

field until after the resonance of the high-mass carrier shown by the data in Fig. 2 is passed. It seems likely that this lack of change is a result of anomalous skin effect conditions, and that the sharp rise observed at a field just above the resonance represents at least partial emergence from the anomalous skin effect region.⁷ This occurs for the sign of field corresponding to electron resonance, and indicates that the carrier of mass $0.43m_0$ observed in Fig. 2 is an electron.

We wish to thank B. B. Cetlin for help in sample preparation, W. H. Richards for growing zinc crystals, and D. F. Gibbons for a residual resistance measurement.

¹Galt, Yager, Merritt, Cetlin, and Dail, Phys. Rev. **100**, 748 (1955).

²Galt, Yager, Merritt, Cetlin, and Brailsford, Phys. Rev. (to be published).

³Galt, Yager, and Dail, Phys. Rev. **103**, 1586 (1956).

⁴M. Ia. Azbel' and E. A. Kaner, Zhur. Eksptl. i Teoret. Fiz. **30**, 811 (1956) [translation: Soviet Phys. JETP **3**, 772 (1956)]; J. Phys. Chem. Solids **6**, 113 (1958).

⁵E. Fawcett, Phys. Rev. **103**, 1582 (1956); Kip, Langenburg, Rosenblum, and Wagoner, Phys. Rev. **108**, 494 (1957); P. A. Bezuglyi and A. A. Galkin, Zhur. Eksptl. i Teoret. Fiz. **33**, 1076 (1957) [translation: Soviet Phys. JETP **6**, 831 (1958)].

⁶D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939).

⁷M. Ia. Azbel' and M. I. Kaganov, Doklady Akad. Nauk S.S.S.R. **95**, 41 (1954).

DIRECT OBSERVATION OF ANTIPARALLEL DOMAINS DURING POLARIZATION REVERSAL IN SINGLE-CRYSTAL BARIUM TITANATE

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(Received March 13, 1959)

This communication describes a new and better method than others previously reported for the continuous, direct observation of the antiparallel ferroelectric domain structure in BaTiO₃ during polarization reversal. This method has been applied to both liquid- and metal-electroded crystals and some of the more interesting results concerning domain growth and domain-wall motion in metal-electroded crystals are given.

The study of the domain dynamics of polariza-

tion reversal in *c*-domain BaTiO₃ crystal plates has been rather severely hampered due to the difficulty experienced in trying to observe directly the antiparallel domains in question.¹ Under conditions where the applied electric field is either parallel or antiparallel to the spontaneous polarization in BaTiO₃, it has generally been considered that domains of opposite polarization cannot be discerned by direct optical observation. Several investigators²⁻⁴ have observed directly the antiparallel domain configuration during polarization reversal; however, in each case it was necessary to subject the BaTiO₃ samples to a "perturbing" electric field applied in a direction normal to the spontaneous polarization. This field rotates the optic axes of the antiparallel domains by small amounts, in opposite directions, so that with the appropriate experimental arrangement, one can discern the antiparallel domain structure. Some of the experimental results of these investigations seem to be in conflict with other work in which the perturbing electric field was omitted. However, it is difficult to interpret some of the results obtained by direct observation, as mentioned above, in terms of polarization reversal in the usual sense where the only applied field is one parallel to the ferroelectric axis.

Two other methods which have frequently been employed to observe a stationary antiparallel domain pattern in BaTiO₃ are the acid etch technique⁵ and the electrostatically charged powder technique.⁶ Unfortunately, although very valuable, these latter two techniques are not suitable for a continuous direct observation of the antiparallel domain configuration during polarization reversal. The ideal method for the study of domain dynamics is, of course, one in which the field is applied parallel to the ferroelectric axis and the domain configuration observed continuously through transparent, or semitransparent, electrodes. The authors have found that this is indeed possible.

In the course of experiments on the electric field dependence of 180° domain-wall velocity in BaTiO₃, it was noted that occasionally one could differentiate antiparallel domains without recourse to any of the aforementioned techniques. That is, portions of the antiparallel domain configuration of liquid-electroded samples⁷ which were partially reversed with fields of the order of a thousand volts per centimeter and then washed in water to remove the electrolyte, were sometimes visible when the sample was mounted

between crossed polaroids and viewed with white light. The reversed domains generally appeared somewhat darker in shade than the surrounding regions.

This most interesting result led to attempts to observe the c -domain structure during polarization reversal by looking along the ferroelectric axis through transparent aqueous lithium chloride electrodes,⁷ again with crossed polaroids. It was found that the antiparallel domain configuration could be discerned in this manner. Furthermore, one could also observe the antiparallel domain structure of semitransparent metal-electroded BaTiO₃ crystals. A photomicrograph of a portion of the antiparallel domain configuration observed directly during polarization reversal with a metal-electroded crystal is shown in Fig. 1. The metal electrodes consisted of 200Å films of gold evaporated on to opposite sides of the crystal plate. Motion pictures of the domain pattern as viewed during polarization reversal have also been made. The visual characteristics of the antiparallel domains are somewhat variable and depend on the lighting conditions. However, it

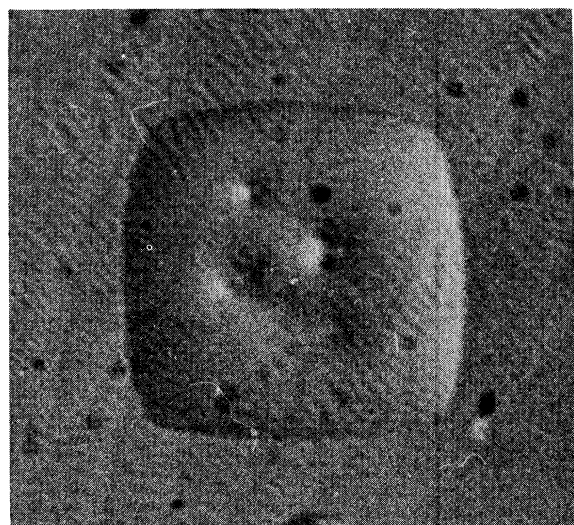


FIG. 1. Photomicrograph showing a portion of the antiparallel domain configuration of a partially reversed BaTiO₃ crystal as observed directly through semitransparent gold electrodes. The single reversed domain shown in the figure is approximately square with the sides at about 45° to the crystalline a axes. The sample was placed between crossed polaroids and viewed with white light.

has been possible to discern the antiparallel domain structure of every sample which has been investigated to date. The origin of the effects which enables one to observe the c -domain structure in the samples viewed in the manner described above is not understood.

Some of the most interesting results obtained using this new technique are those concerned with the domain dynamics of polarization reversal of metal-electroded crystals. "Extensive" sidewise 180° domain-wall motion has been found to occur when the spontaneous polarization of liquid-electroded BaTiO₃ crystals is reversed with applied fields of several hundred volts per centimeter.⁷ The quantitative aspects of this wall motion have also been given.⁸ The authors call sidewise domain wall motion "extensive" if the domain walls in question move sidewise through distances which are a significant fraction of the diameter (≈ 1 mm) of the electroded area. In the case of metal-electroded crystals, the published data on sidewise domain-wall motion are somewhat conflicting. However, there is good evidence that some sidewise 180° domain-wall motion occurs in metal-electroded crystals during polarization reversal with fields of several thousand volts per centimeter^{3,9} and also with fields of several hundred volts per centimeter.^{7,10} Direct observations in the present research indicate that many of the salient features of sidewise wall motion and polarization reversal are the same for metal- and liquid-electroded crystals.^{7,8} In particular, with applied fields of hundreds of volts per centimeter, extensive sidewise wall motion does indeed occur in metal-electroded crystals; and in some cases, the entire electroded area (2.5 mm in diam) can be reversed with a single growing domain, expanding through sidewise 180° domain-wall motion. As in the case of liquid-electroded crystals, the reversed growing domains generally tend to be approximately square in shape, as shown in Fig. 1, with the sides at about 45° to the crystalline a axes. Measurements of the rate of growth of a single reversed domain as a function of the applied field E indicate that the sidewise wall velocity is given by $v \exp[-(\text{const}/E)]$. The same field dependence has been found with liquid-electroded crystals⁸; however, it appears that the sidewise wall velocity measured with metal-electroded crystals is something like several orders of magnitude less than that found for the same field with liquid-electroded crystals.

Since one can now observe directly the anti-

parallel domain structure during polarization reversal under the conditions given above, there are many important experiments which are possible and which will undoubtedly lead to a better understanding of ferroelectric BaTiO_3 . Among those which the authors are currently investigating are the following: the phenomena which give rise the visibility of the antiparallel domains, the quantitative aspects of sidewise wall motion in metal-electroded crystals, the nucleation sites for reversed domains, the origin and characteristics of ferroelectric Barkhausen pulses, and the effects of various electrodes and impurity dopings on the characteristics of polarization reversal.

¹For a general discussion of the published work on this subject, the reader is referred to W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4.

²W. J. Merz, *Phys. Rev.* **88**, 421 (1952). W. J. Merz, *Phys. Rev.* **95**, 690 (1954).

³E. A. Little, *Phys. Rev.* **98**, 978 (1955).

⁴D. Meyerhofer, *Phys. Rev.* **112**, 413 (1958).

⁵J. A. Hooton and W. J. Merz, *Phys. Rev.* **98**, 409 (1955).

⁶G. L. Pearson and W. L. Feldmann, *J. Phys. Chem. Solids* **9**, 28 (1959).

⁷R. C. Miller, *Phys. Rev.* **111**, 736 (1958).

⁸R. C. Miller and A. Savage, *Phys. Rev.* **112**, 755 (1958).

⁹S. Triebwasser and E. F. Hahn, *Bull. Am. Phys. Soc. Ser. II*, **4**, 184 (1959).

¹⁰R. C. Miller and A. Savage (unpublished).

SUPERCONDUCTIVITY OF β MERCURY*

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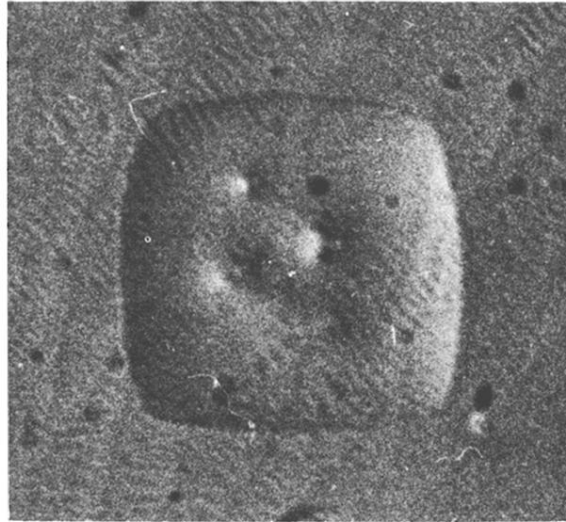
(Received March 12, 1959)

Solid mercury ordinarily crystallizes in a rhombohedral structure which is stable to absolute zero under normal pressures. Recent experiments have shown, however, that a new type of solid mercury can be produced which is actually the more stable form at temperatures below 79°K.¹ The first indications that this new modification existed were found in the course of a series of experiments in which the effect of pressure on the superconducting transition temperature of normal (α) mercury was studied.² The results of these experiments implied (although not conclusively) that the new (β) phase was also

superconducting. The theory of superconductivity, as given by Bardeen, Cooper, and Schrieffer,³ is relatively insensitive to the band structure, and, hence, for a given element, the superconducting transition temperature in zero field should be dependent to a first approximation only on the density.⁴ Lanthanum, which is far from an ideal superconductor,⁵ represents what has been the only known example of an element that exists in two superconducting crystallographic modifications. The two forms of mercury seemed to offer a more ideal opportunity for checking the dependence of the superconducting transition temperature on crystal structure, and in order to investigate this point we have recently investigated the initial part of the critical field curve for β mercury. The zero-field transition temperature which was found for β mercury can be explained quantitatively in terms of the known difference in molar volume¹ (about 1.5%) between the two forms of solid mercury, and the pressure-effect data for α mercury.²

Although β mercury is stable at zero pressure below 79°K, and metastable for temperatures below 90°K, it can be formed only at relatively high pressures (4000 atmos). Above 90°K the low-temperature β phase anneals rapidly into the α phase in an irreversible manner, so care must be taken in handling samples once they have been obtained. In our case, a fine wire of the β phase, 0.4-mm diam, was formed by extruding solid mercury under liquid nitrogen from a 0.250-in. diam cylinder through a 0.016-in. diam hold. A pressure of 8000 atmos was necessary to initiate extrusion, so β mercury was formed in the cylinder before the extrusion began. The extrusion rate was kept small (about one inch of wire per hour) in order to prevent local heating and annealing. A convenient, though destructive, test for the existence of the β phase was made by measuring the resistance of a piece of wire in liquid nitrogen before and after heating in air to 100°K. The existence of the β phase was indicated by an irreversible resistance increase of a factor of two due to the β - α transition.

The critical field curve to 200 gauss was determined by placing the wire in the center of a small solenoid which was later placed in a liquid helium Dewar, all manipulations taking place under liquid nitrogen. The transitions were observed by using an ac mutual inductance method at 33 cps, with a measuring field of 0.02 gauss rms superimposed on the dc field. The results of three runs on both α and β mercury are given



10⁻² CM

FIG. 1. Photomicrograph showing a portion of the antiparallel domain configuration of a partially reversed BaTiO₃ crystal as observed directly through semitransparent gold electrodes. The single reversed domain shown in the figure is approximately square with the sides at about 45° to the crystalline *a* axes. The sample was placed between crossed polaroids and viewed with white light.