The Electric and Optical Behavior of BaTiO₃ Single-Domain Crystals*

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(Received June 16, 1949)

The dielectric constants, the spontaneous polarization, and the optical properties of BaTiO₃ single-domain crystals have been measured as a function of temperature. It is shown that the deformation of the crystal in the tetragonal state is proportional to the square of the spontaneous polarization, in analogy to the behavior of the other ferroelectrics, and that the temperature dependence of the birefringence is proportional to the square of the spontaneous polarization. The change of the polarization at the two lower transition points is consistent with the assumption that the Ti ions in the oxygen octahedra are displaced from the [001] to the [011] and later to the [111] direction.

INTRODUCTION

SINCE the domain structure of BaTiO₃ and its response to electric fields, temperature and pressure[1,2] was discovered, the laws of formation of these domains have been clarified in detail.[3] Single-domain crystals have been grown, and their dielectric constants ϵ_c and ϵ_a, parallel and perpendicular to the polar axis, as well as their spontaneous polarization P_s and the optical properties (refractive index and birefringence), have been investigated over a wide temperature range. The results presented here are discussed in relation to the structure of the crystal, and furnish a basis for the comparison between BaTiO₃ and the two other groups of ferroelectrics.

INITIAL DIELECTRIC CONSTANTS

The single-domain crystals investigated were yellow, transparent plates of a few mm² in area and relatively

high purity, with a Curie temperature of 120°C; their optical axis (c) was, in general, oriented perpendicularly to the plate surface.

Figure 1 shows the initial dielectric constants in the a- and c-directions as a function of temperature[4] and the three well-known transition points.[5] Above the Curie point the crystal is cubic ($\epsilon_a = \epsilon_c$), shifts then by a second-order transition from cubic to tetragonal,[6] while near 0° and −80°C the polar axis changes suddenly in two first-order transitions from the [001] to the [011] and later to the [111] positions of the original cubic system. Due to this shift of the Ti⁺⁴-ions in the oxygen octahedra of the lattice, the crystal structure changes from the tetragonal class (C_{4v}), to the orthorhombic (C_{2v}), and later to the trigonal class (C_{3v}). At these two lower transitions internal strains cause the development of multi domain patterns which may differ from crystal to crystal. This causes variations in the dielectric con-
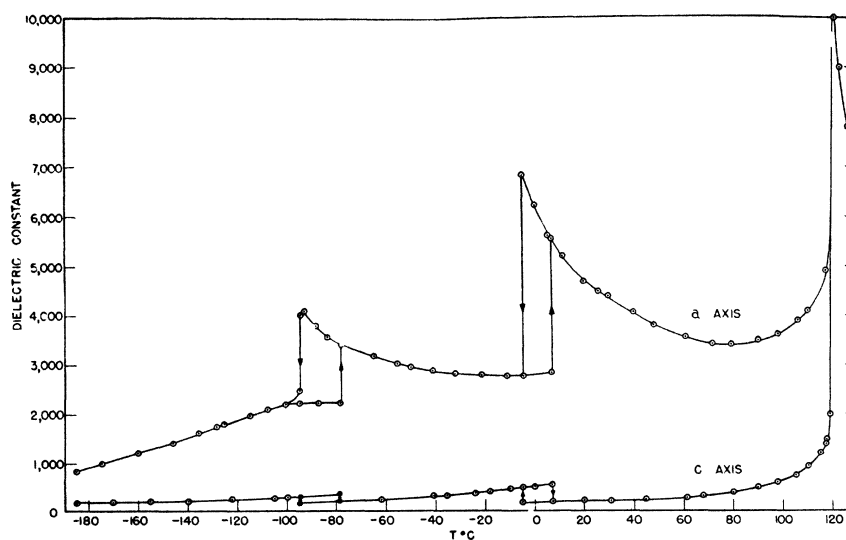

FIG. 1. Dielectric constants ϵ_a and ϵ_c as function of temperature.

* Sponsored by the ONR, the Army Signal Corps, and the Air Force under ONR Contract N5ori-07801.
[1] B. Matthias and A. von Hippel, Phys. Rev. 73, 1378 (1948).
[2] Blattner, Matthias, Merz, and Scherrer, Experientia 3, 148 (1947).
[3] P. Forsbergh, Technical Report XVIII, Laboratory for Insulation Research, M. I. T., 1949.
[4] W. Merz, Phys. Rev. 75, 687 (1949).
[5] Von Hippel, Breckenridge, Chesley, and Tisza, J. Ind. Eng. Chem. 38, 1097 (1946).
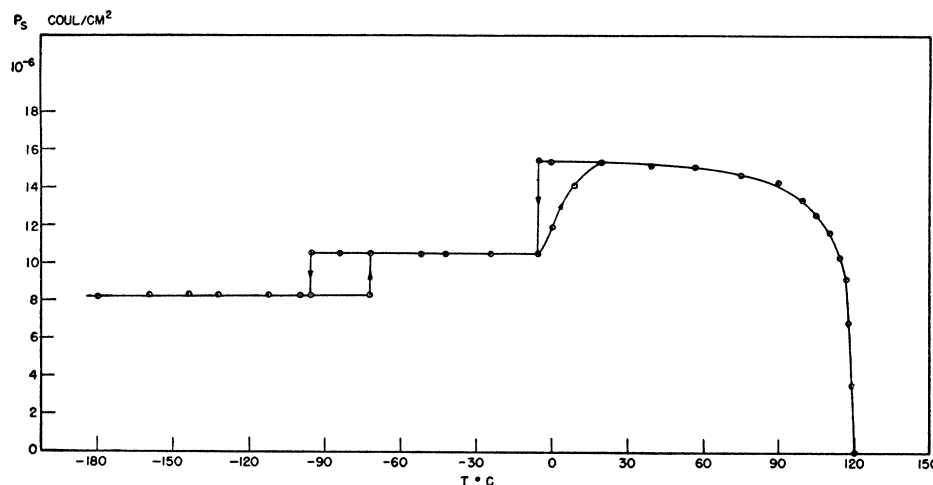[6] H. Megaw, Proc. Roy. Soc. A189, 261 (1947).

FIG. 2. Spontaneous polarization P_s as function of temperature.

stants below 0°C, and is the reason that $\epsilon_a \neq \epsilon_c$ below the transition near −80°C.

SPONTANEOUS POLARIZATION

The spontaneous polarization P_s was measured from the hysteresis loops by the modified method of Sawyer and Tower.[7] In contrast to the loops of multi-domain crystals, these loops can be easily saturated. However, some preconditioning is needed before satisfactory hysteresis loops are obtained. When the field is applied for the first time and the temperature raised, one often finds distorted loops, and the behavior of the spontaneous polarization as a function of temperature is not reproducible. These disturbances disappear after the loops have been taken through several heating cycles with systematically increased field strength. They are probably due to the initial existence of antiparallel domains, of which a smaller part is firmly anchored in its original orientation and can only be made to cooperate by such treatment.

At the two lower transition points near 0° and −80° the spontaneous polarization drops suddenly (Fig. 2) which, as will be explained later, follows from the shift of the polar axis from the [001] to the [011] and then to the [111] orientation. Due to the formation of domains the results below the tetragonal state are not quite reproducible, as in the case of the dielectric constant. Figures 3 to 7 show some of the characteristic hysteresis loops.

RELATION BETWEEN SPONTANEOUS POLARIZATION AND DEFORMATION OF THE CRYSTAL LATTICE

The structure of $BaTiO_3$ above the Curie point is cubic; at the Curie point a polar axis is formed and the crystal changes to tetragonal structure. Megaw[6] has determined the structure as a function of temperature; the relative change of the lattice constants is shown in Fig. 8 where the denominator of $\Delta a/a$ and $\Delta c/c$ refers to the extrapolated cubic value.

It is known that the other two groups of ferroelectric crystals (light and heavy Rochelle salt and the alkali phosphates and arsenates) show, in the Curie region, an intimate relation between the spontaneous polarization and deformation of the crystal lattice, which can be discussed as follows:

Above the Curie point Rochelle salt belongs to the orthorhombic class $(V = D_2)$, and has the following matrix of its piezoelectric constants:

$$\begin{matrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{matrix} \qquad (1)$$

FIG. 3. Hysteresis loop at −100°C.

FIG. 4. Hysteresis loop at −70°C.

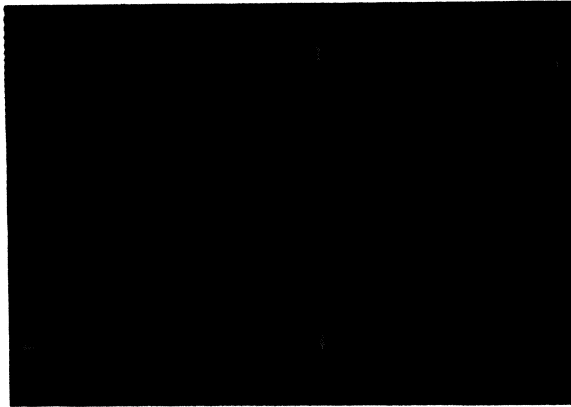[7] C. Sawyer and C. Tower, Phys. Rev. 35, 269 (1930).

FIG. 5. Hysteresis loop at +20°C.

In the Curie region where the crystal has monoclinic symmetry (C_2) the matrix becomes:

$$\begin{matrix} d_{11} & d_{12} & d_{13} & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & d_{26}. \\ 0 & 0 & 0 & 0 & d_{35} & d_{36} \end{matrix} \quad (2)$$

Because the a-axis is the polar axis in Rochelle salt, matrix (2) is written in a cyclical-changed form to allow comparison with matrix (1).

A spontaneous polarization in the x-direction produces corresponding deformations in the x-, y- and z-directions, and a shear in the y–z plane. As Mueller[8] has shown experimentally, the shear y_z is proportional to the spontaneous polarization. This can be understood as a continuation of the normal piezoelectric effect above the Curie point into the Curie region (d_{14}). On the other hand, Mueller found that the 3 normal strains x_x, y_y, z_z are proportional to $P_s{}^2$ and represent therefore a quadratic piezoeffect. As Jaffé[9] has pointed out, this can be understood by the fact that the piezoelectric constants d_{11}, d_{12}, d_{13} which appears now in the monoclinic system must be themselves proportional to the strain and polarization in a first approximation, so that

$$x_x \sim d_{11} P_s{}^2; \quad y_y \sim d_{12} P_s{}^2; \quad z_z \sim d_{13} P_s{}^2.$$

In the case of the alkali phosphates and arsenates the situation is quite analogous. The measurements of de Quervain[10] show that the shear x_y is proportional to the spontaneous polarization P_s in the z-direction, which again can be explained as a continuation of the piezo-effect (d_{36}), and the other strains are proportional to $P_s{}^2$.

For the cubic BaTiO₃ above the Curie point all the piezoelectric constants d_{ik} are zero. Below it, the crystal changes from cubic to tetragonal (C_{4v}) with the matrix:

$$\begin{matrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{matrix} \quad (3)$$

[8] H. Mueller, Phys. Rev. **58**, 805 (1940).
[9] H. Jaffé, Phys. Rev. **51**, 43 (1937).
[10] M. de Quervain, Helv. Phys. Acta **17**, 509 (1944).

Consequently there must be strain components x_x, y_y and z_z caused by the spontaneous polarization P_s in the z-direction. In analogy to the other ferroelectrics one would expect that these normal strains are proportional to the square of P_s because the constants d_{31} and d_{33} should themselves be proportional to P_s.

The measurements of P_s (Fig. 2) and the values of $\Delta a/a$ and $\Delta c/c$ (Fig. 8), calculated with the aid of Megaw's measurements, show, in fact, the expected relation (Fig. 9)

$$(z_z)^{\frac{1}{2}} = (\Delta c/c)^{\frac{1}{2}} \sim P_s, \quad (4)$$

$$(x_x)^{\frac{1}{2}} = (y_y)^{\frac{1}{2}} = (|\Delta a/a|)^{\frac{1}{2}} \sim P_s. \quad (5)$$

This relation, however, was confirmed only from the Curie point (120°C) down to about 90°C. At lower temperatures the measured values of P_s are smaller than expected. It is found that this deviation decreases with increasing field strength, and with the temperature pretreatment at the high field strengths described above. One must therefore assume that this difference is, at least in part, due to the existence of domains oriented in other directions, especially the anti parallel, which at lower temperatures persist long enough at 60 cycles so that the crystal does not polarize completely. This makes it understandable that the absolute value of the spontaneous polarization at room temperature varies from crystal to crystal. As an average we mea-
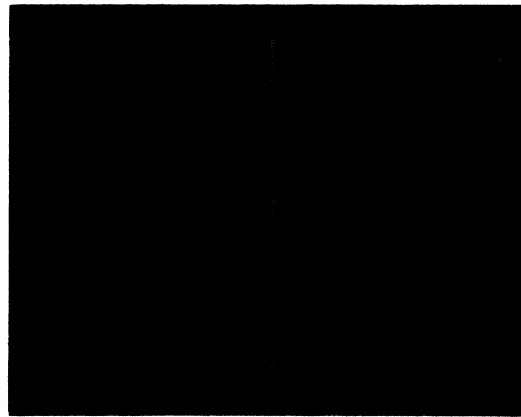

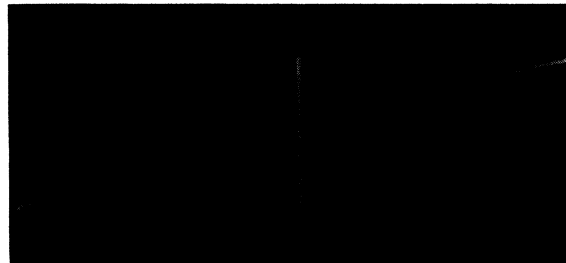FIG. 6. Hysteresis loop at a few degrees below the Curie point.
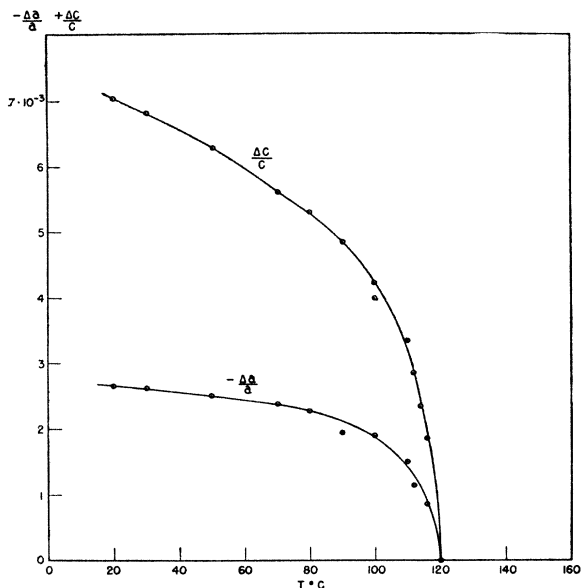

FIG. 7. Hysteresis loop at +120°C.

FIG. 8. $\Delta a/a$ and $\Delta c/c$ as function of temperature, calculated from Megaw's measurements.

sured the value

$$P_s = (15.5 \pm 1.5) \times 10^{-6} \text{ coulomb/cm}^2, \qquad (6)$$

in good agreement with Hulm's value[11] of 16×10^{-6} coulomb/cm² for multidomain crystals.

It is interesting to note that the curve of P_s/P_∞ plotted against the reduced temperature T/θ (θ = Curie temperature) for BaTiO₃ is about the same as that for KH₂PO₄, that is, it rises much more steeply than the Langevin theory would predict. In the ferroelectric region the polarization P is a function of the temperature and of the applied field strength E. With small values of E (less than the coercive field strength) P becomes very small and drops to zero with decreasing field. Besides this, one can observe a decrease of the

polarization in the form of sudden jumps after the field is removed. These facts show that even the "single-domain" crystals split up into domains as soon as the external field approaches zero. These domains must be antiparallel because optically the crystal appears uniformly tetragonal. Thus there seem to exist crystals that are not really single-domain, but that contain only parallel and antiparallel domains, as in the cases of Rochelle salt and KH₂PO₄.

The behavior of the spontaneous polarization at the two lower transitions is characterized by sudden drops of P_s (Fig. 2). With the conclusion derived from optical and dielectric measurements one can understand this behavior. Since at the 0°C transition the [011] position of the polar axis becomes the most stable one, a drop of the spontaneous polarization perpendicular to the crystal face of the order of $1/\sqrt{2}$ should be expected. This value is, in fact, found (Fig. 2). At the second transition point at about $-80°$C a further drop should result because the polar axis moves into the [111] position. The measured change is larger than expected, which may be understood by the assumption that not only the direction changes but also the magnitude of the dipole moment decreases. However, it should be kept in mind that the values of P_s below the 0°C transition are never completely reproducible due to the formation of domains and consequently increasing internal strains.

Just as the d_{31} and d_{33} constants play an important part in the tetragonal region, the change to the ortho-rhombic and trigonal modification expresses itself in the high values and temperature dependence of the shear constants d_{15} and d_{24}.

THE OPTICAL BEHAVIOR OF BaTiO₃

We measured previously the refractive index of BaTiO₃ on thin crystal plates using Chaulnes's method to determine the ratio of the actual to the optical thickness.[12] At the Curie point one finds a peak in the
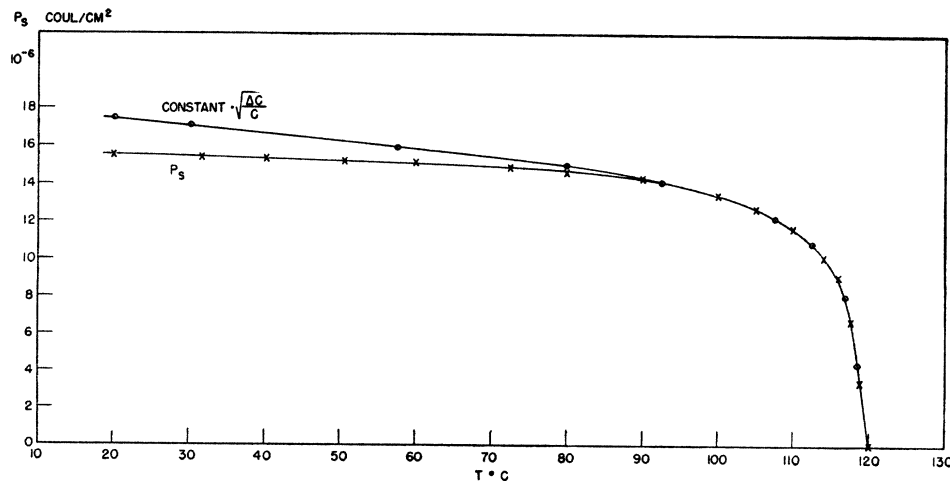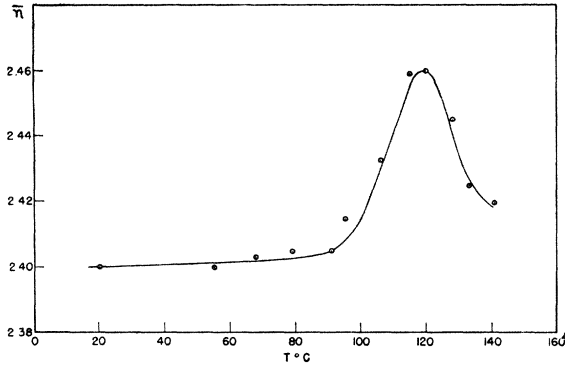

FIG. 9. P_s and constants $\times (\Delta c/c)^{\frac{1}{2}}$ as function of temperature.

[11] J. Hulm, Nature 160, 127 (1947).
[12] Busch, Flury, and Merz, Helv. Phys. Acta 21, 212 (1948).

FIG. 10. Refractive index $\bar{n}$ as function of temperature.

curve of the refractive index (Fig. 10). It is interesting to note that the activation energy of the electrical conductivity is lowered in this region.[12] Besides the refractive index it was of interest to know the behavior of the birefringence of BaTiO₃ because it is related to the spontaneous polarization of the crystal. The birefringence Δn of BaTiO₃ was measured by Forsbergh[3] with the result shown in Fig. 11.

The theory of the electro-optical and elasto-optical effect gives, for the index ellipsoid, the form

$$\sum_{i, k=1}^{3} \frac{a_i' a_k'}{v_{ik}^2} = 1, \qquad (7)$$

where for a piezoelectric crystal[13] v_{ik} has the value

$$\frac{1}{v_{ik}^2} = \frac{1}{n_{ik}^2} + \sum_{m=1}^{6} q_{ik,m} X_m + \sum_{l=1}^{3} f_{ik,l} E_l$$

$$+ \frac{1}{2} \sum_{l=1}^{3} \sum_{j=1}^{3} h_{ik,lj} E_l E_j, \qquad (8)$$

where $q_{ik,m}$ represents piezo-optical constants, $f_{ik,l}$ represents electro-optical constants of the 1st order, and $h_{ik,lj}$ represents electro-optical constants of the 2nd order.

The measurements of Δn were made without external stresses ($X_m = 0$) and without external fields. But the spontaneous polarization P_s in the z-direction is the reason for a spontaneous change in the birefringence (spontaneous Kerr effect). With the conditions $E_a = E_b = 0$; $E_c \neq 0$; $n_1 = n_2$ and $n_{ik} = 0$ for $i \neq k$ and by using only the terms of first order Eq. (8) becomes, with the matrix of f_{hl}, that is, with

$$\begin{array}{ccc} 0 & 0 & f_{13} \\ 0 & 0 & f_{13} \\ 0 & 0 & f_{33} \\ 0 & f_{51} & 0 \\ f_{51} & 0 & 0 \\ 0 & 0 & 0 \end{array} \qquad (9)$$

[13] F. Pockels, *Lehrbuch der Kristalloptik* (B. G. Teubner, Leipzig, 1906).
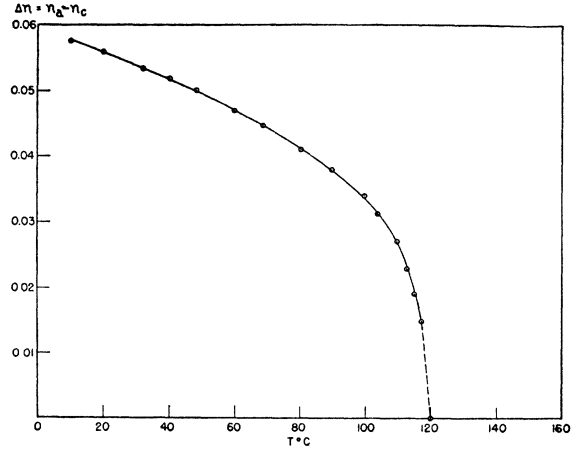
FIG. 11. Birefringence Δn as function of temperature.

as follows:

$$(a^2+b^2)[1/n_1^2 - f_{13}E_c] + c^2[1/n_3^2 + f_{33}E_c] = 1. \qquad (10)$$

As in the case of Rochelle salt and KH₂PO₄, one must assume that the electro-optical constants of the first order (f_{hl}), which do not exist above the Curie point but arise below it due to the deformation of the crystal, behave quite analogously to those of the piezo-effect. Because the f_{hl}'s must be proportional to P_s in the Curie region, the spontaneous Kerr effect becomes proportional to P_s^2

$$\Delta n = n_c - n_a = \frac{n_3}{(1+f_{33}E_c n_3^2)^{\frac{1}{2}}} - \frac{n_1}{(1-f_{13}E_c n_1^2)^{\frac{1}{2}}}$$

$$= (n_3 - n_1) - \frac{1}{2}E_c(f_{33}n_3^3 + f_{13}n_1^3) \qquad (11)$$

$$= \Delta n_0 + \text{const.} \times P_s^2,$$

where $\Delta n_0 (= n_3 - n_1)$, the natural birefringence of BaTiO₃, is zero.

In fact, one finds good agreement between the measured value of Δn and of P_s^2, but again only at higher temperatures. On the other hand, in the whole tetragonal region, Δn is exactly proportional to $\Delta c/c$. That means that the measured values of P_s are too small at lower temperatures, which leads again to the conclusion that the crystal has the tendency to form parallel and antiparallel domains. This does not influence the birefringence and the x-ray measurements but only the values of P_s. In the tetragonal region, n_a^2 and n_c^2 have a similar temperature dependence as ϵ_a and ϵ_c. The dispersion of the refractive indices and of the birefringence is very strong. At both lower transition points one finds a sudden change in Δn due to the change of the crystal system.

The author is grateful to Professor A. von Hippel for many helpful discussions during the course of this work.
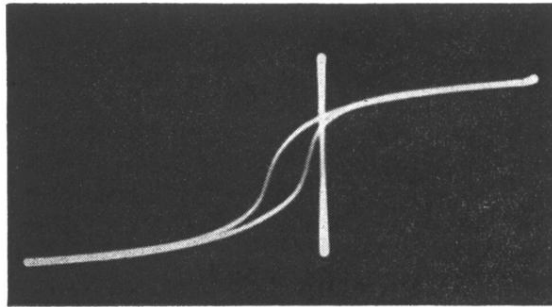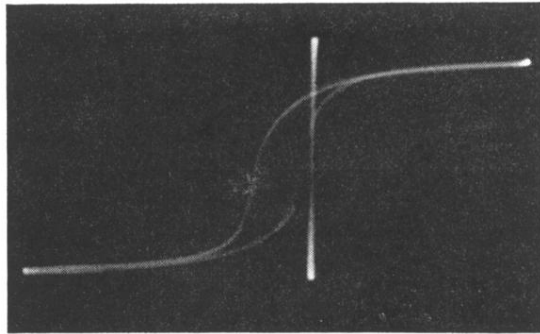
FIG. 3. Hysteresis loop at −100°C.
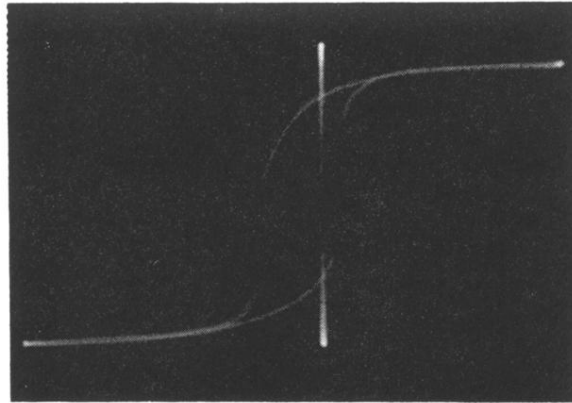
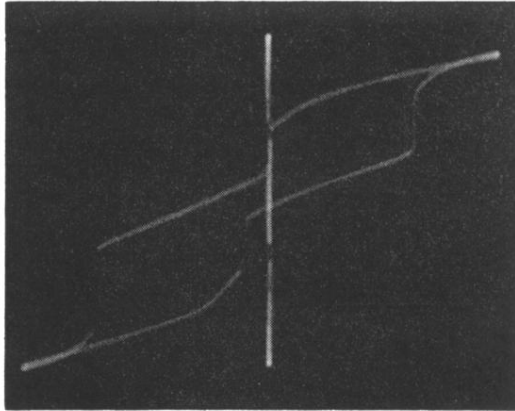Fig. 4. Hysteresis loop at $-70°C$.

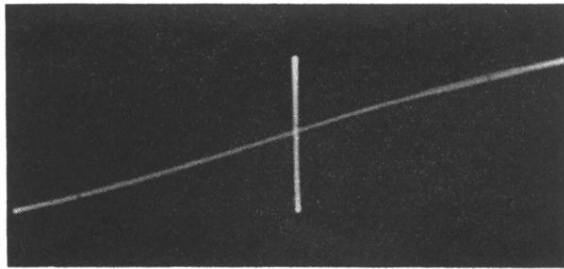FIG. 5. Hysteresis loop at +20°C.

Fig. 6. Hysteresis loop at a few degrees below the Curie point.

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