Letters to the Editor

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Single-Crystal Neutron Analysis of Tetragonal BaTiO₃†

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ABOVE its ferroelectric Curie temperature BaTiO₃ has the cubic perovskite-type structure with Ba on the cell corners, Ti at the center, and O's on the cube faces. In the transition to the ferroelectric tetragonal phase, the atoms are freed from symmetry restrictions on their z coordinates. With Ba at the cell origin, the coordinate parameters may be written: Ba at $(0,0,0)$; Ti at $(\frac{1}{2},\frac{1}{2},\frac{1}{2}+\delta z_{Ti})$; O_I at $(\frac{1}{2},\frac{1}{2},\delta z_{OI})$; O_{II} at $(\frac{1}{2},0,\frac{1}{2}+\delta z_{OII})$ and $(0,\frac{1}{2},\frac{1}{2}+\delta z_{OII})$. The δz displacements from cubic positions must be known accurately before theoretical understanding of ferroelectricity in BaTiO₃ can be achieved.

The most thorough of the several x-ray attempts on this structure were those of Kaenzig[1] and Evans.[2] The especially careful analysis of Evans finally showed that a unique x-ray solution of the problem is not possible. Because of the high Ba scattering and the small values of the δz's one is not able to separate the effects of coordinate and temperature parameters in the interpretation of diffraction data. As Evans suggested, the structure can be solved with neutrons, however. Here the scattering factors do not differ very greatly in magnitude. Moreover, they are constant with angle, and hence the range of observation may be extended without a great loss in intensity and without the problem of extending scattering factor curves beyond their known range.

A successful determination of the tetragonal PbTiO₃ structure was recently reported,[3] as deduced from a combined single-crystal x-ray and powder neutron diffraction study. The large tetragonal distortion of the lattice (about 6% as compared to only 1% for BaTiO₃) suggested at the outset that the δz's might be large enough to permit a determination by x-rays alone. After arriving at a structure that agreed very well with observed x-ray data, it was found that the agreement was not significantly affected by choosing any of the four possible combinations of algebraic signs for the displacement directions. The large cell distortion permitted sufficient resolution in a neutron powder pattern to obtain data which showed conclusive agreement with

only one of the models. This study further emphasized the necessity of using neutrons on BaTiO₃. Because of the small cell distortion, powder methods cannot be employed. The availability of good single crystals of BaTiO₃ has permitted a single-crystal study, which has resulted in an unambiguous solution of the tetragonal structure.

A c-plate was cut with dimensions 12 mm×2.5 mm ×0.38 mm, with an a-axis parallel to the length. Electrodes were applied to permit unidirectional domain alignment by an electric field during the neutron observations (350 volts across the c-plate≅9200 volts/cm). Scattering data were collected on about 50 symmetry-unrelated (HOL) reflections at mean neutron wavelengths of 1.063 A and 0.905 A.

Kaenzig had reported $\delta z_{Ti}=0.014$, $\delta z_{OI}=-0.032$, and $\delta z_{OII}=0$. Evans found two structures which gave almost equally satisfactory agreement between observed and calculated data: (1) $\delta z_{Ti}=0.012$, $\delta z_{OI}=-0.026$, $\delta z_{OII}=0$; (2) $\delta z_{Ti}=0.015$, $\delta z_{OI}=-0.024$, $\delta z_{OII}=-0.020$. In addition to the coordinate parameters, Evans took into account nine anisotropic temperature parameters: 2 each for Ba, Ti, and O_I, and 3 for O_{II}. He discarded the (2) structure because the temperature parameters seemed improbable.

Trial calculations were made based on the above structures and the additional models obtained by taking all combinations of signs. The correct structure appeared to lie somewhere between Evans' two structures. Trial and error calculations were made on this basis, and followed by least squares refinement. This analysis led to the following coordinate parameters: $\delta z_{Ti}=0.014$, $\delta z_{OI}=-0.023$, and $\delta z_{OII}=-0.014$. Structure factors were calculated using these coordinates and the following isotropic temperature parameters: $B_{Ba}=0.273$, $B_{Ti}=0.152$, $B_{OI}=0.334$, and $B_{OII}=0.267$. While this structure shows excellent agreement between calculated and observed data (reliability index $=0.0296$) it is being checked by further measurements at high Bragg angles and by observation of (HHL) spectra from another sample.

Using the cell dimensions of Megaw,[4] $a=3.995$ A and $c=4.034$ A, the neutron results indicate a Ti shift of 0.06 A, and opposite O shifts of -0.09 A for O_I and -0.06 A for O_{II}. While at first sight these displacements are surprising when compared with those in PbTiO₃, since in that study the Ti and O displacements were all in the same direction, a consistent picture is obtained if one views the two structures in terms of shifts of Ti, Pb, and Ba relative to the oxygen framework, instead of fixing the origin at the Ba (or Pb) position. The shifts are then all in same direction. In PbTiO₃, the oxygen octahedra are deformed by the same amount as the lattice. Pb shifts 0.46 A and Ti shifts 0.30 A. In BaTiO₃ there is a small tetragonal distortion of the oxygen octahedra over the lattice distortion. Depending on which oxygen is "fixed," Ba shifts 0.06 A or 0.09 A, and Ti shifts 0.12 A or 0.15 A.

The $PbTiO_3$ shifts are much larger than those in $BaTiO_3$, but this might be expected from the greater lattice distortion and high polarizability of the Pb ion.

Excellent single crystals for this investigation were furnished by Dr. Kohman of the Bell Telephone Laboratories, Dr. Karan of International Business Machines in Poughkeepsie, Dr. Lefkowitz of the Glenco Corporation, and Dr. Jaffe of the Brush Development Company. The research has been supported jointly by the Brookhaven National Laboratory and contracts with the U. S. Atomic Energy Commission and the Signal Corps Engineering Laboratories.

[1] W. Kaenzig, Helv. Phys. Acta 24, 175–216 (1951).
[2] H. T. Evans, Jr., Technical Report No. 54, Philips Laboratories, Inc., Irvington-on-Hudson, New York, 1952 (unpublished).
[3] Shirane, Pepinsky, and Frazer, Phys. Rev. 97, 1179 (1955).
[4] H. D. Megaw, Proc. Phys. Soc. (London) 58, 133 (1946).

Magnetic Domains in Thin Films of Nickel-Iron*

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CONSIDERABLE attention has been given recently to the problem of the magnetic behavior of thin ferromagnetic films.[1-5] Measurements of certain of the magnetic properties have seemed to indicate that domain configurations in general depend upon the thickness and the constants of the films in the manner predicted by Kittel,[6] namely, a single domain parallel to the film when the thickness is less than a critical value and domains oriented normal to the film surface when this value is exceeded. Direct observation of the domain structure in films has apparently been unsuccessful, although an indirect observation by optical transmission through very thin films has been reported by König.[7]

By employing the longitudinal Kerr magneto-optic method of domain observation, previously described,[8] we have succeeded in photographing the domain structure of an evaporated NiFe film (80% nickel) 5000 angstroms thick, measuring 1 in.$\times 1\frac{1}{4}$ in. on the surface. Figure 1(A) is a composite photograph of the several portions of the complete film surface, the composite being necessary because of the rather limited photographic field of our Kerr setup. The pattern consists of a number of antiparallel, gently curving domains several millimeters wide and separated near certain of the film edges by dagger-like domains of various lengths. There is no evidence of closure domains at any of the film edges. By photographing through the microscope cover glass which serves as a backing for the evaporated
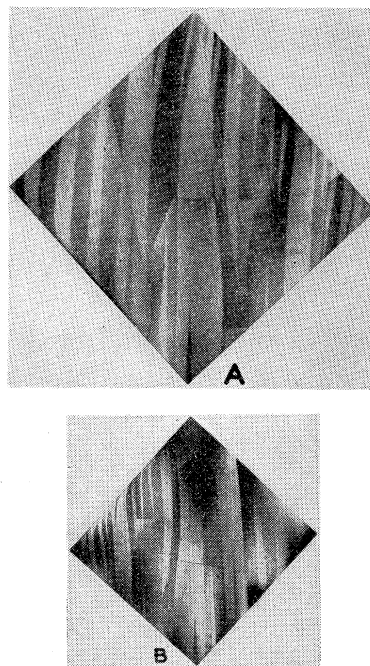

FIG. 1. Composite photographs of the domain configurations in the top (A) and the bottom (B) surfaces of a NiFe film 5000 A thick. The specimen was turned over about an axis connecting the top and bottom corners of the pictures.

alloy, the Kerr technique has revealed the domain configuration on the reverse side of the film, and this proves to be a mirror image of the front side when the film has been turned over about a longitudinal axis [see Fig. 1(B)]. Thus it follows that each domain extends completely through the film, as expected.

The domains are exceedingly sensitive to external magnetic fields. Figure 2 illustrates their behavior in a portion of the surface as the S pole of a small compass needle is brought up to the edge of the film and then withdrawn. These three photographs are part of a longer sequence which indicates that the changes caused by the small field of the perturbing pole occur by movement of the domain walls. When the pole is replaced by an unmagnetized steel needle, a smaller but still significant domain shift is observed. We have even observed changes in domain configuration to occur overnight, presumably caused by small stray fields in the laboratory.

Investigation of two other films of this material but with thicknesses of 10 000 angstroms and 20 000 angstroms, respectively, showed no evidence of surface domains. It is possible that these thicker films contain the predicted normal domains, perhaps very much smaller in surface area than those of Fig. 1. We are now attempting to photograph or otherwise detect these as a part of a systematic experimental study of the domain behavior in films of this thickness down to those of 100 angstroms or less, in a controlled uniform magnetic field.