Acta Cryst. (1975). A31, 753

On the Cubic–Rhombohedral Transformation in Magnetite

BY L. J. VIELAND

RCA Laboratories, Princeton, New Jersey 08540, *U.S.A.*

(*Received* 14 *October* 1974; *accepted* 5 *February* 1975)

It has been found by means of single-crystal X-ray diffractometry that the symmetry of the low-temperature phase of magnetite is rhombohedral, rather than orthorhombic as required by the commonly accepted theories of the transformation. The reason for the discrepancy between the observed structure and the uniaxial symmetry required to explain magnetic anisotropy measurements is found to lie in the discovery that cooling through the transition in the presence of a field causes the development of a superlattice of monoclinic symmetry and a twinned martensitic structure of pseudo-orthorhombic symmetry.

The phase transition occurring well below the Curie point (585 °C) in the ferrimagnetic spinel Fe_3O_4 has been a subject of interest ever since the discovery of a strong specific-heat anomaly near 120 °K over 40 years ago (Millar, 1929). In 1932 a change in magnetocrystalline symmetry from cubic to uniaxial was reported (Li, 1932), and in the 1940's Verwey and coworkers (Verwey, Haayman & Romeijin, 1947) put forth a model of electronic ordering at low temperatures which was designed to explain the large increase in resistivity accompanying the transformation, and was consistent with orthorhombic symmetry. This model, which postulates alternate (001) layering of octahedral Fe^{2+} and Fe^{3+} ions along [110] and [1$\bar{1}$0] rows, has come to be regarded as substantially correct (Bacon, 1962), although recent experiments point to a somewhat more complex situation (Samuelson, Bleecker, Drobrzynski & Riste, 1968; Yamada, Suzuki & Chikazumi, 1968; Rubenstein & Forester, 1971). In 1951, the transition was observed by means of X-ray powder diffraction photographs (Toombs & Rooksby, 1951), and the low-temperature phase was reported as being rhombohedral. In response to conflicting X-ray data (Abrahams & Calhoun, 1953), the measurements were repeated by Rooksby & Willis (1953), who reasserted the claim of Toombs & Rooksby. Nevertheless, the weight of the magnetic evidence (Li, 1932; Williams, Bozorth & Goertz, 1953; Bickford, 1953) some additional (though indirect) X-ray work (Abrahams & Calhoun, 1955), and above all the appealing simplicity of the Verwey model, all served to settle the issue clearly in favor of orthorhombic symmetry. The assumption of such symmetry forms the basis of all recent treatments of the electronic transition in Fe_3O_4.

Here we present some single-crystal X-ray diffractometry results which show unambiguously that the symmetry of the low-temperature phase is rhombohedral, confirming the results of Toombs & Rooksby and Rooksby & Willis in all particulars. In addition, data taken after cooling in a magnetic field are presented, which provide a link between the lattice and magnetic symmetries.

The data were obtained for the most part on synthetic (vapor-grown) single crystals provided by Dr H. Pinch of this laboratory. These crystals had well developed (111) faces with areas up to ~ 10 mm^2, and sharp resistive transitions at $T_c \simeq 120$ °K. Some additional measurements on natural crystal confirmed that the results were not sample dependent. Although T_c was 10° lower for natural crystal, the spontaneous strains at 77 °K were essentially the same for both materials. A diffractometer with provision for separately scanning θ at fixed 2θ (ω scan) was employed. All peak positions were obtained by separately maximizing for θ and 2θ with fine slits (0·2 to 0·4 mm entrance, 0·05 to 0·1 mm receiving), while intensity measurements were performed in the ω-scan mode with the receiving slit removed. Back-reflection peaks observed with Mo $K\alpha$ radiation (16,16,0; 13,13,13) gave line splittings accompanying the transformation about 25 times the resolvable dispersion.

The transformation was observed in one crystal while monitoring the resistivity, by keeping the detector fixed at the cubic ($hh0$) position. The maximum increase in resistivity ($\partial\varrho/\partial T$) occurred simultaneously with the maximum decrease in peak intensity, and the rounding of the transition, over about 1 °K above T_c, and a somewhat greater range below, likewise corresponded to changes seen in ϱ. The transformation is first order, with the spontaneous strain at T_c of the same magnitude as at 77 °K. No hysteresis in T_c was observable. However, the volume fraction of lower-symmetry phase is a function of thermal history, the transition being sharper when approached from below T_c.

The crystal transforms martensitically into a multi-domained structure, and some peak broadening occurs as a result of the small domain tilts. Nevertheless, it is apparent that no peak splitting arising from strains other than the rhombohedral distortion can be present with a magnitude within one order of the main strain. Table 1 shows the observed peaks on both sides of T_c, about 10 °K apart.

Taking $\pi/2-\varepsilon$ as the angle between the coordinate

Table 1. *Observed peak splittings for the rhombohedral transformation, and calculated values of the angular and axial distortions*

$X \wedge Y = Y \wedge Z = Z \wedge X = \pi/2 - \varepsilon$. Mo $K\alpha$ radiation.

Peak	2θ (°) $T > T_c$	$T < T_c$	$10^3\varepsilon$ (rad.)	$10^5\ (a-a_0)/a_0$
{16,16,0}	146·12	145·54 146·63	2·88 ± 0·05	9 ± 8
{13,13,13}	144·28	143·23 144·59	2·90 ± 0·04	7 ± 6

axes in the low-temperature phase, $\{hh0\}$ reflections are split with an equal displacement to lower and higher angles, with $\Delta d/d_0 = \pm\varepsilon/2$, while $\{hhh\}$ reflections give splittings of $(d_e - d_0)/d_0 = \varepsilon$, and $(d_s - d_0)/d_0 = -\varepsilon/3$, where the subscripts e and s refer to elongated and shortened axes. Intensity measurements show the appropriate multiplicity of domains, with the unique (long [hhh]) axis contributing $\frac{1}{4}$ of the $\{hhh\}$ intensity, and the $\{hh0\}$ peak split in two equal parts. In addition, a small volume change is observed, manifest as a shift in the centroid of the peak positions away from the cubic peaks. The rhombohedral strain and axial strain calculated separately for the two peaks are given in Table 1. The rhombohedral angle defined as $\alpha = \pi/3 - 2\varepsilon/\sqrt{3}$ is 59°48·5′ ± 0·2′ for this crystal at about 110°K. Rooksby & Willis reported $\alpha = 59°47{\cdot}5'$ at 80°K.

Additional experiments were undertaken in which the crystal was cooled through the transition in an 8 kG field oriented at various positions in the [1$\bar{1}$0] zone. Since it was necessary to demount the X-ray Dewar from the diffractometer in order to apply the field, the assumption is made that the field effects are frozen in by the transformation, as appears to be the case.

The effect of cooling in a field **H**‖[001] is threefold: a small orthorhombic distortion is superimposed on the rhombohedral cell, lowering the symmetry to monoclinic; the distribution of crystallographic domains is greatly simplified; and superlattice lines appear. Taking the rhombohedral axis to be [111], the symmetry change is describable as a contraction along [001] and [1$\bar{1}$0], and an expansion along [110], with values of ε'/ε of −0·054, −0·066, and +0·12, respectively, where ε is the rhombohedral strain. The c-axis [001] contraction was calculated by assuming negligible volume striction. Large uncertainties in the absolute values of these small strains are introduced by demounting the camera between measurements, but the distortion symmetry is inferred from peak splittings, and is sensitive to about $\pm\varepsilon/50$.* The difference in length between [001] and [100] or [010] axes inferred from the assumption of zero volume striction is $2{\cdot}4 \times 10^{-4}$, in agreement with strain-gauge measurements (Bickford, 1953). The cell defined by a‖[110], b‖[1$\bar{1}$0], c‖[001] is just the orthorhombic lattice associated with the Verwey model, and differs from the observed monoclinic symmetry only in the tilt of the c axis ($c \wedge a \neq 90°$) by an amount given by the rhombohedral distortion, and unaffected by the field. The small orthorhombic distortion is not simply attributable to magnetostriction, but in agreement with conclusions drawn from magnetic studies, indicates that the [monoclinic] c axis lies near the cube axis closest to the applied field.

The more striking aspects of this effect of field are shown in Fig. 1, which shows rocking curves for $\{16,16,l\}$ reflections. The crystal was first demagnetized by heating above the Curie point. The room-temperature trace shows the natural linewidth, and a slight graininess is observable. Upon cooling in the absence of a field, the rhombohedral distortion splits the $\{hh0\}$ reflections in two. A large number of domain tilts (zero-layer component) are observable, and characteristically, the intensity patterns show the same distribution of tilts for both peaks. The maximum tilt between domains is about 0·3°, or 2ε. After field cooling, the two peaks represent reflections from planes perpendicular to the a and b reciprocal-lattice vectors of the monoclinic unit cell where the b axis is the shorter of the two, and is the unique axis for this cell. The $(h00)_M$ peak is split into an orientation doublet with components of approximately equal intensity separated by an angle of 0·47°, which is $2\sqrt{2}\varepsilon$, while the $(0k0)_M$ appears as a sharp singlet. This result implies stacks of domains twin related by rotations of 180° about the original z axis. Finally, it is seen that at a slightly higher angle than the $(0k0)_M$ reflection, and separated from it by rotations of ±1·27°, new peaks appear which are identifiable as $16,\bar{1}\bar{6},\pm\frac{1}{2}$ in cubic indices. These satellites have intensities about $\frac{1}{4}$ of the $16,\bar{1}\bar{6},0$. A search for this superlattice reflection in the demagnetized crystal revealed trace peaks, down in intensity by a factor of more than 25. By contrast, cooling in a field **H**‖[111] gives a threefold reduction in intensity, consistent with a random distribution of c axes along x, y, and z (*cf.* Samuelson *et al.*, 1968). There is no corresponding superlattice peak associated with the $[h00]_M$ axis.

The macroscopic distribution of domains as a function of the angle between the cooling field and the cubic [001] direction is shown in Fig. 2. The intensities are normalized to the total intensity observed for the particular $\{hkl\}$ form. As the field orientation departs from [001], the a peak (long [110]) diminishes in intensity and breaks up into a more complex pattern, but always with peaks occurring in pairs separated by $2\sqrt{2}\varepsilon$. The centroid of the ω scan is also displaced from zero. Thereafter, and until **H**‖[111], only the short [110] is observed, and always as a singlet. For **H** just

* For example, with **H**‖ [110], reflections equivalent to 011, 01$\bar{1}$, 101, and 10$\bar{1}$ are observed with equal intensities, because of the domain distribution. Only a doublet (in 2θ) is observed, and the splitting is the same as for the $H = 0$ case. Therefore the distortion matrix has components $\varepsilon'_{13} = \varepsilon'_{23} = 0$, and the principal strains are $\varepsilon'_x + \varepsilon'_{12}/2$, [110]; $\varepsilon'_x - \varepsilon'_{12}/2$, [1$\bar{1}$0]; and ε'_z, [001].

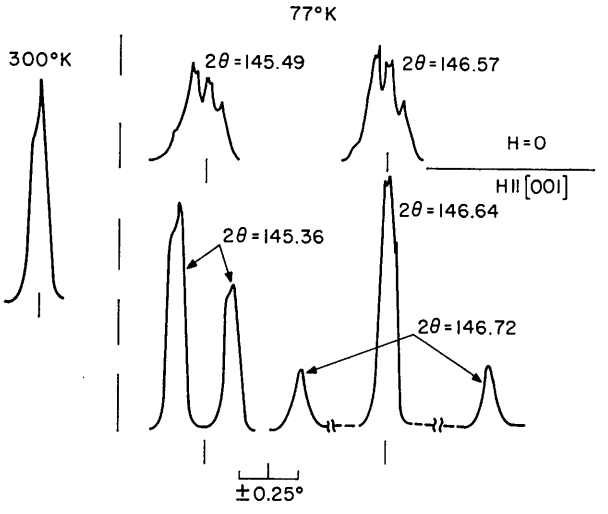

Fig. 1. Rocking curves for 16,16,0 and 16,16,$\pm\frac{1}{2}$ reflections, Mo $K\alpha_1$ radiation. Vertical bars mark the peak position in the cubic state. Rotation axis [1$\bar{1}$0]. The 16,16,$\pm\frac{1}{2}$ peaks appear at a slightly higher d value than the corresponding 16,16,0, and $\pm 1{\cdot}27°$ away in θ.

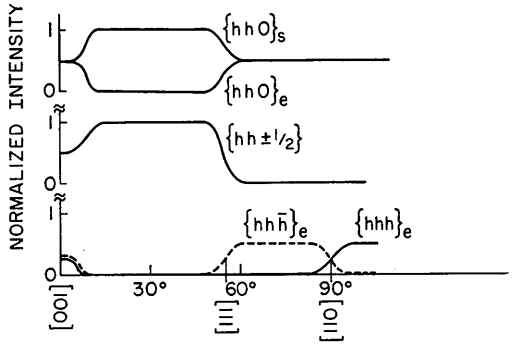

Fig. 2. Peak intensities normalized to maximum total intensity for each {hkl} as a function of the angle between [001] and **H**. Subscripts signify axes elongated or shortened by the rhombohedral transformation. The monoclinic distortion is ignored. [1$\bar{1}$0] crystal rotation axis.

past [111], the superlattice peak disappears, and the tilt distributions of {hh0} peaks are similar. No domains with [111] unique are observed for $0<\mathbf{H}<90°$, while for [111]$<\mathbf{H}<$[110], one half of the domains have [11$\bar{1}$] unique.

These results are consistent with the ideas developed by Williams, Bozorth & Goertz (1953) in a study of magnetic anisotropy, even though their observations appeared to verify the orthorhombic symmetry of the low-temperature phase. The significant new features are that the crystal anisotropy is dominated by the [111] direction nearest the applied field always becoming a shortened (non-unique) axis, while the twins occur in pairs given by 180° rotations about the c axis. Specification of the orthorhombic c and a (or b) axes as given by Williams *et al.* defines the orientation of just such *pairs* of monoclinic twins, so that additional twofold axes appear in the magnetic-anisotropy experiment, *i.e.* at least for fields applied in high-symmetry planes such as {100} and {110}, the macroscopic pseudo-symmetry is orthorhombic.

Whatever the reason for the microscopic symmetry change due to the external field, it is clear that, if the phase transformation is the result of charge ordering, such ordering must be consistent with rhombohedral symmetry. This is clearly not so for Verwey ordering, nor is it strictly possible for any scheme subject to the constraint (Anderson, 1956) of two Fe^{2+} and two Fe^{3+} on each tetrahedron made up of groups of four nearest-neighbor sites. Perfect triangular ordering on (111) sheets comprising the densely packed 'Kagome' planes (Anderson, 1956) [and the intermediate (111) planes with $\frac{1}{3}$ the density of octahedral sites], *is* possible but the threefold axis cannot be common in adjacent 'Kagome' layers. Rhombohedral symmetry might therefore bespeak the absence of phase ordering along the unique [111] axis. Thermodynamically, the effect of such disorder is negligible, the contribution to the zero point entropy being proportional to only $N^{1/3}$.

The author is indebted to H. Pinch for providing the crystals, R. Smith and J. White for varied assistance with the X-ray data, and to I. Balberg, who brought the problem to his attention.

References

ABRAHAMS, S. C. & CALHOUN, B. A. (1953). *Acta Cryst.* **6**, 105–106.

ABRAHAMS, S. C. & CALHOUN, B. A. (1955). *Acta Cryst.* **8**, 257–260.

ANDERSON, P. W. (1956). *Phys. Rev.* **102**, 1008–1013.

BACON, G. E. (1962). *Neutron Diffraction.* Oxford: Clarendon Press.

BICKFORD, L. R. (1953). *Rev. Mod. Phys.* **25**, 75–79.

LI, C. H. (1932). *Phys. Rev.* **40**, 1002–1012.

MILLAR, R. W. (1929). *J. Amer. Chem. Soc.* **51**, 215–222.

ROOKSBY, H. P. & WILLIS, B. T. M. (1953). *Acta Cryst.* **6**, 565–566.

RUBENSTEIN, M. & FORESTER, D. W. (1971). *Sol. State. Commun.* **9**, 1675–1679.

SAMUELSON, E. J., BLEECKER, E. J., DROBRZYNSKI, L. & RISTE, T. (1968). *J. Appl. Phys.* **39**, 1114–1115.

TOOMBS, N. C. & ROOKSBY, H. P. (1951). *Acta Cryst.* **4**, 474–475.

VERWEY, E. J., HAAYMAN, P. W. & ROMEIJAN, F. C. (1947). *J. Chem. Phys.* **15**, 181–187.

WILLIAMS, H. J., BOZORTH, R. B. & GOERTZ, M. (1953). *Phys. Rev.* **91**, 1107–1115.

YAMADA, T., SUZUKI, K. & CHIKAZUMI, S. (1968). *Appl. Phys. Let.* **13**, 172–174.