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Neutron Diffraction Investigation of the 119°K Transition in Magnetite*

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Neutron diffraction measurements on synthetic single crystals of magnetite confirm the orthorhombic ordering scheme proposed by Verwey and co-workers to explain the changes in physical properties which magnetite undergoes when cooled below 119°K. A magnetic field suitably applied during cooling prevents the multiple twinning which occurs in the absence of a field and allows one to make the following deductions: The spins of all magnetic ions align themselves parallel to the cubic [001] direction nearest the direction of the external field. The face diagonals of the cube orthogonal to this **c** axis become the orthorhombic **a** and **b** axes. If these are labeled such that **a** is magnetically harder than **b**, the ferric ions in octahedral sites lie in rows parallel to **a** and the ferrous ions in rows parallel to **b**. Although the average oxygen position is unchanged, there are presumably shifts in the four oxygen parameters which compensate for the effect of the ordering on the ionic sizes at the various sites. In attempting to reproduce the results on natural crystals, which had a transition temperature some five to ten degrees lower, it was found impossible to remove the [**a**,**b**] twinning by use of a magnetic field; furthermore, failure to observe an (002) reflection would seem to indicate that the twinning persists on a micro basis, that is, that there is only short-range order. A least-squares fit was made to the intensities of the cubic phase at 296°K; a value of $u=0.2548\pm0.0002$ was obtained for the oxygen parameter in the spinel structure. The severe primary and secondary extinction encountered was satisfactorily accounted for by methods previously described by the author.

INTRODUCTION

MAGNETITE, Fe_3O_4, exhibits between 110° and 120°K (the exact temperature depending on the purity of the sample) remarkable changes in its physical properties. This transition is accompanied by a heat capacity anomaly,[1–3] a decrease in ease of magnetization,[4,5] and a large decrease in the electrical conductivity.[6–8] Verwey and co-workers have postulated[8,9] that the high conductivity of magnetite above the transition temperature is due to rapid electron transfer between ferric and ferrous ions in the octahedrally coordinated sites, i.e., that there is a dynamic disorder of ferric and ferrous ions. The transition to the low-temperature phase is then associated with a cessation of electron transfer and an accompanying ordering of the ions. The particular ordering scheme proposed by Verwey *et al.* has orthorhombic symmetry, with ferric and ferrous ions lying in mutually perpendicular rows as indicated in Fig. 1, which shows only the ions in octahedral sites. Verwey suggested that the cube edge perpendicular to these rows becomes the direction of easy magnetization. The transition was first confirmed as a change in crystal structure by the x-ray work of Tombs and Rooksby[10] who observed splitting of some of the powder lines. Subsequent powder x-ray work led to some controversy as to whether the symmetry below the transition was rhombohedral[10,11] or orthorhombic,[12] but later work on synthetic single crystals seems to indicate unambiguously that the symmetry is orthorhombic or lower[13]; the powder pattern of Abrahams and Calhoun[12] was indexed on the basis of an orthorhombic unit cell with dimensions

$$a_0=5.912\text{ A},$$
$$b_0=5.945\text{ A},$$
$$c_0=8.388\text{ A}.$$

Orthorhombic symmetry is also strongly indicated by the strain gauge measurements of Bickford,[14] who found that the dimensional changes below the transition relative to a_0 at 130°K were

$$\Delta a=-0.0696\%,$$
$$\Delta b=+0.0594\%,$$
$$\Delta c=-0.0302\%,$$

in general qualitative agreement with the x-ray cell dimensions.[15]

The work of Li[5] had shown that the direction of easy magnetization below the transition temperature could be influenced by a magnetic field applied as the crystal was cooled through the transition temperature. More recent studies[16–19] have established that the cubic [001] axis lying nearest the direction of the applied field

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[1] G. S. Parks and K. K. Kelley, J. Phys. Chem. **30**, 47 (1926).

[2] R. W. Millar, J. Am. Chem. Soc. **51**, 215 (1929).

[3] B. S. Ellefson and N. W. Taylor, J. Chem. Phys. **2**, 58 (1934).

[4] P. Weiss and R. Forrer, Ann. phys. **12**, 279 (1929).

[5] C. H. Li, Phys. Rev. **40**, 1002 (1932).

[6] T. Okamura, Science Repts. Tôhoku Imp. Univ. **21**, 231 (1932).

[7] E. J. W. Verwey, Nature **144**, 327 (1939).

[8] E. J. W. Verwey and P. W. Haayman, Physica **8**, 979 (1941).

[9] Verwey, Haayman, and Romeijn, J. Chem. Phys. **15**, 181 (1947).

[10] N. C. Tombs and H. P. Rooksby, Acta Cryst. **4**, 474 (1951).

[11] H. P. Rooksby and B. T. M. Willis, Acta Cryst. **6**, 565 (1953).

[12] S. C. Abrahams and B. A. Calhoun, Acta Cryst. **6**, 105 (1953).

[13] S. C. Abrahams and B. A. Calhoun, Acta Cryst. **8**, 257 (1955).

[14] L. R. Bickford, Jr., Revs. Modern Phys. **25**, 75 (1953).

[15] Bickford's results would give $a_0=5.926$ A, $b_0=5.934$ A, $c_0=8.384$ A for a cell of the same volume as the x-ray cell.

[16] L. R. Bickford, Jr., Phys. Rev. **78**, 449 (1950).

[17] Williams, Bozorth, and Goertz, Phys. Rev. **91**, 1107 (1953).

[18] C. A. Domenicali, Phys. Rev. **78**, 458 (1950).

[19] B. A. Calhoun, Phys. Rev. **94**, 1577 (1954).

becomes the orthorhombic **c** axis, and that the orthorhombic **a** and **b** axes have less and different tendencies to lie in the field direction.

THE STRUCTURE

Magnetite is the simplest of the compounds $M^{+2}M_2{}^{+3}O_4{}^{=}$ crystallizing in the spinel structure.[20] The space group, $Fd3m-O_h{}^7$, has atoms in the following positions,[21] the origin being taken at the center of symmetry[22]:

32 oxygen atoms in (e):

$$\pm(u,u,u;\ u,\tfrac{1}{4}-u,\tfrac{1}{4}-u;\ \tfrac{1}{4}-u,u,\tfrac{1}{4}-u;\ \tfrac{1}{4}-u,\tfrac{1}{4}-u,u)$$
$$+\text{face-centering translations (FC)},$$

16 metal atoms in (d):

$$\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2};\ \tfrac{1}{2},\tfrac{1}{4},\tfrac{1}{4};\ \tfrac{1}{4},\tfrac{1}{2},\tfrac{1}{4};\ \tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{2};\ +\text{FC},$$

8 metal atoms in (a): $\tfrac{1}{8},\tfrac{1}{8},\tfrac{1}{8};\ \tfrac{7}{8},\tfrac{7}{8},\tfrac{7}{8};\ +\text{FC}$.

Bragg[20] found u for magnetite to be approximately $\tfrac{1}{4}$, a value which was revised a few years later by the careful work of Claasen[23] to $u=0.254\pm0.001$. The value of the u parameter and packing considerations led Verwey and de Boer[24] to the conclusion that magnetite has the *inverse* spinel structure, i.e., half of the sixteen ferric ions are in (a), and the remainder together with the eight ferrous ions are distributed randomly in (d).[25] This structure has approximately the correct metal-oxygen distances for both sites and also explains the abnormally high conductivity. Such a structure was shown by Néel[26] to account satisfactorily for the saturation magnetic moment, which corresponds to that to be expected for the ferrous ions alone, 4 Bohr magnetons per Fe_3O_4 molecule. The octahedral sites are assumed to be coupled antiferromagnetically to the tetrahedral sites, thus leading to a resultant moment of zero for the ferric ions. This antiferromagnetic ordering has been confirmed by the neutron diffraction work of Shull, Wollan, and Koehler.[27]

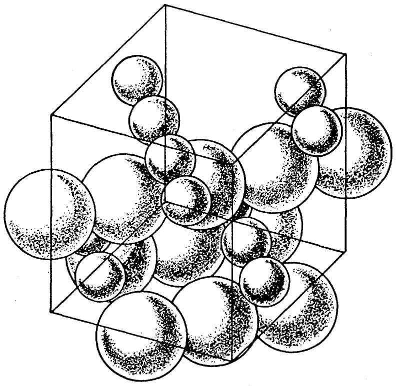

FIG. 1. Octahedrally coordinated ions in unit cube of Fe_3O_4. In the ordered structure, the large balls represent Fe^{+2}, the small one Fe^{+3}.

The most symmetric space group which fits the ordering scheme proposed by Verwey is the body-centered orthorhombic space group $Imma-D_{2h}$,[28] which is obtained from $Fd3m$ by the following transformation:

$$\mathbf{a}_{\text{ortho}}=\mathbf{S}\mathbf{a}_{\text{cubic}} \tag{1}$$

where $\mathbf{a}_{\text{ortho}}$ and $\mathbf{a}_{\text{cubic}}$ are the vector triples defining the orthorhombic and cubic unit cells, and S is given by

$$\mathbf{S}=\begin{bmatrix}\tfrac{1}{2} & -\tfrac{1}{2} & 0\\ \tfrac{1}{2} & \tfrac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}. \tag{2}$$

Thus, the cubic and orthorhombic **c** axes are identical, and the orthorhombic **a** and **b** axes are half the face diagonals of the cube. The atomic positions in the orthorhombic space group are given by

$$\mathbf{x}_{\text{ortho}}=(\mathbf{S}')^{-1}\mathbf{x}_{\text{cubic}}\equiv\begin{bmatrix}1 & -1 & 0\\ 1 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}\mathbf{x}_{\text{cubic}}. \tag{3}$$

Applying (3), we find that the following coordinates describe the structure in the orthorhombic space group:

8 oxygen atoms in (h): $\pm(0,y,z;\ 0,\tfrac{1}{2}+y,\bar{z})$
$+$body-centering translation (BC),
with $y\approx 2u$, $z\approx u$.

8 oxygen atoms in (i): $\pm(x,\tfrac{1}{4},z;\ \bar{x},\tfrac{1}{4},z)+\text{BC}$,
with $x\approx 2u-\tfrac{1}{4}$, $z\approx\tfrac{1}{4}-u$.

4 Fe^{+3} ions (tetrahedral) in (e): $\pm(0,\tfrac{1}{4},z)+\text{BC}$,
with $z\approx\tfrac{1}{8}$.

$$\left.\begin{matrix}4\ Fe^{+3}\\ \\ 4\ Fe^{+2}\end{matrix}\right\}\text{(octahedral) in}\left\{\begin{matrix}(b):\ (0,0,\tfrac{1}{2};\ 0,\tfrac{1}{2},\tfrac{1}{2})+\text{BC}\\ \\ (d):\ (\tfrac{1}{4},\tfrac{1}{4},\tfrac{3}{4};\ \tfrac{3}{4},\tfrac{1}{4},\tfrac{3}{4})+\text{BC}.\end{matrix}\right.$$

The assignment of the ferric and ferrous ions to (b) and (d) as well as the exact parameter values are to be determined (if this model is indeed correct).

Now if the crystal is cooled through the transition with no magnetic field applied, any of the three [001] directions can become the orthorhombic **c** axis. Furthermore, for each of the three choices of **c** axis, there are two possible choices for **a** and **b**.[28] The most likely state

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[20] W. H. Bragg, Phil. Mag. **30**, 305 (1915).

[21] The labeling of positions and symmetry elements follows the conventions of the *International Tables for X-Ray Crystallography*, (Kynoch Press, Birmingham, 1952).

[22] The alternative origin on $\bar{4}3m$ at $-\tfrac{1}{8}$, $-\tfrac{1}{8}$, $-\tfrac{1}{8}$ from the center is often used. In such a case u is approximately $\tfrac{3}{8}$ rather than $\tfrac{1}{4}$.

[23] A. A. Claasen, Proc. Phys. Soc. (London) **38**, 482 (1925–26).

[24] E. J. W. Verwey and J. H. de Boer, Rec. trav. chim. **55**, 531 (1936).

[25] Sites (a) and (d) are known respectively as the *tetrahedral* and *octahedral* sites because of the oxygen coordination about the metal ion. In the ferrite literature, these sites are often referred to as A and B.

[26] L. Néel, Ann. Physik **3**, 137 (1948).

[27] Shull, Wollan, and Koehler, Phys. Rev. **84**, 912 (1951).

[28] There are of course 48 different transformations possible from the cubic to the orthorhombic axes. These correspond to the six possible ways of ordering the rows in **S** and the eight possible sign combinations for each row arrangement. We cannot distinguish between the different choices of sign and thus need only consider the six basically different transformations.

for the crystal to be in, below the transition, is then a multiply twinned state—a mosaic of many single crystals, each with one of the six distinguishable axial relationships. The crystal in such a state will exhibit isotropic behavior, albeit with different properties than the cubic crystal existing above the transition. Most of the changes to be expected in the neutron diffraction intensities are almost averaged out by this twinning.

The ambiguity regarding the **c** axis may be removed by application of a field along one of the [001] cube directions as the crystal is cooled through the transition. Although this [001] direction will become the orthorhombic **c** axis, there still remains the possibility of [**a**,**b**] twinning. Bickford has shown[14] that this twinning may be removed by application of pressure along one of the cubic [110] directions while the crystal is being cooled in a magnetic field along **c**. This face diagonal of the cube will become the short axis of the orthorhombic cell, and one might suppose that the rows of the smaller ferric ions would lie parallel to this axis.[29] Calhoun, in a thorough study of the magnetic and electrical behavior of synthetic single crystals below the transition, concluded[19] that a complete removal of twinning could also be achieved by use of a magnetic field applied in an appropriate direction, since the **a** and **b** axes differ in magnetic hardness. Removal of the twinning appeared to be less straightforward for natural crystals[17]—due perhaps to the influence on local fields of impurities and defects.

EXPERIMENTAL

Unless otherwise noted, all of the measurements were made on fragments of synthetic single crystals grown from the melt by Smiltens,[30] who reported a stoichiometric ratio of Fe^{+3}/Fe^{+2} and a density 99.58% of the x-ray calculated density. The crystals were cut from the same block as those on which Calhoun's magnetic measurements were made[19]; he found the transition to occur sharply at 119.4°K, although the extent of the order, as measured by the conductivity anisotropy, increased as the temperature was lowered to that of boiling nitrogen. Bickford's nuclear magnetic-resonance results[16] indicate that the range of the transition for these crystals is about 3°K. The crystal used for most of the quantitative work reported here was a rectangular pillar 0.96 mm×2.50 mm in cross section and 11.04 mm high. The long axis was parallel to a cubic [110] direction. Other less extensive measurements were made on a crystal similar in shape but with the long axis a [100] direction; the data obtained relevant to the transition agreed in every way with those for the first crystal.

The low temperatures were reached by blowing a stream of vapor from boiling nitrogen over the crystal, which was surrounded by a small quartz Dewar. Care was taken to insure that no condensed water or ice was present in the path of the incident and diffracted beams. Temperatures down to 100°K, as measured by a copper-constantan thermocouple attached to the crystal, were easily obtained.

The neutron diffraction apparatus was similar to that described by Corliss, Hastings, and Brockman,[31] but with certain modifications dictated by its design for use primarily as a single-crystal spectrometer. The magnetic field was applied parallel to the plane of the spectrometer with an electromagnet capable of producing fields of 10 000 gauss with a $\frac{3}{4}$-in. gap between the pole faces. The fields were measured with a search coil and a ballistic galvanometer, calibrated at low fields against a G.E. Gaussmeter.

A monochromatic beam of neutrons with a mean wave length of 1.067 A was used. The effective flux at the crystal was approximately 10^5 neutrons cm^{-2} sec^{-1}, the absolute value being obtained by measuring the diffracted intensity from a small potassium-bromide crystal of known weight. A fission counter on an adjacent experimental hole was used to detect changes in incident intensity due to variations in the power level of the reactor.

EXTINCTION

The synthetic single crystals used in this investigation suffered severely from extinction effects, the most intense reflections having only 0.20–0.25 of the calculated intensities for the correct structure. The author has shown in a recent paper[32] that, for the less severely extinguished reflections from a cylindrical crystal, a secondary extinction correction of exponential form is a good approximation, i.e.,

$$I_{\mathrm{obs}}=I_{\mathrm{calc}}\exp(-c_sI_{\mathrm{calc}}), \tag{4}$$

with

$$c_s=\frac{8\lambda^3A^{\frac{1}{2}}}{(3\pi)^{\frac{3}{2}}V_c^2\eta}, \tag{5}$$

and

$$I_{\mathrm{calc}}=F^2/\sin2\theta. \tag{6}$$

I_{obs} and I_{calc} are the observed and calculated intensities, λ is the neutron wave length, A is the cross-sectional area of the cylinder, V_c is the unit cell volume, η is the mosaic-spread standard deviation, θ is the Bragg angle, and F^2 is the square of the structure factor. Equation (4) is accurate to about 5% for cylindrical crystals provided that $\exp(-c_sI_{\mathrm{calc}})$ is greater than 0.70. It will also be valid, with somewhat less accuracy, for crystals of rectangular cross section, if the length-to-width ratio is not too great. A least-squares determination of c_s, and hence η, has been carried out for several experimental situations, with the results shown in Table I. The estimated standard deviation in η is about 0.3η. One of the interesting features is that the synthetic

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[29] See, for example, M. E. Fine and N. T. Kenney, Phys. Rev. **94**, 1573 (1954).

[30] J. Smiltens, J. Chem. Phys. **20**, 990 (1952).

[31] Corliss, Hastings, and Brockman, Phys. Rev. **90**, 1013 (1953).

[32] W. C. Hamilton, Acta Cryst. **10**, 629 (1957).

crystal is much more nearly perfect than the natural crystal. Furthermore, below the transition, the effective mosaic spread is large for crystals which have been cooled with no field, i.e., where there is a random arrangement of orthorhombic axes among the possible positions. If a unique axial system has been established, however, there is no significant change in the mosaic spread and, hence, the extinction.

The estimates of mosaic spread in Table I were obtained under the assumption that only *secondary* extinction is important. An indication that *primary* extinction may also play a role is the fact that the intensities of the partially magnetic reflections were consistently too low, even after the secondary extinction correction calculated to give the best fit to the pure nuclear reflections had been made. In a forthcoming paper,[33] curves are presented which permit one to calculate the amount of primary extinction and hence t_0, the average linear dimension of the mosaic blocks, by comparison of the actual observed intensity with that to be expected for a pure nuclear reflection of the same calculated intensity and at the same scattering angle. This technique was applied to several reflections from the synthetic magnetite crystal, the resulting estimate for t_0 being 0.0014 cm. Although this estimate certainly lacks precision ($\sigma=0.0007$ cm), it is believed that the order of magnitude is correct, the agreement between observed and calculated intensities being better in several respects than for the case of no primary extinction.

The amount of primary extinction estimated to be present is not enough to affect the estimate of η for the synthetic crystal in its near-perfect state. It is, however, comparable to the total amount of extinction present after the crystal has been cooled through the transition with no magnetic field. This would seem to suggest that all the secondary extinction has been removed by the cooling process with its resultant twinning, but that the primary extinction remains. One may write, for small amounts of primary extinction,

$$I_{\mathrm{obs}}=I_{\mathrm{calc}}(1-c_p I_{\mathrm{calc}}\sin 2\theta), \tag{7}$$

with

$$c_p=\lambda^2 t_0^2/(3V_c^2). \tag{8}$$

Comparing these expressions with (4)–(5) for secondary extinction, we find that the two are equivalent if

$$\eta t_0^2=1.7\times 10^5 A^{\frac{1}{2}}\lambda/\sin 2\theta, \tag{9}$$

η being expressed in seconds of arc, the other quantities in cm. For our crystal of magnetite, this reduces to

$$\eta t_0^2=2.84\times 10^{-4}/\sin 2\theta. \tag{10}$$

Assuming t_0 to be 0.0014 cm, and taking a value of unity for $\sin 2\theta$, we find that the corresponding η is 142″, a value which is almost identical to the estimate in Table I.

The agreement between the observed and calculated intensities (see Table II) is gratifying in view of the fact that but two extinction parameters (η and t_0), based on simple models, have been used for the entire range of intensities, and particularly that the calculated secondary extinction corrections are for a cylinder instead of for the 2×1 rectangular pillar actually used. Most of the deviations observed can be explained in the light of the latter factor.

TABLE I. Estimates of mosaic-spread parameter from the extinction observed in several experimental situations. *H* indicates that the crystal was cooled with an axis-establishing magnetic field.

Crystal	Temperature (°K)	Mosaic spread (seconds)
Synthetic	296	15
Synthetic	105 (*H*)	17
Synthetic	105	147
Natural	296	327
Natural	105	613

REFINEMENT OF THE CUBIC STRUCTURE

The intensities of 60 (*hhl*) reflections with $\sin\theta/\lambda<0.88$ were measured at room temperature. A sequence of least-squares adjustments of the oxygen parameter u, a single isotropic temperature factor $2B$,[34] a scale factor K, and an exponential extinction parameter c_s was carried out on the weakest 36 of the reflections (marked with asterisks in Table II). The results of the final iteration were as follows:

$$\begin{aligned} u&=0.2548, & \sigma&=0.0002,\\ 2B&=0.98, & \sigma&=0.19,\\ K&=1.0, & \sigma&=0.1,\\ c_s&=0.002, & \sigma&=0.0007, \end{aligned}$$

the only large correlation coefficient being, as expected, that between the scale and temperature factor parameters. Intensities calculated for this structure are presented in Table II, the extinction corrections being made as previously described. Nuclear scattering amplitudes of 0.96×10^{-12} and 0.58×10^{-12} were used for iron and oxygen,[35] and magnetic scattering amplitudes of $1.08f\times 10^{-12}$ and $1.35f\times 10^{-12}$ corresponding to $S=2$ and $S=\frac{5}{2}$ were used for Fe^{+2} and Fe^{+3}. The form factor f was assumed to be the same as for the Fe^{+3} ions in magnesium ferrite.[31] The value 0.89 for $(\sigma/\sigma_0)^2$ was taken from the data of Weiss and Forrer.[4]

The interatomic distances calculated for this value

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[33] W. C. Hamilton, Acta Cryst. (to be published).

[34] One refinement was carried out with separate temperature factors for oxygen and iron, but the difference proved to be not statistically significant for the reflections used in the refinement. Compare the standard deviation quoted below for the temperature factor.

[35] C. G. Shull and E. O. Wollan, Phys. Rev. **81**, 527 (1951).

TABLE II. Observed and calculated intensities for cubic magnetite at 296°K. I_{obs} has been corrected for second-order contamination

$$I_{\mathrm{calc}}=\frac{10^{24}}{\sin 2\theta}(F_{\mathrm{nuclear}}{}^2+\tfrac{2}{3}\times 0.89F_{\mathrm{magnetic}}{}^2)\exp[-0.98(\sin\theta/\lambda)^2].$$

E, the extinction correction, is equal to E_pE_s, where E_p is $\tanh(k_1|F|)/k_1|F|$ with $k_1=0.025\times 10^{12}$, an additional correction being made for magnetic reflections as discussed in the text. E_s is calculated for a cylinder with a cross-sectional area of 0.024 cm² and a rectangular mosaic distribution function of standard deviation $15.4''=7.47\times 10^{-5}$ radian. The reflections marked with asterisks were used in the least-squares refinements discussed in the text.

h	h	l	$F_{\mathrm{nuc}}{}^2$	$F_{\mathrm{mag}}{}^2$	I_{calc}	$I_{\mathrm{calc}}E$	I_{obs}
0	0	4	682	339	1726	297	347
0	0	8	1688	1	1535	321	384
0	0	12	629	0	386	219	186
1	1	1	9	227	646	259	220
1	1	3	165	2	386	209	180
1	1	5	226	0	328	192	154
1	1	7*	1	17	11	11	11
1	1	9*	27	1	22	21	22
1	1	11*	114	0	74	64	59
1	1	13	292	0	175	129	127
2	2	0	60	62	264	167	133
2	2	2	10	163	236	155	116
2	2	4	58	29	116	94	79
2	2	6*	8	38	33	31	27
2	2	8*	60	1	52	45	45
2	2	10*	5	0	4	4	4
2	2	12*	58	0	35	33	36
2	2	14*	3	0	2	2	3
3	3	1*	1	97	101	83	60
3	3	3	113	0	165	123	113
3	3	5	165	0	187	134	118
3	3	7*	2	6	4	4	5
3	3	9*	10	0	7	7	5
3	3	11*	74	0	46	42	42
3	3	13	227	0	138	109	111
4	4	0	1709	13	2281	378	509
4	4	2*	0	0	0	0	0
4	4	4	669	71	758	277	263
4	4	6*	0	0	0	0	0
4	4	8	1668	0	1221	326	347
4	4	10*	0	0	0	0	0
4	4	12	618	0	370	213	196
5	5	1*	27	17	38	35	34
5	5	3	224	0	213	148	126
5	5	5	294	0	245	161	146
5	5	7*	9	0	6	6	7
5	5	9*	53	0	34	33	32
5	5	11*	162	0	97	81	76
6	6	0*	68	1	59	52	50
6	6	2*	7	2	7	7	9
6	6	4*	51	0	39	37	38
6	6	6*	5	0	4	4	5
6	6	8*	68	0	42	39	41
6	6	10*	3	0	2	2	2
6	6	12*	51	0	37	35	36
7	7	1*	1	0	1	1	3
7	7	3*	73	0	51	46	47
7	7	5*	116	0	76	65	61
7	7	7*	11	0	7	7	10
7	7	9*	1	0	1	1	1
8	8	0	1648	0	1054	326	347
8	8	2*	1	0	1	1	0
8	8	4	631	0	387	216	205
8	8	6*	1	0	1	1	1
8	8	8	1609	0	993	333	397
9	9	1*	52	0	31	29	30
9	9	3	288	0	172	128	121
9	9	5	366	0	223	152	130
9	9	7*	25	0	17	17	12
10	10	0*	86	0	55	49	53

of the parameter u and[12] $a_0=8.3940$ A are

6 Fe(octahedral)−O	2.0590±0.0016 A
4 Fe(tetrahedral)−O	1.8871±0.0029 A
3 O−O	2.8538±0.0046 A
6 O−O	2.9689±0.0003 A
3 O−O	3.0817±0.0046 A.

Using Pauling's octahedral radii of $r(\mathrm{Fe}^{+3})=0.60$, $r(\mathrm{Fe}^{+2})=0.75$, $r(\mathrm{O}^{=})=1.40$, and assuming $r(\text{tetrahedral})/r(\text{octahedral})=0.946$,[36] on obtains

$$\left.\begin{array}{ll}\mathrm{Fe}^{+3}(\text{octahedral})-\mathrm{O} & 2.00\ \mathrm{A}\\ \mathrm{Fe}^{+2}(\text{octahedral})-\mathrm{O} & 2.15\ \mathrm{A}\end{array}\right\}\ \text{Mean value 2.075 A,}$$

$$\mathrm{Fe}^{+3}(\text{tetrahedral})-\mathrm{O}\quad 1.89\ \mathrm{A},$$

in fair agreement with the observed values.

STRUCTURE OF THE ORTHORHOMBIC PHASE

The crystal was cooled to 105°K in the absence of a magnetic field, and the intensities of a number of reflections were measured. Although most details of any ordering in the octahedral sites would be obscured by the multiple twinning, the intensities are sensitive to any change in the parameter associated with the tetrahedral sites and the average oxygen parameter defined by

$$\bar{u}=(\tfrac{1}{2}+y_h+z_h+x_i-z_i)/6.$$

A least-squares refinement was carried out on a group of fifteen reflections, with the following results:

$$\begin{array}{ll} z(e)=0.125, & \sigma=0.004,\\ \bar{u}=0.2547, & \sigma=0.0002,\\ 2B=0.35, & \sigma=0.05. \end{array}$$

Thus, there is no appreciable change in the *average* geometric structure. The observed and calculated intensities are given in Table III. The higher intensity reflections not used in the least squares were used to obtain an estimate of the extinction correction: $c_s=0.00022$.[37]

One of the most convincing confirmations of the Verwey ordering scheme would be the observation of an (002) reflection. This reflection, absent in the cubic structure, has a structure factor proportional to the difference between the scattering factors for Fe^{+3} and Fe^{+2}, if the ordering scheme is correct. A magnetic field of 10 000 gauss was applied during cooling along

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[36] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948), pp. 350, 367–368.

[37] As indicated above, the extinction remaining here is quite likely primary. However, a reasonable fit is obtained considering a correction of the secondary type.

the [001] direction parallel to the plane of the spectrometer in order to establish a unique **c** axis along that direction. As the ionic moments lie along the **c** axis, there is no diffracted magnetic intensity in the (002) reflection unless the moments are turned out of this direction by a magnetic field; the intensity to be expected for the Verwey model is 13 q^2.[38] The crystal and counter were rotated to the proper position for observation of the (002) reflection, and counts of twenty minutes duration were made at intervals of one-half degree in 2θ, both with zero magnetic field and with a magnetic field of 10 000 gauss at 26° to the [001] direction, i.e., with $q^2=0$ and with $q^2=0.19$.[39] Several runs were made, all showing a distinct peak at almost precisely the proper angle ($2\theta=14.7°$); a composite of the results is shown in Fig. 2. The observed integrated intensity was 2.0±0.6, while that calculated for the Verwey model is 2.47. The peak is rather more broad than a normal peak at this angle, indicating that the order is perhaps not complete.[40]

TABLE III. Observed and calculated intensities for multiply-twinned orthorhombic magnetite at 105°K. $I_{\text{calc}}E$ includes extinction correction of the form $E=\exp(-0.00022I_{\text{calc}})$. The intensities are defined as in Table II but with $\sigma/\sigma_0=1$, and are for the cubic cell size which is twice the orthorhombic. The reflections marked with asterisks were used in the least-squares refinements discussed in the text.

h h l (cubic)	$I_{\text{calc}}E$	I_{obs}
0 0 4	1197	1105
0 0 8	1191	1224
1 1 1	548	543
1 1 11*	95	88
2 2 2	221	222
2 2 4	118	121
2 2 6*	41	40
2 2 8*	60	58
2 2 12*	48	43
3 3 1*	120	112
3 3 11*	61	65
4 4 0	1423	1452
5 5 1*	45	47
5 5 9*	44	39
5 5 11*	137	123
6 6 0*	68	67
6 6 4*	46	46
6 6 8*	56	56
7 7 3*	64	68
7 7 5*	97	99
8 8 0	1012	995
10 10 0*	82	81

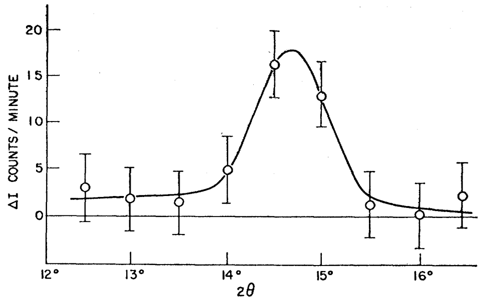

FIG. 2. Intensity curve for (002) reflection in orthorhombic magnetite, plotted as difference between counts received with and without magnetic field at 26° to [001].

The (002) reflection should appear even if [**a**,**b**] twinning exists. More information about the structure can be obtained by consideration of changes in other intensities under circumstances when the twinning is removed. Following the experience of Calhoun,[19] the magnetic field was applied during cooling at 40° to the **c** axis in an attempt to remove the [**a**,**b**] twinning (see Fig. 3). This was indeed successful, as indicated by the low mosaic spread and the observed intensities of the reflections. The intensities of a number of reflections which are particularly sensitive to the ordering were measured, together with several reflections with no magnetic contribution in order to be absolutely sure of the scale factor and the situation with regard to extinction. The intensities observed (Table IV) indicate strongly that the Fe^{+3} ions must be assigned to set (d) of $D_{2h}{}^{28}$ and the Fe^{+2} ions to set (b). As the experiment was performed, this assignment places the ferrous ions in rows parallel to the cubic [110] direction in the plane of the **c** axis and **H**, and the ferric ions in rows perpendicular to this plane, i.e., if **a** is magnetically the harder of the **a** and **b** axes, the Fe^{+3} ions will lie along **a**. Although the resolution of our spectrometer is not high enough to measure easily the small difference between a_0 and b_0, some magnetization measurements by

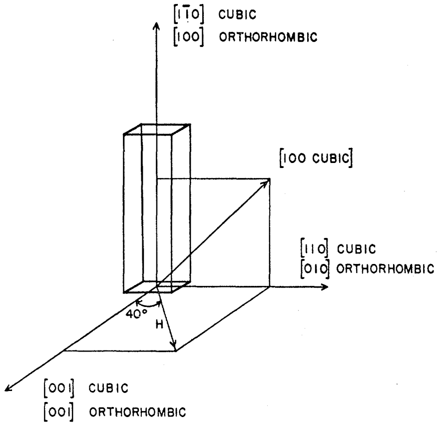

FIG. 3. Axial relationships in experimental arrangement. Incident and diffracted beams were in the plane of [001] and **H**, which is shown oriented in the position which satisfactorily removed the [**a**,**b**] twinning.

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[38] $q^2=\sin^2\tau$, where τ is the angle between the magnetic axis and the scattering vector.

[39] That the applied field was large enough to saturate the crystal was demonstrated by observation of its effect on other magnetic reflections.

[40] It should be noted here that the quartz Dewar gave rise to a broad diffuse peak in this region. However, the effect of this is eliminated by the difference technique as described above. The second order peak from the (004) reflection was eliminated by use of a filter of Pu^{239} which has a transmission of 0.40 for the primary wavelength, but 0.0016 for the $\lambda/2$ component.

TABLE IV. Calculated and observed intensities for orthorhombic magnetite for three axial relationships. The intensities are defined as in Table III, but have been multiplied by 1/10. Extinction corrections have been applied to the observed intensities to make the intensities in the three cases directly comparable.

c axis	Random		Fixed		Fixed		
a and b axes	Random		Random		Fixed		
hhl (cubic)	Calc	Obs	Calc	Obs	Fe^{+3} in (*b*)	Fe^{+3} in (*d*)	Obs
004	184	184	138	134	138	138	133
444	84	80	84	83	84	84	84
111	73	74	73	75	65	82	84
220	28	28	35	34	42	28	24
331	12	13	17	16	15	19	18

Bickford[41] indicate that the magnetically easier axis **b** is the shorter of the two. Thus, the larger ferrous ions lie in rows parallel to the shorter axis, contrary to one's first expectations. However, the detailed discussion of interionic distances below suggests that the situation is not unreasonable.

Insufficient data were collected on the untwinned specimens to refine the oxygen parameters. However, using the information from the twinned sample that the average value is essentially unchanged and information as to the ionic radii, we may make an informed guess of these parameter values. The parameters were adjusted by least squares to fit the distances as closely as possible to those given by the Pauling radii,[36] at the same time satisfying the condition that $\bar{u}=0.2547$. The resulting set of coordinates for the orthorhombic phase is given in Table V together with the corresponding coordinate for the cubic phase with $u=0.2548$. Also presented are the metal-oxygen distances calculated for the orthorhombic structure with an average cell dimension of $a_0\sqrt{2}=b_0\sqrt{2}=c_0=8.3854$ A. The metal-oxygen distances are approximately those calculated by the Pauling radii. The packing is not simple enough to give a wholly convincing argument that **a** should be longer than **b**, although detailed considerations which will not be repeated here indicate that this is perhaps reasonable.

TABLE V. Probable parameters and interatomic distances in orthorhombic magnetite. Parameters *A* are adjusted to fit Pauling radii. Parameters *B* are those for a structure with atomic positions unchanged from those in the cubic form.

	A	*B*
$x(i)$	0.2445	0.2596
$z(i)$	−0.0154	−0.0048
$y(h)$	0.5237	0.5096
$z(h)$	0.2445	0.2548
Octahedral $Fe^{+3}-O$	2.000 and 1.968	
Octahedral $Fe^{+2}-O$	2.123 and 2.147	
Tetrahedral $Fe^{+3}-O$	1.867 and 1.908	
Range of $O-O$	2.683 to 3.176	
Average $O-O$	2.966	

NATURAL CRYSTALS

Some crystals of natural magnetite, kindly furnished by Dr. Robert Nathans, were also examined below the transition, which for these crystals occurred between 110 and 115°K. The intensities observed for the magnetic peaks indicated that a unique **c** axis was readily established by cooling in a magnetic field. However, attempts to remove the [*a*,*b*] twinning by use of the magnetic field were unsuccessful. Furthermore, a distinct (002) reflection could not be observed, though there may well have been a broad diffuse peak obscured by the background. This would indicate that the [**a**,**b**] twinning persists on a micro-basis, i.e., there is very little long-range order. This is possibly due to the fact that the working temperature was little more than 5° below the transition, whereas for the natural magnetite it was 15°. One would expect the transition to be considerably sharper for the synthetic crystals.

Although no extensive investigation into the *axis switching* phenomenon was made, a few pertinent observations were made in passing. A natural crystal was cooled with an axis establishing field along [001]. The field was removed and applied along the [110] direction in the plane thus moving the magnetic moments into the (001) plane. After removal of the field, the moments remained in the (001) plane, as indicated by the intensity of the (004) reflection. This is an example of the axis switching noticed by earlier investigators.[17,19] The [010] and [100] direction presumably become orthorhombic **c** axes in equal amounts, although the exact distribution may depend on a variety of factors such as crystal and domain shape, impurities, etc. This behavior did not appear to hold for the synthetic crystal (at 105°K and fields up to 10 000 gauss). The moments could be turned around to other directions, but returned to their original direction when the field was removed.

CONCLUSION

The Verwey structure may be regarded as being established. If the orthorhombic axes are labeled such that the anisotropy energies E_i satisfy

$$E_a > E_b > E_c = 0,$$

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[41] L. R. Bickford, Jr., U. S. Office of Naval Research, Physics Branch Report NR 018-606, January, 1954 (unpublished).

i.e., **c** is the direction of easy magnetization, then the following statements hold:

(1) The octahedral ferric ions lie in rows parallel to **a**.
(2) The octahedral ferrous ions lie in rows parallel to **b**.
(3) The magnetic moments of all ions are parallel or antiparallel to **c**.
(4) The **a** axis is longer than the **b** axis.

ACKNOWLEDGMENTS

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Effect of Degree of Orientation and Crystal Size on the Scattering of 20-kev Electrons by Aluminum*

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The energy distribution of 20-kev electrons scattered by aluminum has been measured as a function of degree of crystalline orientation and foil thickness. For equal physical thickness the foils with higher degree of orientation are electron-optically thinner. Over a range of thickness from 35 to 500 A, the values of the first two characteristic losses are 6.3±0.1 ev and 15.0±0.1 ev. They exhibit no systematic change with thickness greater than the experimental uncertainty. The intensity ratio between the two losses is essentially constant within this range. It is concluded that the low-lying (6.3 ev) loss is not due to the depolarization effect of grain boundaries.

In an earlier publication[1] it was noted that the distribution of electrons scattered by gold was strongly influenced by the degree of crystalline orientation, but the instrumental resolution was insufficient to show detail. When a new analyzer became available that had an energy resolution of less than 1 ev and an angular resolution less than 1 milliradian, it became possible to obtain quantitative data.

Foils of cp aluminum were prepared by vacuum evaporation at a residual gas pressure of less than 10^{-4} mm Hg on a freshly cleaved rocksalt substrate. In the case of the polycrystalline samples this was at room temperature, and in the single-crystal samples at the known epitaxy temperature of 440°C. A few partially oriented samples were prepared with substrates at intermediate temperatures obtained by use of a gradient furnace.[2] The evaporation rate was uncontrolled but rapid, so that the process was completed in less than 1 minute. The rocksalt was masked to give four $\frac{1}{8}$-in. disks. The four disks were floated off the rocksalt onto a water surface and then three were picked up, one over a 0.014-in. hole in the scattering mount, another on a standard 200-mesh diffraction camera mount and the third on a microscope slide for thickness measurements in a Tolansky[3] interferometer.

Figures 1 and 2 show typical diffraction patterns of "unoriented" and "oriented" films prepared in this way. Figure 3 presents a typical energy distribution at zero scattering angle for a polycrystalline sample. The char-

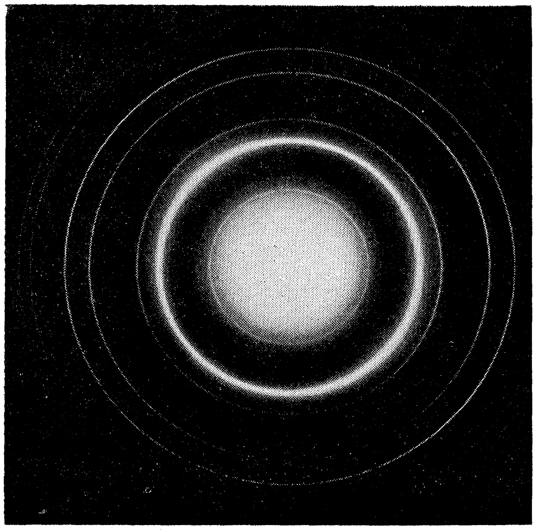

FIG. 1. The electron diffraction pattern of a typical unoriented sample of thickness 900 A.

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[1] Marton, Simpson, and McCraw, Phys. Rev. **99**, 495 (1955).

[2] L. Marton and J. A. Suddeth, Rev. Sci. Instr. **29**, 440 (1958).

[3] S. Tolansky, *Multiple Beam Interferometry* (Oxford University Press, New York, 1948).