The Low Temperature Transformation in Ferrites

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The general behavior of magnetite (iron ferrite) at its low temperature transformation (*ca* 118°K) is reviewed. One of the properties which undergoes a large change is the magnetocrystalline anisotropy, which is larger in magnitude and has a lower symmetry below the transformation. The magnetic symmetry axis below the transition temperature can be predetermined by cooling a single crystal through the transition in a magnetic field, and can be changed from one cube edge to another below the transformation by means of a strong magnetic field.

Directional pressure also appears to be effective in establishing the axis. Hysteresis loop measurements show that if a compressive stress is applied along the length of a rod-shaped specimen cut parallel to [100] as it cools through the transition, the specimen is more easily magnetized in this direction. No such effect was observed along [110] or [111] directions.

Changes in dimension occurring at the transition have been measured by means of resistance strain gages cemented along the principal crystallographic directions. Data were obtained as the crystal warmed through the transition in the demagnetized state after having been cooled in various conditions of biasing magnetic field and pressure. It is concluded that the large changes in magnetic symmetry accompany small changes in crystal structure. The low temperature form appears to be orthorhombic, the maximum distortion from cubic symmetry, along [110], amounting to *ca* 0.07 percent. All three orthorhombic axes can be established unambiguously by cooling the crystal through the transformation in a magnetic field along [100] with pressure applied simultaneously along [011]. The change in direction of easy magnetization above the transition from [111] to [100] is accompanied by a small dimension change (*ca* 0.002 percent).

Similarities with the behavior of barium titanate at its ferroelectric Curie temperature are pointed out. Evidence for the existence of similar transformations in the other ferrites is discussed briefly.

I. INTRODUCTION

NUMEROUS investigations over the past twenty-five years have brought to light many interesting changes occurring in magnetite (iron ferrite) at its low temperature transformation (*ca* 118°K). Three of the more significant changes are illustrated in Fig. 1. Weiss and Forrer[1] found that the magnetization decreases abruptly at the transition, as shown in Fig. 1(a). The magnitude of the discontinuity is smaller for larger magnetic fields, the saturation magnetization remaining unchanged through the transformation. The specific heat curve[2] shows an anomalous peak (Fig. 1(b)), and the electrical resistivity[3] changes rapidly with temperature (Fig. 1(c)). Li[4] found that the magnetocrystalline symmetry decreases from cubic to uniaxial, with a large increase in anisotropy energy. He also demonstrated that a magnetic memory effect exists; that is, the direction of easy magnetization, or magnetic axis, below the transformation temperature can be predetermined by cooling the crystal in a magnetic field. It has been established that the magnetic axis becomes the cube edge most nearly parallel to the direction of this biasing magnetic field and that it can be shifted from [100] to [010] or [001] below the transformation by means of a strong magnetic field.[5]

Verwey[6] has proposed that the transformation is an electronic ordering phenomenon, in which the random distribution of ferrous and ferric ions on the octahedral sites of the cubic inverse spinel lattice changes, on cooling, to an ordered arrangement. If one makes use of this picture, some of the physical changes characteristic of the transition can be attributed directly to the ordering (specific heat and resistivity), and others to a small crystallographic change accompanying the ordering (magnetic properties).

The crystalline structure change must be very small, since a large single crystal will withstand numerous traversals through the transformation without shattering. Several attempts[3,4,7] to detect a crystal structure change by means of x-ray diffraction ended in failure.

Experimental investigation of magnetite below its transformation temperature is somewhat unsatisfactory because the physical properties depend on the condition in which the crystal was cooled through the transition. Exact reproducibility in the measurements is difficult to obtain even when these conditions are controlled as closely as possible.

II. HYSTERESIS LOOP MEASUREMENTS

Directional pressure has been found to be effective in selecting the magnetic symmetry axis, but to a lesser extent than magnetic field. The ease of magnetization

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[1] P. Weiss and R. Forrer, Ann. phys. **12**, 279 (1929).
[2] R. W. Millar, J. Am. Chem. Soc. **51**, 215 (1929).
[3] T. Okamura, Sci. Repts. Tôhoku Imp. Univ. **21**, 231 (1932).
[4] C. H. Li, Phys. Rev. **40**, 1002 (1932).
[5] L. R. Bickford, Jr., Phys. Rev. **78**, 449 (1950).
[6] Verwey, Haayman, and Romeijn, J. Chem. Phys. **15**, 181 (1947).
[7] H. Shôji, Sci. Repts. Tôhoku Imp. Univ. **24**, 250 (1935).

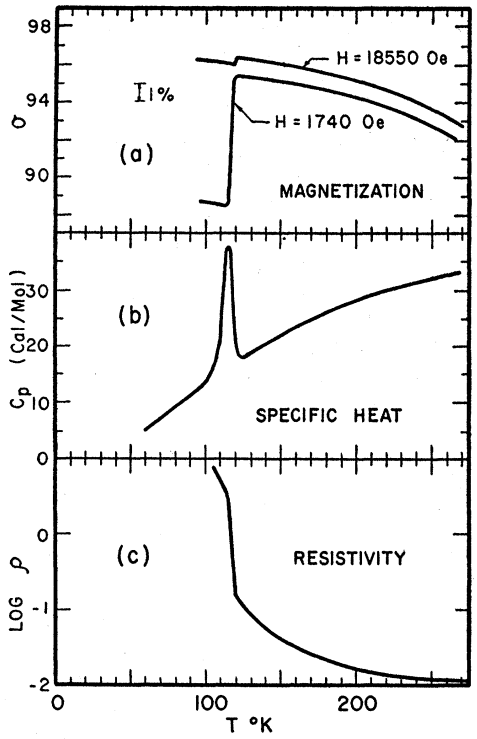

FIG. 1. Anomalies in magnetization, specific heat, and electrical resistivity at the magnetite low temperature transformation.

of a rod-shaped specimen with its axis parallel to [100] is increased below the transformation by cooling under compressive stress along the axis. This effect is not observed in specimens cut parallel to [110] or [111].

Figure 2 shows a photographic sequence of oscilloscope traces representing hysteresis loops obtained below the transformation with a 60-cycle magnetic field parallel to the axis of a [100] specimen cut from a natural single crystal. Curves (b) through (e) were obtained under identical conditions during measurement, as indicated in (a). The differences arise entirely from the different conditions under which the crystal was cooled through the transformation, as shown schematically by each inset.

Curve (b) was obtained after the crystal had been cooled with a magnetic field applied along the specimen axis and corresponds to a measurement along the magnetic axis. The crystal was cooled in a magnetic field along [010] (perpendicular to the specimen axis) prior to obtaining curve (c). As a result of this treatment the specimen axis is the direction of most difficult magnetization. The measuring field was much too weak to saturate the crystal. A comparison of curves (b) and (c) will serve to illustrate the large magnetic anisotropy.

Curve (d) was photographed after the crystal had been cooled in the absence of a magnetic field and is intermediate in appearance between (b) and (c). Curve (e) was obtained after the crystal had been cooled in a compressive stress of 4 kg/mm^2 parallel to the specimen axis. It shows the effect of a directional pressure. The behavior of the crystal in the transformation region is illustrated in Fig. 2(f), in which is superimposed a number of hysteresis loops photographed as the crystal warmed slowly through the transformation.

III. STRAIN GAUGE MEASUREMENTS AT THE TRANSFORMATION

Although dilatometric measurements[3,8] had shown that an anisotropy exists in linear thermal expansion along different crystal directions, Tombs and Rooksby[9] reported the first concrete evidence of a change in crystalline structure, obtained through an x-ray analysis of powder samples. They concluded that the low temperature modification is rhombohedral, with the maximum distortion from cubic symmetry amounting to 0.1 percent along the body diagonal at 95°K.

Rhombohedral symmetry, however, does not seem to fit in with the magnetic behavior, which indicates that the magnetic symmetry axis is one of the cube edges. The magnetic symmetry should be related to the crystalline symmetry. Moreover, it is of fundamental importance to know just how intimately magnetic symmetry is related to crystalline symmetry; whether for example, the switching of the magnetic axis is accompanied by a corresponding change in crystalline structure.

Our approach to these questions has been to measure macroscopically the changes in length of magnetite single crystals in the transformation region. Resistance strain gauges were cemented along the principal crystallographic directions of disk-shaped specimens cut from

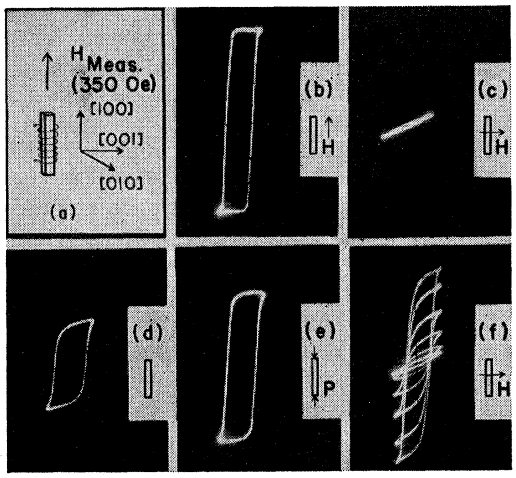

FIG. 2. Sixty-cycle hysteresis loops at 88°K for natural single crystal of magnetite after different conditions of cooling through transformation (schematically represented by each inset). In (f) are superimposed loops obtained as crystal warmed through transformation.

[8] C. A. Domenicali, Phys. Rev. **78**, 458 (1950).
[9] N. C. Tombs and H. P. Rooksby, Acta Cryst. **4**, 474 (1951).

a synthetic single crystal.† The strain was measured as the sample warmed slowly through the transition, after having been cooled under various conditions of magnetic field and stress. This method has two distinct advantages over x-ray analysis: one, greater sensitivity ($\Delta l/l = 10^{-6}$ or better); and two, ability to observe the changes taking place. The structure cannot be determined directly in a single measurement but can be deduced by measuring total dimension changes occurring along the different directions as the crystal transforms from the unknown state to one in which its symmetry and lattice constant are known. For the known state, we chose a point 12° above the transition (130°K). The magnetocrystalline anisotropy energy is extremely low at this temperature, and therefore the symmetry most nearly cubic.

The first significant observation from the strain gauge measurements was that the cube edge which becomes the magnetic axis contracts by *ca* 0.027 percent with respect to the others, which actually expand on cooling through the transition. Warming curves corresponding to these two conditions are shown in Fig. 3, along with a curve for [111].

The magnetic axis transfer from one cube edge to another below the transformation is also accompanied by a dimension change. Figure 4 shows the relative dimensional change along [100] as the direction of a strong magnetic field oscillates slowly in the (001) plane between [100] and [010]. An abrupt contraction occurs as the magnetic axis transfers to [100] and an elongation, as it transfers to [010]. The amount of angular hysteresis depends upon the temperature and magnitude of the magnetic field.

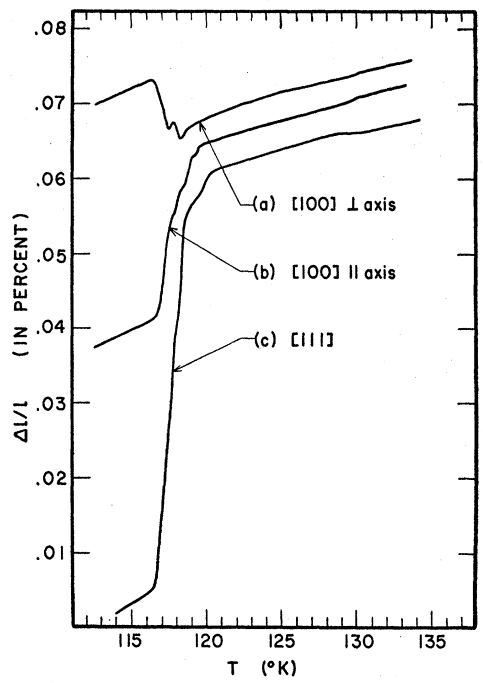

FIG. 3. Thermal expanison behavior of magnetite single crystal along [100] and [111] in the transformation region.

† Kindly furnished by Professor A. R. von Hippel, Laboratory for Insulation Research, MIT; see J. Smiltens, Tech. Rept. 49, Lab. Ins. Res., MIT (December, 1951).

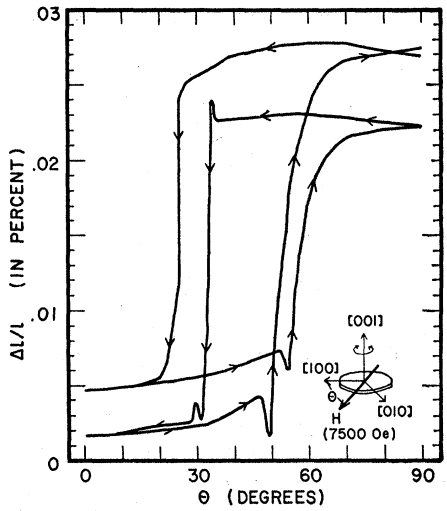

FIG. 4. Dimensional change along [100] accompanying switching of magnetic axis in magnetite single crystal between [100] and [010] at 98°K.

1. Structure of the Low Temperature Modification

The orthorhombic structure shown in Fig. 5(a) has been worked out tentatively for magnetite at 115°K. (just below the transformation), on the basis of strain gauge measurements completed to date. The numbers on the diagram refer to measured percentage changes relative to the dimensions of the cubic crystal at 130°K (indicated by the dotted lines). The relatively large changes for the face diagonals in the plane perpendicular to the *c* axis (i.e., along *a* and *b* axes) were measured only after the crystal had been cooled through the transformation under the simultaneous influence of a magnetic field and a directional pressure (*ca* 3 kg/mm²), orineted as shown in Fig. 5(b). Without pressure, both diagonals displayed roughly the same expansion behavior. All other measurements were made without pressure.

The volume change at the transformation, calculated on the basis of this model, only amounts to 0.025 percent. Figure 5(c) shows the ordered arrangement of ferrous and ferric ions on the octahedral sites, as proposed by Verwey. Our tentative structure is compatible with this arrangement.

2. Crystallographic Interpretation of the Transformation

The interpretation which suggests itself is that the large change in magnetocrystalline anisotropy occurring at the transformation is intimately associated with a

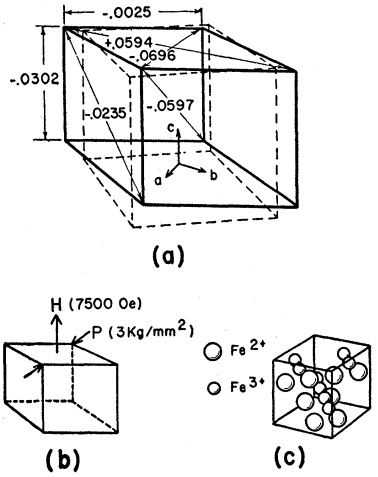

FIG. 5. (a) Tentative orthorhombic structure for magnetite at 115°K, with measured percentage changes in dimension relative to the cubic crystal at 130°K. (b) Experimental cooling conditions prior to obtaining data for plane perpendicular to c axis. (c) Verwey model of low temperature form.

very small orthorhombic distortion of the cubic crystal structure, the magnetic axis coinciding with the orthorhombic c axis. If a single crystal is cooled through the transformation in a demagnetized condition and in the absence of external stress, the resultant state is determined by the internal stress pattern and magnetic domain pattern. The domain pattern predominates because the large crystal anisotropy discourages any arrangement not resulting in the alignment of the magnetization with the magnetic axis. As a result, the crystal is no longer a single crystal below the transition temperature, but is rather a "hybrid" in which the orthorhombic c axis coincides with different original cubical axes in different regions. In this condition, the crystal is not easily magnetized in any direction.

Cooling the crystal in a magnetic field partially removes the hybridization by establishing the c axis along the same [100] (most nearly parallel to the magnetic field) throughout the crystal. Some twinning remains, however, in that the a and b axes are interchanged in different regions. This partial twinning is probably determined by the internal stresses, which appear to be especially significant in the synthetic crystals. Calhoun[10] has already suggested the existence of such a situation as an explanation for the double absorption peaks below the transition observed in microwave resonance experiments.[5]

It is suggested that the hybridization can be completely removed by cooling the crystal in a strong magnetic field along one of the cube axes [100] and at the same time applying pressure along one of the body diagonals [011] in the plane perpendicular to this axis.

[10] B. A. Calhoun, Prog. Rept. IX, Lab. for Ins. Res., MIT, p. 50 (May, 1951).

3. Comparison with the Titanates

The phenomenon of hybridization is known to exist in titanates. Megaw[11] has found direct x-ray evidence for its occurrence in a titanate cooled through the Curie region in the absence of an electric field. Certain other similarities with the behavior of barium titanate at its ferroelectric Curie point are suggestive. It is perhaps unusual to point this out, since comparisons are usually made the other way around; that is, ferroelectric behavior is usually described by analogy with ferromagnetic behavior. Moreover, the magnetite transformation is not a Curie point transformation. However, the intimate association of domain structure with crystalline structure displayed by magnetite below the transformation is more characteristic of ferroelectrics than of ferromagnetics. Barium titanate shows the effects of predetermination of the crystallographic c axis by an electric field applied as the crystal cools through the transformation and of the switching of the axis below the Curie point by an electric field. Ferroelectric barium titanate has a tetragonal structure, however, so there is no ambiguity regarding a and b axes.

IV. DIMENSIONAL CHANGES ABOVE THE TRANSFORMATION

The direction of easy magnetization in cubic magnetite changes, on cooling, from [111] to [100] above the transformation at *ca* 130°K. We have found by strain gauge measurements that this change is accompanied in a demagnetized single crystal by dimensional changes: one, a small shrinkage in the direction which becomes the direction of easy magnetization; and two, a small elongation in the direction along which magnetization becomes more difficult. Figure 6(a) shows the thermal expansion along a [100] direction in the region of the direction of easy magnetization change-over. The effect is most apparent when one measures the differential expansion between two crystallographic

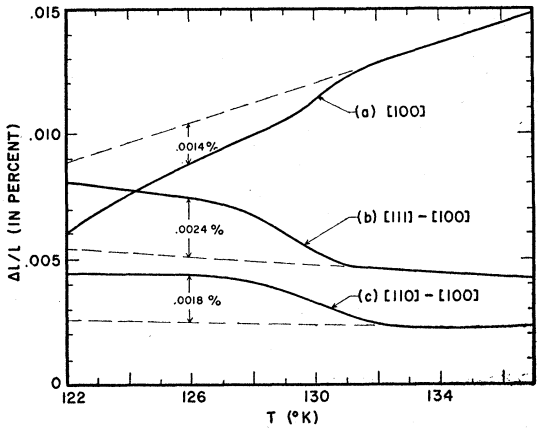

FIG. 6. Dimensional changes accompanying change-over of direction of easy magnetization in magnetite from [111] to [100] above transformation temperature.

[11] H. D. Megaw, Nature **157**, 20 (1946).

directions. Strain gauges are particularly suitable for making this type of measurement directly. Figure 6(b) shows differential expansion between [111] and [100], and (c), between [110] and [100]. The shape of these curves, obtained as the crystal warmed, was found to be independent of the condition of the crystal below the transformation.

V. TRANSFORMATION IN THE OTHER FERRITES

Several references have been made in the literature to a low temperature transformation in other ferrites, including those of cobalt,[12] nickel,[13] and manganese.[13] The most convincing evidence is the magnetization data of Guillaud for cobalt ferrite, which show discontinuities similar to those displayed by magnetite. However, present evidence is insufficient to determine whether any of the reported anomalies can be classified along with the magnetite transformation. Healy's microwave resonance absorption study[14] of nickel ferrite has shown that no sudden change in magnetic symmetry occurs between the Curie temperature and 78°K, although the anisotropy constants change in a manner somewhat similar to those of magnetite. If the interpretation of the magnetite transformation as an ordering phenomenon is correct, it is difficult to understand how a similar transformation could occur in other ferrites in the same temperature region, since ordering in any other ferrite would necessitate ionic motion.

[12] C. Guillaud and H. Creveaux, Comp. rend. **230**, 1256 (1950).
[13] T. Okamura and J. Simoizaka, Phys. Rev. **83**, 664 (1951).
[14] D. W. Healy, Jr., Phys. Rev. **86**, 1009 (1952).

ACKNOWLEDGMENTS

The writer would like to acknowledge his indebtedness to Dr. C. A. Domenicali of the Franklin Institute, who was associated with this work during its early stages; to Mr. M. Nerenstone, for assistance in the strain gauge measurements; to Dr. J. E. Goldman of Carnegie Institute, for having suggested the use of strain gauges in studies of magnetite; and to Dr. E. A. Wood, of Bell Telephone Laboratories, for an illuminating discussion of low temperature structure possibilities, during which the idea for the experiment of Fig. 5(b) was evolved.

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Magnetic Study of Low Temperature Transformation in Magnetite

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THE magnetic crystal anisotropy of magnetite has been investigated with special reference to the effect of cooling through the transformation at about −160°C in the presence of a magnetic field. In a natural crystal we have found an anisotropy such that the difference in energy between the directions of easy and of hard magnetization is 1.07×10^6 ergs/cm^3. When the field is applied in a (100) plane parallel to a [001] direction, this direction becomes the easy direction whereas [010] becomes the hard direction. This confirms the observation first reported by Li.[1]

When fields are applied along other directions in this plane, the relation between the direction of applied field and the consequent direction of easy magnetization is shown in Fig. 1, and similar data for the (011) plane are given in Fig. 2. A set of torque curves for the (100) plane are shown in Fig. 3.

The results for the (100) plane can be explained as follows: When the field used during cooling was applied within about 40 degrees of a [001] direction, that direction becomes the direction of easy magnetization for all of the crystal; the directions [010] and [001] being hard directions. When the field during cooling is near a [011] direction, some portions of the crystal

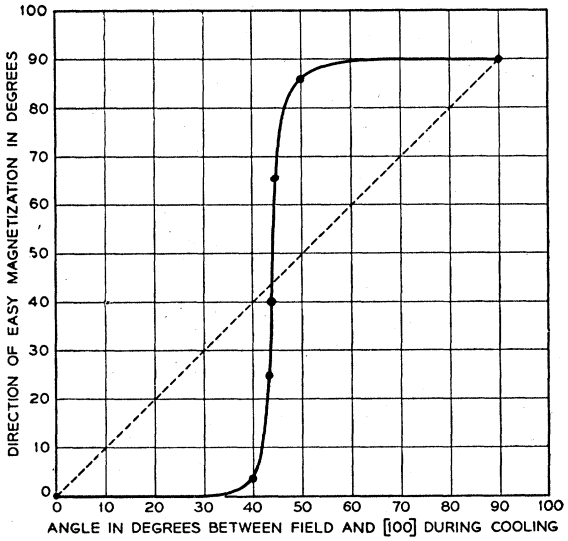

FIG. 1. Natural magnetite crystal, liquid N_2 temperature. Relation between direction of magnetic field present during cooling, and resultant direction of easy magnetization, in (100) plane.

[1] C. H. Li, Phys. Rev. **40**, 1002 (1932); see also Domenicali, Phys. Rev. **78**, 458 (1950).

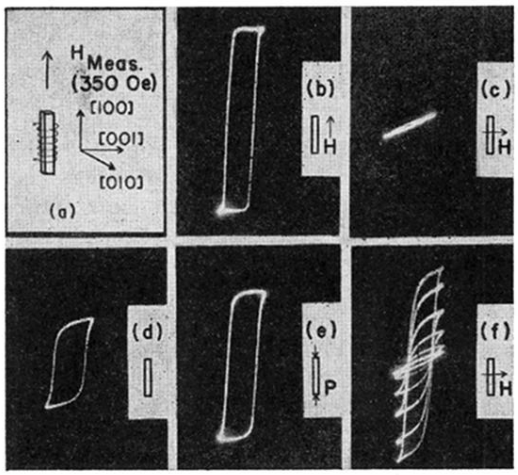

FIG. 2. Sixty-cycle hysteresis loops at 88°K for natural single crystal of magnetite after different conditions of cooling through transformation (schematically represented by each inset). In (f) are superimposed loops obtained as crystal warmed through transformation.