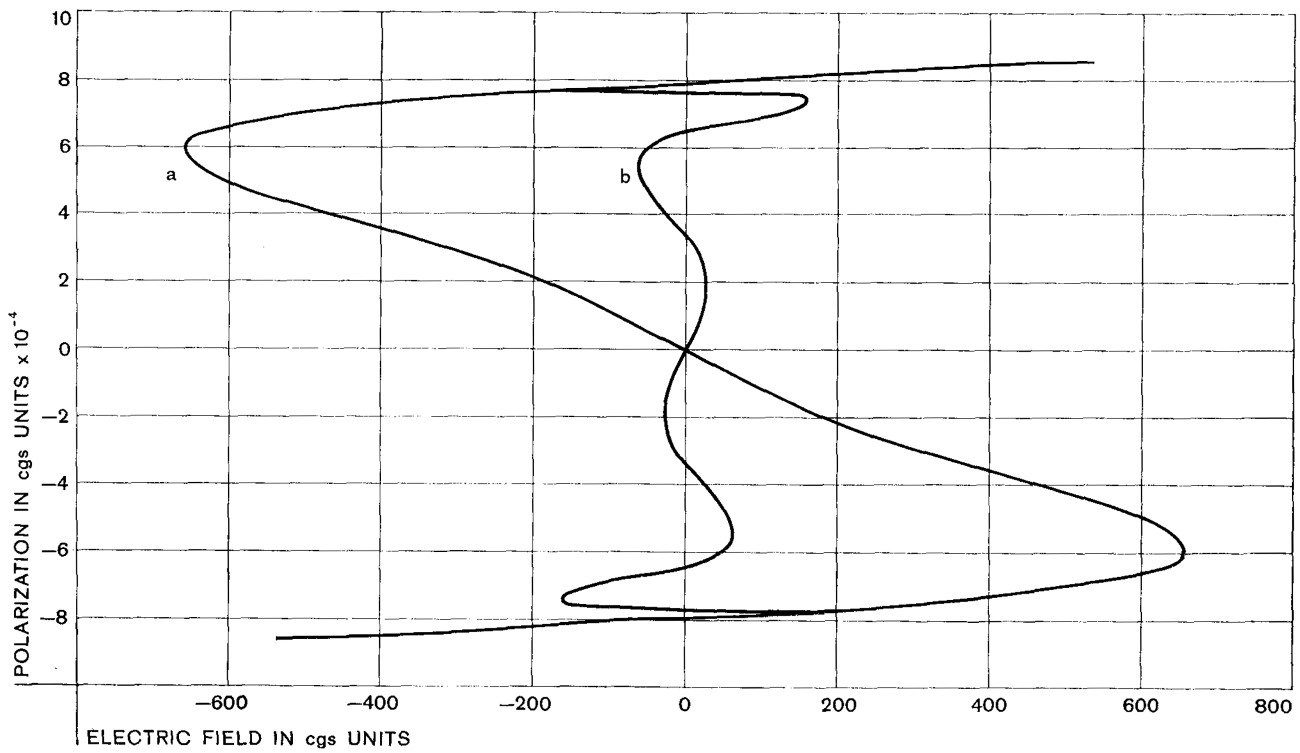


Figure 8 **A plot of the polarization P_z versus the electric field E_z, evaluated for 5°C.** *Curve a is obtained for $P_x = 0$, and curve b is obtained when P_x is read from the curve in Fig. 7.*

plots such as shown in Fig. 8 vary with temperature; the curves shown in Fig. 8 have been drawn for coefficients evaluated at 5°C. Two curves are drawn in Fig. 8: the long sweeping curve (a), having the two extremal points, obtains if $P_x = 0$, while the wavy curve (b) near the $E = 0$ axis results from the elimination of P_x through the curve shown in Fig. 7. The E vs P curve in Fig. 8 will be discussed after two experimental observations of the effect of an electric field on the transition are described.

The behavior of two physical properties through the transition region have been observed as functions of the field. Corresponding to the double loops which appear at the Curie point, we have observed hysteresis loops (polarization vs field) at suitable temperatures for which the two states both appear. In a small temperature range just below 5°C the orthorhombic state is stable for zero and low fields, but the tetragonal state can be induced through the application of large fields. If a crystal is kept at a temperature just below the transition temperature and is subjected to a low-amplitude alternating field, a hysteresis loop appears as the polarization is reversed between two opposite orthorhombic directions. The slope of the loop in the saturated regions is greater than the corresponding part of a tetragonal hysteresis loop because of its higher dielectric constant. If, however, the amplitude of the a-c field is continuously increased to a critical field for the particular temperature, a discontinuous increase in the polarization is observed as the crystal flips into the tetragonal state at high fields. A photograph of a typical high-field hysteresis loop is shown in Fig. 9. The tetragonal polarization is slightly greater than the z-component of the orthorhombic polarization, which accounts for the increase shown at I in Fig. 9. The crystal remains in the tetragonal state until the field has decreased to that magnitude which is no longer sufficient to hold it tetragonal (M in Fig. 9), at which time the orthorhombic state appears with lower polarization at N. We refer to the hysteresis phenomena displayed in Fig. 9 as a "triple loop."

The repeated transitions between the two crystal states are severe shocks to the crystal, and it was found that only at very low frequencies, around 5 cps, was it possible to observe these triple hysteresis loops without shattering the crystal. At 60 cps all crystals shattered.

The change in the appearance of the triple loop as the temperature is decreased is in agreement with expectations. A decrease in temperature makes the crystal more strongly orthorhombic; hence fields of greater magnitude are required to produce the tetragonal portions of the loop. The two tetragonal loops move out along the saturated portions of the orthorhombic loop away from the $E = 0$ axis, until they become all but indistinguishable because the polarization in the two states becomes equal. Photographs of triple loops at different temperatures, Fig. 10, verify these predictions.

In Fig. 11, an experimental triple loop is shown superimposed on the theoretical P_z vs E_z plot of Fig. 8. The orthorhombic coercive field at I is smaller by a factor

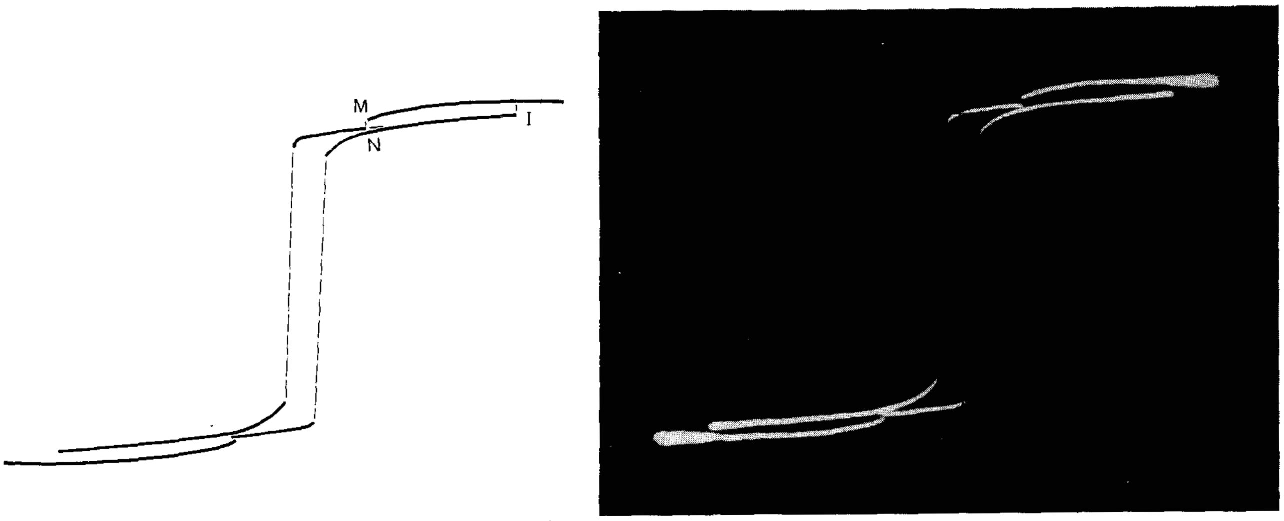


Figure 9 **A photograph of a triple hysteresis loop.**
The orthorhombic-to-tetragonal transition occurs at the point I, while the reverse transition occurs at the much smaller field, M.

4°C 3°C 2°C

Figure 10 **The effect of temperature on the hysteresis loops.**
Decreasing temperature requires greater fields for the tetragonal state to appear.

of 25 than the field at N for which the slope dP_z/dE_z is infinite. The field at K for which the transition from the orthorhombic to the tetragonal state occurs is only slightly smaller than the theoretically predicted field for which this slope is infinite. On the other hand, the return from the tetragonal into the orthorhombic state at M occurs for a value of dP_z/dE_z far from infinite. These apparent inconsistencies are treated in the discussion.

The behavior of the dielectric constant as a function of the electric field has also been observed through the transition region. A completely electroded single crystal, kept at some temperature just below the 5°C transition, is subjected to a slowly varying field as the 20 kc dielectric constant is being plotted. At zero and low fields the crystal is in the orthorhombic state and is characterized by a high dielectric constant, Fig. 12. At D, where the slope is rapidly approaching a vertical tangent, the electric field reaches a critical magnitude sufficient to flip the polarization into the tetragonal direction. Since this state has a much lower dielectric constant, there is a discontinuous drop from D to F. The dielectric constant plot shows the transition more strikingly than does a triple loop because the change in dielectric constant is an order of magnitude, compared to a few percent for the polarization change. The crystal remains in the tetragonal state until the field decreases to a value H, at which time it spontaneously reverts back to the orthorhombic state at B. The two minima at M and N show that a decrease in dielectric constant occurs during the reversal of the polarization in the orthorhombic loop.

Similar plots of dielectric constant have been obtained for various temperatures, with the expected result that lowering the temperature delayed the transition to the tetragonal state, requiring greater fields. A further conclusion of these temperature observations was that the temperature hysteresis did not decrease with increasing field, contrary to what would appear from the two curves of Fig. 6. In the varying-temperature experiment of Fig. 6, high fields were applied to a crystal for periods of two to four hours, whereas in the varying-field experiment

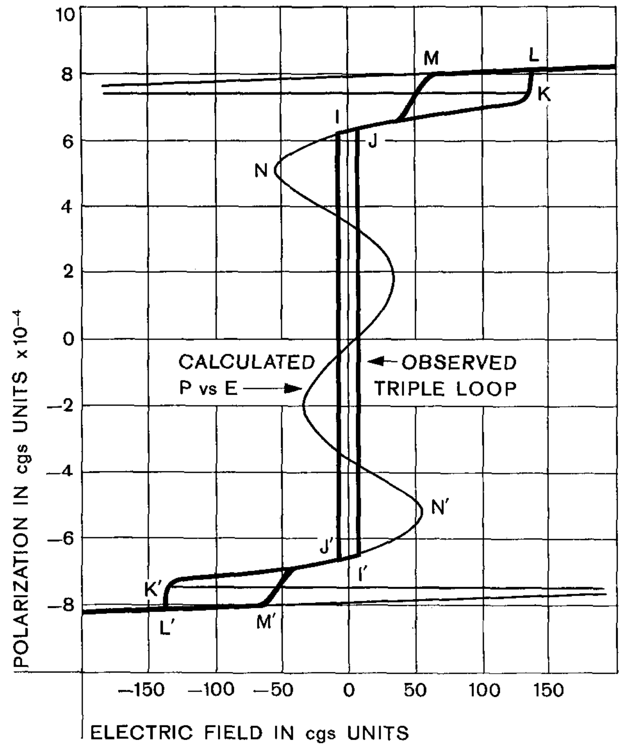


Figure 11 **Comparison of a triple loop with the theoretically determined plot of P_z versus E_z (curve *b* of Fig. 8).**
The observed coercive field in the orthorhombic state, I, is much smaller than the calculated field for vertical slope, N, but the transition coercive field, K, agrees well with the value computed from the free energy function.

high fields were applied for a matter of two to three minutes. Consequently, the effect of space charge is much less in the varying-field experiment, and in this case the temperature hysteresis is independent of the applied field.

The behavior of the dielectric constant with field in the 5°C transition region will now be computed from the free energy function, and compared with the data just presented in Fig. 12. The particular dielectric constant under consideration is ε_{zz}, since P and E are both in the z-direction. Since ε_{zz} is large compared with unity there is negligible error in letting $\varepsilon_{zz} = 4\pi\chi_{zz}$. The susceptibility, χ_{zz}, is related to components of polarization and field by the relation:

$$\chi_{ij} = dP_i/dE_j. \tag{16}$$

Hence, $\chi_{zz} = dP_z/dE_z \cong \varepsilon_{zz}/4\pi$. (17)

Since P_z is a continuous function of E_z (Fig. 8), and because in Eq. (15) P is the independent variable,

$$4\pi/\varepsilon_{zz} = dE_z/dP_z. \tag{18}$$

Since E_z is a function of both P_x and P_z, Eq. (18) becomes

$$4\pi/\varepsilon_{zz} = \partial E_z/\partial P_z + (\partial E_z/\partial P_x)(dP_x/dP_z). \tag{19}$$

The two partial derivatives can be evaluated from Eq. (15), and dP_x/dP_z is the reciprocal of the slope of the curve in Fig. 7. The right hand side of Eq. (19) computed for both the tetragonal and orthorhombic states is plotted in Fig. 13. For the tetragonal state $P_x = 0$ (and $dP_x/dP_z = 0$), and only the first term in Eq. (19) is needed; the whole expression is used for the computations for the orthorhombic state.

Eq. (19) yields curve *ABCDE* for the orthorhombic state and *HFG* for the tetragonal state. The decrease with field for low fields, the minimum, and the rapid increase towards infinity predicted in this way is in good agreement with the observation (Fig. 12). A comparison is made in Fig. 13 of the theoretical curve and the experimental data, the latter shown with dotted lines. The observed transition from orthorhombic to tetragonal occurs at a field *D* slightly less than that for vertical slope, *E*. The inverse transition, which is observed to occur at a field *H*, is not predicted by the theory. The general slope

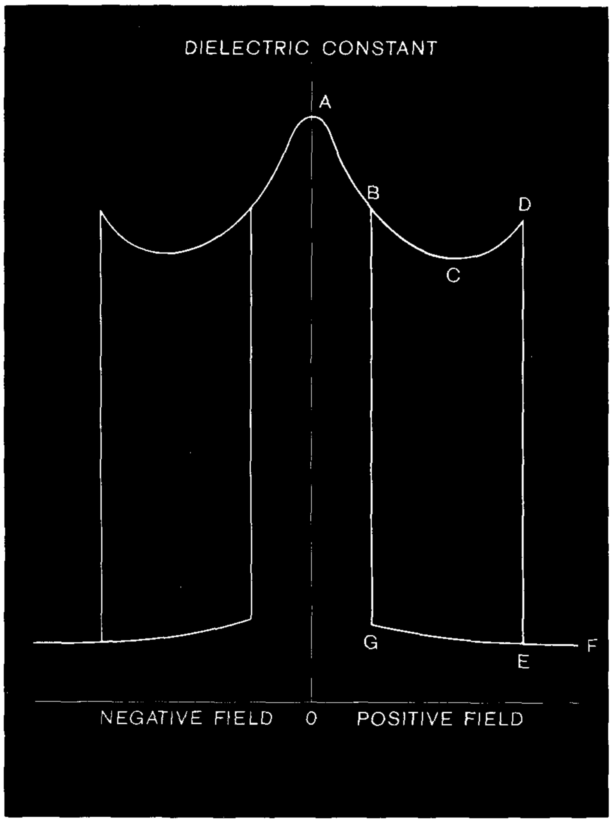


Figure 12 **The dielectric constant ε_{zz}, plotted experimentally versus electric field for a constant temperature slightly below the 5°C transition.**
The plot ABCD is the behavior in the orthorhombic state, while the curve through GEF is the dielectric constant in the tetragonal state. The transitions occur from D to F, and G to B, respectively.

of the curves and the quantitative aspects of the computed behavior of the dielectric constant agree with the experimental observation.

Discussion

Many of the experimental results presented above are in obvious agreement with the form of the free-energy function hypothesized by Devonshire. The coefficients of this function can be determined to make the theory predict qualitatively and quantitatively the details of the two transitions described in this paper; exceptions are the exact transition temperatures, coercive fields (in ordinary hysteresis loops) and transition fields (in double and triple hysteresis loops).

These apparent failures of the theory do not in any sense mean that Devonshire's free-energy function is incorrect. In all the transitions involved the material goes from a metastable to a stable state. All that a thermodynamic theory can do is to predict the range of a transition parameter (temperature, electric field, etc.) in which one state is stable and the other state is metastable. A thermodynamic treatment cannot yield the exact value of this parameter for which the transition will actually take place. The actual value of the parameter at transition may depend on variables not considered in the theory, e.g., the rate of change of the transition parameter.

There are only two ways in which the experiments could invalidate the theory: first, if a transition were found to occur for a value of the transition parameter, the theory predicts that the material must be in a well-defined stable state; and, secondly, if a transition were found to take place from a state which the theory says is stable (absolute minimum of free energy) to a state which the theory claims to be metastable (relative minimum of the free energy). Since no such instance presents itself in the experiments that have been discussed, we conclude that the predictions of the free-energy function are in excellent agreement with the experimental results. The quantitative agreement between experimental results and theoretical predictions depends upon the choice of the coefficients in the free-energy function. To determine these coefficients, use has been made of certain experimental results and of the extrapolation of the coefficient A from the cubic state. An experimental result that might have been used in place of this extrapolation is the value of the dielectric constant ε_{zz} in the orthorhombic state. This would seem a more logical approach than one relying on the extrapolation of A. This procedure was not followed because it turns out that small errors in ε_{zz} would have resulted in large errors in the coefficients. On the other hand, the Curie-Weiss plots (inverse dielectric constant versus temperature) yield such good straight lines in the cubic region (120°C to 160°C) that an extrapolation to 0°C can be made with a high degree of certainty. That the value obtained for A by this method is satisfactory is well borne out by the excellent agreement of the orthorhombic dielectric constant as shown in Fig. 13.

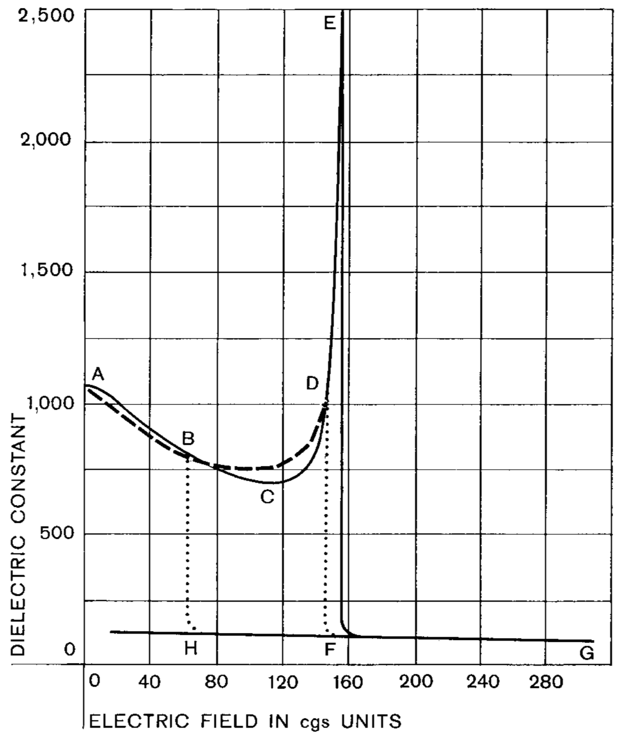


Figure 13 **A plot of the computed dielectric constant versus electric field.**
Theory gives the solid portions of the plot. The two dotted lines have been drawn to indicate the relationship between the computed curve and the observed effect plotted in Fig. 12.

Since A can be extrapolated from the cubic region, it is not surprising to find that the same may be done for B. The value of B determined for 0°C, lies very near an extrapolation of data obtained in earlier measurements.[4]

All the points of agreement mentioned in this paper make it appear that the behavior of barium titanate is well described by the Devonshire free-energy polynomial approximation, and that we have obtained reliable values for the coefficient involved.

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