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A Magneto-X-ray Study of Magnetite at 78°K.*

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The X-ray diffraction pattern produced by a small single crystal of magnetite after cooling through the transition at 119° K. has been examined. It is demonstrated, by using orientated magnetic fields during the cooling process, that up to six different domain orientations are present in the crystal at 78° K. This number of domain orientations can be produced only if the symmetry of the low-temperature phase of magnetite is orthorhombic or lower.

Introduction

The crystal structure of magnetite, Fe_3O_4, below its transition at 119° K. has recently attracted considerable interest. Verwey & Haayman (1941) suggested that magnetite has the inverse spinel structure at room temperature and that the transition is due to an ordering of the ferrous and ferric ions in the octahedral positions of the spinel lattice. This ordered arrangement, Verwey, Haayman & Romeijn (1947) proposed, possesses orthorhombic symmetry.§ Measurements of the deformation of circular disks cooled through the transition in a magnetic field, by strain-gauge techniques (Bickford, 1953), were consistent with an orthorhombic structure, and it has been shown that

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§ The cell they gave was tetragonal, but it really has orthorhombic symmetry.

the anisotropy of the electrical conductivity below the transition (Calhoun, 1954) also agrees with Verwey's model. Further, the anisotropy energy of both natural (Williams, Bozorth & Goertz, 1953) and synthetic (Calhoun, 1954) crystals of magnetite below 119° K. has the form expected from holohedral orthorhombic symmetry.

The deformation of the unit cell at the transition is very small and a number of early attempts to detect it by X-ray methods failed. Tombs & Rooksby (1951) first reported definite evidence of the deformation, based on powder patterns taken with a 19 cm. camera. They interpreted the pattern at 95° K. in terms of a rhombohedral cell. Since this appeared to conflict with all the other evidence, we examined a magnetite powder sample with a Norelco wide-range diffractometer (Abrahams & Calhoun, 1953) and found a small splitting of the cubic 800 line below the transition. This was consistent with the orthorhombic model and appeared to eliminate the rhombohedral model.

Rooksby & Willis (1953) have now presented new data supporting the view that magnetite transforms from the cubic to the rhombohedral system below 119° K. Within the limits of resolution of a 19 cm. powder camera, they could observe no splitting in 800. The splitting previously observed by the present writers (the diffractometer has a diameter of 34 cm.) was small: $d_{(008)} = 1{\cdot}0481$ and $d_{(440)} = 1{\cdot}0476$ Å for Fe $K\alpha$ radiation. Hence, a new experiment was designed to examine this and several other important reflections, as diffracted by a small single crystal. Each such reflection could then be analysed by cooling the crystal through the transition in a strong magnetic field, thus obtaining different portions of the pattern for each magnetic field direction.

Experimental

A Norelco wide-range diffractometer was modified for use with a small single-crystal specimen. The adaptor described by Abrahams & Grenville-Wells (1954) was used in conjunction with a Geiger counter, and an oscillation attachment to this adaptor was used with photographic recording. Two crystals were examined, both prepared from a large single crystal of magnetite grown by Smiltens (1952). The first crystal was ground to a sphere and then etched by sulfuric acid to a cube. The other crystal was kept as a sphere, to avoid the large demagnetizing fields along the edges and in the corners of the cube. Each crystal was mounted within a thin-walled glass capillary, and, in the case of the spherical crystal, a small quantity of Vinylseal* was inserted around the crystal to prevent it from moving on application of the magnetic field. Both crystals had a maximum dimension of about 0·30 mm.

The specimens were completely bathed in a collimated X-ray beam and, in using the Geiger counter, both receiving and scatter slits were removed. In this case, the counter was kept stationary while the crystal was rotated through the reflecting position with a constant angular velocity of $\frac{1}{8}° \theta$ per minute. With the photographic method, the film was contained in a paper cassette and replaced the receiving slit. The film remained stationary while the crystal was oscillated through about $3° \theta$ with a constant angular velocity.

The low temperature was attained by a method similar to that of Lonsdale & Smith (1941) in which a stream of liquid nitrogen about $\frac{1}{16}$ in. in diameter was allowed to flow over the crystal, contained within the capillary, at a rate of about 5 l. per hour. This rate of delivery was maintained by a head of about 30 in. liquid nitrogen above the exit nozzle. The filtered nitrogen was continuously pumped from a 25-l. can to a 3-l. metal container, insulated with $\frac{1}{2}$ in. of Styrofoam*.

The magnetic field was applied, using a small permanent magnet fitted with specially designed pole pieces, so that the crystal could be surrounded by a fairly homogeneous field. The field strength at the crystal was about 3200 oersteds, and the field required to saturate the specimen was computed to be about 2000 oersteds.

Unfiltered iron X radiation was used throughout.

Discussion

An analysis of Rooksby & Willis's low-temperature experimental data, on the basis of which they reject the orthorhombic in favor of the rhombohedral model, reveals that their interpretation depends upon three powder lines.† These are the lines that were cubic 440, 444 and 800 at room temperature; the other two lines studied, 533 and 840, fit either model about equally well. Particular significance is attached to the be-

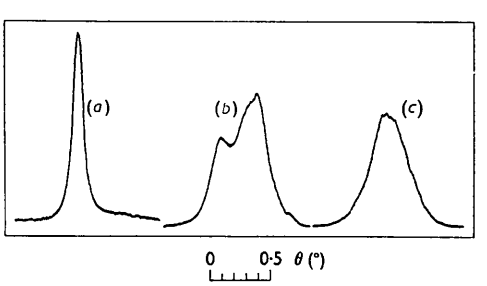

Fig. 1. (*a*) Profile of magnetite 800, recorded with Fe $K\beta$ radiation, at room temperature; (*b*) same line at liquid-nitrogen temperature; (*c*) same line cooled through the transition, with magnetic field applied parallel to rotation direction [100].

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† Mr Rooksby (private communication) has pointed out that, to a first approximation, *all* the powder lines fit a rhombohedral symmetry, and it is only in the fine details of the diffraction data not detectable on powder photographs that a departure from a relatively strong [111] dilatation becomes apparent.

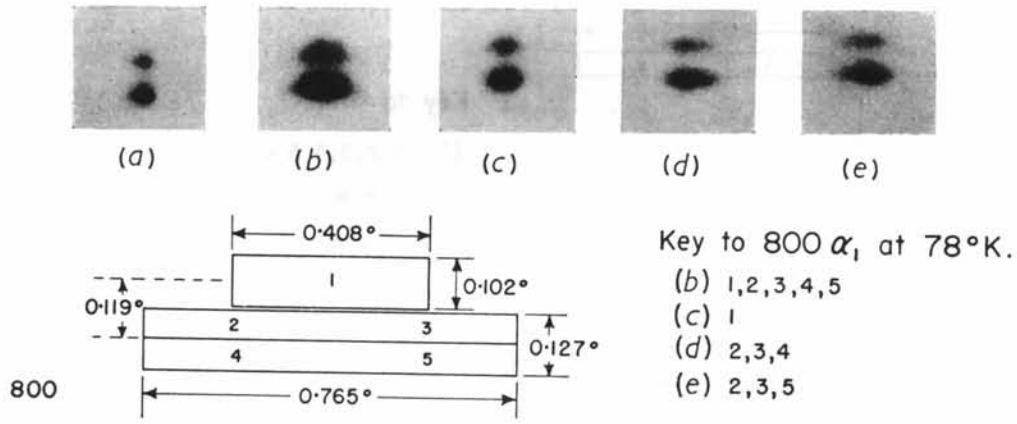

Fig. 2. Magnetite 800 α_1 and α_2 reflections: (*a*) at 298° K.; (*b*) at 78° K.; (*c*)–(*e*) at 78° K. after cooling through transition with magnetic field aligned along each cube edge in turn. The key gives the angular dimensions of the reflections subtended at the crystal.

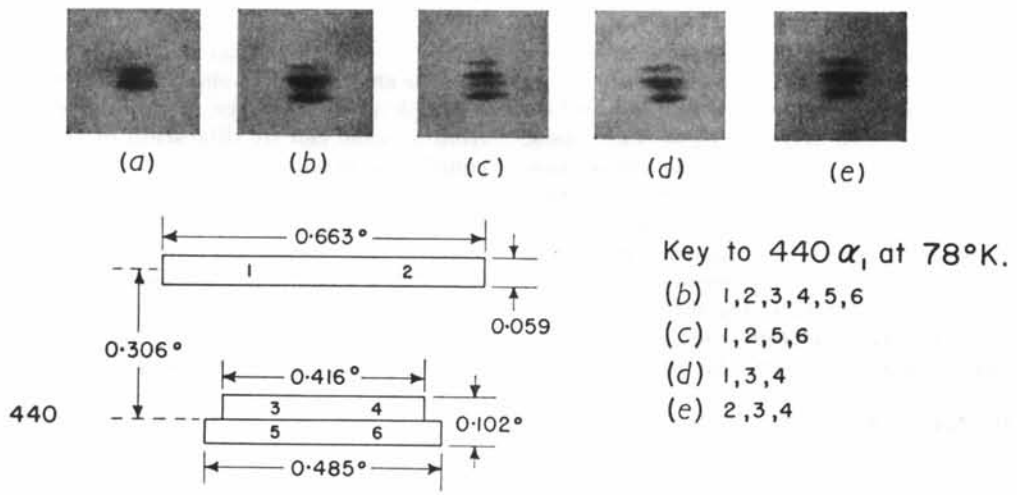

Fig. 3. 440 α_1 and α_2 reflections: (*a*)–(*e*) as in Fig. 2.

havior of 440 at 80° K., which is reported to split into two lines of about equal intensity with a separation about equal to that of the $\alpha_1\alpha_2$ doublet for this line. Attempts to repeat Rooksby & Willis's observations on 440, using a powder sample and Cr radiation as they did, were not successful owing to the low efficiency of the Geiger-counter tubes available to us.

In using a single crystal, 800 was initially examined with the cubic-shaped crystal, recording the diffraction pattern with the Geiger counter. Fig. 1 shows the profile of this line first at 298°, then at 78° and finally after cooling the crystal through the transition to 78° K. with a magnetic field applied parallel to the rotation axis [100]. The line clearly splits into two unequal components, one of which has been removed by the field. A consideration of the region of reciprocal space around the cubic 800 point, at 78° K., indicates that part of the resultant composite reflection might lie out of the zero layer. The present techniques would not distinguish such a reflection from others in the zero layer, unless a special receiving slit were used. The introduction of a suitable slit was found to reduce the intensity too much.

Resort was then made to photographic recording methods. Fig. 2 shows 800, diffracted by the spherical crystal, at 298°, at 78° and then after cooling through the transition to 78° K. with the magnetic field aligned along each of the cubic axes in turn. In Figs. 2, 3 and 4, [110] is the rotation axis.

Reference to Fig. 2 shows that 800 splits into five components at 78° K., of which one is in the zero layer, the other four being symmetrically arrayed slightly out of this layer. It has been shown by Calhoun (1954) that on cooling a single crystal of magnetite through the transition in the presence of a magnetic field, the *c* axis of an orthorhombic cell will be established in the direction of the cube edge closest to the applied field. In Fig. 2(*c*), where the magnetic field was applied in the plane of the focal spot, the crystal and the recording film, this effect is clearly illustrated, and on

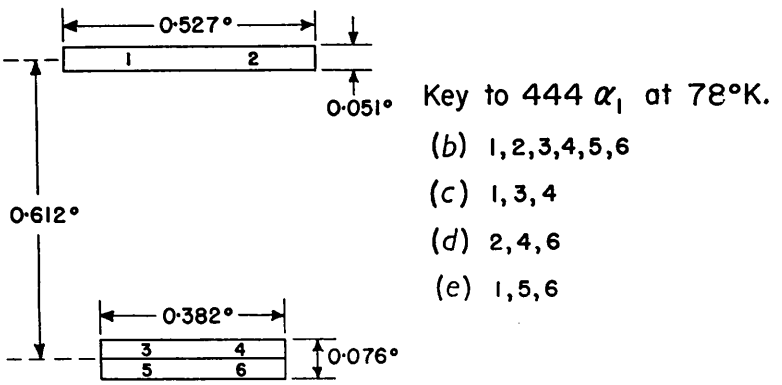

Fig. 4. 444 reflections: (*b*)–(*e*) as in Fig. 2.

the basis of the orthorhombic structure previously proposed (Abrahams & Calhoun, 1953) the single spot in the zero layer is the orthorhombic 008. The interpretation of Fig. 2(*d*) and (*e*), in which the orthorhombic 440 reflections appear, is more complicated, since the presence of three reflections in each photograph indicates that the *c* axis has not been uniquely established along a single cube edge in those two cases. The failure to establish a unique *c*-axis orientation could be due to the strain distribution near the surface of the sample, produced by the large dimensional changes which occur on cooling through the transition. Since the diffraction process here predominantly takes place close to the sample surface, the diffraction data will be sensitive to strain effects which are known (Calhoun, 1954) to interfere with the orientation of the *c* axis.

In Fig. 3, the behavior of 440 is shown, under similar conditions to those in Fig. 2. In this case, below the transition, the single cubic reciprocal point splits into two widely separated groups with an intensity relation of about 1:2. Fig. 3 indicates the presence of two reflections in the weaker line, both out of the zero layer, and of four reflections in the stronger line, each not quite as far out of this layer. These data may be reconciled with Rooksby & Willis's observation that 440 splits into two powder lines of about equal intensity if there was some line broadening present which could have affected their intensity estimate.

The behavior of 444 has similarly been studied, but is not reproduced here because of the reduced intensity of this reflection, and the consequent difficulty in printing. It is very similar to 440 and splits into two reflections of the same θ values, both out of the zero layer, and a group of four others close together, and not quite as far out of the zero layer. The intensity relation of the two groups is again about 1:2, in the order given. The angular dimensions of this reflection are given in Fig. 4.

In summary, an orthorhombic cell which is derived from the cubic cell by replacing a cube edge with the orthorhombic *c* axis, and the two normal face diagonals with the orthorhombic *a* and *b* axes (as suggested for the low-temperature form of magnetite by Abrahams & Calhoun, 1953) could, in general, assume up to six different domain orientations below the transition: since for each of the three possible *c*-axis orientations there is an alternative choice for the orientations of the *a* and *b* axes. However, a rhombohedral cell derived from a cubic cell by dilatation of the body diagonals could assume only a maximum of four different domain orientations. The data given in the present paper show that for the reflections 800, 440 and 444 there are 5, 6 and 6 domain orientations formed, respectively. It thus appears that an orthorhombic cell (or one of lower symmetry with angles close to 90°) can account for all the magnetic, electric, strain-gauge and X-ray measurements on magnetite below the transition.

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