The Structure of Magnetite: Two Annealed Natural Magnetites, $Fe_{3.005}O_4$ and $Fe_{2.96}Mg_{0.04}O_4$

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Abstract. $Fe_{3.005}O_4$: $M_r = 231.8$, cubic, $Fd3m$, $a = 8.3969$ (8) Å, $V = 592.0$ Å^3, $Z = 8$, $D_x = 5.202$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 14.7$ mm^{-1}, $F(000) = 881.0$, room temperature, final $R = 0.015$ for 146 unique averaged reflections; natural magnetite annealed at 1373 K. $Fe_{2.96}Mg_{0.04}O_4$: $M_r = 230.3$, cubic, $Fd3m$, $a = 8.3975$ (7) Å, $V = 592.2$ Å^3, $Z = 8$, $D_x = 5.166$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 14.5$ mm^{-1}, $F(000) = 875.5$, room temperature, final $R = 0.014$ for 146 unique averaged reflections; natural magnetite annealed at 1073 K. Both annealed magnetites have the ideal inverse-spinel structure. Interstitial cation defects, present in the unannealed natural specimens, are not observed.

Introduction. Recent X-ray refinements of the crystal structures of natural magnetite specimens resolved a significant proportion of disordered point defects (Fleet, 1981, 1982*a*). Magnetite No. 633 ($Fe_{3.000}O_4$, $a = 8.3941$ Å) has about 0.3% of total Fe cations in an interstitial tetrahedral position $T(2)$. Magnetite No. 2741 ($Fe_{2.961}Mg_{0.039}O_4$, $a = 8.3930$ Å) has about 5% of total cations as interstitials in a second tetrahedral position $T(3)$ and a second octahedral position $M(2)$. These results were surprising since previous indirect studies on the structure of magnetite (*e.g.* Dieckmann, 1982) had recognized only cation interstitials intrinsic to the metal-excess $Fe_{3-\delta}O_4$ ($\delta < 0$) composition, which are generally present at concentrations below the resolution of X-ray structure methods.

The point defects in natural magnetites appeared to be randomly distributed Frenkel defects unrelated to nonstoichiometry and the discussion in Fleet (1982*b*) tacitly anticipated that they are present at equilibrium concentrations for the conditions of original crystal growth. The latter hypothesis may be tested experimentally, since the equilibrium concentration of such Frenkel defects should increase with increasing temperature (*T*) according to $\exp(-E/RT)$ (where E is the energy of formation of one mole of Frenkel defects, and R is the gas constant: *e.g.* Greenwood, 1968). The present paper reports on the crystal structures at room temperature of annealed magnetite 633 and 2741.

Experimental. Magnetite 633, MT1, was annealed at 1373 K for 7 d in a sealed silica-glass tube with a wustite/magnetite buffer and quenched in air. The equilibrium concentration for the conditions of annealing is $Fe_{3.005}O_4$ (Dieckmann, 1982), with about 0.17% of the total cations as interstitials related to the nonstoichiometry. X-ray precession-camera investigation on grain fragments of MT1 revealed a diffraction pattern similar to that of the unannealed material. Crystal approximately rectangular-prismatic, $0.14 \times 0.15 \times 0.20$ mm. Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Unit cell: 18 reflections in 2θ range 57.1–60.9°. θ–2θ scan. All reflections with $h+k$, $k+l$, $l+h=2n$ within hemisphere out to $2\theta=90°$ measured. Variation of standard reflections (440, 4$\bar{4}$0 and 008) insignificant. Background, Lorentz, polarization and absorption corrections applied; transmission factors (by Gaussian integration with a $12 \times 12 \times 12$ grid and $\mu = 14.7$ mm^{-1}) varied from 0.149 for 111 to 0.239 for $8,\bar{12},8$. 2560 reflections were reduced to 146 reflections non-equivalent in $Fd3m$. σ calculated from agreement between equivalent reflections, giving $\sigma(F) < 0.01|F|$ for reflections with $I > 0$. 22 reflections with $I = 0$, assigned if more than 25% of set of equivalent reflections had $I <$(background + 1σ). Refinement with defect structure I starting parameters (Fleet, 1981) gave $R = 0.015$. However, refined cation site occupancies, $T(1) = 1.001$ (12), $M(1) = 1.011$ (12) and $T(2) = 0.0012$ (5), indicated an insignificant occupancy for the $T(2)$ interstitial cation position. Final refinement made with the ideal three-position magnetite structure; $\sum w(\Delta F)^2$ minimized, $R = 0.015$, $R_w = 0.016$, $S = 1.8$, $w = 1/\sigma^2(F)$. Isotropic-extinction parameter for type I extinction (Coppens & Hamilton, 1970): 0.12 (2) $\times 10^{-4}$. $F_o - F_c$ residual electron density at the $T(2)$ position of defect structure I was negligible, and there was no significant residual density at other possible interstitial cation positions. $(\Delta/\sigma)_{max} = 0.0011$. Scattering factors for neutral atomic species and f', f'' taken, respectively, from Tables 2.2B and 2.3.1 of *International Tables for X-ray Crystallography* (1974). Computations carried out with *DATAP77* and *LINEX77* (SUNY at Buffalo).

Magnetite 2741, MT9, was annealed at 1073 K for 7 d in a sealed silica-glass tube and quenched in air and finally in water. Since an oxygen buffer was not used, the Fe–O composition of MT9 is not precisely known within the range $Fe_{3.008}O_4$ to $Fe_{2.997}O_4$ (Dieckmann, 1982). The maximum possible concentration of cation interstitials related to the nonstoichiometry is about 0·27% of total cations, which is insignificant compared to the concentration of defects in the unannealed material. Extensive X-ray precession camera investigation of grain fragments of MT9 revealed a diffraction pattern similar to that of magnetite 633. Weak $\langle 110 \rangle$* diffraction streaks, which characterize the diffraction pattern of unannealed magnetite 2741, were not present. Equidimensional crystal, well faceted and rather small ($0·61 \times 10^{-3}$ mm³). Transmission factors ($\mu = 14·5$ mm⁻¹) from 0·340 for 10,10,8 to 0·435 for 13,5,9. 26 reflections with $I = 0$. Refinement with defect structure II starting parameters (Fleet, 1982a) and fixed site occupancies gave $R = 0·026$. However, final refinement with the ideal three-position magnetite structure, with Mg^{2+} randomly distributed over the $T(1)$ and $M(1)$ sites, significantly reduced R to 0·014 ($R_w = 0·013$, $S = 1·3$). Isotropic-extinction parameter for type I extinction (Coppens & Hamilton, 1970): $0·05 (2) \times 10^{-4}$. F_o-F_c residual electron densities at the $T(3)$ and $M(2)$ positions of defect structure II were negligible and there was no significant residual density at other possible interstitial cation positions. $(\Delta/\sigma)_{max} = 0·00012$. All other experimental conditions are identical to those above for magnetite 633.

Discussion. Positional parameters are given in Table 1 and selected interatomic distances and bond angles are given in Table 2.† The refined, room-temperature crystal structures of the two annealed magnetites 633 and 2741 are virtually identical to each other and are very similar to the ideal inverse-spinel components of the structures of the corresponding natural magnetites. The annealed magnetites do exhibit a slight increase in unit-cell parameter and thermal vibration and a significant decrease in secondary extinction compared to the natural magnetites. The latter is attributed to thermal-shock effects on quenching from high temperature.

Thus, natural magnetites annealed at high temperature and quenched to room temperature have the ideal inverse-spinel structure, in agreement with previous experimental and theoretical work. Significant concentrations of interstitial cations unrelated to nonstoichiometry are not present. Discontinuous weak ripples, concentric about electron density peaks, were

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39426 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Occupancy, positional and thermal parameters for refined structures of annealed natural magnetite*

Origin at centre ($\bar{3}m$); $y,z=x$ in all equipoint positions. MT1 is magnetite No. 633 annealed at 1373 K; MT9 is magnetite No. 2741 annealed at 1073 K. Thermal parameters ($\times 10^3$ Å²) are calculated from $T = \exp\{-\frac{1}{4}[B_{11}a^{*2}(h^2+k^2+l^2)+2B_{12}a^{*2}(hk+kl+hl)]\}$.

Site	Equi-point	Occupancy	x	B_{11}	B_{12}
Magnetite 633,MT1					
$T(1)$	8(a)	1·0	$\frac{1}{8}$	388 (7)	
$M(1)$	16(d)	1·0	$\frac{1}{2}$	504 (8)	59 (3)
O	32(e)	1·0	0·25468 (7)	597 (13)	−41 (12)
Magnetite 2741,MT9					
$T(1)$	8(a)	0·987	$\frac{1}{8}$	367 (6)	
		Mg,0·013			
$M(1)$	16(d)	0·987	$\frac{1}{2}$	501 (6)	51 (3)
		Mg,0·013			
O	32(e)	1·0	0·25491 (6)	585 (10)	−33 (11)

Table 2. *Some interatomic distances (Å) and bond angles (°) in annealed natural magnetite*

	MT1	MT9
$T(1)$–O	1·8861 (10)	1·8895 (9)
$M(1)$–O	2·0607 (6)	2·0590 (5)
$M(1)$–$M(1')$*	2·9688 (3)	2·9690 (3)
O–O′	3·0799 (17)	3·0856 (15)
O–O″	2·9698 (3)	2·9701 (3)
O–O‴	2·8576 (17)	2·8523 (15)
O–$M(1)$–O‴	87·79 (3)	87·68 (3)

* M' at $(\frac{1}{4}+x,\frac{3}{4}+y,\bar{z})$; O′ at $(x,\frac{1}{4}-y,\frac{1}{4}-z)$, O″ at $(\frac{1}{2}-x,\frac{1}{4}+y,\frac{1}{4}+z)$, O‴ at $(x,\frac{3}{4}-y,\frac{3}{4}-z)$.

resolved in F_o maps of both MT1 and MT9. However, the ripple distributions were essentially identical in the F_o maps of both structure refinements and corresponding residual electron density was not present in the F_o-F_c maps. Therefore, the F_o-map ripple was attributed to Fourier series termination error (due to truncation of the data set at $2\theta = 90°$). This was confirmed by the magnitude of the ripple period (about 0·5 Å) and by the progressive change in ripple pattern with truncation of the data set at progressively decreasing 2θ. It is appreciated that the two magnetite structures were partially inverse at the temperatures of annealing (Wu & Mason, 1981). This disordered cation distribution, which involves only the exchange of electrons between the tetrahedral and octahedral sublattices, is not quenchable. In contrast, cation interstitials are more likely to be quenchable. Furthermore, the incomplete inversion on quenching of large concentrations of interstitials would result in appreciable non-Bragg scattering.

Since the point defects observed in natural magnetite crystals anneal-out at high temperature, they appear to be a metastable feature. Commonly recognized metastable crystal defects include twin and stacking fault composition planes, crystal growth zonation, and dislocations. The association of the defects with twin

and stacking fault composition planes seems unlikely (Fleet, 1982a). No evidence for either coherent or incoherent twinning in magnetite has been observed in the recent studies by the author. Striated magnetites, such as 2741, have been subjected to particularly close scrutiny in this regard. The striations appear to be the traces of {111} growth planes.

One explanation consistent with the available data is that the defects were introduced during crystal growth. The present limited data do point to a correlation between point defect concentration and density of growth striations. Hence the interstitial cation defects may be concentrated on {111} growth planes. However, the density of such planes would have to be appreciably greater than the microscopically resolved striation density to account for the defect concentration observed in magnetite 2741.

References

COPPENS, P. & HAMILTON, W. C. (1970). Acta Cryst. A26, 71–83.
DIECKMANN, R. (1982). Ber. Bunsenges. Phys. Chem. 86, 112–118.
FLEET, M. E. (1981). Acta Cryst. B37, 917–920.
FLEET, M. E. (1982a). Acta Cryst. B38, 1718–1723.
FLEET, M. E. (1982b). J. Can. Ceram. Soc. 51, 13–15.
GREENWOOD, N. N. (1968). Ionic Crystals, Lattice Defects and Nonstoichiometry. London: Butterworths.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
WU, C. C. & MASON, T. O. (1981). J. Am. Ceram. Soc. 64, 520–522.

Structure of Dealuminated Linde Y-Zeolite; $Si_{139.7}Al_{52.3}O_{384}$ and $Si_{173.1}Al_{18.9}O_{384}$: Presence of Non-framework Al Species

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Abstract. Neutron powder diffraction techniques ($\lambda = 2.3841$ Å) have been used to study samples of Linde Y-zeolite treated with NH_3/steam and gaseous $SiCl_4$. The respective compositions from chemical analysis are $Si_{139.7}Al_{52.3}O_{384}$ and $Si_{173.1}Al_{18.9}O_{384}$ ($Z = 1$), and Si/Al framework ratios from magic-angle spinning nuclear magnetic resonance are 10·5 and 10·8. The space group is $Fd3m$, origin at center ($\bar{3}m$). A combination of Rietveld refinement and difference Fourier techniques gives clear evidence for the presence of a four-coordinated Al species in the center of the sodalite unit in both materials, but no six-coordinated species nor the previously reported $Na^+AlCl_4^-$ species could be detected in the difference maps. The refinements give $a = 24.358$ (1) Å, $V = 14451$ (1) Å³, $R_{wp} = 10.77$, R_e = 6·57, $R_I = 6·95$ for the NH_3/steamed sample at 293 K; $a = 24.188$ (1) Å, $V = 14152$ (2) Å³, $R_{wp} = 10·61$, $R_e = 6·02$, $R_I = 5·61$, for the $SiCl_4$-treated sample at 293 K; and $a = 24.171$ (1) Å, $V = 14122$ (2) Å³, $R_{wp} = 10·48$, $R_e = 5·95$, $R_I = 5·29$ for the $SiCl_4$-treated sample at 573 K.

Introduction. The removal of aluminum from the framework of Y-type zeolite by the action of steam (Scherzer, 1978, and references therein) or by treatment with gaseous $SiCl_4$ (Beyer & Belenykaja, 1980) has been discussed extensively. Such treatments produce so called 'ultrastable' zeolite Y, a form of the compound resistant to degradation and the mainstay of the petroleum cracking industry. Recent applications of magic-angle spinning nuclear magnetic resonance (MASNMR) have confirmed the removal of aluminum from the framework of the zeolite under the conditions of steaming (Maxwell, van Erp, Hays, Couperus, Huis & Clague, 1982) and also the entrainment of

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