Symmetry of the Low-Temperature Phase of BaTiO$_3$†

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X-ray Weissenberg patterns of a barium titanate crystal in the low-temperature phase (below −90°C) show that the spacings along the perovskite cubic axes are equal and that the cube faces are sheared through a small angle, i.e., the unit cell has rhombohedral character. Optical examination of these crystals in electric fields, together with dielectric constant measurements, suggest that the cell is only pseudorhombohedral. The true symmetry appears to be lower and may possibly be monoclinic (point group 2 or m). The contradictions in the early dielectric measurements are explained by this assumption.

I. INTRODUCTION

BARIUM titanate, BaTiO$_3$, the best known representative of the perovskite-type ferroelectrics, undergoes three well-described phase transitions. Above 120°C the crystal is cubic and nonpolar. Below 120°C tetragonal symmetry appears, with an axial ratio c/a of 1.01 at room temperature, and exhibits ferroelectric properties along the direction of the tetragonal c axis. Tetragonal barium titanate has been studied in great detail,[1] and its structure has been completely determined in a neutron diffraction study by Frazer, Danner, and Pepinsky.[2]

A second phase transition occurs at about 0°C, with the symmetry becoming orthorhombic. The crystal is still ferroelectric, but the direction of spontaneous polarization is now inclined at 45° to the original cubic [100] direction. The structure of this phase was recently determined with neutrons by Shirane, Danner, and Pepinsky.[3]

If the crystal is cooled below −90°C, a third phase transition occurs. The symmetry of this phase is reportedly rhombohedral, with the direction of spontaneous polarization along the original cubic [111] direction. The experimental data indicating such symmetry for this low-temperature phase have been very convincing. The most important points are the following:

(1) An x-ray study of the low-temperature phase by Kay and Vousden[4] reveals that all reflections can be indexed on the assumption that the symmetry is rhombohedral. The spacings along the cube axes are found to be equal, and the cube faces are sheared through a small angle.

(2) Optical studies[4,5] show that the extinction of a BaTiO$_3$ plate with pseudocubic habit is always symmetrical in the low-temperature phase. This is in accordance with the assumption of a rhombohedral phase, which is the only pseudocubic form which gives twinning and extinction independent of the cube axis of viewing. Moreover, Kay and Vousden showed that electric fields applied along the original cubic [100] direction cause no orientation of the crystal before breakdown occurs. This again is in accord with the assumption of a polar axis along [111], since the twinning of such a crystal permits four different polar directions equally inclined to the field.[4]

(3) Because the polar axis is supposedly lying along the original body diagonal below −90°C, the value of the spontaneous polarization measured along the cube axis was expected to be √3 times smaller than the room-temperature value. The measurements of Merz[6] show that this relationship is approximately fulfilled.

Although the above results are all in agreement with a rhombohedral symmetry for the low-temperature phase, they do not provide conclusive proof. Optically, such proof appears very difficult because no crystal with (111) faces is available. Crystal-structural studies also encounter difficulties. The presence or absence of threefold symmetry could only be established by a full neutron analysis, using a cylindrical single-domain specimen of adequate size; and no such specimen has been preparable.

There exist two other reasons for questioning the assumption of rhombohedral symmetry. The first of these is of a general nature, and is based on the well-known empirical fact that crystal transitions *generally* result in a *decrease* in symmetry as temperature decreases. In BaTiO$_3$ this rule is indeed fulfilled at the two upper transitions. Starting with cubic symmetry, space group $Pm3m$, the crystal loses the threefold symmetry at 120°C and assumes the tetragonal space group $P4mm$. At 0°C, the fourfold symmetry disappears, and the result is the orthorhombic space group $Amm2$. The reassumption of a threefold symmetry (space group $R3m$) at −90°C, if true, is remarkable but not impossible. The loss of the mirror plane symmetry (leading to monoclinic $C2$) or the twofold axis (leading to monoclinic Cm) would be more in agreement with previous experience.

[1] See, e.g., Shirane, Jona, and Pepinsky, Proc. Inst. Radio Engrs. 43, 1738 (1955).
[2] Frazer, Danner, and Pepinsky, Phys. Rev. 100, 745 (1955).
[3] Shirane, Danner, and Pepinsky, preceding paper [Phys. Rev. 105, 856 (1957)].
[4] H. F. Kay and P. Vousden, Phil. Mag. 40, 1019 (1949).
[5] P. W. Forsbergh, Phys. Rev. 76, 1187 (1949).
[6] W. J. Merz, Phys. Rev. 76, 1221 (1949).

A re-examination of the dielectric measurements made on single crystals of $BaTiO_3$ by Merz[6] lead to the second reason for skepticism about the supposed rhombohedral symmetry. The reported data, plotted as dielectric constant *versus* temperature, were obtained from specimens which were a- and c-single-domain plates in the room-temperature tetragonal phase; but the curves corresponding to the two samples were remarkably different in the low-temperature phase. It has been repeatedly pointed out[1,7] that the existence of two branches on such a plot in the temperature region below $-90°C$ is incompatible with the accepted rhombohedral symmetry of the lowest phase.

The purpose of this investigation is to obtain additional information concerning the low-temperature phase of $BaTiO_3$, and to show that the previously assumed rhombohedral symmetry is unlikely.

II. X-RAY STUDY

A small parallelepiped was cut from a large plate of $BaTiO_3$, in such a way that its major dimension lay along the original cubic [100] direction. The crystal was then mounted on the goniometer head of a low-temperature Weissenberg camera[8] so that the cubic axis coincided with the axis of rotation. As a control, room-temperature Weissenberg photographs were taken with both Cu $K\alpha$ and Mo $K\alpha$ radiation. The Cu $K\alpha$ wavelength allowed recording of reflections up to the fifth order; and Mo $K\alpha$ gave data as high as the eleventh order. The sample was not ground to cylindrical shape and a single-domain crystal was not sought, since intensity data were not required. Unit cell dimensions for the room-temperature phase were found to be

$$a = 3.992 \text{ A}, \quad c = 4.031 \text{ A},$$

in good agreement with the published data.

A Weissenberg photograph was taken with Mo $K\alpha$ radiation at $-168°C$, and the splitting of reflections due to twinning was carefully studied. No splitting was observed for reflections of the type $(h00)$ and $(0k0)$, but a definite splitting occurred for reflections of the general type $(hk0)$. The splitting is proof of the multidomain nature of the crystal in the low-temperature phase, and the lack of splitting for $(h00)$ and $(0k0)$ type reflections confirms the early work of Kay and Vousden.[4]

The unit cell for the low-temperature phase proved to be rhombohedral in the sense that the spacings along the three axes which coincide with the original cubic [100] directions are indeed equal. This "rhombohedral" cell was found to have the following dimensions:

$$a_r = 4.001 \text{ A}, \quad \alpha_r = 89°51'.$$

Of course, these measurements do not prove that the true symmetry of this phase is rhombohedral. It is

conceivable, for example, that the symmetry could be monoclinic, or even triclinic, in which case the existence of a pseudocell with rhombohedral character would be purely accidental. Such accidental pseudocells of higher symmetry are not unusual for low-temperature phases arising from slight distortions of a cubic lattice. The most recent example is that of the low-temperature phase of $NaNbO_3$[9]; older examples are $PbZrO_3$,[10] and magnetite at low temperatures.[11] If a monoclinic lattice is chosen for the low-temperature phase of $BaTiO_3$, measurements of the unit cell dimensions give the following values:

$$a = 5.666 \text{ A}, \quad b = 5.651 \text{ A}, \quad c = 4.001 \text{ A}, \quad \beta = 90°13'.$$

Figure 1 shows the relative positions of the previously chosen rhombohedral axes and the monoclinic axes chosen above.

III. OPTICAL STUDY

If it is true that the symmetry of the lowest phase is monoclinic, both symmetrical and parallel extinction should be observed. However, the fact that only symmetrical extinction is observed does not exclude the possibility of monoclinic symmetry.

In the first place, it is conceivable that the domains which show parallel extinction are oriented so that the polarized light travels almost in the direction of an optic axis. In such a case, the existence of these domains in a highly twinned crystal (and *every* $BaTiO_3$ crystal is highly twinned in the low-temperature phase) would escape the attention of an observer, because their only effect would be to render the predominantly symmetrical extinction imperfect. In actual fact, it was found that a multidomain crystal of $BaTiO_3$ does not extinguish perfectly in the low-temperature phase.

Secondly, it was observed that a multidomain crystal in the *orthorhombic* phase shows predominantly symmetrical extinction, which indicates that the polar axis
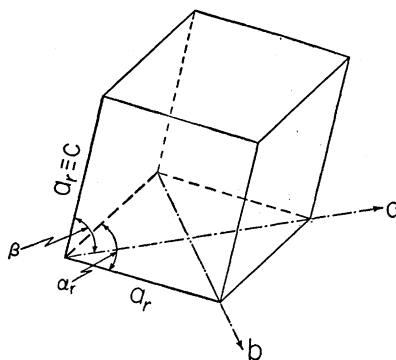

FIG. 1. Orientation of rhombohedral axes a_r relative to monoclinic axes a, b, c in low-temperature phase of $BaTiO_3$.

[7] C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), p. 119.

[8] Keeling, Frazer, and Pepinsky, Rev. Sci. Instr. 24, 1087 (1953).

[9] Johns, Shirane, Jona, and Pepinsky (to be published).

[10] Sawaguchi, Maniwa, and Hoshino, Phys. Rev. 83, 1078 (1951).

[11] S. C. Abraham and B. A. Calhoun, Acta Cryst. 6, 105 (1953).

in this phase lies in general within the plane of the crystal plate. If the polar axis coincides with the monoclinic b axis in the low-temperature phase (see Fig. 1), it is quite possible that the same situation occurs. As a consequence, a majority of the domains will show symmetrical extinction.

Observation of the crystal between crossed nicols and in the presence of a strong dc field should provide a conclusive answer to the problem. However, Kay and Vousden,[4] who performed such an experiment, obtained data which showed only that one or the other of the two following assumptions may be correct: (i) the polar axis lies in the direction of the body diagonal; or (ii) the polar axis lies in the direction of the monoclinic b axis, which coincides with an original cubic $\langle 110 \rangle$ direction. Their inability to distinguish between these two possibilities is due to the fact that the field was applied along the cube axis, which was oriented perpendicular to the direction of propagation of the light. However, if the field is applied in the $\langle 100 \rangle$ direction *parallel* to the light beam, the two possibilities give rise to different effects, and a choice can be made. In the first case, a parallel field should cause no domain orientation which could affect the symmetrical extinction. In the second case, there should be a change from symmetrical to parallel extinction in the presence of the field.

The above experiment was performed using BaTiO₃ crystals of approximately 5×10^{-3} cm thickness and with areas as large as 25 mm². These were kindly furnished by Professor Pulvari of the Catholic University in Washington, D. C. The major surfaces of the plates were, as usual, perpendicular to a $\langle 100 \rangle$ cubic axis. Semi-transparent electrodes about 2 mm in diameter were evaporated *in vacuo* on opposite surfaces of the crystal plates, and electrical contact was made to a dc power supply. The crystals were then mounted in a special holder designed for optical studies at low temperatures.

The experimental arrangement was checked in the following ways:

(a) At room temperature, where between crossed nicols the plates show a large number of a domains (parallel extinction), application of the field caused darkening of the coated region. Here the polar axis is forced to assume the same direction as the field, i.e., parallel to the light beam.

(b) In the orthorhombic phase, where the crystals appear to be highly twinned and where the extinction is symmetrical, the field causes orientation of the domains under the coated region in such a way that the extinction changes from symmetrical to parallel. This can be considered additional proof that the polar axis of the orthorhombic phase *does* lie along one of the original cubic $\langle 110 \rangle$ directions. The latter fact had recently questioned by Berlincourt *et al.*,[12] but was reconfirmed by the structural analysis of Shirane *et al.*[3]

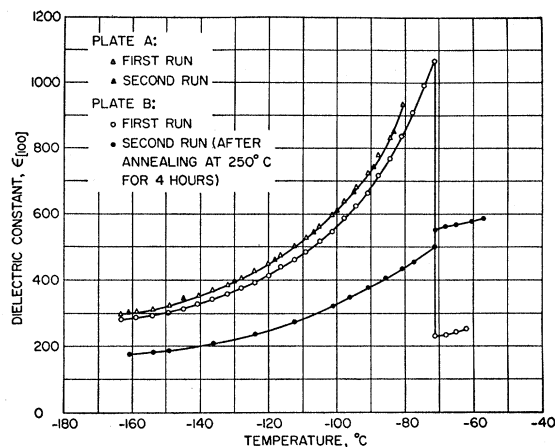[12] Berlincourt, Jaffe, and Shiozawa, Bull. Am. Phys. Soc. **1**, 132 (1956).

FIG. 2. Dielectric constant $\epsilon_{[100]}$ of multidomain BaTiO₃ crystals in low-temperature phase.

After the above tests of the experimental arrangement, the temperature was dropped below $-90°$C, the multidomain crystals were rotated into one of the (symmetrical) extinction positions, and electric fields ranging up to 10^5 v/cm were applied. In the presence of the field, *a definite brightening of the coated region is observed;* and this is found to disappear as soon as the field is removed. This optical experiment, more than any of the indications discussed above, would seem to point to some symmetry other than rhombohedral for the low-temperature phase of BaTiO₃.

IV. DIELECTRIC STUDY

The early dielectric measurements made on BaTiO₃ by Merz,[6] which show two branches on the dielectric constant curve below $-90°$C, also indicate other than rhombohedral symmetry for the low-temperature phase. Merz's data can be explained if it is assumed that the true symmetry is monoclinic and that the two crystals investigated had very different domain configurations in the low-temperature phase.

To show that these assumptions hold, it was decided to determine the dielectric constant $\epsilon_{[100]}$ (i.e., measured along the cube axis) for several different crystals in the low-temperature phase. Six crystals of different sizes and origins were used (four from the Bell Telephone Research Laboratory and two from the Clevite-Brush Development Company). Rhombohedral symmetry should result in identical $\epsilon_{[100]}$ values for all the crystals; but the measured values differed widely. For example, one series of measurements at $-108°$C gave 273, 239, 486, 528, 515, and 217 for the $\epsilon_{[100]}$ of the six crystals. It seems unlikely that such a wide spread of values could be due to experimental error, even if this error (due to thickness and area determinations, edge effects, etc.) is pessimistically estimated at 20%. However, there still remains the possibility that these crystals from different sources might have different dielectric

behavior as a result of variations in growth conditions, impurities, etc.

To eliminate this criticism, the following experiment was performed. A single-crystal plate about 35 mm² in area and 0.4 mm in thickness was cut in half after being coated with evaporated silver electrodes. The dielectric constants of the two plates thus obtained (plates A and B) were measured at the same time in the same crystal holder. The measuring field was 2.5 v/cm and the frequency 10 kc/sec. The results are shown graphically in Fig. 2 (curves with open circles and open triangles). With identical experimental conditions for the two samples, the only source of error in $|\epsilon_{[100]}{}^{A} - \epsilon_{[100]}{}^{B}|$ is due to error in the surface area measurements. At most such an error should not exceed 5%, so that differences larger than 5% must be due to a true difference in dielectric behavior, which corresponds here to slightly different domain configurations in A and B.

If the two plates are heated to room temperature and then cooled to the low-temperature phase, there is a high probability that the domains will return to their original configuration. This was confirmed by optical observation of the domain patterns below $-90°C$ after repeated warmings to room temperature.

One of the plates (B) was then heated to 250°C in a Nichrome furnace, kept at this temperature for 4 hours, and cooled to room temperature over a period of 8 hours. It was hoped that this annealing process would eliminate some of the strains and thus favor the establishment of a different domain configuration in the low-temperature phase. Plate A was not subjected to this heat treatment. A low-temperature dielectric constant measurement was then made under the same conditions as before. The results are included in Fig. 2 (black circles and black triangles). Plate A exhibits the same dielectric constant $\epsilon_{[100]}$ as in the first run, as expected. Plate B shows drastically different behavior, thus confirming the supposition that a new domain configuration was assumed during cooling to the low-temperature phase. The *relative* error in the curves obtained in the two runs is the error of the capacitance bridge, which is essentially negligible.

The above dielectric tests confirm the results of the optical investigation, and clearly indicate that the differences in the values of $\epsilon_{[100]}$ obtained for $BaTiO_3$ crystals in the low-temperature phase are due to the presence of different domain patterns in the individual plates.

V. CONCLUSION

The above experiments strongly suggest that, even though the low-temperature phase of $BaTiO_3$ can be described in terms of a unit cell with rhombohedral dimensions, the true symmetry is nonetheless lower. In view of the sequence of phase transitions exhibited by barium titanate, it would seem logical to assign monoclinic symmetry (point group 2 or m). However, the possibility of triclinic symmetry cannot be ruled out on the basis of present evidence.

If the polar axis is taken as lying along the face diagonal (monoclinic b) in the low-temperature phase, the conclusion—that the spontaneous polarization along the cube axis below $-90°C$ is about $\sqrt{3}$ times smaller than that of the tetragonal phase *because* the polar axis lies along a body diagonal—is invalidated. Clearly, such a statement implies that only the direction of the spontaneous polarization changes at the transition points, and not the magnitude. It should not be necessary to emphasize that there is no reason for the magnitude of the spontaneous polarization to remain constant at the transitions. In fact, it would be rather surprising if it did.

There is admittedly a large amount of experimental and theoretical work to be done before the question raised by this paper is definitely settled. This involves: the correlation between the optical and the dielectric results; the study of a possible effect of strains which may be created in the crystal by the field in the optical experiment; the possibility of microscopic cracks influencing the magnitude of the dielectric constant below $-90°C$[1]; the effects of domain clamping; and the theoretical treatment of the low-temperature phase on the basis of Devonshire theory.[13] The determination of the true symmetry of the low-temperature phase must finally be based on a detailed x-ray and neutron study of a single-domain crystal in this phase.

VI. ACKNOWLEDGMENTS

[13] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949); **42**, 1065 (1951).