# Transition to the Ferroelectric State in Barium Titanate\*

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The phase transition in BaTiO3 at the Curie point was investigated on single crystals with optical and electrical techniques. Besides raising the cubic-tetragonal transition about 15°C in the usual way with an electric field along the cube-edge direction, an orthorhombic phase was induced above the Curie point by a field along a face-diagonal direction. Birefringence, polarization, and dielectric constant were measured above and below the Curie point as functions of field strength and field direction. The data fit a unified description using the free energy equation of Devonshire. An atomic model for the induced orthorhombic phase is proposed with Ti ions displaced in alternate cube-edge directions. The shift of the ferroelectric transition with electric field was observed optically and compared with predictions derived from the freeenergy curves. Two types of transition were observed: In the slow transition the new phase nucleates at the edges of the crystal and grows by domain-wall motion; in the fast transition, which occurs only if the electric field is changed faster than about 1 kv/cm sec, the entire crystal switches in a uniform, continuous motion in 1 to 2  $\mu$ sec.

### I. INTRODUCTION

HE study of the spontaneous orientation of dipole moments in ferroelectrics and ferromagnetics is one of the long-range research projects of the Laboratory for Insulation Research.<sup>1,2</sup> The present investigation is concerned with the creation of the ferroelectric state in BaTiO<sub>3</sub>, with particular attention to questions of shortvs long-range interaction near the Curie point, the nucleation of the ferroelectric state, and the speed of its formation. Only a limited amount of information on the spontaneous formation of dipoles can be obtained from the dielectric measurements of previous investigations. A combination of electrical and optical tools. as used in this study, gives a more complete picture of the onset of the ferroelectric phase.

BaTiO<sub>3</sub> is used preferentially for ferroelectric studies because of its simple perovskite structure, its availability in the form of single-crystal plates, the wide variation of properties obtainable by cation substitution, and the predominant technical importance of titanate ceramics.<sup>1</sup> The dielectric constant and polarization of single crystals of BaTiO<sub>3</sub> have been measured extensively since they became available. The most recent data were from single crystals grown from KF flux by the Remeika method,<sup>3</sup> since they are larger and less strained than those grown by other methods. These crystals yield higher values of polarization and dielectric constant both above and below the Curie point.4-6

A deeper understanding of the electrical properties

has been acquired by investigating the dynamic behavior of the domains.<sup>7,8</sup> The phase transitions themselves have been investigated only scantily. The Curie point was found to represent a first order transition, as Merz<sup>4</sup> proved conclusively by double hysteresis loops. For 15° above the Curie point the crystal can be switched from the paraelectric to an induced ferroelectric phase by application of an electric field, i.e., the Curie point can be raised by the field. Huibregtse and Young<sup>9</sup> made a similar study of the tetragonal-orthorhombic transition.

#### **II. EXPERIMENTAL**

The polarizing microscope was the primary tool used in these investigations. It allows clear observation of domain and phase boundaries and accurate birefringence measurements. Larger values of birefringence were measured with a quartz wedge and small ones with a quarter-wave plate.<sup>10</sup> The values could be obtained also by recording the light output with a photomultiplier tube mounted on top of the microscope; the output of the tube was fed into an oscilloscope and photographed. Since the birefringence of BaTiO<sub>3</sub> shows a strong dispersion near 5450A, the green mercury line was chosen for illumination.

Thin, single-crystal samples of simple geometric shape were required for these observations. Electrodes had to be attached intimately and permanently to two opposite edges, covering them completely because of the high dielectric constant and piezoelectric coefficients.6

Samples about 1.0 by 1.5 mm were cut from singlecrystal plates grown by the Remeika method and the edges were polished to microscopic smoothness. The crystals were then etched to the desired thickness of 15

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<sup>&</sup>lt;sup>2</sup> Miles, Westphal, and von Hippel, Revs. Modern Phys. 29, 279 (1957).

 <sup>&</sup>lt;sup>5</sup> J. P. Remeika, J. Am. Chem. Soc. 76, 940 (1954).
 <sup>4</sup> W. J. Merz, Phys. Rev. 91, 513 (1953).
 <sup>5</sup> M. E. Drougard and D. R. Young, Phys. Rev. 95, 1152 (1954).
 <sup>6</sup> Drougard, Landauer, and Young, Phys. Rev. 98, 1010 (1955).

<sup>&</sup>lt;sup>7</sup> E. A. Little, Phys. Rev. 98, 978 (1955).

<sup>&</sup>lt;sup>6</sup> W. J. Merz, Phys. Rev. **95**, 690 (1954); H. H. Wieder, J. Appl. Phys. **27**, 413 (1956). E. J. Huibregtse and D. R. Young, Phys. Rev. 103, 1705

<sup>(1956).</sup> <sup>10</sup> See, e.g., C. Burri, Das Polarisations Mikroskop (Birkhauser, Basel, Switzerland, 1950), pp. 138-158.



FIG. 1. Electrode geometry used for simultaneous electrical and optical measurements.

to 100  $\mu$  by concentrated phosphoric acid above 120°C a process which leaves all surfaces plane-parallel and smooth.<sup>11</sup> The electrodes were formed by depositing a semiconducting layer of tin oxide on the crystal surface because evaporated metals were found not to adhere well enough. A layer of gold was evaporated on top of the semiconducting layer and the crystals were mounted in a sample holder between two soft springs of goldcoated tungsten wire (Fig. 1).

Two microscope stages were provided with temperature control  $(-40^{\circ} \text{ to } 150^{\circ}\text{C})$  and electrical connections to the sample holder. A solid copper stage, heated by circulating oil, was used for precise temperature measurements. With it the temperature of the sample changed much less than 0.1°C in several hours.





<sup>11</sup> J. T. Last, Phys. Rev. 105, 1740 (1957),

#### **III. STEADY-STATE INVESTIGATION OF THE** FERROELECTRIC TRANSITION

### **General Problems**

Space-charge build-up, causing inhomogeneous fields, is a problem in all steady-state measurements, especially at high temperatures. For this reason, previous measurements near the Curie point have been made with alternating fields.6

Space-charge effects could be eliminated in the birefringence measurements by using square waves with a period much longer than the response time of the crystal. Observations of polarization and dielectric constant were made with low-frequency ac fields. Both techniques may raise the crystal temperature by hysteresis effects; hence only frequencies low enough to make this effect negligible were used. The crystal may also heat reversibly by the electrocaloric effect (inverse pyroelectric effect), but this influence was previously shown to be small.6

The permanent space-charge layer observed by Chynoweth<sup>12</sup> might also interfere with the measurements. He reports that this layer can produce considerable fields in the crystal which may change some of the measurements above the Curie point. In the present case, however, the geometry of the samples is such that any built-in fields would be reduced by a factor 10 to 20 below those observed by Chynoweth, and therefore they may be neglected.

The crystals were polarized to the single-domain state whenever possible to avoid internal clamping. This can be checked visually since both 90° and 180° walls can be observed under the microscope.<sup>7</sup>

### Observations below the Curie Point

A [100] crystal [electrodes in the (100) plane] could always be polarized parallel to the field in the tetragonal phase. The birefringence  $(\Delta n)$  was measured (Fig. 2) for several samples at zero field. The samples have differing Curie temperatures due to the different amounts of impurities they contain. The average value of  $\Delta n$  is 0.073 at 20°. Even if all the curves are adjusted to this value to correct for inaccuracies in thickness measurements, the curves differ considerably for the various crystals. There is a general trend for the birefringence to decrease more slowly with temperature in crystals with higher Curie points.

The polarization of the  $\lceil 100 \rceil$  crystals was measured by a display of hysteresis loops in the usual Sawyer and Tower circuit.<sup>13</sup> The domain structure was observed at the some time to insure that the entire crystal reversed its polarization. The loops [Fig. 3(a)] did not change shape for ac fields as high as 5000 v/cm. The values of spontaneous polarization obtained from these loops showed the same variations as the birefringence values

 <sup>&</sup>lt;sup>12</sup> A. G. Chynoweth, Phys. Rev. **102**, 705 (1956).
 <sup>13</sup> C. Sawyer and C. Tower, Phys. Rev. **35**, 269 (1930).



FIG. 3. Hysteresis loops: (a) typical hysteresis loop in the tetragonal phase; (b) double loop in the [100] direction; (c) double loop in the [110] direction; (d) quadruple loop in the [110] direction.

(Fig. 2). The average values were equal to those previously reported.<sup>4</sup>

The dielectric constant of [100] crystals was measured parallel ( $\kappa_c'$ ) and perpendicular ( $\kappa_a'$ ) to the polar axis (Fig. 4). The values of  $\kappa_c'$  are the same as those previously reported.<sup>5</sup>  $\kappa_a'$  has not been measured previously on crystals grown from KF flux, because this measurement is possible only if the permanent electrodes are on the sides of the sample, as in the present case. The crystals can then be polarized in a direction perpendicular to the plate by using temporary glycerin electrodes.

## **Observations Above the Curie Point**

In Fig. 5 the dependence of birefringence on electric field in the [100] direction is shown for various temperatures around the Curie point, and also the discontinuous transition between the para- and ferro-electric phases with the fields and hysteresis observed



FIG. 4. Dielectric constant in the cubic and tetragonal phases: perpendicular ( $\kappa_{\alpha}'$ ) and parallel ( $\kappa_{\alpha}'$ ) to the direction of spontaneous polarization.



FIG. 5. Induced birefringence vs electric field in the [100] direction.

in the polarization measurements.<sup>4</sup> The value of birefringence in the paraelectric phase can be expressed as  $\Delta n = d_1 E^2 + d_2 E^4 + \cdots$ . There will be sixth and higher order terms, which cannot be measured at these field strengths but become important in the induced ferroelectric phase. The values of  $d_1$  and  $d_2$  are shown as functions of temperature in Fig. 6.

When a field of 3000 to 6000 v/cm was applied to a [110] sample below the Curie point, the domain structure nearly always changed to that shown in Fig. 7. The



FIG. 6. Induced birefringence in the paraelectric phase: coefficients of the equation  $\Delta n = d_1 E^2 + d_2 E^4$  vs temperature (in °C above the average Curie point) for various crystals.

number of 90° walls tended to increase with field. The individual domains were quite narrow. At about 500 v/cm, if the field direction was reversed, the domain polarization was reversed by 180°. The induced birefringence was parallel to the field ([110] direction) in the paraelectric phase. The sample transformed to an induced ferroelectric phase at higher fields. This phase could be identified by the direction of the polar axis. It was entirely orthorhombic [110] at higher temperatures, but contained a mixture of tetragonal [100] and orthorombic domains near the Curie point. The dependence of birefringence on the strength of the electric field in the [110] direction is shown in Fig. 8. Some of the values in the orthorhombic ferroelectric phase were difficult to obtain accurately because the orthorhombic regions were small and intermixed with tetragonal regions. However, the values were reproducible for various crystals. As in the  $\lceil 100 \rceil$  direction, the birefringence in the paraelectric phase could be expressed by  $\Delta n = d_1 E^2 + d_2 E^4 + \cdots$  (Fig. 6).

To clarify the dependence of  $\Delta n$  on intermediate directions of the electric field, a set of crystals was prepared with edges approximately halfway between



FIG. 7. Domain configuration in the tetragonal phase below the Curie point after a field has been applied in the [110] direction.

the [100] and the [110] axes. In the paraelectric phase the coefficients  $d_1$  and  $d_2$  fall between the curves of Fig. 6 ( $d_2$  is very small and negative). The induced ferroelectric phase above the Curie point is completely tetragonal with many 90° walls. A very small orthorhombic region appeared in only one case.

Polarization measurements on [100] crystals showed the same double hysteresis loops as the birefringence measurements (see Fig. 5). From these [Fig. 3(b)] the dependence of polarization on electric field and temperature was obtained. Hysteresis heating effects were considered negligible because the curves were independent of frequency. In the paraelectric phase the curves can be expressed as  $P = \epsilon E + \lambda E^3 + \cdots$ .  $\epsilon$  and  $\lambda$  are shown in Fig. 9 as functions of temperature with a curve of  $\lambda/\epsilon^4$  for comparison with the thermodynamic theory (see below).

Double hysteresis loops appear also for fields applied in the [110] direction above the Curie point [Fig. 3(c)] and give similar characteristics (Fig. 9). The induced phase is orthorhombic in this case, as confirmed by optical observation. Some crystals show two induced phases. The first change to the orthorhombic phase is followed by another one at higher fields to a new configuration which cannot be determined by electrical and optical methods alone. It has a smaller birefringence than the orthorhombic phase and a poorly defined optical axis approximately along the [110] axis. Since the polarization along the field is larger than in the orthorhombic phase, quadruple hysteresis loops are obtained [Fig. 3(d)].

All steady-state measurements were repeated on various crystals which contained different, but unknown amounts of impurities and strain, and therefore had different Curie points. However, most results were reproducible if they were plotted relative to the Curie point temperature (see Figs. 6 and 9 which contain measurements from many different samples). The maximum variations of  $\pm 10\%$  occurred at high field strengths.

#### Discussion

The polarization and dielectric constant data can be fitted into a unified picture by using the relatively simple thermodynamic formulation developed by Devonshire.<sup>14</sup>

TABLE I. Coefficients of the Devonshire equation.

\*  $T_0$  varies with the Curie point  $T_c$ ;  $T_c - T_0 = 13.5$  °C.

He expresses the free-energy difference between the actual ferroelectric or paraelectric state and a hypothetical cubic state as a power series in polarization for *zero stress*:

$$\begin{aligned} G_{1}(T,P) - G_{10}(T) \\ &= \frac{1}{2}\beta_{0}(P_{x}^{2} + P_{y}^{2} + P_{z}^{2}) + \frac{1}{4}\xi_{11}(P_{x}^{4} + P_{y}^{4} + P_{z}^{4}) \\ &+ \frac{1}{2}\xi_{12}(P_{y}^{2}P_{z}^{2} + P_{z}^{2}P_{x}^{2} + P_{x}^{2}P_{y}^{2}) \\ &+ \frac{1}{6}\zeta_{111}(P_{x}^{6} + P_{y}^{6} + P_{z}^{6}) + \frac{1}{2}\zeta_{112}[P_{x}^{2}(P_{y}^{4} + P_{z}^{4}) \\ &+ P_{y}^{2}(P_{z}^{4} + P_{x}^{4}) + P_{z}^{2}(P_{x}^{4} + P_{y}^{4})] + \frac{1}{2}\zeta_{123}P_{x}^{2}P_{y}^{2}P_{z}^{2} \end{aligned}$$

(The last two terms have been added to the original formulation to complete the power series to the sixth order of the polarization.<sup>9</sup>) The coefficients are isothermal and depend, in general, on temperature, although Devonshire assumed this only for the Curie-Weiss law coefficient  $\beta_0$ . The relations between polarization, dielectric constant and electric field are derived by differentiating the free-energy function.

The coefficients of the free-energy function were determined from all the measurements of dielectric constant and polarization except those of the polari-



FIG. 8. Induced birefringence vs field strength in the [110] direction.

zation in the induced orthorhombic phase, where measured values are ca 30% smaller than those calculated (Table I).

Birefringence can be related to the square of the polarization because in first approximation both quantities are proportional to the spontaneous strain.<sup>4,15</sup> The measured values of  $P^2/\Delta n$  in the [100] direction always fell between 0.9 and 1.25 coul<sup>2</sup>/m<sup>4</sup>. The birefringence behaved similarly in the orthorhombic phase: at 0°C,  $P=0.31 \text{ coul/m}^2, \Delta n=0.1150 \text{ and } P^2/\Delta n=0.83 \text{ coul}^2/m^4$ . This is not the case for the [110] direction above the Curie point. In the paraelectric phase  $\Delta n$  was expressed by  $d_1$  and  $d_2$ :  $d_1$  was approximately the same for the



FIG. 9. Induced polarization in the paraelectric phase: coefficients of  $P = \kappa E + \lambda E^3$  vs temperature in the [100] and [110] direction.

<sup>15</sup> H. Kay and P. Vousden, Phil. Mag. 40, 1019 (1949).

<sup>&</sup>lt;sup>14</sup> A. F. Devonshire, Phil. Mag. 40, 1040 (1949); 42, 1065 (1951). A. F. Devonshire, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 85.



FIG. 10. Models of the perovskite lattice projected onto the (100) plane parallel to the polar axis: (a) tetragonal, (b) orthorhombic-ferroelectric phase, (c) proposed induced orthorhombic phase, with movement of the Ti ions only, (d) with movement of all the ions.

[100] and [110] direction, but  $d_2$  proved to be positive in the [100] and negative in the [110] direction (Fig. 6). This effect became much more pronounced in the transition to the induced ferroelectric orthorhombic phase. The birefringence decreased discontinuously (Fig. 8) while the polarization increased [Fig. 3(c)], resulting in values of  $P^2/\Delta n$  as high as 5 instead of 1. This shows that the induced orthorhombic phase must be different from the one below 5°C.

The atomic configuration which leads to the thermodynamic behavior described above can be represented by the following simplified model. Let the Ba and O ions have zero polarizability and let them be positioned at the corners and face centers of the perovskite lattice, leaving only the Ti ion free to polarize and move. Neutron diffraction showed that the Ti ion is displaced



FIG. 11. Potential energy curves for coherent movement of all Ti ions (schematic).

relative to the oxygen octahedron along the  $\lceil 100 \rceil$  axis in the tetragonal phase, with the displacement x proportional to the polarization.<sup>16</sup> Similarly, the polarization in the orthorhombic phase is due to the Ti displacement in the [110] direction.<sup>17</sup> The birefringence is proportional to the strains and to the square of the polarization in both cases. Figure 10 shows projections of the perovskite lattice onto the (100) plane parallel to the polar axis; a and b are simplified configurations for the tetragonal and orthorhombic phases. It can be assumed that the same proportionality will hold approximately in the induced orthorhombic phase, which therefore requires a model with a large Ti displacement and a small strain. Such a model is shown in Fig. 10(c). The Ti's are displaced alternately in the  $\lceil 100 \rceil$  and [010] directions. In a first approximation the other ions are held in their cubic positions; a square lattice without birefringence results. Actually, they are shifted slightly to keep the interatomic distances approximately the same, producing a small orthorhombic shear in the unit cell [Fig. 10(d)]. The resulting birefringence is much smaller than in model b; the net polarization along the axis is also somewhat smaller than for b because  $P = mx/\frac{1}{2}$ rather than mx, corresponding to the experimental observations. Obviously, other models might be constructed with similar properties and a thorough structure analysis is required to select the right one.

According to model d, the potential minima for the Ti ions in the induced orthorhombic phase lie near the [100] axes; they must be the ones that are occupied in the tetragonal phase. The potential energy is spherically symmetrical near the origin, as shown by the behavior in the paraelectric phase (Figs. 6 and 9). The Ti ion tends to be displaced along the [110] axis when a small field is applied in that direction. The strongly anisotropic second-order terms become important at higher fields and the Ti ion moves away from the [110] axis. The potential-energy curves for coherent movement of all Ti ions and positions of the Ti ions as a function of



FIG. 12. Phase-transition temperatures of a good single crystal vs time: A to C and a to n refer to microphotographs (Figs. 13 and 14) of the crystal made at the time shown.

<sup>16</sup> Frazer, Danner, and Pepinsky, Phys. Rev. 100, 745 (1955); Bull. Am. Phys. Soc. Ser. II, 2, 23 (1957).

<sup>17</sup> Shirane, Danner, and Pepinsky, Phys. Rev. 105, 856 (1957).

the field in the [110] direction are schematically sketched in Fig. 11.

## IV. DYNAMICS OF THE PHASE TRANSITION

### Phase Transition at Zero Field

Careful observation with the polarizing microscope showed that the crystals did not transform abruptly from cubic to tetragonal and vice versa, but formed one or more domains of the new phase which grew slowly, continuously or in steps. The nucleation took place at special points along the edges of the crystal. The walls between the phases were straight lines that might or might not be orientated in the direction of any of the simple crystal axes. The temperature for nucleation, the domain pattern, and the speed of growth of the domain walls varied with temperature, even for the same crystal under identical external conditions.

The statistical switching behavior of a strain-free sample is illustrated in Fig. 12, where the temperature range of each transition is indicated. The temperature was changed by  $0.1^{\circ}/\text{min}$ ; no movement of the phase boundaries occurred when the temperature was held constant part way through the transition. The crystal randomly assumed one of three distinctly different final domain configurations (A, B, or C, Fig. 13) upon transforming to the tetragonal phase. The mixed phase regions took on a large number of different forms de-



FIG. 13. Photomicrographs of tetragonal domain configurations (see Fig. 12).

pending on the final tetragonal configuration. The photographs of some of these, taken at times a to n of Fig. 12, are shown in Fig. 14. (The black regions are cubic, the others tetragonal.) From the single-domain state (A) the transition usually proceeded by the continuous movement of a single phase boundary





FIG. 15. Change of the first-order transition with the electric field in the [100] direction: (I) slow, (II) fast transition.

 $(a \rightarrow b \rightarrow c \rightarrow d)$ . The two-phase regions (*f* to *n*, Fig. 14) were more complex when they started with the configurations *B* or *C* (Fig. 13).

Some samples appeared to have more built-in strains or impurities and always transformed to the same domain pattern in the tetragonal phase. In those cases the transformation in one direction was the exact inverse of that in the other direction indicating that different parts of the crystal had different Curie temperatures. This behavior could be changed, sometimes permanently, by changing the domain pattern in the tetragonal phase with an electric field.

The average temperature<sup>18</sup> hysteresis  $(T_{c2}-T_{c1})$  varied from 1.0 to 2.2°C for various crystals. The average Curie point  $(T_{c1}+T_{c2})/2$  ranged from 115.6° to 119.9°C for our crystals grown by the Remeika technique in air; other samples had Curie point temperatures from 106.2° to 115.6°C.

#### **Field-Induced** Transition

The influence of electric field on the Curie point was studied first by varying the temperature at constant field. The transition proceeded by nucleation and growth of the new phase, as in the zero-field case, but the crystal always assumed the single domain status (A, Fig. 13) in the tetragonal phase and the transition points shifted to higher temperatures (Fig.15, curve I). The external fields shown do not completely correspond to the internal situation because of space-charge buildup during the long time required for these measurements; they vary considerably from crystal to crystal. Above 5000 v/cm, field distortion made the transition point relatively uncertain.

Next, the field was varied at constant temperature. This gave more quantitative information because the field could be changed much faster and space-charge build-up avoided. For very slow changes of field (<0.1 kv/cm sec) the transition proceeded exactly as when the temperature was varied. One or more domains of the opposite phase nucleated at the edges of the crystal and grew. The average transition points coincided approximately with those induced by temperature variation (Fig. 15, curve I).

The transition behaved quite differently if the field was changed rapidly (>0.1 kv/cm sec). The entire crystal changed abruptly from one phase to the other without any evidence of boundary motion as far as optical observations could discern. The fields at which this transition took place (Fig. 15, curves II) were well reproducible for various crystals except at high temperatures, where the two phases nearly coalesce. In the regions of positive field (curve IIa and curve IIb for  $T>T_1$ ) the curves were independent of the rate of change of field as long as the whole crystal switched at once. This was checked from 10<sup>7</sup> to 0.1 kv/cm sec.

The reverse transition from the tetragonal to the cubic phase took place at negative fields in the temperature region between  $T_{c2}$  and  $T_1$  (Fig. 15, curve IIb) as long as the field was varied faster than 100 kv/cm sec. At lower rates of change all crystals switched back to the cubic state near zero field, either suddenly or gradually by wall motion. The reason apparently is that the tetragonal phase could break up into a variety of domain patterns at that point if given enough time. The crystal transformed only partially to the cubic phase below  $T_{c2}$  and not at all below  $T_{c1}$ .

The transition to the induced orthorhombic phase was investigated in the same manner. The tetragonal phase, stable below the Curie point, interfered with the orthorhombic phase in the cases of slow transitions and no definite transition points could be assigned. For rapid changes of the field the crystal transformed suddenly from the cubic to the orthorhombic phase analogously to the tetragonal case (Fig. 16).

#### Discussion

The temperature of the first order transition as a function of field strength cannot yet be derived from



FIG. 16. Change of the first-order cubic-orthorhombic phase transition with electric field in the [110] direction.

<sup>&</sup>lt;sup>18</sup> From here on the Curie temperature of a crystal will be defined as the temperature at which, on the average, one half of the crystal has changed phase:  $T_{c1}$  for the cubic  $\rightarrow$  tetragonal transition,  $T_{c2}$  for tetragonal  $\rightarrow$  cubic.

atomic theory because the free energies cannot be calculated very accurately. It is therefore necessary to use the phenomenological thermodynamic theory as a basis for a discussion. The stable phase at each value of temperature and electric field is the one with the lowest total energy. Since  $(G_1 - G_{10})$  represents only the reversible work needed to change the polarization of the crystal from zero to P at zero field, the total energy W must include an electrostatic term  $W(E,T,P) = G_1(T,P) - \mathbf{E} \cdot \mathbf{P}$ . W can be plotted as function of E, T, and P, using the coefficients of Table I. There is always at least one energy minimum, for high temperatures near P=0(paraelectric phase) and for low temperatures at a large value of P (ferroelectric phase). In an intermediate range there are two minima as long as  $E < E_c$ .  $(E_c = 11 \text{ kv/cm for the } [100] \text{ direction.})$ 

At what temperature the transition from one minimum to the other takes place will depend on the relative depth of the minima, the height of the potential barrier between them, and the temperature vibrations. Two special cases can be considered: (1) The temperature (or the field) is changed slowly and the thermal vibrations are large enough so that the crystal is always in its most stable state, in which case the transition must take place where the two minima are equally deep, i.e., there will be no thermal hysteresis. (2) The temperature (field) is changed very fast so that the crystal has no chance to move out of the higher potential well until the well completely disappears when  $\partial^2 G_1 / \partial P^2 = 0$ .

These special transition points are shown for the  $\lceil 100 \rceil$  direction in Fig. 15 (dashed lines); the middle line refers to case 1 while the other two lines refer to case 2. The actual observation of the slow transition compares to case 1 except that it shows a small amount of temperature hysteresis. The activation energy between the minima must be high even at the special points along the edges where the new phases nucleate. The slope of the experimental curves also differs from that of the theoretical one because, due to space charge, the measured fields are higher than the actual fields. The curves of the fast transition show the same shape as case 2 but the temperature hysteresis is 40% of the theoretical one. This is to be expected since the total transition time could not be decreased below 1  $\mu$ sec, even with rapidly rising fields (see below); the temperature vibrations cannot be neglected during such a period.

This analysis can be made for the cubic-orthorhombic transition, except that only the fast transition could be measured. The temperature hysteresis is here only 14% of the theoretical (Fig. 16), while the qualitative behavior is again the same as theoretically predicted. The potential barriers between the two phases must be smaller than in the previous case.

#### **Pulse Measurements**

Since the field-induced transition can be made to take place very rapidly, detailed information about the



FIG. 17. Change in light output and birefringence during a  $3-\mu$ sec electrical pulse large enough to switch the crystal from the cubic to the tetragonal phase.

actual process requires pulse techniques. Pulses and step functions of 0.1  $\mu$ sec rise time were applied to the samples and the light output recorded (the recording system had a time constant of slightly less than 0.1  $\mu$ sec). For monochromatic light polarized at 45° to the optical axis, the light output under crossed polarizers is related to the birefringence as  $I = I_0 \sin^2(\Delta \phi/2) = I_0 \sin^2(\pi \Delta n d/\lambda)$ , with  $\Delta \phi$  the phase difference between the ordinary and the extraordinary ray, d the crystal thickness, and  $\lambda$ the light wavelength.

In the paraelectric phase a quadratic Kerr effect was observed since  $\Delta n \propto E^2$ . For a 3-µsec pulse the birefringence followed the electric field strength without delay, indicating that the time constant for the Kerr effect was less than 0.1 µsec. This corresponds to the observations of Koelsch,<sup>19</sup> who observed a time constant of 40 mµsec or less. The birefringence continued to increase slightly after the voltage pulse had reached its maximum value. This effect was smaller on a crystal with gold electrodes only; the distributed circuit elements of the tin oxide and surface layers may be responsible for it.

The light output shows a more complicated behavior when the crystal is switched to the induced tetragonal ferroelectric phase (Fig. 17). A typical high-speed oscillogram shows a number of large oscillations in light intensity at the beginning of the pulse (A). These were accurately reproducible and were caused by a continuous change of birefringence from zero to its final value, which fell on the same curve as the dc measurements (Fig. 5).

Subsections of the crystal, investigated by masking sections of its image on the surface of the photomultiplier, showed the same behavior of the birefringence as the whole crystal. Hence, for high-speed pulses, the crystals transformed uniformly and continuously from one phase to the other without evidence of wall motion.

<sup>&</sup>lt;sup>19</sup> A. G. Koelsch, Institute for Radio Engineers Convention Record (Institute for Radio Engineers, New York, 1957), Part 3, pp. 169 ft.

The time of the transition from 10 to 90% varied between 1 and 2.5  $\mu$ sec, depending on the crystal and sample holder but not on temperature or electric field. Pulses were applied to a much smaller crystal (0.26 mm between electrodes) to investigate the effect of crystal geometry. The sample did not behave as well as the larger crystals, probably because of electrode-edge effects; the oscillations in light output (A) were only barely noticeable, but the transition definitely took place in about 0.5  $\mu$ sec, considerably faster than for the larger samples.

After  $\Delta n$  reached its final value, the average light output was constant for the remainder of the voltage pulse (B).

The behavior after the pulse ended (C) depended on temperature. Above  $T_1$  (Fig. 15) the crystal switched back to the cubic phase immediately. The light output curve was approximately the inverse of that observed at the rise of the field. The number of large oscillations was the same but they were less pronounced possibly due to induced strains. It took 2 to 3  $\mu$ sec for most of the light to disappear.

The crystal did not change immediately to the cubic phase when the pulse was removed between  $T_{c2}$  and  $T_{1}$ , but remained for a while in the ferroelectric state with only a slight change of  $\Delta n$  (C). After a time the light output changed by one or more sudden jumps, and eventually reached zero. The intermediate states were evidently partly tetragonal with various domain structures. This reiterates the importance of domain formation to the break-up of the tetragonal state in this temperature region. The first jump led to zero in about half the cases and occurred from 200 to 1500  $\mu$ sec after the pulse ended. This time varied only slightly for a given crystal at constant temperature, decreasing with increasing temperature. This could not be determined quantitatively since the range between  $T_{c2}$  and  $T_1$  was only 2°.

Small sinusoidal oscillations were superimposed on the constant values of light output in both regions (*B* and *C*, Fig. 17). They continued undiminished sometimes for long periods and were also observed in the paraelectric phase. Their period was between 0.5 and 0.8  $\mu$ sec for samples 1.0 to 1.5 mm long, and 0.2  $\mu$ sec for the short crystal (0.23 mm long), an average of 0.6  $\mu$ sec/mm. Piezoelectric resonances observed in the dielectric constant spectrum of these samples at room temperature<sup>20</sup> showed that the fundamental longitudinal vibration occurs at 0.5  $\mu$ sec/mm. This indicates that the oscillations were electromechanical vibrations excited by the electric pulse.

Pulse measurements were also made on [110] crystals. In this case the birefringence in the induced ferroelectric phase is only slightly different from that in the paraelectric one and the transitions were difficult to detect and investigate by this method. However, it could be seen that the transition required about the same time as in the [100] case and the decay from the orthorhombic to the cubic phase was similar.

The behavior differed if pulses were applied to the samples with edges halfway between the [110] and [100] directions. The induced state was multidomain tetragonal, and the transition took place in 1 to 2  $\mu$ sec with only one or two noticeable oscillations. The formation of domain walls evidently proceeds during the transition, and not after its completion.

## The Transition Process

The fast transition, during which the crystal switched as a whole, allowed a more quantitative investigation by measurements of the change in birefringence (see Fig. 17). The ultimate limit of the speed of transition must be the time it takes for the feed-back effect to build up. The ions will be displaced a small amount by the external field, thereby producing a larger local field which in turn increases the displacement, and so on. The temperature will influence this effect because it will produce variations in the local field. The magnitude of the electric field should also change the speed of transition. No such dependence on temperature and field was observed, hence the feed-back mechanism takes effect faster than the observed transition time of 1  $\mu$ sec and a slower process must limit the speed of transition.

The slower process must be connected with the mechanical deformation occurring during the transition. as demonstrated by the shorter transition time of the smaller crystal. The deformation is a longitudinal extension along the polar axis and a considerable rearrangement of the ions in the crystal lattice is associated with it. A type of shock-wave pattern can be expected to form during the transient state to keep the deformation and ion rearrangements uniform throughout the crystal and cause the transition to be somewhat longer than the transit time of a sound wave. The shock-wave pattern will create a high attenuation and account for the "relaxation-type" rise in birefringence (see Fig. 17). This is the same process that determines the highfrequency relaxation spectrum of the dielectric constant as postulated by von Hippel.<sup>21</sup>

In contrast, the piezoelectric resonances observed once the crystal had switched were attenuated only slightly (see Fig. 17). Their frequency corresponds exactly to the transit time of a sound wave and therefore they have a shorter period than the damped transition (0.6 vs 1.5  $\mu$ sec/m). They are identical to the piezoelectric resonances observed in the dielectric constant spectrum, as was mentioned previously.

The fact that the fast transition takes place at the same value of electric field under all conditions shows that it always occurs in the manner discussed in this

<sup>&</sup>lt;sup>20</sup> W. B. Westphal, Massachusetts Institute of Technology (private communication).

<sup>&</sup>lt;sup>21</sup> A. von Hippel, Technical Report 99, Laboratory for Insulation Research, Massachusetts Institute of Technology, August, 1955 (unpublished).

section. Every part of the crystal starts to transform at the same time, in contrast to the slow transition with its one or two nucleation points. The transition process is also very different from the polarization reversal in the tetragonal phase. The latter always takes place through nucleation and growth of antiparallel domains. The reversal time varies continuously and exponentially with the electric field except that it must also be limited by the velocity of sound.<sup>8</sup> This is as expected since it must be more difficult to reverse an already established polarization than create or destroy one.

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# Optical Absorption and Photoconductivity in Magnesium Oxide Crystals\*

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Optical absorption and photoconductivity spectra of magnesium oxide crystals from various sources are presented. The effects of ultraviolet and x-ray irradiation are described, and the results are interpreted in terms of valence changes of impurities, principally iron. A method for the analysis of the photoconductivity data is given. This method corrects for the effects of strong nonionizing absorption, which may lead to spurious peaks in photoconductivity spectra. The sign of the optically excited charge carriers was deduced by a method which involves the formation of a space-charge field by the motion of carriers in an applied electric field, and the detection of the asymmetry in this space-charge field when carriers are subsequently allowed to move under the influence of the space-charge field only.

A band centered at 5.05 ev has been detected in all specimens measured and this is believed to be due to the impurity  $Fe^{2+}$ . Irradiation in this band provides free electrons some of which are believed to be trapped by other  $Fe^{2+}$  ions. Three absorption bands previously observed by other authors are believed to be associated with the impurity Fe<sup>3+</sup>.

### 1. INTRODUCTION

HE work to be described in this paper was part of a program<sup>1,2</sup> whose purpose was the determination of the nature of certain imperfections in magnesium oxide crystals. The imperfections of interest are those which evidence themselves as electronic excitation processes occurring in a region of the spectrum where light is not absorbed by the perfect crystal. According to the usual usage of the term, they may therefore be denoted as "color centers."

One of the principal reasons for the interest in color centers in MgO is the desirability of extending the information and understanding that has been gained in the study of the alkali halide group of compounds,<sup>3</sup> to

a compound of divalent elements with a similar type of binding. So far as the author is aware, there is not in the present nor in any previous work, any evidence that an analog to any of the well-known color centers has been found in MgO. There are known, however, several optical transitions<sup>4,5</sup> which can be introduced in certain ways. The purpose of this work was to study these transitions by the measurement of absorption and photoconductivity spectra and to attempt to determine the nature of the corresponding imperfections.

Measurements of this sort have previously been published: optical absorption spectra by Weber<sup>4</sup> and photoconductivity spectra by Day.<sup>5</sup> Their conclusions have been extensively used by other authors in the discussion of measurements of conductivity,6 ultraviolet activation,7 luminescence,8 and Hall effect9 of MgO crystals.

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FIG. 13. Photomicrographs of tetragonal domain configurations (see Fig. 12).





FIG. 3. Hysteresis loops: (a) typical hysteresis loop in the tetragonal phase; (b) double loop in the [100] direction; (c) double loop in the [110] direction; (d) quadruple loop in the [110] direction.