Table 2. *Bond lengths* (Å) *and angles* (°)

		X-ray data*
S(1)–O(1)	1·448 (9)	1·44 (1)
S(1)–O(2)	1·500 (6)	1·47 (1)
S(1)–O(3)	1·505 (9)	1·47 (1)
O(4)–O(4^{i})	1·37 (1)	1·33 (2)
D(1)–O(4)	0·96 (1)	–
O(1)–S(1)–O(2)	111·4 (4)	110·4 (3)
O(1)–S(1)–O(3)	110·9 (6)	110·0 (6)
O(1)–S(1)–O(2^{ii})	111·4 (4)	110·4 (3)
O(2)–S(1)–O(3)	108·1 (4)	109·0 (3)
O(2)–S(1)–O(2^{ii})	106·8 (5)	107·9 (5)
O(3)–S(1)–O(2^{ii})	108·1 (4)	109·0 (3)

The dihedral angle for D_2O_2 is 100·1 (6)°

Symmetry code

(i)	$1-x, -y, z$	(x)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
(ii)	$x, y, -z$	(xi)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(iii)	$x, 1+y, z$	(xii)	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}+z$
(iv)	$1-x, 1-y, z$	(xiii)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}+z$
(v)	$1-y, x, z$	(xiv)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$
(vi)	$1\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	(xv)	$-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$
(vii)	$\frac{1}{2}+y, \frac{1}{2}+x, \frac{1}{2}-z$	(xvi)	$y, 1-x, z$
(viii)	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$	(xvii)	$1+x, 1+y, z$
(ix)	$-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$		

* Adams & Pritchard (1978).

Table 3. *Coordination around the cations*

Na(1)–O(3^{iii})	2·485 (8) Å		Na(2)–O(2^{viii})	2·557 (3) Å
Na(1)–O(4^{iv})	2·707 (13) ←		O(2^{ix})	
Na(1)–O(1^{v})	2·290 (7)		O(2^{x})	
Na(1)–O(2^{vi})	2·347 (7)	or	O(2^{xi})	
Na(1)–O(2^{vii})	2·316 (7)		O(2^{xii})	
Na(1)–O(4^{vii})	2·249 (11) ←		O(2^{xiii})	
Na(1)–Cl(1^{xvii})	3·029 (7)		O(2^{xiv})	
			O(2^{xv})	

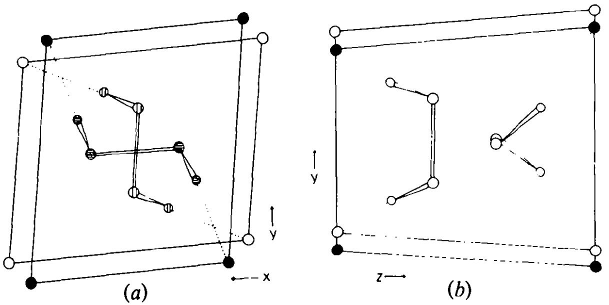

Fig. 1. View of the D_2O_2 molecules. Each molecule has a site occupancy of 0·5. The hydrogen-bonding scheme O(4)–D(1)···O(3) is shown. (*a*) Projection on to (001). The centre of the diagram is at $x = 0·5$, $y = 0·0$. (*b*) Projection on to (100). The centre of the diagram is at $y = 0·0$, $z = 0·25$.

hydrogen-bonding scheme. In the previous X-ray study (Adams & Pritchard, 1978) it was shown that the peroxide O(4) was close to the sulphate O(3) and O(1^{xvi}) and it was therefore possible that the hydrogen bond could be to either of these O atoms since the O···O distances were similar, 2·71 (2) and 2·68 (2) Å respectively. We have found in the neutron study that the O···O distances are less similar than those for the non-deuterated compound: O(4)···O(3) 2·51 (1) and O(4)···O(1^{xvi}) 2·85(1) Å. It is likely from these figures that O(4)···O(3) is the hydrogen bond since the O(4)···O(1^{xvi}) distance is close to the van der Waals diameter for an O atom. In addition the D atom lies close to the line between O(4) and O(3). We have O(4)–D(1) 0·95 (1), D(1)···O(3) 1·62 (1) Å, O(4)–D(1)···O(3) 163 (1)°.

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The Structure of Magnetite

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Abstract. Fe_3O_4, cubic, *Fd*3*m*, $a = 8·3941$ (7) Å. The structure has been refined to a weighted *R* of 0·033, using 147 unique averaged reflexions collected at room temperature on a single-crystal diffractometer with Mo $K\alpha$ ($\lambda = 0·7107$ Å) radiation. The oxygen positional parameter (u) is 0·2549 (1). The observed *M*—O bond

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distance and electron density distribution in the vicinity of the O atom are consistent with a common Fe^{3+} nucleus for *M* site atoms. Residual electron density at equipoint position 8(*b*) is assigned to interstitial Fe^{3+} in a second tetrahedrally coordinated position. Thus natural magnetite at room temperature has a defect structure with an interstitial-vacancy couple similar to that reported for ferrous oxide.

Introduction. Magnetite has the inverse-spinel structure with space group *Fd*3*m* (Bragg, 1915; Claasen, 1926; Verwey & de Boer, 1936; Shull, Wollan & Koehler, 1951). The O atoms, at equipoint position 32(*e*), form an approximate cubic close-packed array, with one Fe^{3+} per formula unit at a tetrahedrally coordinated position, equipoint 8(*a*), and Fe^{2+} and the remaining Fe^{3+} randomly distributed at an octahedrally coordinated position, equipoint 16(*d*) (Fig. 1). The single positional parameter (*u*) locates the O atom. The structure was most recently refined by Hamilton (1958), using neutron diffraction data, to give u = 0·2548 (2). Due to their remarkable solid-state properties, magnetite and related spinel ferrites have been extensively examined by scientists of diverse specialities, and this has resulted in some confusion in structural terminology. In the present paper, tetrahedral and octahedral metal positions will be referred to either explicitly or as *T* and *M* sites respectively. The familiar '*A*' and '*B*' notation is not adopted as these symbols are already used in the general chemical formula, AB_2O_4.

The inverse-spinel configuration was originally suggested by Verwey & de Boer (1936) to account for the anomalously high electrical conductivity of magnetite (~2 × 10^4 S m^{-1}) through continuous exchange of electrons between Fe^{2+} and Fe^{3+} in the octahedrally coordinated position. This fast electron-hopping hypothesis is also supported by Mössbauer spectra of magnetite above the Verwey phase transition, which indicate a single six-line hyperfine spectrum for *M* site atoms (Bauminger, Cohen, Marinov, Ofer & Segal, 1961; Ito, Ono & Ishikawa, 1963). The relaxation time for fast electron hopping is assumed to be appreciably less than that expected for Fe^{2+}—O and Fe^{3+}—O bonds, and *M* site Fe^{2+} and Fe^{3+} should appear in X-ray structure analysis as one atom. Certainly, modern theories on the electronic structure of magnetite predict a common Fe^{3+} nucleus for *M* site Fe atoms, with an itinerant 3*d* electron either having a fast electron-hopping role (Lotgering & van Diepen, 1977) or delocalized within a conduction band (Evans, 1975). At the outset of the present investigation it was intended to ascertain whether the thermal parameters and residual electron density, particularly of the O atom, were consistent with a common nucleus for *M* site atoms, or with an average structure of short-range ordered discrete Fe^{2+} and Fe^{3+} atoms.

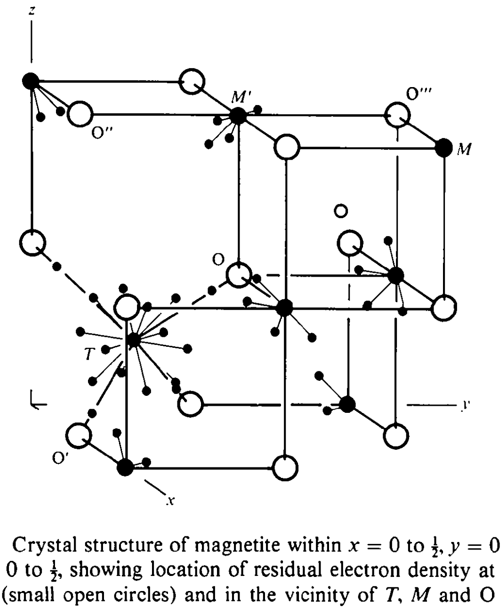

Fig. 1. Crystal structure of magnetite within $x = 0$ to $\frac{1}{2}$, $y = 0$ to $\frac{1}{2}$, $z = 0$ to $\frac{1}{2}$, showing location of residual electron density at *T*(2) site (small open circles) and in the vicinity of *T*, *M* and O sites (dots).

The present investigation was made on natural magnetite occurring as euhedral octahedra in a magnetite–chlorite schist (No. 633, Dana Collection, University of Western Ontario). This material was thoroughly characterized by polished-section petrographic examination, electron microprobe analysis, and single-crystal X-ray diffraction procedures as single-phase, essentially end-member magnetite. Observed reflexions on precession and Weissenberg films are consistent with space group *Fd*3*m*. Sporadic, very weak *hk*0 reflexions with $h + k = 4n + 2$ (*e.g.* 420), observed on long-exposure films, were confirmed as multiple reflexions (Samuelsen, 1974) by varying the conditions of diffraction. Least-squares refinement of 17 centred reflexions measured on a four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ (λ = 0·7107 Å) radiation gave a = 8·3941 (7) Å, which is in good agreement with published data for Fe_3O_4 (Hamilton, 1958).

The crystal selected for the structure refinement was an approximately equidimensional single-crystal fragment bounded by (100), (0$\bar{1}$0), ($\bar{1}$12) and ($\bar{1}$1$\bar{2}$), with a calculated volume of 1·8 × 10^{-3} mm^3. The X-ray intensity data were collected at room temperature on a Picker FACS1 four-circle diffractometer system by the θ–2θ scan technique: 40 s stationary background counts, peak-base widths of 2° 2θ and a scanning rate of 2° min^{-1}. All *hkl* and $\bar{h}\bar{k}\bar{l}$ reflexions with $h + k$, $k + l$, $l + h = 2n$ out to 2θ = 90° were measured. The resulting data were processed with program *DATAP*77 (SUNY at Buffalo) and corrected for background, Lorentz and polarization effects, and absorption. Transmission factors for the absorption correction were calculated by Gaussian integration with a 12 × 12

Table 1. *Positional and thermal* (Å^2) *parameters for magnetite*

Anisotropic thermal parameters ($\times 10^5$) are calculated from $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^*\cos\gamma^* + 2B_{13}hla^*c^*\cos\beta^* + 2B_{23}klb^*c^*\cos\alpha^*)]$.

	Equipoint position	x	y	z	B_{11}	B_{12}	(B)
T	8(a)*	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	349 (14)	0	0·34 (2)
M	16(d)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	461 (14)	45 (5)	0·46 (2)
O	32(e)	0·2549 (1)	0·2549 (1)	0·2549 (1)	541 (24)	−3 (17)	0·49 (3)

* Origin at centre ($\bar{3}m$).

Table 2. *Residual peaks on* $F_o - F_c$ *maps for refinement with anisotropic thermal parameters*

Equipoint position	x	y	z	Relative electron density (%)*
8(b)	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	1·0
96(g)	0·06	0·06	0·125	0·7
96(h)	0	0·205	0·795	0·6
32(e)	0·22	0·22	0·22	0·7

* Relative electron density is percentage of peak F_o electron density at position of T site.

× 12 grid using a linear absorption coefficient of 14·65 mm^{-1}. The crystal was oriented with [220] parallel to the φ axis. The calculated transmission factors varied from 0·245 for $0\bar{2}0$ to 0·348 for 0,12,10. The original data list of 2565 reflexions was reduced to 147 reflexions non-equivalent in $Fd3m$. Standard deviations were calculated from the agreement between equivalent reflexions. Zero intensity was assigned if more than 25% of a set of equivalent reflexions had peak intensities less than background plus one standard deviation.

The magnetite crystal structure was refined in space group $Fd3m$ using program *LINEX*77 (SUNY at Buffalo). Initial structural parameters were from Hamilton (1958). Scattering curves for the neutral atomic species, and real and imaginary components of the anomalous-dispersion corrections were taken, respectively, from Tables 2.2B and 2.3.1 of *International Tables for X-ray Crystallography* (1974). The refinement with anisotropic thermal parameters and isotropic extinction converged on values for the weighted and conventional residual indices of 0·033 and 0·024, respectively. Equivalent data for refinement with isotropic thermal parameters are 0·039 and 0·027, respectively. Final positional and thermal parameters are given in Table 1.* The isotropic extinction parameter for type I extinction, Lorentzian distribution (Coppens & Hamilton, 1970), is 1·32 (10) × 10^{-4}, for refinement with anisotropic thermal parameters.

Very weak residual peaks are present in $F_o - F_c$ maps for the refined magnetite structure (Table 2, Fig. 1). The most prominent residual electron density, that in the 8(b) equipoint position, was tentatively assigned to a second tetrahedrally coordinated position for iron, T(2). Further refinement with anisotropic thermal parameters and an assumed T(2) occupancy proportional to the residual electron density (Table 2) reduced the weighted and conventional residual indices to 0·032 and 0·023 respectively.

Discussion. The present results for the oxygen positional parameters (u) and interatomic distances and bond angles in magnetite at room temperature (Table 3) are similar to the earlier data of Hamilton (1958), with improved precision. Comparison of the observed u parameter and metal–oxygen bond distances with values calculated from effective ionic radii (Shannon & Prewitt, 1969, 1970) favours both the inverse-spinel configuration (Verwey & de Boer, 1936; Hamilton, 1958) and a single Fe^{3+} nucleus for M-site Fe atoms (Table 4).

Table 3. *Some interatomic distances and bond angle in magnetite*

T–O	1·8883 (17) Å	O–O''	2·9689 (3) Å
M–O	2·0584 (9)	O–O'''	2·8519 (27)
M–M'*	2·9678 (3)		
O–O'	3·0836 (27)	O–M–O'''	87·70 (6)°

* M' at $[\frac{3}{4}+x, \frac{3}{4}+y, \bar{z}]$, O' at $[x, \frac{1}{4}-y, \frac{1}{4}-z]$, O'' at $[\frac{1}{2}-x, \frac{3}{4}+y, \frac{1}{4}+z]$, O''' at $[x, \frac{3}{4}-y, \frac{3}{4}-z]$.

Table 4. *Observed and calculated bond distances and u parameters*

Bond distances (Å)		
Tetrahedral: Fe^{2+}–O	2·03	
Fe^{3+}–O	1·89	1·888 (2)
Octahedral: (Fe^{2+},Fe^{3+})–O	2·113	
Fe^{3+}–O	2·045	2·0584 (9)
Parameter u		
Normal structure	0·2618	
Inverse structure	0·2527	0·2549 (1)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35901 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The isotropic temperature factors (Table 1) are generally similar to the respective B parameters in well-refined room-temperature structures of end-member-composition oxide spinels and related phases (*e.g.* Morimoto, Tokonami, Watanabe & Koto, 1974; Yagi, Marumo & Akimato, 1974), and are significantly lower than the respective data for a natural titanomagnetite (Stout & Bayliss, 1975). However, many well-refined structures of related phases with mixed metal-site occupancies yield relatively low B parameters, and this correlation is probably not significant. For example, the mean B parameters of the T, M and O positions in a natural olivine ($Mg_{0.98}Fe_{1.01}SiO_4$) are 0·41 (2), 0·48 (2) and 0·58 (5), respectively (Finger, 1970).

The bulk electron density distribution in the vicinity of the O atom is not noticeably bimodal or anisotropic. This observation favours a common nucleus for most, if not all, M site atoms in the magnetite structure.

The weak but significant residual electron density at equipoint position $8(b)$ must logically be associated with one of the following possibilities: (i) incoherent twinning, (ii) coherent twinning, (iii) interstitial Fe atoms in the $T(2)$ position. Additional reflexions consistent with incoherent twinning have not been observed in spite of extensive precession and Weissenberg work on this magnetite. Furthermore, continuous diffraction streaks consistent with coherent twinning have not been observed. However, magnetite crystals from another locality did exhibit markedly anisotropic diffuse scattering in the vicinity of certain Bragg reflexions. These diffraction streaks are non-systematically distributed in reciprocal space: streaks on neighbouring Bragg reflexions are not parallel to common or symmetry-related reciprocal-lattice directions. Hence, this diffuse scattering may be attributed to point defects. Subsequently, long-exposure precession films of magnetite crystals of the present investigation showed similar diffuse scattering but of weaker intensity. Thus, it is provisionally concluded that at room temperature natural magnetite has a defect structure, with interstitial Fe^{3+} atoms in the $T(2)$ position and corresponding vacancies in, most probably, the octahedral position. This interstitial-vacancy couple is similar to that reported for the defect structure of ferrous oxide (Roth, 1960).

The weak residual electron density at equipoint positions $96(g)$, $96(h)$ and $32(e)$ is consistent with the local displacements of neighbouring T, O and M atoms, respectively, required for equilibrium $T(2)$–O and $T(2)$–M bond distances (Fig. 1). However, the spatial distribution of this residual electron density is also consistent with, respectively, occupied t_2 orbitals on T atoms, occupied t_{2g} orbitals on M atoms (as surmised by Fleet, 1975), and even a singly occupied sp^3 orbital lobe on O atoms.

The presently proposed crystal structure may have profound ramifications for interpretation of the solid-state properties of magnetite and related ferrites. The anomalously high electrical conductivity of magnetite may be more appropriately described by a semiconductor band model than by fast electron hopping. Investigation of other magnetite specimens, particularly those exhibiting diffuse scattering, is continuing.

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