Charge ordered structure of magnetite Fe₃O₄ below the Verwey transition

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The crystal structure of highly stoichiometric magnetite (Fe₃O₄) below the Verwey transition has been refined from high-resolution neutron and synchrotron x-ray powder-diffraction data. The refined model has a monoclinic P2/c symmetry cell with orthorhombic *Pmca* pseudosymmetry constraints on the atomic positions, and contains four independent octahedral *B* site iron atoms. Charge ordering is evidenced by the presence of expanded and contracted BO_6 octahedra, and by the distribution of *B-B* distances resulting from unequal Coulombic repulsions between the different *B* site charges. The *B-B* distances are inconsistent with dimer formation. Competition between the *B*-O and *B-B* interactions results in polar displacements of two of the *B* site cations. The charge ordering has a predominant [001] density modulation, which relieves a nesting instability in the electronic density of states, but a second $[00\frac{1}{2}]$ phase modulation also occurs. The monoclinic distortion at the Verwey transition is consistent with a macroscopic rhombohedral magnetostriction, driven by the localization of orbitally degenerate Fe²⁺, coincident with the microscopic charge ordering distortions that have an orthorhombic lattice symmetry.

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I. INTRODUCTION

The magnetic properties of magnetite (Fe₃O₄) minerals were first recorded by Greek writers ~800 B.C. and magnetite lodestones were used as a compass by early navigators. During the twentieth century, derived materials such as γ -Fe₂O₂ for magnetic recording and the spinel ferrites for high-frequency applications in transformers, inductors, and radio antenna were developed. The magnetoresistive properties of polycrystalline and thin films of magnetite are of current interest for spin electronics.¹ The ferrimagnetism and moderate electrical conductivity ($\sim 10^{-2} \Omega$ cm at 300 K) of magnetite arise from its inverse spinel-type crystal structure. This is formally written as $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$ to show that the first (A type) Fe^{3+} is tetrahedrally coordinated, whereas the bracketed Fe^{2+} and Fe^{3+} ions occupy (*B* type) octahedrally coordinated sites. At ambient temperatures, the incomplete cancellation of the two B site magnetic moments by the antiparallel A site cation moment results in ferrimagnetism, and delocalization or hopping of the minority-spin "extra" electron between the *B* site Fe^{2+} and Fe^{3+} ions renders the *B* sites structurally and spectroscopically equivalent, and gives rise to the electronic conductivity.

Followed an earlier report of a heat-capacity anomaly,² Verwey made the fundamental discovery that magnetite undergoes a sharp, first-order transition on cooling below ~ 120 K, at which the resistivity increases sharply by two orders of magnitude,³ and the structure distorts from cubic symmetry.

This is consistent with charge ordering of the Fe^{2+} and Fe^{3+} states on the *B* sublattice, and an orthorhombic superstructure model (Verwey model) was proposed.⁴ Despite much research, no conclusive structural model of the low-temperature phase has emerged. The Verwey model was apparently confirmed by neutron diffraction,⁵ however, later research showed that multiple-scattering effects flawed this experiment and disproved the model.⁶

Further observations of superstructure reflections⁷ indexed as $(h,k,l+\frac{1}{2})_c$ on the cubic unit cell (the "c" subscript refers to the high-temperature cubic cell throughout), and not predicted by the Verwey model, show the symmetry to be monoclinic. The low-temperature structure was shown to have a $\sqrt{2}a_c \times \sqrt{2}a_c \times 2a_c$ crystallographic supercell with space group Cc, from a neutron-diffraction study of a partially detwinned single crystal.8 The observation of monoclinic lattice symmetry was also confirmed by a singlecrystal x-ray study.9 The observation of a magnetoelectric effect¹⁰ indicated the symmetry in the low-temperature phase should be no higher than P1, and an x-ray topography study¹¹ showed twins that were interpreted as being due to a triclinic distortion. However, a recent spectroscopic investigation failed to observe the Raman and infrared phonon modes that should be active if the low-temperature phase lacks inversion symmetry.¹² Thus, the question of the symmetry of the low-temperature phase remains controversial, although any distortion from the Cc monoclinic cell is accepted to be very small, compared to the distortion from cubic to monoclinic symmetry.

The most detailed structure refinement below T_V resulted from a neutron-diffraction study of an almost fully detwinned single crystal by Iizumi *et al.*¹³ The authors used an $a_c/\sqrt{2} \times a_c/\sqrt{2} \times 2a_c$ subcell of the unit cell identified above and imposed orthorhombic symmetry constraints on the atomic positions to reduce the number of free parameters in the low-temperature crystal structure. Centric space group *Pmca* (a nonstandard setting of *Pbcm*) and acentric *Pmc2*₁ refinements were reported. By grouping the observed superstructure reflections according to symmetry requirements it was shown that these higher-symmetry models account for the bulk of the atomic displacements, and any further distortions are very small. Although large atomic displacements of Fe and O atoms were found, no charge ordered arrangement was identified in the refined structure.

Diffuse streaking has been reported in electron-14 and neutron-¹⁵ scattering experiments above T_V , evidencing a marked softening of the phonon modes at temperatures up to 200 K. Diffuse resonant x-ray scattering at the Fe K edge above T_V , that disappeared when the energy was tuned away from the edge,¹⁶ was explained as a 1:3 (or 3:1) ordering of Fe^{2+} and Fe^{3+} ions along [110]_c directions, suggesting that the charge disproportionation is coupled to the phonon mode softening above T_V . DAFS (differential anomalous fine structure) measurements of the (002) and (004) reflections above T_V indicate that the octahedral sites are equivalent on a time scale of 10^{-16} s, ¹⁷ suggesting that the valence electrons are delocalized, rather than hopping rapidly above T_V . DAFS measurements below T_V (Ref. 18) place an upper limit of any charge disproportionation at \sim 25%, provided that Cc symmetry and the Anderson criterion (see below) are fulfilled. However, $(0 4 \frac{1}{2})$ superstructure peak intensities measured as a function of x-ray energy around the Fe K edge in a different study showed features that strongly suggest charge ordering.19

Mossbauer spectra demonstrate that localized Fe^{2+} and Fe^{3+} are present at the octahedral sites, and a recent study resolved two environments for each cation in addition to the tetrahedral Fe^{3+} signal.²⁰ An ⁵⁷Fe NMR study²¹ has resolved 8 tetrahedral and 15 octahedral iron environments, in keeping with the 8 unique *A* and 16 unique *B* sites expected in the monoclinic *Cc* symmetry supercell. However, the chemical shifts of the octahedral cations were intermediate between those of normal Fe^{2+} and Fe^{3+} . More recent ⁵⁷Fe NMR data from a single crystal have resolved all 16 octahedral site signals and measured their angular dependence.²²

Several proposed charge ordered models^{23–25} have been compared to electron-diffraction data. Reference 25 provides a useful list of models for charge order on the 16 octahedral sites in the crystallographic unit cell and space group Cc, which satisfy the Anderson criterion²⁶ for minimal electrostatic repulsion. The octahedral *B* sites in the spinel structure make up a network of corner-sharing B_4 tetrahedra, and the Anderson criterion is that each tetrahedron contains two Fe²⁺ and two Fe³⁺ states. These constraints allow only ten possible charge ordered models with *Cc* symmetry.



FIG. 1. (440) and (800) synchrotron x-ray-diffraction peaks from Fe_3O_4 below (90 K) and above (130 K) the Verwey transition. The 90 K data are displaced above the 130 K data for clarity.

In the absence of a definitive structure, many theoretical models for the low-temperature structure of Fe₃O₄ have been proposed. Purely electronic²⁷ and electron-phonon models for charge ordering have been described.^{28,29} A bond dimerized ground state without charge separation has also been proposed recently.³⁰

The problems of multiple-scattering, extinction, and twinning effects, which beset single-crystal studies of magnetite below T_V , gave rise to the present powder-diffraction study. Multiple scattering is much reduced in a powder sample due the reduced size of the crystallites, primary extinction usually has a minimal effect on the reflection intensities, and twinning is irrelevant. We have previously investigated the temperature dependence of the pseudorhombohedral distortion in the low-temperature structure of Fe₃O₄ using neutron powder diffraction.³¹ Loss of information due to peak overlap is the main disadvantage of powder methods. To overcome this, very high-resolution diffractometers are used, and powder x-ray and neutron data from the same sample may be combined in the Rietveld data analysis. We report here the detailed structure of Fe₃O₄ at 90 K from combined synchrotron x-ray and neutron studies of a highly stoichiometric sample. Initial results have been reported previously.³²

II. EXPERIMENT

A highly stoichiometric magnetite powder (Fe_{3-3 δ}O₄ with $\delta \approx 0.000$) was obtained by grinding single crystals



FIG. 2. Relationships between the unit cells referred to in the text.

grown by the skull melter technique. A trace of Fe_2O_3 (0.8) wt % by Rietveld analysis), perhaps arising from surface oxidation of the powder during grinding, was found in the diffraction patterns for this sample. High-resolution neutron powder-diffraction data were collected at 90 and 130 K using the high-resolution neutron powder-diffractometer (HRPD) instrument at the ISIS spallation source, United Kingdom.³³ Approximately 10 g of sample was loaded into a vanadium sample can and mounted in a closed-cycle refrigerator to maintain temperature control while retaining a low instrumental background. Data were collected at 90 K for a total of 460 μ A h and at 130 K for 330 μ A h in a time of flight (ToF) range of 15–215 ms, which corresponds to a *d*-spacing range of 0.31–4.45 Å. Data from the backscattering detector bank were summed and corrected for the incident neutron spectrum and detector efficiency.

Synchrotron x-ray powder data were collected at 90 and 130 K for approximately 18 h at each temperature using the BM16 instrument at European Synchrotron Radiation Facility (ESRF), Grenoble, France.³⁴ The sample was ground manually to reduce the particle size and ensure a good powder average. A wavelength of 0.493 95 Å, defined by Si(111) monochromator and Ge(111) analyzer crystals, was used to minimize absorption, and the sample was spun in a 0.7 mm capillary cooled by an Oxford Cryosystems cryostream. Rapid temperature scans were also carried out for 2 min per pattern in the angular range $2\theta = 5.0^{\circ} - 23.5^{\circ}$, warming in steps of 2.3 K from 102 K through the transition. The General Structure Analysis System package was used for Rietveld fits to the data.

III. RESULTS

A. Unit-cell metric

Figure 1 shows the (800) and (440) reflections from the synchrotron x-ray data at 130 and 90 K. A large 1:1 splitting of the (440) peak is observed, confirming that the distortion of the unit cell is principally rhombohedral. The unequal widths of the (440) and ($4\overline{40}$) peaks, and the shoulder on the (800) peak, result from the smaller monoclinic distortion. No

further distortions were required to account for the peak broadenings and splittings. Figure 2 shows the relationships between the unit cells in the low- and high-temperature phases.

Numerous superstructure peaks were identified by comparing the 90 and 130 K profiles. All of these superstructure peaks were indexed on the monoclinic unit cell previously proposed,⁸ which has Cc symmetry and axes;

$$\mathbf{a}_{\mathbf{m}} = -(\mathbf{a}_{\mathbf{c}} + \mathbf{b}_{\mathbf{c}}),$$
$$\mathbf{b}_{\mathbf{m}} = (\mathbf{a}_{\mathbf{c}} - \mathbf{b}_{\mathbf{c}}),$$
$$\mathbf{c}_{\mathbf{m}} = 2\mathbf{c}_{\mathbf{c}}.$$

However, the reduced cell with $\mathbf{a} = \mathbf{a}_m/2$, $\mathbf{b} = \mathbf{b}_m/2$, and $\mathbf{c} = \mathbf{c}_m$ was able to account for all observed superstructure intensities except for three very weak reflections. This reduced cell was used in the previous single-crystal neutron-diffraction study.¹³ Unit-cell parameters determined by fitting the 90-K synchrotron x-ray peaks were a = 5.94441(2), b = 5.92472(2), and c = 16.77508(6) Å, and $\beta = 90.2365(2)^\circ$. The thermal evolution of the (440) x-ray peak (Fig. 3) shows that the first-order structural transition from monoclinic to cubic symmetry occurs rapidly between 116 K and $T_V = 122$ K.

B. Structure refinements

Fitting the x-ray intensities was initially problematic, since the peaks displayed significant tails that could not be accounted for using standard functions. However, the shapes were described well by a sum of two Lorentzian functions with different full widths at half maximum. Figure 4 illustrates the improvement in fit achieved using this peak shape description. This effect reflects the exceptionally high instrumental resolution of BM16; the second, broader, Lorentzian results from the Ge analyzer crystals and the presence of a tail of very small crystallites in the mechanically ground sample. The neutron-diffraction peaks were described by a standard ToF peak shape,³⁵ convoluted with a Lorentzian sample broadening function.



FIG. 3. Thermal evolution of the magnetite (404) x-raydiffraction peak through the Verwey transition.

The refined models at 130 K were used to generate starting models at 90 K by transforming the unit cell to space group P2/m with conventional monoclinic axes (Fig. 2). $Fd\overline{3}m$ symmetry constraints were applied to the atomic parameters, so that there was still only one variable positional parameter (the oxide *u* coordinate). Table I summarizes the results of the Rietveld refinements with pseudocubic symmetry. All of the intense peaks in the 90 K data sets were fitted well by this model, although it does not account for the superstructure peaks.

Magnetic moments in the low- and high-temperature models were aligned along the *c* axis, which is coincident for the cells (Fig. 2). For the cubic phase, neutron powder data are insensitive to moment directions, since only their relative orientations affect the intensities. The magnitudes of the moments for the *A* and *B* sites are in keeping with the inverse $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$ charge distribution. In the lowtemperature phase, the approximately rhombohedral cell distortion allows components of the moments parallel and perpendicular to the pseudothreefold axis to be refined



FIG. 4. Fits to the Fe₃O₄ (400) x-ray-diffraction peak at T = 130 K using a pseudo-Voigt function (lower difference curve) and a sum of two Lorentzians (upper difference curve). The difference curves are shown as $50 \times (\text{difference/e.s.d.})$ (e.s.d.= estimated standard deviation).

independently. However, we found that good fits were obtained with the moments remaining along the c axis and fixed the moment directions accordingly. Significant magnetic intensities are only observed at long d spacings, due to the magnetic form factor, and the majority of superstructure peaks did not fall into this range. All octahedral B sites were therefore constrained to have the same magnetic moment value, since the HRPD data did not give stable refinements of independent moments for the various octahedral sites.

Initial attempts at refinement of the low-temperature structure in space group P2/c (Fig. 2) were unstable and the data did not support such a large number of variable parameters. Pseudosymmetry constraints were necessary in order to obtain a convergent refinement. Combined refinements with both the x-ray and neutron data were carried out in order to maximize the observations to parameters ratio for the lowtemperature phase. A number of space groups that may be derived from a descent in symmetry from $Fd\overline{3}m$ were tested. The orthorhombic group *Pmca* (as used by Iizumi *et al.*¹³) gave a much better fit than any other space group. We were unable to fit the superstructure reflections using higher symmetries, and removal of any of the *Pmca* pseudosymmetry elements such as the inversion center (which results in $Pmc2_1$ symmetry) led to instabilities. Refinements were started by applying small random displacements to the atomic positions to avoid ill-conditioning of the least-squares matrix. The refinements in Pmca were found to be robust and returned to the same minimum after atoms were displaced away from the refined positions. Several pairs of sites in the P2/c cell were constrained to have equivalent coordinates by the Pmca symmetry operators; these sites are labeled "a" and "b", e.g., B(1a) and B(1b), in Table II. The four inequivalent sites B(1)-B(4) in our model each represent an averaging over 4 of the 16 unique B sites in the larger Cc supercell.

Atomic coordinates, thermal displacement parameters, and magnetic moments are listed in Table II with a comparison to the values obtained previously.¹³ Interatomic distances are listed in Table III, and bond valence sums (BVS's) (calculated from standard parameters³⁶) and renormalized valences V are given in Table IV. The renormalized valences were obtained by setting the tetrahedral sites to +3 and rescaling the B site values to average to +2.5, in keeping with the accepted inverse charge distribution between the A and B sites in Fe₃O₄. The profile fits are displayed in Fig. 5, using a logarithmic intensity scale to make the superstructure peaks visible. Figure 6 shows a comparison of the structures refined at 90 K with cubic and Pmca symmetry constraints. The distortions from the $Fd\overline{3}m$ structure have been exaggerated by a factor of 3 to make the displacements more obvious.

IV. DISCUSSION

A. Evidence for Charge Order

The primary structural evidence for a charge ordering transition is the appearance of distinct metal sites with significantly different mean distances to the surrounding anions

TABLE I. Results from initial Rietveld fits to powder neutron (HRPD) and x-ray (BM16) data using a standard spinel model with $Fd\overline{3}m$ symmetry at 130 K [A site Fe at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$; B site Fe at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; O at $(\frac{1}{4}+u, \frac{1}{4}+u, \frac{1}{4}+u)$] and a monoclinic P2/m cell (Fig. 2) at 90 K with $Fd\overline{3}m$ symmetry constraints on the atomic positions. Cell parameters, residuals, the O coordinate *u*, isotropic thermal parameters, and magnetic moments for the neutron fits are listed. Distances and bond valence sums (BVS's) from the 130 K HRPD refinement are also given.

Variable] T	HRPD 7=90 K	HRPD T = 130 K	BM16 T=90 K	Т	BM16 = 130 K
a/Å	5.	9419(1)	8.3939(2)	5.944 41(2)	8.3	90 405(3)
b/Å	5.	9251(1)		5.924 72(2)		
$c/\text{\AA}$	8.	3858(1)		8.387 54(3)		
eta / $^{\circ}$	90).255(5)		90.23 65(2)		
R_p (%)		8.29	7.67	6.02		4.29
$R_{wp}^{'}$ (%)		9.26	7.51	8.26		5.35
χ^2		11.50	4.75	6.80		3.18
$u(\times 1000)$	4	5.07(5)	4.90(5)	5.21(5)		5.21(3)
$U_{\rm iso}$ A	(0.16(1)	0.117(8)	0.051(3)	().134(3)
(×100) B	(0.54(1)	0.307(9)	0.265(3)	().298(2)
Å ² O	(0.25(1)	0.285(11)	0.280(9)	().395(6)
μ/μ_B A	2	1.44(4)	4.20(3)			
В	_	4.10(2)	-3.97(2)			
130 K (HRPD) res	sults:					
Distances (Å)	A-O (×4)	1.8885(6)	<i>B</i> -O (×6)	2.0582(4)	<i>B-B</i> (×6)	2.9677(1)
BVS	Α	2.82	В	2.57	0	1.99

in the low-temperature phase. The mean B-site-to-oxygen distances (Table III) or the equivalent BVS calculations (Table IV) show that the octahedral iron sites are split into two groups below the Verwey transition with V = 2.4 and 2.6, as discussed previously.³² The magnitude of the charge separation is only 20% of that expected for ideal Fe²⁺ and Fe³⁺ states. This may result in part from structural averaging, since each B site in the *Pmca* model is averaged over four inequivalent subsites in the larger $\sqrt{2}a_c \times \sqrt{2}a_c \times 2a_c$ Cc supercell, so that our large [B(1) and B(4)] and small [B(2)and B(3)] subsites could, respectively, be averaged over four Fe^{2+} and four Fe^{3+} subsites (which we refer to as class-I charge order), or over (three $Fe^{2+} + Fe^{3+}$) and $(Fe^{2+} + three Fe^{3+})$ subsites (class-II charge order). Hence, in the class-II models the charge separation would be 40% in the full Cc superstructure, but is averaged to 20% in our Pmca-constrained subcell. The Anderson criterion is not met by either class.

In comparing several transition-metal oxides that undergo a Verwey-like transition from a high-temperature chargeaveraged state to a low-temperature charge ordered state,³⁷ the charge separation estimated from bond distances or BVS's ranges from 24% (in $Y_2Ni^{2+}Ni^{4+}O_6$) to 60% (in YBaCo²⁺Co³⁺O₅) of the ideal value. Forty percent of the ideal separation between Fe²⁺ and Fe³⁺ is found in TbBaFe₂O₅.³⁸ The charge disproportionation is significantly reduced from the ideal value in all experimentally determined structures. The observed charge difference of 20% (for class-I charge order) or 40% (for class-II) of the ideal value in Fe₃O₄ is therefore not anomalous in comparison to other oxides. This effect was not known when the previous low-temperature refinement of Fe₃O₄ was published,¹³ which may explain why the differences between average Fe-O distances were not thought to evidence charge order. Although some of the previously determined coordinates differ significantly from ours (see Table II), the mean Fe-O distances of 2.071, 2.039, 2.053, and 2.062 Å for sites B(1)-B(4), respectively, in the previous model do not differ significantly from the values in Table III. However, the distribution of these mean distances is less bimodal than in our model, perhaps making the charge ordering less apparent.

The reason why the apparent charge separation in metal oxides is so reduced from the expected value is an unresolved issue requiring further theoretical analysis. One possible explanation is that the mixing of the ionic ground state $Fe^{2+}...Fe^{3+}...Fe^{3+}...Fe^{3+}...$ with excited states such as $Fe^{2+}...Fe^{2+}...Fe^{3+}...Fe^{3+}...$, etc. is strong in charge disproportionated oxides, because the symmetry equivalence of sites is broken only by the charge order. Other explanations such as strained charge states or intersite disorder may also be relevant. However, since the magnitude of the apparent charge ordered oxides, it is justifiable to describe magnetite as being charge ordered insofar as any transition-metal oxide is considered to be charge ordered.

B. Periodicity of the charge order

The $P2/c \ a_c/\sqrt{2} \times a_c/\sqrt{2} \times 2a_c$ cell used in the present refinement has the same **c** cell vector as the large Cc supercell, but only half the **a** and **b** vector lengths. Hence, the periodicity of the charge ordering along **c** is evident, but ab-plane modulations in the Cc structure are mostly lost by averaging in the P2/c cell and by the imposition of Pmca symmetry constraints.

TABLE II. Refined atomic coordinates for Fe₃O₄ at 90 K with values from the previous 10 K refinement (Ref. 13) shown underneath in italics for comparison. The cell has monoclinic *P2/c* symmetry, but the coordinates were constrained by the symmetry operations of orthorhombic space group *Pmca*. Residuals: $R_{wp} = 6.86\%$, $R_p = 4.87\%$, $R_{F^2} = 9.23\%$, and $\chi^2 = 5.99$. Cell parameters: a = 5.944407(14), b = 5.924701(17), and c = 16.77515(14) Å, and $\beta = 90.2363(2)^{\circ}$.

Atom	<i>x</i>	У	<i>z</i>	$U_{\rm iso}$ (Å ²)	$\mu (\mu_B)$
A(1)	1/4	0.0034(4)	0.06366(7)	0.00005(4)	4.44(3)
		0.0049(3)	0.0635(1)	0.0006(5)	
A(2)	1/4	0.5061(2)	0.18867(8)	0.00005(4)	4.44(4)
		0.5067(2)	0.1887(1)	0.0006(5)	
<i>B</i> (1a)	0	1/2	0	0.000 70(3)	-4.17(2)
				0.0016(6)	
<i>B</i> (1b)	1/2	1/2	0	0.000 70(3)	-4.17(2)
				0.0016(6)	
<i>B</i> (2a)	0	0.0096(3)	1/4	0.000 70(3)	-4.17(2)
		0.0099(3)		0.0018(6)	
<i>B</i> (2b)	1/2	0.0096(3)	1/4	0.000 70(3)	-4.17(2)
		0.0099(3)		0.0018(6)	
B(3)	1/4	0.2659(2)	0.38010(9)	0.000 70(3)	-4.17(2)
		0.2643(4)	0.3789(1)	0.0013(6)	
B(4)	1/4	0.7520(2)	0.37659(9)	0.000 70(3)	-4.17(2)
		0.7549(5)	0.3746(2)	0.0001(4)	
O(1)	1/4	0.2637(7)	-0.0023(3)	0.002 27(8)	
		0.2630(6)	-0.0027(2)	0.0020(8)	
O(2)	1/4	0.7461(6)	-0.0029(3)	0.002 27(8)	
		0.7477(6)	-0.0009(2)	0.0016(8)	
O(3)	1/4	0.2447(8)	0.2542(3)	0.002 27(8)	
		0.2461(7)	0.2450(2)	0.0034(8)	
O(4)	1/4	0.7738(8)	0.2525(3)	0.002 27(8)	
		0.7696(6)	0.2427(2)	0.0025(6)	
O(5a)	-0.0091(4)	0.0095(6)	0.1277(2)	0.002 27(8)	
	-0.0116(6)	0.0089(3)	0.1295(2)	0.0022(6)	
O(5b)	0.4909(4)	0.0095(6)	0.3723(2)	0.002 27(8)	
	0.4884(6)	0.0089(3)	0.3705(2)	0.0022(6)	
O(6a)	-0.0081(4)	0.5046(6)	0.1246(2)	0.002 27(8)	
	-0.0067(6)	0.5050(3)	0.1244(1)	0.0014(6)	
O(6b)	0.4919(4)	0.5046(6)	0.3754(2)	0.002 27(8)	
	0.4933(6)	0.5050(3)	0.3756(1)	0.0014(6)	

The arrangement of the two *B* cation charge states in the refined model is shown in Fig. 7. Two charge modulations parallel to c are apparent. The average charge density has a [001], modulation, as reported previously.³² Band-structure calculations³⁹ of the cubic phase show nesting on the Fermi surface at the $[001]_c$ (X) point, corresponding to an instability in the states of the "extra" (minority-spin) t_{2g} electrons. The small [001], deformations open up a gap in the energy spectrum (estimated to be 150 meV from photoemission studies⁴⁰) leading to the observed loss of conductivity at the Verwey transition. This is essentially a charge-density wave (CDW) mechanism, but with strong electron-lattice coupling that leads to a commensurate CDW as electrons are localized at atomic sites. A frozen $[001]_c$ charge-density wave model has recently been proposed from NMR measurements by Mizoguchi²² and the observed critical scattering above T_V strongly supports such a mechanism.⁴¹

The electron-lattice coupling in oxides such as magnetite is much stronger than in classic CDW materials such as metal chalcogenides, so that electrons are essentially localized on distinct Fe sites. This forces a second charge modulation because the nodal planes of the $[001]_c$ wave contain chains of *B* site irons at $z = \frac{1}{8}$, $\frac{3}{8}$, etc. Ordering of electrons on alternate sites in these chains leads to a $[00\frac{1}{2}]_c$ charge modulation, since the ordering at $z = \frac{1}{8}$ has the opposite phase to that at $z = \frac{5}{8}$ [see Fig. 7(a)]. Thus, the charge order in magnetite is described by both $[001]_c$ and $[00\frac{1}{2}]_c$ vectors. The charge density has the $[001]_c$ modulation while the phase of the charge order in the $[001]_c$ nodal planes has the $[00\frac{1}{2}]_c$ vector. The condensation of $[001]_c$ (*X*-type) and $[00\frac{1}{2}]_c$ (Δ type) phonons at the Verwey transition has been reported previously, and these distortions result from the charge order as discussed later.

Two classes of charge ordering over the 16 Fe sites in the Cc supercell are consistent with the 4 observed B sites in the present Pmca refinement. There is a single class-I model

TABLE III. Fe-O distances in Fe_3O_4 at 90 K with mean values for the $A\text{O}_4$ tetrahedra and $B\text{O}_6$ octahedra shown.

Bond	Length (Å)	Bond	Length (Å)
A(1)-O(1)	1.898(4)	A(2)-O(4)	1.913(5)
A(1)-O(5)	1.875(2)	A(2)-O(6)	1.870(2)
A(1)-O(5)	1.882(2)	A(2)-O(6)	1.877(2)
A(1)-O(2)	1.890(4)	A(2)-O(3)	1.899(5)
$\langle A(1)-O \rangle$	1.886(3)	$\langle A(2)-O \rangle$	1.890(4)
B(1)-O(1) ×2	2.042(3)	$B(2)-O(5) \times 2$	2.052(3)
$B(1)-O(6) \times 2$	2.091(3)	$B(2)$ -O(4) $\times 2$	2.040(3)
B(1)-O(2) ×2	2.082(3)	B(2)-O(3) ×2	2.038(4)
$\langle B(1)-O \rangle$	2.072(3)	$\langle B(2)$ -O \rangle	2.043(3)
$B(3)-O(5) \times 2$	2.092(3)	$B(4)-O(5) \times 2$	2.094(3)
$B(3)-O(6) \times 2$	2.018(3)	$B(4)-O(6) \times 2$	2.053(3)
B(3)-O(2)	1.964(5)	B(4)-O(1)	2.033(5)
B(3)-O(3)	2.116(5)	B(4)-O(4)	2.086(5)
$\langle B(3)-O\rangle$	2.050(4)	$\langle B(4)-\mathrm{O}\rangle$	2.069(4)

with Fe²⁺ at the B(1) and B(4) sites, and Fe³⁺ at B(2) and B(3), 32 class-II models with (three Fe²⁺ + Fe³⁺) at the B(1) and B(4) sites, and (Fe²⁺ + three Fe³⁺) at the B(2) and B(3) sites. Class-II models appear more plausible than the class-I arrangement, since they can account for the larger Cc superstructure, the 16 *B* site resonances seen by NMR, and have lower electron-electron Coulombic repulsions. The latter is clearly not a strong constraint, since the Anderson criterion is not satisfied by any of the class-I or II models. However, calculations of the electrostatic energies show that one class-II model minimizes the repulsions between the localized electrons, and we previously proposed this model as a plausible charge ordered structure for magnetite.³² Reliable intensities for the additional Cc superstructure reflections would be required to distinguish between the 33 class-I and

TABLE IV. Bond valence sums (BVS's) and renormalized valences (V) for all sites in the refined 90 K structure of Fe₃O₄.

Atom	BVS	V
A(1)	2.80	3.00
A(2)	2.77	3.00
<i>B</i> (1a)	2.49	2.38
<i>B</i> (1b)	2.50	2.39
<i>B</i> (2a)	2.73	2.61
<i>B</i> (2b)	2.73	2.61
<i>B</i> (3)	2.71	2.59
B(4)	2.52	2.41
O(1)	2.04	2.00
O(2)	2.06	2.00
O(3)	1.97	2.00
O(4)	1.97	2.00
O(5a)	1.94	2.00
O(5b)	1.96	2.00
O(6a)	2.03	2.00
O(6b)	2.05	2.00

-II models. We estimate the average difference in Fe-O distances between the present *Pmca*-averaged model and a fully charge ordered class-II *Cc* structure (with 40% of the ideal Fe^{2+}/Fe^{3+} size difference) to be 0.012 Å, and this represents the uncertainty limit in approximating the "true" *Cc* structure by the *P2/c* subcell when discussing the structural features in later sections. The difference of 0.012 Å is only about three times the typical refinement error in Fe-O distances (Table III), so the deviations of the present structure from the "true" *Cc* structure are marginal within the error estimates. This is corroborated by the very weak x-ray and neutron intensities of the *Cc* superstructure peaks, only three of which were observed in our data.

C. Lattice Distortion

A sharp, first-order structural change occurs at the Verwey temperature. The structural symmetry is lowered from cubic $Fd\overline{3}m$ to a monoclinic Cc, $\sqrt{2}a_c \times \sqrt{2}a_c \times 2a_c$ supercell although the previous¹³ and the current structure refinements show that virtually all the diffracted intensity is described by a smaller $a_c/\sqrt{2} \times a_c/\sqrt{2} \times 2a_c$ cell (the *P2/c* cell in Fig. 2). The symmetry and periodicity of this cell are consistent with two consequences of electron localization on the B sites at the Verwey transition. The first of these is the charge order (Fig. 7), which, as described above, gives rise to X-type $[001]_c$ and Δ -type $[00\frac{1}{2}]_c$ modulations and lowers the cell symmetry to orthorhombic *Pmca* $a_c/\sqrt{2} \times a_c/\sqrt{2} \times 2a_c$. The resulting microscopic distortions are discussed in the next section. Further ab-plane charge order according to the class-II models can account for the larger $\sqrt{2}a_c \times \sqrt{2}a_c$ $\times 2a_c$ supercell.

A second consequence of charge localization is that Fe²⁺ states in a magnetically ordered material can give rise to a magnetostriction, as the orbital moment couples to the magnetization easy axis, which is [111], below the Verwey transition. The low-temperature cell can be described to a first approximation by an $F\overline{3}m$ rhombohedral cell, with parameters $a_c = 8.390$ Å, $\alpha = 89.82^{\circ}$ for the present Fe₃O₄ sample at 90 K. Magnetostrictions are usually observed when insulating materials are cooled through a magnetic ordering transition, for example, cubic FeO undergoes a rhombohedral distortion at the 200 K Néel transition. The low-temperature structure can be described as Fe₄O₄ having an F3 symmetry cell with parameters $a_c = 8.629$ Å, $\alpha = 89.42^{\circ}$ for near-stoichiometric FeO at 10 K.⁴² The magnitudes of the rhombohedral distortions per Fe^{2+} ion are comparable for the two materials, showing that the rhombohedral distortion in Fe₃O₄ is consistent with the single-ion magnetostriction from localization of Fe²⁺. Large magnetostrictions have been observed in doped magnetites with Fe^{2+} localized on B sites, for example, $CrFe_2O_4$ ($Fe^{3+}[Fe^{2+}Cr^{3+}]O_4$).⁴³ The coupling of a magnetic field to the Verwey cell distortion was used to detwin the crystal in the previous study.¹³

The combination of the orthorhombic charge ordering distortion and the rhombohedral magnetostriction lowers the lattice symmetry to monoclinic. The magnetostriction is a macroscopic lattice distortion and so is the predominant fac-



FIG. 5. Observed, calculated, and (offset below) difference/e.s.d. curves for the simultaneous Rietveld fit to (a) synchrotron and (b) neutron 90 K powder-diffraction data of Fe_3O_4 . Observed and calculated intensities are plotted on a logarithmic scale. 130 K data are shown for comparison, offset one decade above the 90 K profiles for clarity. Fe_2O_3 impurity peaks are marked.

tor in the cell distortion, but is not apparent in the internal distortions. The charge order leads to large microscopic distortions that are evident in the internal coordinates, but gives only a small lattice distortion that lowers the symmetry from rhombohedral to monoclinic.

D. B site Fe-Fe distances

The pattern of *B*-*B* distances is important as it enables the possibility of Fe-Fe dimerization³⁰ to be investigated. A large range of *B*-*B* distances, from 2.86 to 3.05 Å, is observed in our model (Table V), comparable to the dispersion of *B*-O



FIG. 6. Pattern of atomic displacements in the 90 K refined Fe_3O_4 model (filled circles) compared to the high-temperature cubic phase positions (open circles). The displacements have been exaggerated by a factor of 3 for clarity.

distances. In a dimerization scenario, one-in-six of the *B-B* distances are short and five-out-of-six are long, with each *B* site participating in one of the short bonded contacts. This is not supported by the observed pattern of distances (Table V) in which three of the twelve *B-B* distances are notably shorter than the rest, and these all originate at the same site, B(3). Goodenough⁴⁴ estimated the critical distances below which metal-metal bonding occurs in oxides to be 2.58 Å for Fe³⁺-Fe³⁺ and 2.95 Å for Fe²⁺-Fe²⁺. Dimers in Fe₃O₄

would formally be Fe^{2+} - Fe^{3+} bonds with a critical distance of ≈ 2.77 Å, which is 0.1 Å below the shortest observed distance.

The pattern of B-B distances can be rationalized by considering only the Coulombic repulsions between ordered B site charges. Each B cation is at the shared apex of two B_4 tetrahedra and so has six nearest-neighbor cations. In the high-temperature cubic phase, the B cations all have averaged +2.5 formal charges and are located at inversion centers, so the repulsions from neighboring cations cancel out. However, in the low-temperature phase, charge ordering breaks the symmetry at the *B* sites. The $Fe^{2+}-Fe^{2+}-Fe^{3+}-Fe^{3+}$ interactions are relatively attractive/neutral/repulsive in the low-temperature phase and their Coulombic forces are in the ratio 4:6:9. (Integral charge states are assumed for descriptive convenience, although the apparent magnitude of the charge separation is smaller.) Hence, the magnitude of the Fe^{3+} - Fe^{3+} repulsion is greater than the Fe^{2+} - Fe^{2+} attraction, relative to the Fe²⁺-Fe³⁺ interactions. The six Fe-Fe interactions around each octahedral site cancel out for the B(1) sites, but lead to resultant forces in the vz plane (neglecting the deviation of β from 90°) for the other sites, as shown in Fig. 8. [The repulsions within the B(1) and B(2) chains parallel to **a** are also unequal, but lattice symmetry imposes the condition that the B(1)-B(1) and B(2)-B(2) distances both equal a/2.] The observed pattern of long and short distances, also shown, is consistent with these nearest-neighbor forces. The strong $Fe^{3+}-Fe^{3+}$ repulsion between B(2) and B(3) cations displaces B(3) directly towards the B(1) chains, resulting in short B(1)-B(3) and long B(2)-B(3) distances. The weaker $Fe^{2+}-Fe^{2+}$ attraction between B(4) and B(1) reduces their separation and lengthens the B(4)-B(2) distances, but by a smaller amount than the former repulsion. The displacements of B(3) and B(4) towards the B(1) chains lead to alternating long and short B(3)-B(4) separations in the **b** direction.

Hence, the pattern of *B* site Fe-Fe distances in the lowtemperature structure corroborates the charge ordered arrangement inferred from the mean Fe-O distances. *B* site dimerization is not consistent with the observed *B*-*B* distances, nor with the formation of expanded and contracted FeO_6 octahedra, and so we reject the dimerization hypothesis.

The oxygen and the *B* site Fe atoms define a network of distorted B_4O_4 cubes consisting of interpenetrating B_4 and O_4 tetrahedra. The cubes share corners through the Fe atoms so that every BO_6 octahedra is divided between two cubes, with three oxygens participating in each. Our *Pmca*-constrained refinement model contains two crystallographically independent B_4O_4 cubes. The *B*-*B* and *B*-O distances within each of these are shown in Table V. There is a striking segregation of the *B*-*B* distances between the two cubes as a result of the unequal Coulombic repulsions described above. Although the model symmetry constrains the cubes to have one value in common [the a/2 B(1)-B(1) and B(2)-B(2) separation], the other five distances are all larger than this value in one cube but smaller in the other. The average *B*-*B* distances in the two cubes differ by 0.1 Å. There is also a



FIG. 7. The arrangement of charge states in the refined P2/c cell. The B(1) and B(4) sites (V=+2.4) are shown as filled circles and B(2) and B(3) (V=+2.6) as open circles. The chains of *B* sites parallel to *x* or *y* are shown in (a). The mean charges at each *z* height, shown relative to the average (amplitude q=0.1 e/at.), define the $[001]_c$ charge-density wave. The additional $[00\frac{1}{2}]_c$ modulation is apparent from the phase of the charge order in the $z=\frac{1}{8}$ and $\frac{5}{8}$ planes. (b) shows the arrangement of electron-rich (dark shading) and -poor (light shading) Fe₄O₄ cubes.

smaller difference of 0.02 Å between the mean Fe-O distances in the two cubes. The smaller ("electron-rich") cube contains the higher electron (Fe²⁺) concentration, with three V=2.4 and one V=2.6 B sites at its apexes. The larger ("electron-poor") cube is defined by one V=2.4 and three V=2.6 B sites. The structure consists of alternating double layers of electron-rich and poor cubes [Fig. 7(b)]; this is another description of the [001]_c charge-density wave.

The appearance of large and small Fe_4O_4 cubes could be in keeping with the formation of electron clusters, with the extra electrons delocalized unequally over *B* sites within the electron-rich cubes. This cannot be ruled out on the basis of structural studies alone, however, we note that a purely charge ordered scenario is sufficient to explain the expansion and contraction of the cubes from the imbalance of electrostatic repulsions between nonbonded *B* site Fe ions.

E. Octahedral distortions

The above description of the low-temperature magnetite structure in terms of electron-rich and -poor cubes creates an

apparent structural paradox. The electron-rich Fe_4O_4 cubes contract because of the diminished Fe-Fe repulsions, leading to a mean Fe-O distance for the cube *below* the global structural average, and yet the electron-rich (V=2.4) *B* sites at three-quarters of the cube corners were identified from the *above average* Fe-O distances within their octahedra. The opposite is true for the electron-poor cubes, which have an *above average* mean Fe-O distance and yet are defined by *contracted* (V=2.6) octahedra at three-quarters of the corners.

This apparent paradox reveals why the low-temperature structure is highly distorted internally. Charge order in the highly constrained spinel network, which (unlike perovskites) contains short distances between charge ordered cations in addition to the shortest cation-anion bonds, leads to a competition between Coulombic cation-anion and cation-cation interactions. Electron localization creates an Fe²⁺ state, which tends to expand the six Fe-O bonds around it, but also tends to contract the six Fe-Fe distances. Conversely, an electron-unoccupied Fe³⁺ tends to contract the

B(1a B-B), <i>B</i> (1b), <i>B</i> (3), <i>B</i> (4), O(1) distances (Å)	, O(2), O(6a), O(6b) cubes (ele <i>B</i> -O d	ectron rich) istances (Å)
$\overline{B(1a)}$ - $B(1b)$	2.972 18(1)	B(1a)-O(1)	2.043(3)
B(1a) - B(3)	2.864(1)	B(1a)-O(2)	2.083(3)
<i>B</i> (1b)- <i>B</i> (3)	2.855(1)	B(1a)-O(6b)	2.091(3)
B(1a) - B(4)	2.958(1)	<i>B</i> (1b)-O(1)	2.043(3)
B(1b) - B(4)	2.950(1)	B(1b)-O(2)	2.083(3)
B(3)-B(4)	2.880(1)	<i>B</i> (1b)-O(6a)	2.090(3)
		B(3)-O(2)	1.964(5)
		B(3)-O(6a)	2.019(3)
		<i>B</i> (3)-O(6b)	2.018(3)
		B(4)-O(1)	2.033(5)
		<i>B</i> (4)-O(6a)	2.054(3)
		<i>B</i> (4)-O(6b)	2.053(3)
$\langle B - B \rangle$	2.913(1)	$\langle B - O \rangle$	2.048(3)
B(2a) B-B), $B(2b)$, $B(3)$, $B(4)$, $O(3)$, distances (Å)	, O(4), O(5a), O(5b) cubes (ele <i>B</i> -O d	ectron poor) istances (Å)
<i>B</i> (2a)- <i>B</i> (2b)	2.972 18(1)	B(2a)-O(3)	2.038(4)
B(2a) - B(3)	3.041(1)	B(2a)-O(4)	2.041(3)
<i>B</i> (2b)- <i>B</i> (3)	3.050(1)	B(2a)-O(5a)	2.051(3)
B(2a) - B(4)	3.003(1)	<i>B</i> (2b)-O(3)	2.039(4)
<i>B</i> (2b)- <i>B</i> (4)	3.012(1)	<i>B</i> (2b)-O(4)	2.041(3)
B(3)- $B(4)$	3.046(1)	<i>B</i> (2b)-O(5b)	2.051(3)
		<i>B</i> (3)-O(3)	2.116(5)
		<i>B</i> (3)-O(5a)	2.092(3)
		<i>B</i> (3)-O(5b)	2.092(3)
		B(4)-O(4)	2.085(5)
		<i>B</i> (4)-O(5a)	2.093(3)
		<i>B</i> (4)-O(5b)	2.094(3)
$\langle B-B \rangle$	3.021(1)	$\langle B - O \rangle$	2.069(4)

TABLE V. B site Fe-O and Fe-Fe distances in the two structurally distinct Fe_4O_4 cubes.

bonds to oxygen but expand the distances to neighboring *B* sites.

The result of this competition, and the resolution of the apparent paradox, comes from the distortion of some of the BO_6 octahedra according to whether they are shared between like (two electron-rich or two -poor) or unlike (one rich and one poor) cubes. Taking the distances within each BO_6 octahedron (Tables III and V) in turn we find the following:

(i) B(1) (V=2.4) lies at the corner of two electron-rich cubes and at a center of inversion symmetry. The $B(1)O_6$ octahedron is expanded and is near regular but with a slight tetragonal compression. This could result from orbital order, since the localized $t_{2g}^4 e_g^2$ configuration of Fe²⁺ is triply degenerate, and tetragonal compression along the local z axis gives orbital ordering $d_{xy}^2 d_{xz}^1 d_{yx}^1$ within the t_{2g} set and so is a Jahn-Teller active distortion mode.

(ii) B(2) (V=2.6) lies at the corner of two electron-poor cubes, and has an almost regular, contracted octahedron. In comparison to B(1), the lack of an orbital ordering distortion is consistent with the presence of nondegenerate Fe³⁺. (iii) B(3) (V=2.6) is at the shared corner of electron-rich and poor cubes. There is thus the tendency to shorten the three B(3)-O bonds in the electron-rich cube, and to lengthen the other three B(3)-O bonds in the electron-poor cube. This splitting is increased because six of the twelve Fe-O bonds in the electron-rich cube [from the $B(1)O_6$ octahedron above] are on average longer than the global mean *B*-O, and six of the twelve distances from $B(2)O_6$ in the electron-poor cube are on average shorter than the B-O mean. Hence, the three B(3)-O bonds in the electron-rich cube are very short, and the three bonds in the electron-poor cube are lengthened to a lesser degree, so as to satisfy the requirements of the cubes (driven by B-B repulsions) and the overall compression of the electron-poor (V=2.6) $B(3)O_6$ octahedron. The net effect of creating three long and three short B(3)-O distances is a trigonal polar displacement of the cation towards one face of the octahedron, which is evident in Fig. 6.

(iv) B(4) (V=2.4) also lies between electron-rich and -poor cubes, and so has a polar distortion like that of the $B(3)O_6$ octahedron, although with an overall expansion of the octahedron.

The observed local distortions in Fe_3O_4 are thus consistent with the charge ordering below the Verwey transition.



FIG. 8. [100] projection of the *B* sites (shaded as in Fig. 7) in the low-temperature Fe_3O_4 structure. Attractive $Fe^{2+}-Fe^{2+}$ (filled bonds) and repulsive $Fe^{3+}-Fe^{3+}$ (open bonds) interactions are shown together with the resultant Coulombic forces at the unique *B* sites. The observed *B*-*B* distances (Å) are also displayed.

The charge localization expands the octahedra around B(1)and B(4) but contracts those around B(2) and B(3), and expands or contracts the B_4O_4 cubes as a result of differing B-B repulsions. The competition between these Coulombic effects leads to a polar distortion of the B(3) and B(4) octahedra. Orbital ordering is evident only at the B(1) site, since the B(4) octahedron is distorted by the Coulombic forces. The distortions in the B_2O_4 network inevitably distort the AO_4 tetrahedra. The mean A-O distances and BVS's (Tables III and IV) and the BVS summations for the O sites (Table IV) show a very small dispersion and are close to the values in the high-temperature cubic phase (Table I). Each O atom is bonded to one A cation and three B cations, so the AO_4 distortions compensate for the changes in electron density around the oxygen atoms caused by the charge order very effectively, subject to the constraint of maintaining the correct bonding density around the A site Fe³⁺ cations.

F. Displacement Modes

The low-temperature structure of Fe₃O₄ is shown in Fig. 6, with the atomic displacements exaggerated so as to be visible. The lattice and local distortions described above result from the condensation of several phonons at the Verwey transition. At least three types of phonon are needed to account for the magnetostriction (Γ -type) and the charge ordering (*X*- and Δ -types) distortions in the $a_c/\sqrt{2} \times a_c/\sqrt{2} \times 2a_c$ monoclinic supercell. An additional Γ mode is present if the structure is acentric, and further modes are needed to account for the full $\sqrt{2}a_c \times \sqrt{2}a_c \times 2a_c$ *Cc* supercell and any triclinic distortions.

Of the two microscopic modes that are driven by the charge ordering, the Δ type has been identified as the Δ_5 mode.⁴⁵ This is an incommensurate $[0\ 0\ q]$ vector that becomes commensurate with $q_c = \frac{1}{2}$ because it condenses with an X-type $[0\ 0\ 1]_c$ mode. This was originally identified as the X_1 phonon,⁹ however, subsequent diffuse scattering experiments have suggested that the X_3 mode is involved.⁴¹

The *Pmca* symmetry operations used here heavily constrain the pattern of displacements so it is not possible to distinguish decisively between the possible modes. Instead, the refined displacements have been decomposed according to their symmetry in the xy plane to enable their wave vectors and amplitudes in the z direction to be compared.

The $a_c\sqrt{2} \times a_c\sqrt{2} \times 2a_c$ monoclinic supercell is conveniently described as a stack of B_2O_4 layers in the *xy* plane stacked at heights z=0, $\frac{1}{8}$, $\frac{1}{4}$, $\frac{3}{8}$, etc. with the tetrahedral *A* sites between the layers at $z=\frac{1}{16}$, $\frac{3}{16}$, $\frac{5}{16}$, etc. The *B* cations in each B_2O_4 layer are arranged in chains that are parallel to **a** in the z=0, $\frac{1}{4}$, $\frac{1}{2}$, etc. planes, and parallel to **b** at $z=\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$, etc. The sites in each layer are listed in Table VI. The *Pmca*-constrained model allows the determination of three symmetry-independent B_2O_4 layers at z=0, $\frac{1}{8}$, and $\frac{1}{4}$.

The displacements of atoms in each B_2O_4 layer can be classified according to whether they are longitudinal (L), i.e.,

TABLE VI. The *B* and O sites present at each *z* height for $z=0-\frac{3}{8}$, with the coordinates of the central positions relative to which the displacements of the B_2 pair and O_4 square are measured. The sequence repeats for $z=\frac{1}{2}-\frac{7}{8}$.

z	B atoms	B_2 center (x,y)	O atoms	O_4 center (x,y)
$\begin{array}{c} 0\\ \frac{1}{8}\\ \frac{1}{4}\\ \frac{3}{8}\end{array}$	B(1a), B(1b) B(3), B(4) B(2a), B(2b) B(3), B(4)	$(\frac{1}{4}, \frac{1}{2}) (\frac{3}{4}, \frac{1}{2}) (\frac{1}{4}, 0) (\frac{1}{4}, \frac{1}{2})$	$\begin{array}{l} O(1) \ (\times 2), \ O(2) \ (\times 2) \\ O(5a), \ O(5b), \ O(6a), \ O(6b) \\ O(3) \ (\times 2), \ O(4) \ (\times 2) \\ O(5a), \ O(5b), \ O(6a), \ O(6b) \end{array}$	$ \begin{array}{c} (\frac{1}{2}, \frac{1}{2}) \\ (\frac{3}{4}, \frac{1}{4}) \\ (\frac{1}{2}, 0) \\ (\frac{1}{4}, \frac{1}{4}) \end{array} $



FIG. 9. The B_2O_4 arrangement in the z=0 plane of the P2/c cell magnetite structure, showing the four modes used to describe the displacements of the oxygen atoms from the positions in the high-temperature, cubic spinel structure.

parallel to **c**, or transverse (T), perpendicular to **c**. The transverse displacements may be parallel (//) or perpendicular (\perp) to the chain direction. The displacements of the square of O atoms surrounding a *B* cation in each layer have been de-



FIG. 10. Amplitudes of the longitudinal displacements (Å) of the *A* and *B* site Fe and the O atoms for $0 < z < \frac{1}{2}$: (a) the L(0), (b) the L(1//), and (c) the L(1 \perp) and L(2) modes.

composed into a combination of four normal modes as shown in Fig. 9. The modes are the totally symmetric (0) displacement; the antisymmetric (1//) and (1 \perp) modes in which the normal to the nodal plane is, respectively, parallel or perpendicular to the chain direction; and the (2) mode. The positions of the centers of the O₄ squares in each layer are shown in Table VI. The displacements of the pair of *B* cations around the center positions in Table VI can similarly be decomposed into a combination of (0) and (1//) modes. As an example, the T(1 \perp): O \perp displacement describes transverse, (1 \perp) symmetry, displacements of oxygen that are perpendicular to the chain direction.

The amplitudes of the L and T displacement modes along **c** are, respectively, plotted in Figs. 10 and 11. The L(0) are the largest longitudinal displacements, and both the *A* and *B* cation amplitudes are greater than that for oxygen. These and the L(1//) modes both have a $[001]_c$ periodicity, whereas the L(1 \perp) and L(2) modes have a small $[00\frac{1}{2}]_c$ modulation. The



FIG. 11. Amplitudes of the transverse displacements (Å) of the *A* and *B* site Fe and the O atoms for $0 < z < \frac{1}{2}$: (a) the T(0), (b) the T(1//), and (c) the T(1 \perp) mode.

transverse modes mostly have $[00\frac{1}{2}]_c$ periodicities imposed by the space-group symmetry. However, the T(1//): O \perp displacements have a $[00\frac{1}{2}]_c$ and a $[000]_c$ mode, although the amplitude of the latter is not significant. The three transverse *B* cation modes have large amplitudes of 0.05–0.07Å whereas the $[00\frac{1}{2}]_c$ and $[001]_c$ O amplitudes are in the range 0.01–0.06 Å.

As discussed above, the electron localization below the Verwey transition in Fe₃O₄ imposes expansion or compression of FeO₆ octahedra driven by *B*-O interactions, and expansion or compression of Fe₄O₄ cubes driven by the *B*-*B* repulsions. Each octahedron is made up of a BO_4 group in a given *z* plane with two more oxygens at $z \pm \frac{1}{8}$. The in-plane displacements that describe the expansion or compression of the octahedra are the T(1//):O|| and T(1⊥):O⊥. The former

leads to an alternation of large and small BO_4 groups along the chains, corresponding to charge ordering on every other site, whereas the $T(1\perp):O\perp$ describes an expansion of all the BO_4 groups consistent with a uniform charge density. The $T(1//):O\perp$ and $T(1\perp):O//$ displacements correspond to volume-preserving deformations and twists. The longitudinal displacements that describe expansion or compression of the octahedra centered in the *z* plane are those that do not have a maximum or minimum at *z*, and therefore have differing displacements at $z \pm \frac{1}{8}$.

The refined displacements in Figs. 10 and 11 show how the observed expansion and compression (charge order) pattern is decomposed into the various modes. The alternation of large B(1) sites at z=0, $\frac{1}{2}$, etc. with small B(2) sites at $z=\frac{1}{4}$, $\frac{3}{4}$, etc. is described by the T(1 \perp):O \perp displacement of amplitude 0.016 Å and the L(0):O (amplitude 0.019 Å) and L(1//):O (amplitude 0.016 Å) displacements. These define the [001]_c charge-density wave. The B(3) and B(4) sites are in chains of alternating compressed and expanded octahedra in each $z=\frac{1}{8}$, $\frac{3}{8}$, etc. plane. This is described by the T(1//):O// displacements of 0.015 Å, and the half amplitudes of the L(2):O (0.014 Å) and the L(1 \perp):O (0.005 Å) displacements. These define the $[00\frac{1}{2}]_c$ charge modulation.

The compression of the B(1a), B(1b), B(3), and B(4) tetrahedron and the expansion of the B(2a), B(2b), B(3), and B(4) tetrahedron are described by the half amplitude (0.056 Å) of the L(0):*B* mode and the T(1//):*B*// displacement of 0.041 Å, in which the B(3) and B(4) cations move from their ideal positions. The other *B* displacements such as the T(0) modes reflect volume-preserving distortions of the tetrahedra that result from the competing distortions from the *B*-*B* and *B*-O interactions.

V. CONCLUSIONS

The structure of Fe_3O_4 below the Verwey transition is described to a good approximation by a monoclinic $a_c/\sqrt{2}$ $\times a_c/\sqrt{2} \times 2a_c$ model with *Pmca* pseudosymmetry, as first proposed by Iizumi et al.¹³ This structure gives a good description of both x-ray and neutron powder-diffraction intensities in the present refinement. The four octahedral B sites in our refined model are split into pairs of large and small sites, providing direct evidence for charge ordering. The magnitude of this splitting is small, and is equivalent to apparent local charges of $Fe^{2.4+}$ and $Fe^{2.6+}$, in keeping with the reduced charge separation found in other charge disproportionated transition-metal oxides. The charge order is described by a dominant $[001]_c$ charge-density wave, and a secondary $[00\frac{1}{2}]_c$ modulation in the phase of the charge order at half the sites. The $[001]_c$ distortion relieves a nesting instability at the Fermi level in the high-temperature cubic phase, and this appears to be the primary cause of the Verwey transition. The charge ordering does not obey the Anderson criterion.

The complex structural distortion at the Verwey transition results from several consequences of the charge localization. These are a macroscopic magnetostriction from the coupling of the Fe^{2+} orbital moments with the magnetization axis, and microscopic distortions from the charge order and a small

orbital ordering at one of the Fe²⁺ sites. Changes in the Coulombic *B-B* repulsions as a result of the charge ordering compete with the changes in *B*-O distances, leading to polar deformations of two of the four octahedra. The *B-B* distances are not consistent with dimer formation. The distortions result in $[001]_c$ and $[00\frac{1}{2}]_c$ modulated displacements of all of the atoms with amplitudes up to 0.07 Å. Additional displacements leading to a *Cc* symmetry $\sqrt{2}a_c \times \sqrt{2}a_c \times 2a_c$

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supercell containing 16 unique *B* sites are likely to be much smaller, ~ 0.01 Å.

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