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**Citation for published version:**

Senn, MS, Wright, JP & Attfield, JP 2012, 'Charge order and three-site distortions in the Verwey structure of magnetite', *Nature*, vol. 481, no. 7380, pp. 173-176. <https://doi.org/10.1038/nature10704>

**Digital Object Identifier (DOI):**

[10.1038/nature10704](https://doi.org/10.1038/nature10704)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Peer reviewed version

**Published In:**

Nature

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Post-print of peer-reviewed article published by the Nature Publishing Group.

Published article available at: <http://dx.doi.org/10.1038/nature10704>

Cite as:

Senn, MS, Wright, JP & Attfield, JP 2012, 'Charge order and three-site distortions in the Verwey structure of magnetite' *Nature*, vol 481, no. 7380, pp. 173-176.

Manuscript received: 01/06/2011; Accepted: 08/11/2011; Article published: 21/12/2011

## Charge Order And Three-Site Distortions In The Verwey Structure Of Magnetite\*\*

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<sup>[\*\*]</sup>We thank Dr. Carole Morrison for supplying code for electrical polarization calculations, Prof. J. Honig for provision of the magnetite sample, the Leverhulme Trust for financial support, and EPSRC and STFC for financial support and provision of continuing access to ESRF.

### Supporting information:

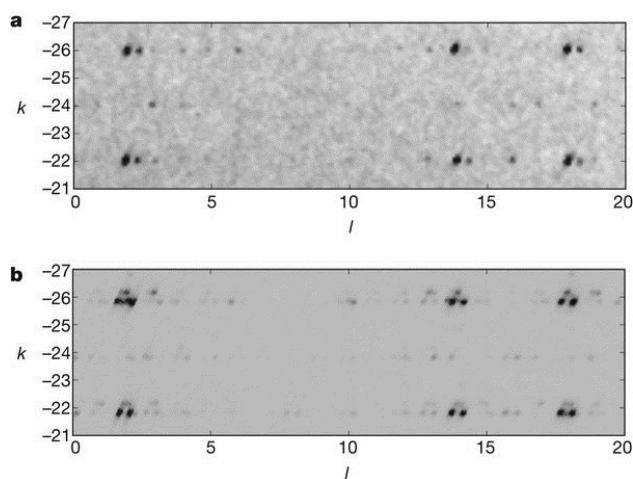
Supplementary Information is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature)

## Abstract

The mineral magnetite ( $\text{Fe}_3\text{O}_4$ ) undergoes a complex structural distortion and becomes electrically insulating at temperatures less than 125 kelvin. Verwey proposed in 1939 that this transition is driven by a charge ordering of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions<sup>1</sup>, but the ground state of the low-temperature phase has remained contentious<sup>2,3</sup> because twinning of crystal domains hampers diffraction studies of the structure<sup>4</sup>. Recent powder diffraction refinements<sup>5,6,7</sup> and resonant X-ray studies<sup>8,9,10,11,12</sup> have led to proposals of a variety of charge-ordered and bond-dimerized ground-state models<sup>13,14,15,16,17,18,19</sup>. Here we report the full low-temperature superstructure of magnetite, determined by high-energy x-ray diffraction from an almost single-domain, 40-micrometre grain, and identify the emergent order. The acentric structure is described by a superposition of 168 atomic displacement waves (frozen phonon modes), all with amplitude 0.24 Å. Distortions of the  $\text{FeO}_6$  octahedra show that Verwey's hypothesis is correct to a first approximation and that the charge and  $\text{Fe}^{2+}$  orbital order are consistent with a recent prediction<sup>17</sup>. However, anomalous shortening of some Fe–Fe distances suggests that the localized electrons are distributed over linear three-Fe-site units, which we call ‘trimerons’. The charge order and three-site distortions induce substantial off-centre atomic displacements and couple the resulting large electrical polarization to the magnetization. Trimerons may be important quasiparticles in magnetite above the Verwey transition and in other transition metal oxides.

## Main text

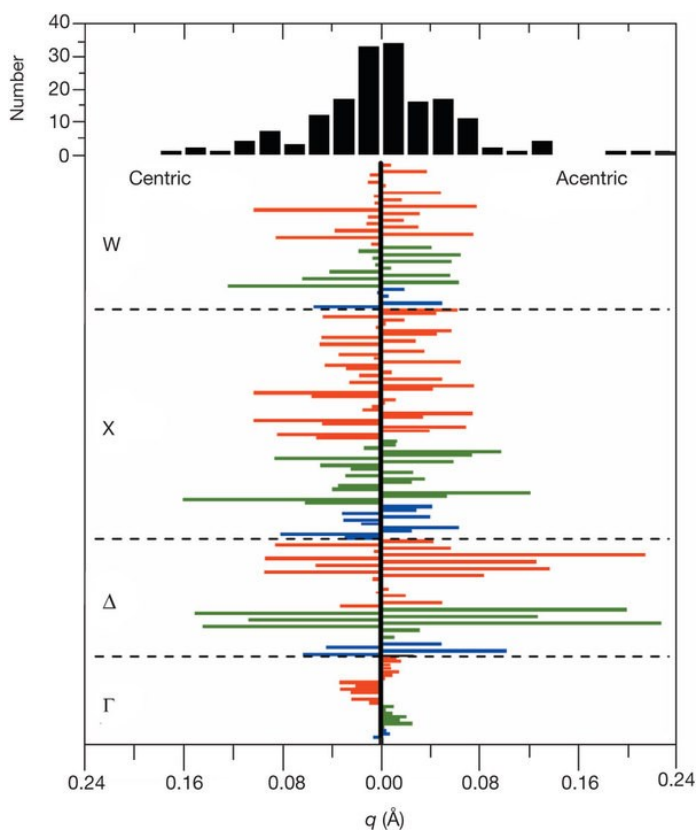
The cubic spinel type structure of magnetite distorts to a monoclinic superstructure with  $Cc$  space group symmetry below the  $T_V \approx 125$  K Verwey transition<sup>4,20</sup>.  $Cc$  domains<sup>21</sup>  $\sim 1$   $\mu\text{m}$  in size are formed in up to 24 orientations within magnetite crystals, and microtwinning of these domains severely hampers diffraction studies. We have investigated the use of small magnetite grains as potential single-domain crystals for high-energy X-ray structure analysis (Fig. 1). In the smallest and least-twinned grain of many that we investigated, 89% of the scattering was from a single orientation and 11% was from a secondary domain (Fig. 1a). The  $Cc$  crystal structure was determined using 91,433 symmetry-unique Bragg reflections from this 40- $\mu\text{m}$  grain (see Methods Summary and Methods section in Supplementary Information for details of the structure and derived quantities used below). No further superstructure or lowering of space group symmetry below  $Cc$  was evident in the diffraction data.



**Figure 1. Reciprocal lattice synchrotron X-ray diffraction intensities for magnetite microcrystal grains at 90 K.** Sections of  $(h k l)$  intensities in the  $h = 50$  plane are shown. **a**, Intensities for an approximately spherical grain of

diameter 40  $\mu\text{m}$ , which was used to determine the crystal structure. The microcrystal is almost single domain; faint spots to the right of the main intensities reveal the secondary twin. **b**, Intensities from an irregular grain of dimension  $\sim 100 \mu\text{m}$  showing multiple twin domains.

The low-temperature  $Cc$  crystal structure of magnetite has 168 variable  $(x, y, z)$  atomic coordinates, of which 166 are independent and two are constrained to fix the cell origin. The coordinates are equivalently described by the same number of amplitudes of frozen displacement waves (phonons), all with values  $q < 0.24 \text{ \AA}$ , as shown graphically in Fig. 2. Only one of these (an O-site  $\Gamma$ -mode) is present in the high-temperature cubic structure and the remainder all freeze at the Verwey transition. The three largest-amplitude modes have  $\Delta_5$  symmetry and are acentric, heralding the large off-centre structural distortions described later, but the smoothly varying distribution of amplitudes shows that many centric and acentric  $\Delta$ , X and W modes contribute significantly. Hence, the superstructure is not approximated well by a few frozen phonons, and even attempts to describe the important features with up to 100 lattice modes were unsuccessful.

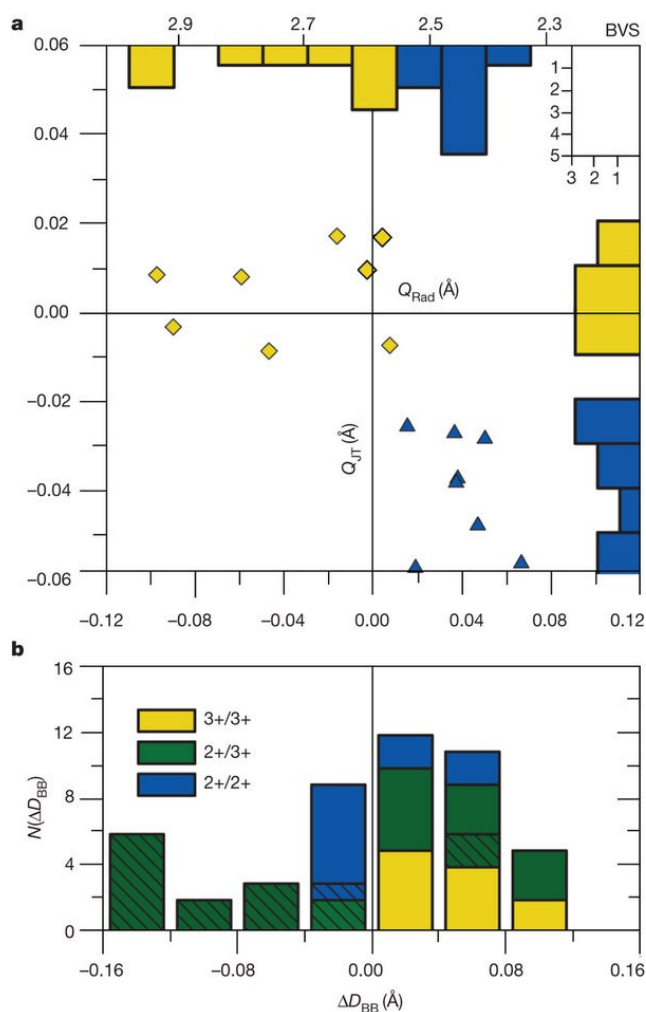


← **Figure 2. The 168 displacement amplitudes of the low-temperature  $Cc$  magnetite structure.**

Main panel: centric and acentric mode amplitudes,  $q$ , which have estimated standard deviations  $< 0.003 \text{ \AA}$ . Top panel: distribution of amplitudes. A, B and O atom modes of the cubic  $Fd\bar{3}m$   $\text{AB}_2\text{O}_4$  spinel type structure are coloured blue, green and red, respectively. The displacement waves have periodicities corresponding to the  $\Gamma$  (0, 0, 0),  $\Delta$  (0, 1/2, 0), X (0, 1, 0) and W (1/2, 1, 0) points in the Brillouin zone of the cubic structure. Many acentric and centric  $\Delta$ , X and W modes involving the B and O sites contribute significantly to the overall superstructure, but the  $\Gamma$  modes are less

Magnetite has an  $\text{AB}_2\text{O}_4$  spinel structure in which  $\text{Fe}^{3+}$  occupies the tetrahedrally coordinated A cation sites, and a 1:1 order of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  is expected over the 16 inequivalent octahedral B sites of the  $Cc$  superstructure in the Verwey hypothesis. Each B-site  $\text{FeO}_6$  octahedron has an irregular distortion from which the amplitudes of radial expansion (breathing) local modes ( $Q_{\text{Rad}}$ ) and tetragonal Jahn–Teller ( $Q_{\text{JT}}$ ) local modes were extracted because these are sensitive to charge-ordering and associated orbital-ordering displacements. For  $Q_{\text{JT}}$  we find a bimodal Verwey-type distribution

(Fig. 3a) in which eight near-zero values are consistent with  $\text{Fe}^{3+}$ , which is Jahn–Teller inactive as the high-spin  $3d^5$  electron configuration is non-degenerate. The other eight  $Q_{\text{JT}}$  values are negative as expected for  $3d^6 \text{Fe}^{2+}$ , where tetragonal Jahn–Teller compression removes the degeneracy created by the extra electron occupying one of the three  $t_{2g}$  symmetry  $d$  orbitals ( $d_{xy}$ ,  $d_{xz}$  or  $d_{yz}$ ). In addition, the plot of  $Q_{\text{Rad}}$  (the increase in octahedral average Fe–O bond distance) against  $Q_{\text{JT}}$  shows that the eight Jahn–Teller-distorted B sites are also the eight most expanded, consistent with  $\text{Fe}^{2+}$ , and that the eight undistorted sites are the least expanded, as expected for  $\text{Fe}^{3+}$ . The bimodal distribution of tetragonal distortions and their correlation with the radial amplitudes demonstrate experimentally that Verwey’s  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  ordering hypothesis is correct to a useful first approximation. However, the distribution of  $Q_{\text{Rad}}$  and equivalent bond valence sum (BVS) estimates of formal Fe charge (Fig. 3a) does not seem bimodal, indicating the more complex electronic order described later.

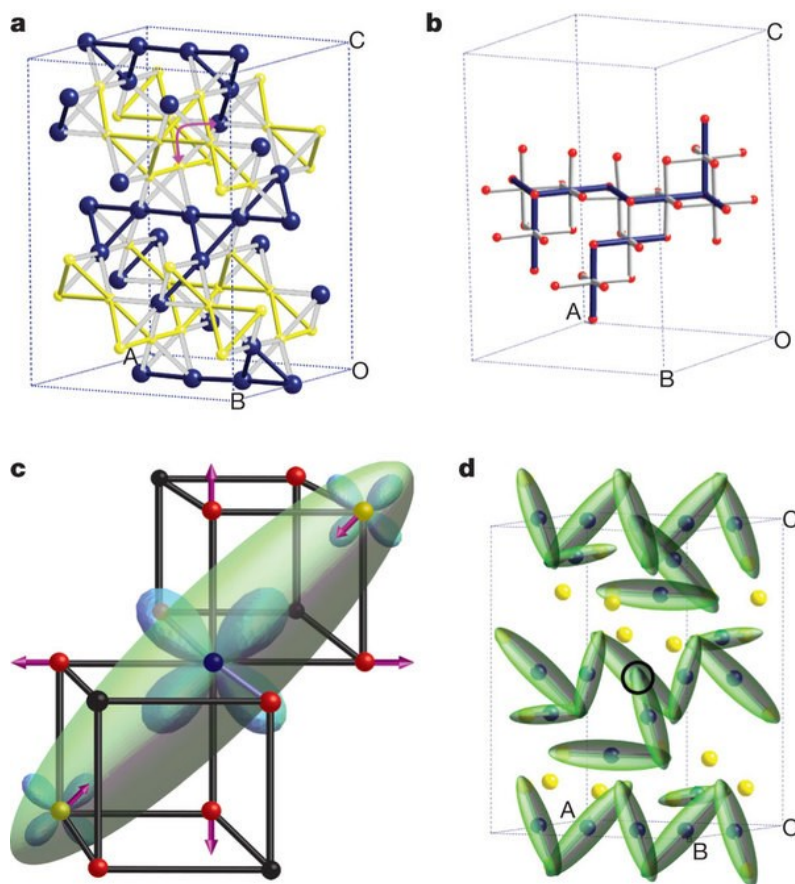


**Figure 3. Local distortion distributions that reveal electronic order in the low-temperature magnetite structure.**

**(a)** Plot of local distortions for the 16 distinct  $\text{FeO}_6$  octahedra.  $Q_{\text{Rad}}$  and  $Q_{\text{JT}}$  are the amplitudes of the radial (breathing) and tetragonal Jahn–Teller distortions. Their estimated standard deviations of  $<0.002 \text{ \AA}$  are smaller than the symbols shown.  $Q_{\text{Rad}}$  is the difference between the average Fe–O bond distance in an  $\text{FeO}_6$  octahedron and the average over all octahedra. The points fall into two groups describing characteristic local distortions for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  (blue and yellow bars and symbols, respectively). The distributions of the two modes (inside top and right edges of plot, with scales top right) show that there is bimodal segregation of the  $Q_{\text{JT}}$  amplitudes but that the  $Q_{\text{Rad}}$  dispersion is more continuous. BVS estimates of formal Fe charge are shown above the  $Q_{\text{Rad}}$  distribution. **(b)**, Distribution of the 48 distinct Fe–Fe

distances between neighbouring B sites, relative to the average  $D_{BB}$  ( $= 2.967 \text{ \AA}$ ), coloured according to the Fe charge states. The 16 distances from the eight  $\text{Fe}^{2+}$  sites to their two neighbours perpendicular to the local orbital ordering axis ( $\text{Fe}^{3+}$  in 15 cases and  $\text{Fe}^{2+}$  once) are hatched. The anomalous shortening of most of these distances indicates the linear three-site (trimeron) distortions as shown in Fig. 4c.

The average BVS formal oxidation states for the eight  $\text{Fe}^{2+}$ - and  $\text{Fe}^{3+}$ -like B sites in the  $C_{cm}$  magnetite structure are 2.47 and 2.75, respectively, consistent with an earlier partial refinement<sup>5,6</sup> and structural results for other charge-ordered transition metal oxides<sup>22</sup>. The  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  arrangement (Fig. 4a) differs from the original prediction of Verwey<sup>23</sup>, but the charge and  $\text{Fe}^{2+}$  orbital ordering (Fig. 4b) are in agreement with a recent model based on electronic structure calculations<sup>17</sup>. The arrangement is close to a centric structure in which the  $\text{Fe}^{2+}$  states form chains of corner-linked ( $\text{Fe}^{2+}$ )<sub>3</sub> triangles, but with a neighbouring  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  pair exchanged at every fourth triangle as shown (Fig. 4a). Anderson's condition<sup>24</sup> that each tetrahedron of four neighbouring B sites should contain two  $\text{Fe}^{2+}$  ions is only satisfied in a quarter of the tetrahedra. The complexity of the charge and orbital ordering may be explained in part by the distribution of Jahn–Teller distortions. The octahedral compressions of the 16  $\text{Fe}^{2+}$  sites in the basic cell act parallel to the  $a$ ,  $b$ , and  $c$  axes of the high-temperature cubic lattice in a 5:5:6 ratio that minimizes strain in the highly connected spinel lattice. More-symmetric charge and orbital orderings tend to have less equal ratios. The small anisotropy arising from excess distortion in the  $c$  direction may account for the change in magnetic easy-axis from cubic [111] to [001] at temperatures less than  $T_V$ .



**Figure 4. Charge, orbital and trimeron order in the low-temperature magnetite structure. (a)** Distribution of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  states (blue and yellow spheres, respectively) in the first-approximation Verwey-type model, shown in

the  $\sqrt{2}a \times \sqrt{2}a \times 2a$   $Cc$  supercell ( $a$  is the high-temperature cubic-cell parameter). Nearest-neighbour  $\text{Fe}^{2+}$ – $\text{Fe}^{2+}$  connections (blue lines) describe irregular chains, parallel to the  $a$  axis, derived from a more symmetric, centric arrangement of corner-linked triangles by exchange of  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  pairs (one pair indicated). **(b)** Jahn–Teller distortions arising from orbital order within a single  $\text{Fe}^{2+}$  chain shown as long and short bonds (grey and blue lines, respectively) to oxygen atoms (red spheres). **(c)** Coupled distribution of a minority-spin electron (with approximate atomic populations indicated by the sizes of blue  $t_{2g}$  orbitals) and associated atomic displacements (purple arrows) within a linear three-Fe-site (trimeron) unit. Orbital order at the central  $\text{Fe}^{2+}$  site (blue) localizes the minority-spin electron in one of the  $t_{2g}$  orbitals and elongates the four Fe–O bonds perpendicular to the local Jahn–Teller axis. Weak bonding interactions transfer minority-spin density into coplanar  $t_{2g}$  orbitals at two neighbouring B sites (shown as yellow  $\text{Fe}^{3+}$ ) and shorten the Fe–Fe distances. The minority-spin electron density is approximated by a scalene ellipsoid encompassing the three Fe sites. Other B-site  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  neighbours (black spheres) do not participate. **(d)** Trimeron distribution in the low-temperature magnetite structure, following the experimentally observed distortions, with  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  states shown as blue and yellow spheres, respectively, and trimeron ellipsoids as in **c**. The trimerons are mainly end-linked through  $\text{Fe}^{3+}$  ions, but one trimeron is terminated by an  $\text{Fe}^{2+}$  ion (circled). Some  $\text{Fe}^{3+}$  sites do not participate in any trimerons.

Edge sharing of  $\text{FeO}_6$  octahedra allows direct B–B electronic interactions within linear chains that extend in six directions. The nearest-neighbour B–B distances,  $D_{\text{BB}}$ , are all equivalent in the cubic magnetite structure, but  $D_{\text{BB}}(\text{Fe}^{2+}$ – $\text{Fe}^{3+})$ , the nearest-neighbour  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  distance, in particular shows a wide distribution in the Verwey phase (Fig. 3b). Electrostatic repulsions tend to disperse the distance values such that  $D_{\text{BB}}(\text{Fe}^{2+}$ – $\text{Fe}^{2+}) < D_{\text{BB}}(\text{Fe}^{2+}$ – $\text{Fe}^{3+}) < D_{\text{BB}}(\text{Fe}^{3+}$ – $\text{Fe}^{3+})$ , so the observed tail of anomalously short  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  distances is not expected in a Verwey model and indicates magnetically driven B–B bonding by the additional  $t_{2g}$  electrons. (The five parallel unpaired  $d$ -electron spins at all B sites are ferromagnetically ordered below the Curie temperature (858 K), so only the additional electron from each  $3d^6$   $\text{Fe}^{2+}$  state has an opposed, minority, spin and may be delocalized between B sites through bonding.) Chains of alternating short and long B–B distances are predicted in bond-dimerized models<sup>13, 16, 19</sup>, but are not observed in our structure. Instead, the two B–B distances perpendicular to the local orbital-ordering axis at each of the eight  $\text{Fe}^{2+}$  positions both tend to be shortened: this is the case for 14 of these 16 distances (Fig. 3b, hatched). This suggests that minority-spin  $t_{2g}$  electron density is significantly delocalized from an  $\text{Fe}^{2+}$  donor onto two adjacent B-site acceptors, which are usually  $\text{Fe}^{3+}$  sites. This single charge, delocalized over three B sites with associated displacements of the two acceptor B sites and surrounding oxygen atoms (Fig. 4c), corresponds to a highly structured small polaron that may be described as a ‘trimeron’, by analogy with dimeron quasiparticles in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  (ref. 25). Fifteen of the 16 trimeron acceptor sites are  $\text{Fe}^{3+}$  ions, but one  $\text{Fe}^{2+}$  (Fig. 4d, circled) accepts into a  $t_{2g}$  orbital that is orthogonal to its own trimeron. Trimeron distortions are intrinsically symmetric (having  $D_{\text{BB}} = 2.832$  and  $2.848$  Å in the most regular environment of the  $Cc$  structure, where  $D_{\text{BB}} = 2.967$  Å on average), but asymmetric connectivity leads to off-centre distortions and long B–B bonds in 2 of 16 cases.

The linear three-site (trimeron) distortions (Fig. 4d) significantly perturb charge order in the  $Cc$  magnetite structure and couple the magnetism to the complex overall distortion. Only two B ions are available per minority-spin electron, so trimeron units are constrained to share sites. End-sharing connections with angles of  $60^\circ$ ,  $120^\circ$  and  $180^\circ$  are possible, but  $180^\circ$  linkages are apparently avoided to maximize charge transfer because two or three different  $t_{2g}$  orbitals are

used by an  $\text{Fe}^{3+}$  ion participating in two or three trimers. This is analogous to the formation of two or three short *cis*-bonds in some  $d^0$  transition metal oxides and oxynitrides<sup>26</sup>, and creates off-centre  $\text{Fe}^{3+}$  displacements that contribute strongly to the acentric lattice modes and electric polarization. High connectivity seems favourable because four of the eight  $\text{Fe}^{3+}$  sites participate in the maximum of three trimers. The orderings of linear three-site, one-electron units along the infinite B chains correspond to charge density waves with wavevector magnitude  $q_c = 1/N$  for a repeat sequence of one trimeron for every  $N$  B sites. The structural average is  $q_c = 1/6$  but only chains with  $q_c = 0, 1/8$  and  $1/4$  are present, in a 1:6:5 ratio. The unique  $q_c = 0$  chain contains only  $\text{Fe}^{2+}$  ions (Fig. 4a, b) but their three-site distortions are always within other chains.

The linear three-site distortions we attribute to trimers also account for the non-Verwey distribution of radial amplitudes ( $Q_{\text{Rad}}$ ) and BVS values for the B-site  $\text{FeO}_6$  octahedra (Fig. 3a). Each  $\text{Fe}^{2+}$  ion donates minority-spin  $t_{2g}$  electron density to two B-site acceptors within a trimeron (Fig. 4c), so the eight  $\text{Fe}^{2+}$ -like sites have a narrow  $Q_{\text{Rad}}$  distribution and  $\text{BVS} \approx 2.4$ . However,  $\text{Fe}^{3+}$  ions are acceptors in varying numbers of trimers. Two  $\text{Fe}^{3+}$  sites do not participate in any trimers and so have the two lowest  $Q_{\text{Rad}}$  values and the highest B-site BVS values,  $\sim 3.0$  (Fig. 3a). The other six  $\text{Fe}^{3+}$  sites are acceptors for one to three trimers and thus have a spread of higher  $Q_{\text{Rad}}$  values and lower valences with  $\text{BVS} \approx 2.6$ – $2.8$ . Charge transfer within trimers tends to equalize the electron density across B sites: in the limit of maximum donor-to-acceptor transfers (of  $0.2e$ , where  $e$  is the electron charge), an  $\text{Fe}^{3+}$  ion participating in three trimers has the same formal charge,  $+2.4e$ , as the  $\text{Fe}^{2+}$  donor sites. However, the two states are still distinguished by their minority-spin  $t_{2g}$  distributions, as the former site has populations  $d_{xy}^{0.2}d_{xz}^{0.2}d_{yz}^{0.2}$  that preserve the high symmetry of  $\text{Fe}^{3+}$ , whereas the latter has a distribution such as  $d_{xy}^{0.6}d_{xz}^0d_{yz}^0$ , retaining the orbital order of  $\text{Fe}^{2+}$ . This justifies the use of formal valence states to describe charge-ordered structures even when the apparent charge separations are small, as here in magnetite.

The discovery of multiferroism in charge-ordered  $\text{LuFe}_2\text{O}_4$  (ref. 27) has led to recent interest in the coupling of magnetism and the ferroelectric polarization expected in the acentric  $Cc$  magnetite superstructure<sup>16, 17</sup>. Measured electric polarization values of  $P \approx 0.05 \text{ C m}^{-2}$  for magnetite crystals and thin films agree with estimates from previous structural models<sup>17</sup>, but an  $\text{Fe}^{2+}\text{--Fe}^{3+}\text{--O}^{2-}$  point-charge calculation for our structure gives a polarization larger by an order of magnitude ( $P_a = 0.118 \text{ C m}^{-2}$ ,  $P_c = 0.405 \text{ C m}^{-2}$ ;  $P = 0.422 \text{ C m}^{-2}$ ; where  $P_a$  and  $P_c$  are the respective magnitudes of the polarization vector components parallel to the crystallographic  $a$  and  $c$  axes and  $P$  is the magnitude of the resultant polarisation vector). The same calculation with average  $\text{Fe}^{2.5+}$  B-site charges gives similar results ( $P_a = 0.080 \text{ C m}^{-2}$ ,  $P_c = 0.346 \text{ C m}^{-2}$ ;  $P = 0.355 \text{ C m}^{-2}$ ), showing that atomic displacements resulting from charge order and three-site distortions are responsible for most of the polarization, with exchange of  $\text{Fe}^{2+}\text{--Fe}^{3+}$  pairs (Fig. 4a) contributing only 16% of the total. The large  $P_c$  component, parallel to the magnetic easy axis, shows that a substantial magnetoelectric coupling is expected in single magnetite domains.

Lattice effects are significant in the cubic phase of magnetite as diffuse scattering is observed above the Verwey transition,<sup>12, 28</sup> and the electrical conductivity rises continuously to a maximum at  $\sim 3\text{TV}$ . Hence, trimeron fluctuations may be significant quasiparticles in the cubic phase. The expected entropy change at the Verwey transition is conventionally assumed to be  $R\ln 4 = 1.4R$  ( $R$  is the molar gas constant) for full disorder of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  charges, but our structure shows that this change should be  $R\ln 12 = 2.5R$  for additional randomisation of the triply-degenerate  $\text{Fe}^{2+}$  orbital states. Hence the observed entropy change of  $\sim 0.7R$  corresponds to only 30% of the possible disorder at  $\text{TV}$ .<sup>29</sup>



Previous estimates have used Anderson or other charge configurations within tetrahedra of four B sites, but trimeron-based models may provide alternative predictions. An approximate calculation based on the above local connectivity of  $\text{Fe}^{3+}$  sites reduces the predicted transition entropy from 2.5R to 2.1R (or from 1.4R to 1.0R if orbital states are neglected) – these estimates are still greater than above the observed value and suggest that trimeron or other correlations persist above  $T_V$ .

In conclusion, we have determined the low temperature structure of magnetite to high experimental precision from high energy x-ray structure analysis of a small, almost single-domain, magnetite grain. Many frozen lattice modes contribute to the  $Cc$  superstructure including substantial acentric amplitudes from which a large electrical polarisation is predicted. Verwey's charge ordering hypothesis is correct to a useful first approximation, but analysis of the Fe-Fe distances indicates that the minority spin  $\text{Fe}^{2+}$  electrons are delocalised over linear three-site (trimeron) units. Selforganisation of the charge and orbital states couples the spin order of this eponymous magnetic material to the complex Verwey distortion. Trimerons may be significant quasiparticles above the Verwey transition and may also be relevant to other transition metal oxides such as superconducting  $\text{LiTi}_2\text{O}_4$  spinel. Finally, we note that a full *ab initio* simulation of the low-temperature magnetite structure starting from calculations on the cubic state presents a future challenge to improve understanding of the Verwey phase, now that the experimental structure has been determined.

## Methods Summary

Grains from a highly stoichiometric powder used in previous studies<sup>5,6,8</sup> were placed in a 100- $\mu\text{m}$ , focused monochromatic beam (wavelength, 0.16653(1) Å; estimated standard deviation shown in parenthesis) on the ID11 diffractometer at ESRF, Grenoble. Multiple scattering and extinction problems were reduced by using small crystallites and a high X-ray energy (74 keV), which also gave access to an abundance of diffraction peaks at very high momentum transfer and reduced absorption effects. Crystals were aligned and de-twinned using a permanent magnet (producing a field of approximately 0.1 T at the sample), and were verified as being cubic single domains at 130 K before cooling through the Verwey transition to 90 K.

The grain used for structure determination was approximately spherical with diameter  $\sim 40$   $\mu\text{m}$ . We used  $\omega$ -scans with varying exposure times to increase the dynamic range of the data from the charge-coupled-device detector (Frelon2K camera) and these were performed at azimuthal angles  $\varphi$  and  $\varphi + 180^\circ$  to improve data redundancy and test for multiple scattering. Reciprocal lattice sections (Fig. 1a) were reconstructed using local software. Small-box integrations were used to identify the orientation of the two observed domains, and large-box integration was performed to encompass intensity from both domains and allow structure refinement as a pseudo-merohedral twin.

2,000 starting models were generated by applying random atomic displacements to the high-temperature structure and were optimized by least-squares refinement. A global minimum at residual  $R[F^2 > 4\sigma] = 4.99\%$  (where  $F$  and  $\sigma$  are the observed magnitude and standard deviation of a structure factor) was observed most frequently (292 times), in addition to local refinement minima ( $R[F^2 > 4\sigma] \geq 5.88\%$ ). The final refinement of the global minimum model used independent anisotropic thermal parameters for all atoms and all data to a resolution of  $d \geq 0.3$  Å, giving  $R$  values  $R[F^2 > 4\sigma] = 3.40\%$ ,  $R[F^2] = 5.18\%$  and weighted residual  $wR_2 = 6.96\%$ . Full crystallographic information and details of the analysis software are given in Supplementary Information.

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