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The Structure of Magnetite: Symmetry of Cubic Spinels

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The structure of magnetite is centrosymmetric to within the resolution of existing X-ray procedures. Systematic intensity measurements made with rotation about the scattering vector show that the *Fd3m*-forbidden reflections (*hk*0 with $h + k = 4n + 2$) are indeed absent, all nonzero intensity measurements for these reflections being attributable to simultaneous diffraction. The intensities of other weak reflections of magnetite are also enhanced by simultaneous diffraction. When data sets are not corrected for this interference, comparative structure refinements favor a noncentrosymmetric $F\bar{4}3m$ structure with anomalously discrepant O(1) and O(2) thermal parameters. Diffraction-related evidence for noncentrosymmetry in other spinel phases should be carefully reviewed.

Introduction

Recent X-ray refinements of the crystal structures of two natural magnetite (Fe_3O_4) specimens (*1, 2*) and of their high-temperature annealed equivalents (*3*) were made in the centrosymmetric space group *Fd3m* (*4*, No. 227, p. 687). *Fd3m*-forbidden reflections (*hk*0 with $h + k = 4n + 2$) with $|F_0| > 0.0$ were collected in all of these data sets but were rejected as simultaneous diffraction on the basis of precession and Weissenberg camera studies.

The reflections 200 and/or 420 are commonly observed in diffraction studies on cubic spinel phases (e.g., *5–11, 1, 2*), and there has been extensive debate on their significance. However, systematic diffraction studies (e.g., *6, 7, 10, 11, 1*) do suggest that most if not all of the observed intensity is attributable to simultaneous diffraction.

In a surprising development, Grimes *et al.* (*12*) refined the structure of $MgAl_2O_4$ in both *Fd3m* and $F\bar{4}3m$ and demonstrated apparent significant improvement in refinement with the noncentrosymmetric space group. $F\bar{4}3m$ was favored on the basis of superior $|F_0|$, $|F_c|$ agreement for weak reflections (especially those with $|F_c| \simeq 0.0$ in *Fd3m*), $|F_0|$, $|F_c|$ agreement for the *Fd3m*-forbidden reflections and the *R*-ratio test (*13*). The crystal investigated had a very large secondary extinction effect.

In light of these results, the structure refinements of magnetite by Fleet (*1–3*) are clearly incomplete without comparative refinements in the noncentrosymmetric space group $F\bar{4}3m$. In the data set for magnetite No. 633 (*1*), for example, 8 of the 147 *Fd3m* reflections have $|F_0| > |F_c| \simeq 0.0$ (Table I) and 3 of the *Fd3m*-forbidden reflections were "observed." At the same time the potential exists for systematic error in the data set of Grimes *et al.* (*12*), through enhancement of weak reflection intensity by simultaneous diffraction.

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TABLE 1

MEASUREMENTS CORRESPONDING TO ZERO REFLECTION INTENSITY IN ψ SCANS

				Number with zero intensity[b]							Number with zero intensity[b]		
h	k	l	$\lvert F_0\rvert$[a]	$N0$	$N1$	$N3$	h	k	l	$\lvert F_0\rvert$[a]	$N0$	$N1$	$N3$
Natural magnetite No. 633													
2	4	4	3.6	5	24	34	0	0	2	4.5	19[c]	23	30
4	4	2	3.6	4	20	34	0	2	0	4.5	10[c]	27	37
2	4	8	3.9	6	19	34	0	0	6	2.2	5	27	35
8	4	2	3.9	10	29	36	0	0	10	0.0	13	33	38
3	3	15	3.1	7	35	40	0	0	14	0.0	6	29	39
3	7	11	5.8	9	28	40	0	2	4	4.1	2	18	31
4	4	6	3.2	4	18	38	0	2	4	4.1	11[c]	23	35
6	4	4	3.2	12	27	39	4	0	2	4.1	2	19	35
4	4	10	3.4	11	29	39	0	2	8	0.0	5	27	35
10	4	4	3.4	8	27	38	0	2	12	0.0	11	31	38
4	6	8	3.2	23	35	39	0	2	16	0.0	10	30	39
4	6	12	5.1	20	38	40	0	4	6	0.0	9	28	34
4	4	14	0.0	13	31	40	0	4	10	0.0	8	28	39
4	8	10	0.0	11	33	40	0	4	14	0.0	13	28	39
4	8	14	0.0	16	36	40	0	6	8	0.0	15	31	39
4	10	12	0.0	15	36	40	0	6	12	0.0	7	30	39
6	8	8	0.0	12	29	39	0	8	10	0.0	19	32	39
8	8	10	0.0	12	34	40							
Annealed magnetite No. 633, MT1													
6	4	4	5.4	5	24	31	0	0	6	0.0	2	22	33
8	8	2	4.6	11	30	36	0	0	10	0.0	10	30	37
10	8	4	4.1	12	30	37	0	0	14	0.0	13	31	40
11	3	1	10.0	0	5	35	0	2	4	2.4	0	4	12
11	7	3	0.0	9	26	39	0	2	8	4.7	8	23	30
11	9	3	0.0	5	21	40	0	2	12	0.0	10	29	40
12	8	2	0.0	14	34	39	0	2	16	0.0	8	33	40
15	1	1	0.0	14	34	40	0	4	6	0.0	3	15	34
15	5	3	0.0	6	30	40	0	4	10	3.3	6	26	37
15	5	5	0.0	7	28	39	0	4	14	0.0	4	20	39
							0	6	8	0.0	9	24	36
							0	6	12	0.0	11	29	40
							0	8	10	4.7	19	31	34

[a] Using Fleet (*1*, *3*) criterion.

[b] Out of 40 ψ scan measurements; $N0$, $I < 0$; $N1$, $I < \sigma_I$; $N3$, $I < 3\sigma_I$.

[c] 30 kV, 26 mA.

In the present paper, the crystals used in the studies of natural magnetite No. 633 (*1*) and annealed natural magnetite No. 633, MT1 (*3*) are reinvestigated. Enhancement of weak and $Fd3m$-forbidden reflection intensity by simultaneous diffraction is demonstrated by intensity measurements made with rotation about the scattering vector (ψ scans). Comparative refinements in space groups $Fd3m$ and $F\bar{4}3m$ show that the

structure of magnetite is centrosymmetric to within the resolution of existing X-ray procedures.

Simultaneous Diffraction Effects

Fd3m-forbidden reflections (*hk*0 with $h + k = 4n + 2$) have been observed routinely in long-exposure single-crystal precession and Weissenburg photographs of magnetite and other spinel phases. Their relative intensities in magnetite Nos. 633 and 2741 (*2*) are $I_{200} \simeq I_{420} > I_{860} \simeq I_{640} > I_{820}$. The 200 and 420 intensities are attributable to simultaneous diffraction effects because the presence and appearance of these reflections varies with the conditions of diffraction, particularly by changing $\bar{\mu}$ in precession photography (e.g., *14*). With unfiltered radiation, K_β reflections are commonly excited without the corresponding K_α reflections. Also, *Fd3m*-forbidden reflections are sharp, they are often not centered on ideal reciprocal lattice points, and Friedel's law is frequently disobeyed. It is emphasized that the latter effect is not directly related to anomalous scattering, because the visibility of *both* reflections of a Friedel pair is dependent on the conditions of diffraction and may be modified by small changes in crystal orientation. 860, 640, and 820 are too weak for systematic study.

Weak and *Fd3m*-forbidden reflection intensities were investigated by ψ scans, using an Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo K_α radiation (40 kV, 20 mA) and the crystals used in the original structural studies (*1, 3*). The crystal for magnetite No. 633 had been stored in an airtight glass vial. It had been remounted in the interim with [212] close to the ϕ axis. ψ scans were made by taking $\theta - 2\theta$ scans at 0.5° intervals in the ψ range −10° to +9.5° (Fig. 1). The $\theta - 2\theta$ scans were made in the manner of those for data collection (below). Peak background was obtained from the mean of the 40 individual

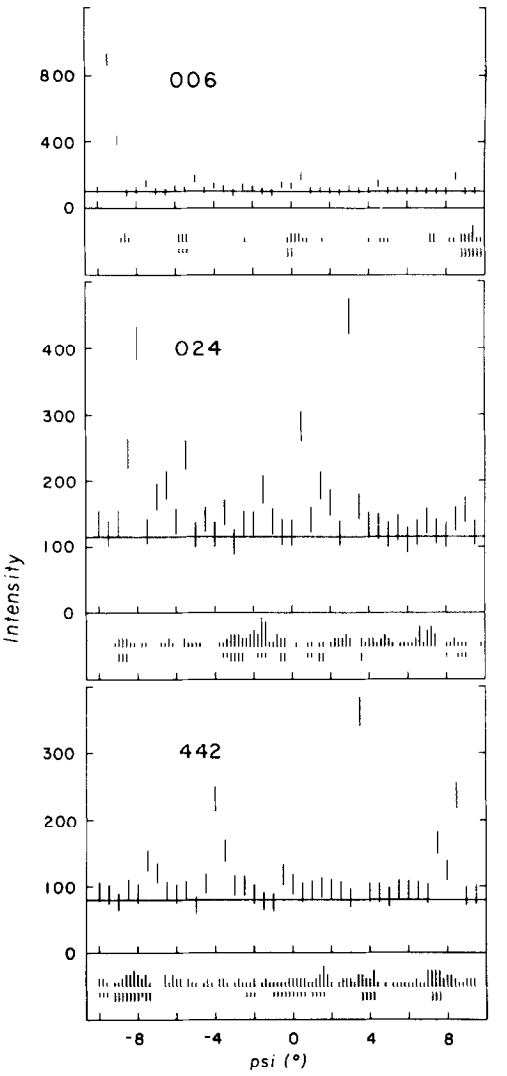

FIG. 1. Intensity measurements made with rotation about the scattering vector for reflections 006, 024, and 442 of magnetite No. 633: data are integrated peak intensities without background subtraction; error bars are $\pm 1\sigma_I$; horizontal line is mean background. MULREF results are shown below each ψ scan: upper row indicates calculated position of Renninger reflections, bar length is proportional to the number of computed reflections; lower row indicates presence of strong operating reflections, short bar—one, long bar—two or more.

$\theta - 2\theta$ scans and the variance of the background measurement was used in calculating σ_I. The ψ scan data for magnetite No.

633 are summarized in Table I as the number of reflections with zero intensity in each of the 40 $\theta - 2\theta$ scans using the discriminants $I < 0$, $I < \sigma_I$, and $I < 3\sigma_I$. Reflection data for 200 were collected at 30 kV because of enhancement by 400 ($\lambda/2$) at 35 and 40 kV. ψ scan data for magnetite No. 633, MT1 were obtained under similar conditions to those for No. 633 (Table I).

The ψ scans for the two crystals investigated (e.g., Fig. 1) are dominated by simultaneous diffraction effects. The overall characteristics of these ψ scans are fully consistent with literature observations on simultaneous diffraction (e.g., *15*). In particular, since $(a/\lambda) = 11.8$ for magnetite, the individual Renninger reflections are expected to complexly overlap as suggested by Cole *et al.* (*16*, Fig. 4). This interpretation is confirmed by calculation with program MULREF (*17*), for strong and intermediate operating reflections and a half-thickness of the sphere of reflection (Δ) of 0.002 A^{-1} (Fig. 1). The latter parameter allows for crystal mosaicity and divergence of the incident beam (*17*). The maximum ω-rotation of the *Fd3m*-forbidden reflections in precession films suggests that the effective value of Δ may be as high as 0.010 A^{-1} in magnetite crystals. Therefore the observed peaks in ψ scans could be displaced by $\pm 0.5°$ or so from the calculated peak positions for $\Delta = 0.002$ A^{-1}, which is sufficient to account for the small discrepancies in Fig. 1. Quantitative explanation of simultaneous diffraction effects is dependent on precise knowledge of the mosaic structure of crystals and is certainly not possible at the present time. Moreover, Mo K_α radiation is too short for good peak resolution in most cases (Fig. 1) and there seems little point in attempting to identify individual reflections in the ψ scans. Minimum values in each scan are more likely to reflect an approach to true reflection intensity than loss of reflection intensity through simultaneous diffraction. Thus, on the basis of the large number of intensity measurements with $I < 0$ and $I < \sigma_I$, all of the 8 *Fd3m* reflections with $|F_0| > |F_c| \simeq 0$ in the original data list for magnetite No. 633 are now recognized as having zero Bragg intensity. Similarly, all of the *Fd3m*-forbidden reflections for both No. 633 and No. 633, MT1 are assigned zero intensity. The reflection 11, 3, 1 in the data list for No. 633, MT1 is assigned a nonzero intensity because of the small number of measurements with $I < \sigma_I$.

Crystal Structure Refinements

The ideal inverse-spinel structure of magnetite has been refined in space groups *Fd3m* and $F\bar{4}3m$ using several data sets for No. 633 and a single data set for No. 633, MT1 (Table II). The data set 633A is the original *Fd3m* reflection list for magnetite No. 633 (*1*). The data set 633B is the 633A list plus data for the *Fd3m*-forbidden reflections. The latter include 11 reflections which have zero intensity by the discriminant used in Fleet (*1*) and which have been assigned nonzero values of $|F_0|$ from a simple average of all the equivalent data collected. 633C is the 633A list with zero intensity assigned to the 8 *Fd3m* reflections with $|F_0| > |F_c| \simeq 0$. 633D is a new data set for magnetite No. 633 collected with the original crystal using the procedure of Fleet (*3*) but with $a = 8.3985(5)$ Å and $2\theta \leq 100°$. All of the weak reflections investigated by ψ scan (Table I) were assigned zero intensity (in fact, of the 8 *Fd3m* reflections with $|F_0| > |F_c| \simeq 0$ in the 633A list only 11, 7, 3 of the 633D data set has nonzero intensity on the basis of the discriminant used in Ref. *1*). Data set 633, MT1B includes the original *Fd3m* list for No. 633, MT1 (*3*) but with 644, 882, and 10, 8, 4 assigned zero intensity on the basis of the present ψ scan data (Table I).

The structure refinements were made as in Fleet (*1*, *3*) and the results are summa-

TABLE II

Fd3m AND $F\bar{4}3m$ STRUCTURE REFINEMENTS OF NATURAL AND ANNEALED NATURAL MAGNETITE

Refinement	Data set	Space group	B_{equiv} (A^2) O, O(1)	O(2)	R_w[a]	R[a]	S	$(\Delta/\sigma)_{max}$
1	633A	*Fd3m*	0.54(2)		0.033	0.025	2.4	0.001
2	633A	$F\bar{4}3m$	0.36(4)	0.80(6)	0.026	0.024	2.0	0.09
3	633B	$F\bar{4}3m$	0.45(5)	0.65(7)	0.029	0.026	2.1	0.08
4	633C	*Fd3m*	0.54(2)		0.024	0.022	1.8	0.001
5	633C	$F\bar{4}3m$	0.45(5)	0.68(6)	0.024	0.023	1.8	1.7
6	633D	*Fd3m*	0.55(1)		0.015	0.022	1.8	0.001
7	633D	$F\bar{4}3m$	0.54(5)	0.55(6)	0.016	0.023	1.9	2.8
8	633, MT1B	*Fd3m*	0.59(1)		0.016	0.017	1.6	0.000002
9	633, MT1B	$F\bar{4}3m$	0.62(7)	0.57(7)	0.015	0.016	1.6	1.0

[a] Including data for reflections with zero intensity.

rized in Tables II–IV.[1] The refinements used a weight of n/σ^2, where σ is calculated from agreement between n equivalent reflections. This procedure gives a lower weight to reflections of low multiplicity. However, the overall improvement in refinement compared to use of a weight of $1/\sigma^2$ was marginal. The weighting scheme of Grimes *et al.* (*12*), which gives a higher weight to weak and high-angle reflections, resulted in somewhat lower values of R_w with data sets 633A, 633B, and 633C but the corresponding values of R were essentially unchanged. Residual electron densities for the refinements of Table III are: refinement 1, $\Delta\rho$ = 0.3 to 3.1 e A^{-3}; 2, $\Delta\rho$ = 0.4 to 2.4; 4, $\Delta\rho$ = 0.3 to 2.6; 6, $\Delta\rho$ = 0.9 to 2.0; 8, $\Delta\rho$ = 0.4 to 4.2.

The $F\bar{4}3m$ refinements with data sets 633A and 633B (2, 3 in Table II) were slow to converge and the other $F\bar{4}3m$ refinements (5, 7, 9 in Table II) did not converge, but oscillated with continued refinement giving shifts in the O(1) and O(2) parameters of the same order of magnitude as the corresponding errors. Applying the Hamilton (*13*) R-ratio test to the refinements with data set 633A (1, 2 in Table II), $R_{5,147}$ = 1.247; the *Fd3m* structure can be rejected at the 99.5% level.

[1] See NAPS document No. 04346 for 12 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

Discussion

Systematic intensity measurements made with rotation about the scattering vector show that the *Fd3m*-forbidden reflections (*hk*0 with $h + k = 4n + 2$) appear to be absent in magnetite. All nonzero intensity measurements for these reflections can be attributed to simultaneous diffraction. The intensities of weak *Fd3m* reflections of magnetite are also enhanced by simultaneous diffraction and the 8 *Fd3m* reflections with $|F_0| > |F_c| \simeq 0$ in the data set used by Fleet (*1*; 633A, Table II) to refine the structure of magnetite No. 633 are properly assigned zero intensity. The 633A data set should not be used for comparative structure refinements since it contains sys-

TABLE III

POSITIONAL, THERMAL, AND EXTINCTION PARAMETERS FOR REFINEMENT OF NATURAL MAGNETITE

Refinement		1	2	4	6	8
		633A	633A	633C	633D	633, MT1B
Site	Parameter	$Fd3m$[a]	$F\bar{4}3m$	$Fd3m$[a]	$Fd3m$[a]	$Fd3m$[a]
$T(1)$	B_{11}[b]	349(14)	351(16)	348(11)	339(6)	387(7)
$T(2)$	B_{11}	—	342(17)	—	—	—
M	x	—	0.6253(1)	—	—	—
	B_{11}	461(14)	473(12)	465(11)	469(6)	503(7)
	B_{12}	45(5)	51(7)	48(3)	52(3)	56(3)
O(1)	x	0.3799(1)	0.8722(8)	0.37986(8)	0.37987(6)	0.37972(6)
	B_{11}	541(24)	355(44)	541(18)	550(9)	593(12)
	B_{12}	−3(17)	124(65)	−44(12)	−31(9)	−29(11)
O(2)	x	—	0.3817(4)	—	—	—
	B_{11}	—	795(61)	—	—	—
	B_{12}	—	−274(46)	—	—	—
	G[c]	1.33(10)	1.32(8)	1.33(7)	1.50(8)	0.21(2)

[a] Origin at $\bar{4}3m$, at $(-\frac{1}{8},-\frac{1}{8},-\frac{1}{8})$ from center $(\bar{3}m)$.

[b] Thermal parameters ($\times 10^3$ A^2) are calculated from $T = \exp\{-[B_{11}a^{*2}(h^2 + k^2 + l^2) + 2B_{12}a^{*2}(hk + kl + hl)]\}$.

[c] Isotropic-extinction parameter for type I extinction ($\times 10^{-4}$).

tematic errors which bias refinement in favor of a noncentrosymmetric structure. Such errors, which emanate from secondary extinction effects as well as simultaneous diffraction, have been reduced in data sets 633C, 633D, and 633, MT1B but not entirely eliminated.

Structure refinements with data sets 633C and 633D (Table II) favor the centrosymmetric $Fd3m$ structure for natural magnetite on the basis of the lack of convergence of the respective $F\bar{4}3m$ refinements. Similarly, the $Fd3m$ structure is also favored for annealed natural magnetite. The $F\bar{4}3m$ refinements 5, 7, and 9 (Table II) fail to converge because the deviations from the centrosymmetric $Fd3m$ model are so small as to be effectively singular. Corresponding O(1) and O(2) parameters are highly correlated (Table III) and sensible refinement cannot be attained.

The present refined $F\bar{4}3m$ structures of magnetite may also be rejected on stereochemical grounds. As illustrated in the data for refinement 2 (Tables II and III) the noncentrosymmetry is manifest very largely in the O(1) and O(2) thermal parameters, which depart markedly from equivalent $Fd3m$ values. In view of the small atomic displacements from centrosymmetry, the O(1) and O(2) thermal ellipsoids would be expected to be very comparable. However, with all of the 633 data sets, the O(1) ellipsoid contracts and the O(2) ellipsoid expands, leaving mean B_{equiv} values similar to corresponding $Fd3m$ values.

Both of the present $Fd3m$ refinements for magnetite No. 633 (4, 6 in Table III) yield essentially the same structure as that of Fleet (*1*). Extending the data set to $2\theta = 100°$ results only in slightly improved precision. The small differences between the annealed magnetite structure and the natural magnetite structure have been discussed elsewhere (*3*).

The present study reaffirms literature reports on the common occurrence of simultaneous diffraction effects in spinel phases. The mere observation of $Fd3m$-forbidden reflections in X-ray precession photo-

graphs, as in the study of thiospinels (*8*), is not sufficient evidence for noncentrosymmetry. Precession studies have to include observations with continuous radiation over a range of $\bar{\mu}$.

Simultaneous diffraction also enhances the intensities of weak reflections to an extent that may invalidate comparison of $Fd3m$ and noncentrosymmetric refinements. No attempt was made to investigate this possibility in the recent study of the structure of $MgAl_2O_4$ (*12*). The improvement in refinement using the $F\bar{4}3m$ structure of $MgAl_2O_4$ resides very largely in data for the weak reflections and the noncentrosymmetry is largely manifest in the O(1) and O(2) thermal parameters. Improved $|F_0|$, $|F_c|$ agreement for weak (and $Fd3m$-forbidden) reflections with $F\bar{4}3m$ is not too significant. Similar agreement was obtained for $F\bar{4}3m$ refinement of magnetite No. 633 with the 633B data set. The $F\bar{4}3m$ refinement of $MgAl_2O_4$ is closely comparable to the misleading $F\bar{4}3m$ refinements of magnetite with the 633A and 633B data sets (2, 3 in Table II). Clearly, further study is required to substantiate the proposed $F\bar{4}3m$ structure of $MgAl_2O_4$.

The structure of magnetite is centrosymmetric to within the resolution of existing X-ray procedures. In the present study, zero reflection intensity corresponds to $|F_{hkl}| < (0.004 - 0.005)\,|F_{000}|$. In view of the enhancement of the intensities of weak reflections by simultaneous diffraction and the diminution of the intensities of strong reflections by complex secondary extinction effects, improved resolution of spinel structure refinements is not anticipated with routine data collection procedures. Certainly intensity data for weak reflections should be regarded as unreliable unless demonstrated otherwise. Also, reduction in R_w and R is not synonymous with an increase in useful information when systematic errors are present in the data set. The present study has not systematically investigated the two other noncentrosymmetric cubic space groups which are maximal nonisomorphic subgroups of $Fd3m$ ($Fd3$ and $F4_132$, *4*, p. 692) because such a detailed comparative analysis does not seem to be warranted by the quality of the available intensity data. Both of these space groups ($Fd3$ and $F4_132$) give magnetite structures which are very similar to the $Fd3m$ structure.

The structure analysis of Fleet (*1*) reported residual electron density at equipoint position 8(*b*), which was attributed to the presence of interstitial Fe^{3+} cations in amounts <0.3% of total Fe cations. $Fd3m$ refinements with data sets 633A, 633B, and 633C show that the presence of this residual density is essentially independent of least-squares weighting scheme, simultaneous diffraction effects, and secondary extinction correction. Refinement without secondary extinction correction yields a residual map with the expected strong minima at the $T(1)$, M, and O(1) positions, and strong minima at all of the possible tetrahedral and octahedral interstitial cation positions except 8(*b*), which has a (relatively) strong maximum. With $F\bar{4}3m$ refinement and the above data sets the 8(*b*) density is no longer the strongest residual maximum but, nevertheless, it is still a significant feature. Refinements 6 and 7, with the data set 633D collected in the present study, yield a weak residual *minimum* at equipoint position 8(*b*) which is replaced by a prominent maximum when these refinements are repeated without secondary extinction correction. This suggests that while the present isotropic secondary extinction correction results in improvement in refinement of the ideal inverse spinel structure it tends to obscure resolution of additional structural features. Comparison of equivalent reflection intensities reveals that secondary extinction in magnetite and $MgAl_2O_4$ (*12*) is, in fact, markedly anisotropic. However, in the absence of a more complete understanding of

the possible effects of extinction terms on the residual map of magnetite, there remains the possibility that the residual electron density in question is not related to the magnetite structure.

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