Magnetism and the Trimeron Bond

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J. Paul Attfield*

ABSTRACT: A review of progress in understanding the Verwey transition in magnetite (Fe₃O₄) over the past decade is presented. This electronic and structural transition at \(T_V \approx 125\) K was reported in 1939 and has since been a contentious issue in magnetism. Long range \(\text{Fe}^{2+}/\text{Fe}^{3+}\) charge ordering has been confirmed below the transition from crystal structure refinement, and \(\text{Fe}^{2+}\) orbital ordering and formation of trimerons through weak bonding of \(\text{Fe}^{2+}\) states to two \(\text{Fe}\) neighbors has been discovered. This model has accounted for many spectroscopic observations such as the \(^{57}\text{Fe}\) NMR frequencies. The trimeron lifetime has been measured, and trimeron soft modes have been observed. The origin of the first to second order crossover of Verwey transitions in doped magnetites has been revealed by a nanoparticle study. Electronic and structural fluctuations are found to persist to temperatures far above \(T_V\) and local structural distortions track the bulk magnetization, disappearing at the 850 K Curie transition. New binary mixed-valent iron oxides discovered at high pressure are found to have electronic transitions and orbital molecule ground states similar to those of magnetite.

INTRODUCTION

Goodenough’s seminal “Magnetism and the Chemical Bond” introduced important concepts such as orbital-based super-exchange rules for explaining magnetism in solids.\(^1\) The magnetic behavior of many transition metal compounds was rationalized using these rules, including the ferrimagnetism of the original magnetic material magnetite (Fe₃O₄), and related ferrite spinels. However, magnetite also undergoes a change in properties at \(T_V \approx 125\) K reported by Verwey in 1939 that reveals further electronic complexity at low temperatures.\(^2\) The full low temperature crystal structure was determined in 2012 and revealed direct magnetically driven Fe–Fe bonding interactions within three-center trimeron units.\(^3\) This paper will review progress on the long-running effort to understand the Verwey transition of magnetite made over the subsequent decade.

At ambient temperature, magnetite adopts the cubic spinel-type structure with an inverse formal charge distribution \(\text{Fe}^{3+}\)[\(\text{Fe}^{2+}\)]₂O₄ over tetrahedral A and octahedral B sites, shown throughout as \(A[B]_2O_4\). Ferrimagnetic order occurs below the Curie transition at \(T_C \approx 850\) K as there are twice as many up-spins at the B sites as there are down-spins at the A sites. Each cation site has a \(\text{Fe}^{3+}\) 3\(d^5\) \(S = \frac{5}{2}\) core spin, and rapid hopping of the one extra down-spin electron for every two B sites results in minority-spin-polarized electronic conductivity so all B-sites are structurally and spectroscopically equivalent. The Verwey transition at \(T_V \approx 125\) K, where magnetite undergoes a structural distortion and becomes electrically insulating, is observed in measurements of heat capacity, conductivity, magnetization, and many other properties. Progress made on understanding this transition during the 20th Century is covered in an extensive review by Walz.\(^4\)

Verwey proposed that the 125 K transition is driven by an ordering of \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) ions at the B-sites equivalent to localization of the minority spin extra electrons,\(^2\) a phenomenon now known as charge ordering that has been verified in many other oxides.\(^5\) However, initial simple charge ordered models were incompatible with crystallographic data, and a complex lattice distortion to a monoclinic \(\sqrt{2} \times \sqrt{2} \times 2\) superstructure of the cubic room temperature spinel lattice was later identified.\(^6,7\) The supercell has \(Cc\) space group symmetry and contains 56 symmetry-unique atoms (compered to three in the cubic \(Fd\overline{3}m\) high temperature cell). The complexity of this acentric superstructure in addition to practical difficulties arising from microtwinning of \(Cc\) domains below the Verwey transition.

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hampered single crystal diffraction studies of the low temperature structure. Several partial structure refinements using powder diffraction data with symmetry constraints,8−10 or Fe K-edge resonant X-ray diffraction studies,11−13 reported some evidence for charge order during 2001−2011.

A full refinement of the low temperature Cc superstructure of magnetite against microcrystal synchrotron diffraction data recorded at 90 K was reported by Senn, Wright, and Attfield (hereafter the SWA model).5 Analysis of the local distortion modes of the BO6 octahedra revealed complex patterns of Fe2+/Fe3+ charge ordering and Fe2+ preferentially oxidized.53 Material reprinted with permission from ref 53. Figure 1a,b. A later ellipsoidal analysis of local coordinations in the SWA model also revealed the charge and orbital ordering features.14 However, additional structural displacements leading to anomalous shortening of some B−B distances showed that the extra down-spin electrons are not fully localized as Fe2+ states but are instead spread over linear three-site units where weak magnetically driven Fe−Fe−Fe bonding results in highly structured three-site polarons termed “trimeron” (Figure 1c). The low temperature structure can thus also be described as a network of corner sharing trimeron (Figure 1d). It is notable that, out of many theoretical predictions made prior to publication of the SWA model, one computational study did correctly predict the charge and orbital ordering patterns within the Cc superstructure of magnetite and also reported some of the trimeron distortions.15

This paper will review progress on magnetite and the Verwey transition over the past decade, showing how experimental and computational results have been used to test and build upon the charge, orbital, and trimeron orderings and other features of the SWA model and describing new iron oxides that have been discovered to have trimeron-based and related ground states. The review is organized into sections that cover insights into (A) the low and (B) the high temperature states of magnetite (below and above Tv); (C) results for off-stoichiometric and cation-doped magnetites; and (D) discoveries of other iron oxides with trimeron-based and related ground states.

■ RESULTS

A. Low Temperature Magnetite (below Tv). The experimental reproducibility of the SWA model for the Cc superstructure was verified by a subsequent study in which 22 high-accuracy structure refinements using synchrotron X-ray data from three different 10−40 μm grains of magnetite were performed at temperatures from 20 to 124 K.16 Analysis of the coordinates showed little variation across the models except for small thermal changes at temperatures just below Tv.

The low temperature Cc crystal structure is complex and difficult to visualize, and so it is useful to represent the 168 independent shifts in (x, y, z) atomic coordinates as 168 equivalent frozen phonon amplitudes. Only one O atom mode is present in the high temperature cubic structure as a static distortion, and the rest all freeze at the Verwey transition. A total of 80 modes are required for the closest centric description (preserving inversion symmetry) in space group C2/c, and an additional 88 are needed for the full acentric Cc description. The 168 modes belong to four classes; Γ, Δ, X, and W point distortions. The magnitudes of all 168 modes in the SWA model have been analyzed5,17 and their thermal variations were also reported.16 Differences between the amplitudes of centric and acentric branches of Δ, X, and W modes were all found to contribute to the significant off-center atomic distortions in the Cc magnetite structure that can lead to ferroelectric and multiferroic properties. It would be convenient to be able to describe the Cc magnetite structure in terms of a few frozen phonon modes, but no good approximation is yet apparent, although brief details of an attempt at mode parametrization are reported.18

Further diffraction evidence for charge order in the Cc phase of magnetite has come from a resonant multilayer X-ray diffraction study.19 The use of three-wave diffraction intensities corrected for self-absorption effects that may have affected earlier studies, giving clear evidence for charge ordering at the B-sites in agreement with the SWA model.

Electronic DFT band structure calculations of the Cc magnetite structure have been reported using the SWA model positions20,21 or with relaxed coordinates.22 These have confirmed the reported charge and orbital orderings and show
that the extra electrons occupy a narrow minority-spin band just below the Fermi level. Real space plots of the electron density show a buildup of charge between Fe atoms that form trimeron units, consistent with a weak bonding effect.\textsuperscript{20} Interplay between the orbital order and spin–orbit coupling was found to account for the reported magnetostrictive effect in the $\text{Cc}$ structure.\textsuperscript{21}

DFT calculations have also been used to investigate how well the SWA model accounts for spectroscopic observations of the low temperature magnetite structure.\textsuperscript{57}Fe NMR is particularly important as it is the only noncrystallographic technique to have resolved signals from all 24 unique Fe atoms (at 8 A sites and 16 B sites) within the $\text{Cc}$ cell.\textsuperscript{23} Hyperfine fields from DFT calculations were used to compute the $\text{57}\text{Fe}$ resonance frequencies,\textsuperscript{24,25} and these are in excellent agreement with reported values as shown for the B sites in Figure 2. These calculations also support the trimeron description as ref\textsuperscript{25} notes “the hyperfine anisotropy data obtained from the DFT calculations support the trimeron concept as the central Fe$^{2+}$ site Fe$^{2+}$ ions with the extra electron in the direction changes around a applied magnetic easy magnetization axis of the structure have shown good agreement with inelastic neutron, X-ray, and nuclear scattering data, revealing strong trimeron–phonon coupling, especially for trimerons oriented parallel to the axes of the monoclinic $\text{Cc}$ cell.\textsuperscript{28}

Dynamics of the low temperature phase of magnetite have been explored using coherent and other light sources. The lifetime of individual trimerons was measured in a pump–probe experiment where the effects of femtosecond laser excitation were followed by soft X-ray diffraction.\textsuperscript{29} This found that metallization of the low temperature state of magnetite proceeds in two steps. Initial trimeron destruction takes place in 300 fs, with phase segregation into metallic and insulating regions following on an $\sim 1500$ fs time scale. A full study of the photoinduced phase segregation through optical conductivity measurements was subsequently reported.\textsuperscript{30} Soft electronic modes of the trimeron order were recently revealed by low temperature optical pump–terahertz probe experiments.\textsuperscript{31} These modes show critical softening and so are associated with the Verwey transition, and they most likely correspond to the sliding of trimerons along their long axes.

The Verwey transition is suppressed at a pressure of 8 GPa as confirmed by changes in elastic constants observed in a high pressure study.\textsuperscript{52} Pronounced elastic anisotropies in acoustic waves along the cubic-[110] direction were attributed to the presence of the long Fe$^{2+}$–Fe$^{3+}$–Fe$^{2+}$ trimeron axis parallel to this direction. The large shape strain at the Verwey transition makes the low temperature phase sensitive to nonhydrostatic stresses, and twin populations are altered.\textsuperscript{53} Uniaxial stresses are found to increase $T_V$ initially as twin orientations with higher $T_V$’s become favored. Twinning of the $\text{Cc}$ structure is eliminated in small particles, and a study of magnetite nanocrystal size effects showed that the Verwey transition is decreased slightly to $T_V \approx 120$ K at a 20 nm particle size and is fully suppressed in particles below 6 nm.\textsuperscript{34} This demonstrates that the minimum coherence distance for the bulk long-range electronic order is around the length of 10 trimerons.

### B. High Temperature Magnetite (above $T_V$)

Above the Verwey transition at $T_V \approx 125$ K, magnetite has the cubic spinel-type structure in space group $\text{Fd}$$\text{3}$$\text{m}$ with formal charge distribution $\text{Fe}^{3+}[\text{Fe}^{2+} \ldots]_2\text{O}_4$, at ambient temperature. A high temperature powder neutron diffraction study revealed changes in the thermal expansion coefficient and variable oxygen coordinate near 700 K that were attributed to the onset of charge transfer between the tetrahedral A and octahedral B sites.\textsuperscript{55} This has been confirmed by recent X-ray spectroscopy measurements which showed that charge transfer from B to A sites is represented by $x$ in the formula $\text{Fe}^{3+}_x \text{Fe}^{2+}_{1-x}\text{Fe}^{3+}_{\frac{x}{2}}[\text{Fe}^{3+}_{\frac{x}{2}}\text{Fe}^{2+}_{\frac{x}{2}-1\frac{x}{2}}]_2\text{O}_4$, starts near 330 K and increases up to $x \approx 0.125$ at 840 K near $T_\text{C}$.\textsuperscript{36} Migration of Fe cations from octahedral sites to tetrahedral vacancies was reported at higher temperatures.

A key question has been whether disordered charge, orbital, and trimeron correlations persist in the high-temperature cubic phase. Observation of diffuse scattering just above $T_V$ shows that local structural correlations are present, and a single crystal X-ray experiment revealed highly structured diffuse scatter that persists to at least 300 K.\textsuperscript{57} This has been corroborated by inelastic scattering studies of the lattice vibrations. Raman studies have shown that changes in vibrational modes associated with the Verwey transition occur from $T_V$ up to $\sim 200$ K,\textsuperscript{38-40} and an inelastic neutron scattering study up to 293 K found discontinuities in transverse acoustic phonons at $T_V$ and a decoupling of electronic and phonon dynamics consistent with slow fluctuations of trimerons in the cubic phase.\textsuperscript{40} Anomalous

![Figure 2](https://doi.org/10.1021/acs.chemmater.2c00275)
broadening of \( \Delta \) and X mode phonons up to at least 293 K was reported from an inelastic X-ray scattering (IXS) study.\(^{41}\) Resonant IXS (RIXS) has been used to explore electronic excitations of the octahedral Fe cations in cubic magnetite, revealing magnetic excitations driven by polaronic distortions that persist to at least 350 K.\(^{42}\) Other RIXS experiments have shown that the orbital components of the magnetic moments are ordered noncollinearly at 300 K, consistent with dynamic distortions associated with polaron formation.\(^{43}\)

However, a RIXS-MLD (magnetic linear dichroism) experiment at 170 K revealed that the polarization dependence of the spin–orbital excitations is incompatible with the purely tetragonal Jahn–Teller distortions of the ideal trimeron quasiparticle (Figure 1c) and suggested that trigonal distortions may be more relevant.\(^{44}\)

Analysis of the PDF (pair distribution function) derived from total scattering experiments has been used to evidence local structural distortions within the cubic phase of magnetite. Room temperature X-ray and neutron PDFs of a nanoparticle magnetite sample were found to be not fitted well by the cubic \( Fd\bar{3}m \) structure, and lower symmetry space groups were used to model the local distortions.\(^{45}\) The SWA model was used to fit the average degree of local distortion over short, medium, and long-range length scales in an X-ray PDF study covering a wide range of temperatures (90–923 K).\(^{46}\) The resulting plots in Figure 3 show that long-range structural distortions fall sharply to zero just above \( T_V \), while medium range distortions persist up to 250–300 K, which matches Raman observations of modes associated with the electronic order.\(^{36,39}\) However, short-range structural correlations, on the length scale of an individual trimeron, remain present above \( T_V \) and decrease to zero near the Curie transition at \( T_C \approx 850 \) K, following a similar temperature dependence to the reported bulk magnetization.\(^{37}\) This also matches the thermal transfer of extra electrons (Fe\(^{3+} \) states) from octahedral to tetrahedral sites seen by X-ray spectroscopy.\(^{36}\) The weak bonding Fe–Fe interactions in a trimeron require ferromagnetic alignment of the three core \( S = S/2 \) spins so that the extra minority spin electron can be delocalized over the three Fe ions, as shown in Figure 1c. Hence, magnetization is coupled to local Fe displacements to which the X-ray PDF is particularly sensitive. Fe cation displacements due to Fe–Fe bonding interactions emerging below \( T_V \) were thus identified as the primary driver of the local structural distortions that give rise to the Verwey transition in magnetite.

### C. Doped Magnetites

Many cations can be substituted into magnetite to generate the cubic spinel family of ferrites. Comparison of room temperature X-ray and neutron PDFs for \( \text{MFe}_2\text{O}_4 \) (M = Mn, Fe, Co, and Ni) spinel nanoparticles showed that the M = Mn, Co, and Ni dopants suppressed the local distortions observed for M = Fe magnetite,\(^{48}\) consistent with loss of the Fe\(^{3+} \) states associated with local charge, orbital, and trimeron orders.

Magnetite has a small intrinsic range of nonstoichiometry due to iron-deficiency as Fe\(_{3+x-0.4}\)O\(_4\) up to \( x = 0.035 \). Studies of nonstoichiometric and lightly cation-doped magnetites showed that \( T_V \) is suppressed by doping, and a change from sharp first order to broad second order Verwey transitions was reported around hole doping of \( x \approx 0.012 \),\(^{48,49}\) as shown in Figure 4.

![Figure 4](https://doi.org/10.1021/acs.chemmater.2c00275)

**Figure 4.** Variations of \( T_V \) and the monoclinic angle of the low temperature \( Cc \) cell with doping parameters for nonstoichiometric and cation-doped magnetites in ref 49. The break between first and second order regimes of the Verwey transition is marked by the vertical line. Reprinted with permission from ref 49. Copyright 2012 Elsevier.

The lattice distortion associated with formation of the low temperature \( Cc \) state is observed in both first and second order regimes, and no change in phonon spectra between the regimes was found in nuclear inelastic scattering experiments.\(^{50}\) \( \text{Zn}^{2+} \) substitutes at the tetrahedral A sites and so provides a clean way to hole-dope the B cation sites as Fe\(_{3−x} \)Zn\(_x\)\( \left[ \text{Fe}^{3+}_{1−x} \text{Zn}^{2+}_x \right] _4 \)O\(_4\) up to \( x = 0.4 \) and detailed characterization of Fe\(_{3−x} \)Zn\(_x\)O\(_4\) samples by Mössbauer spectroscopy and X-ray diffraction has been reported.\(^{51}\)

Insight into the origin of the first and second order regimes of doped magnetites has recently been provided by a study of slow oxidation of magnetite nanoparticles.\(^{52}\) This revealed that the Verwey transition is initially suppressed to a minimum value at \( T_V \approx 80 \) K, but on further oxidation recovers to a persistent value of \( T_V = 95 \) K as shown in Figure 5. This variation demonstrates that the Verwey transition is suppressed not only by the doping...
respectively. The dashed line indicates the time $t$ during oxidation, and this was con
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 richness exterior and oxygen-poor interior of the nanoparticles from the concentration gradient developed between the oxygen-
Figure 5. Variation of the Verwey transition of magnetite nanoparticles with oxidation time in air from ref 52. Square, circle, triangle, and diamond symbols show $T_V$ values from magnetization ($M$), powder X-ray diffraction (XRD), NMR, and heat capacity (C/T) measurements, respectively. The dashed line indicates the time $t_{\text{min}}$, at which the minimum of $T_V$ is observed in the magnetization data. The color density represents the temperature difference of the magnetization, $dM/dT_V$, which shows how the Verwey transition broadens around $t_{\text{min}}$ and later sharpens as the persistent $T_V = 95$ K value is reached near $2t_{\text{min}}$. This persistent value is identified as the limit of the first order (homogeneous) doping regime. Material reprinted from ref 52. Published 2021 by Springer Nature Limited under a Creative Commons license (http://creativecommons.org/licenses/by/4.0/).

The trimerons observed in the low temperature structure of magnetite are an example of orbital molecules, clusters made up of coupled orbital states on several metal ions within an orbitally ordered (and often also charge ordered) solid. Further examples of orbital molecules are found in other transition metal compounds, e.g., the $V_2$ dimers formed in other orbital molecule ordering in their ground states.

D. Other Iron Oxides. The trimerons observed in the low temperature structure of magnetite are an example of orbital molecules, clusters made up of coupled orbital states on several metal ions within an orbitally ordered (and often also charge ordered) solid. Further examples of orbital molecules are found in other transition metal compounds, e.g., the $V_2$ dimers formed below the metal–insulator transition in VO$_2$, and are reviewed elsewhere. Recent discoveries of trimeron and related dimeron cluster orders in iron oxides are described below.

Fe$_3$O$_4$ was previously the only known stoichiometric, binary, mixed-valent iron oxide, but the past decade has seen an explosion of iron oxide discoveries. The breakthrough occurred when geophysicists exploring possible new iron oxides formed at high pressures and temperatures within Earth’s mantle discovered a new composition, Fe$_2$O$_3$ (Figure 6a), that could be recovered to ambient conditions. This has led to discoveries of new binary mixed-valent iron oxides falling into the Fe$_m$O$_{n+1}$ ($n = 4$ and 5) and Fe$_m$O$_{m+2}$ ($m = 5$ and 7) homologous series. The Fe$_{n+1}$ materials show Verwey-type transitions with charge, orbital, and orbital molecule ordering in their ground states.

Figure 6. (a) Projection of the Fe$_3$O$_4$ structure type. This has two inequivalent types of FeO$_6$ octahedra (red and blue) and Fe$^{3+}$ ions within trigonal prismatic tunnels (purple). The latter are replaced by Ca$^{2+}$ in CaFe$_2$O$_4$. Electronic phase separation in lightly doped CaFe$_2$O$_4$ leads to a mixture of (b) a charge ordered (CO) ground state, where groups of three spins have ferromagnetic alignment leading to Fe$^{3+}$–Fe$^{3+}$–Fe$^{3+}$ charge order and trimeron formation (green lines), and (c) a charge averaged (CA) phase where the spins in the same groups are antiferromagnetically coupled and no charge or trimeron order is observed. Material from ref 68, http://creativecommons.org/licenses/by/4.0/.
Fe₂O₃ orders antiferromagnetically below ~320 K and shows a Verwey-type charge ordering transition at 150 K and a further spin canting transition at 85 K.²⁵ The Fe²⁺/Fe³⁺ charge ordered structure is incommensurate and consists of trimerons and also dimerons. “Dimeron” is used to describe two-center units analogous to trimerons, where one extra electron is shared between two neighboring B site cations with parallel S = 5/2 spins, giving a symmetric Fe₃⁵⁺ dimer. Two further high pressure charge ordered phases, one containing dimerons and trimerons and the second based on dimerons alone, have subsequently been discovered from exploration of the low temperature phase diagram up to 50 GPa.²⁰ Fe₂O₃ undergoes a Verwey-type charge ordering transition at 275 K leading to dimer ordering, with long-range antiferromagnetic order of the dimerons below 100 K, and the dimer order is reported to be stable to at least 20 GPa.²⁰

Electronic ordering has also been reported in several ternaries derived from magnetite or the above new iron oxides. High pressure Mössbauer, conductivity, and diffraction studies of the warwickite type oxoborate BFe₂O₄ (Fe₂OBO₃), which is charge ordered without orbital molecule formation below 280 K at ambient pressure,²³ reported formation of an electron-localized dimeron phase from 16 GPa up to at least 50 GPa.²³,²⁴ CaFe₂O₇, the Ca-stabilized version of the as-yet unreported Fe₄O₅ for M = Mn and Ca. Spins in MnFe₃O₅ order at 150 and 60 K. The latter is driven by charge ordering of Fe²⁺ dimerons. Structured is incommensurate and consists of trimerons and also provides a clear demonstration of the conditions for trimeron formation.²⁵,²⁶,²⁷ The trimeron interpretation of the low temperature electronic order has also been supported by subsequent studies; a critical test was again the ⁵⁷Fe NMR spectrum where the trimeron model was shown to give a better description than an alternative orbital picture.²⁵ Measurement of the trimeron lifetime as a distinct step in the photon-induced metallization of magnetite²⁷ and recent observation of trimeron soft modes²⁸ add further weight. Comparison of trimeron and nontrimeron ground states in phase separated CaFe₂O₅ gives direct observation of the conditions for trimeron formation.²⁴,²⁵ Electronic DFT band structure calculations have confirmed the charge, orbital, and trimeron orderings in magnetite²⁶-²⁸ and have enabled quantitative interpretation of many spectroscopic results. A recent study (ref 28) concluded that their “results indicate the validity of trimerons (and trimeron–phonon coupling) to explain the physics of magnetite much beyond their original formulation”, suggesting that further insights may derive from more sophisticated future theoretical treatments of trimeron quasiparticles.

Understanding of the low temperature state of magnetite has assisted interpretation of the high temperature cubic phase. RIXS has been particularly insightful in showing that charge and orbital fluctuations remain active far above Tₘ.²⁹ Two studies have revealed similar variations in local distortions²⁹ and B to A site charge transfer as temperature increases toward Tₘ ≈ 850 K. These paint a consistent picture that long-range magnetic order creates the trimeron bonding distortions that drive charge and orbital ordering, thereby suppressing B to A site charge transfer. Critical fluctuations in the magnetization as temperature increases toward Tₘ thus lead to loss of the local structural distortions and the onset of intersite charge transfer.

However, studies of local structure in the cubic phase of magnetite have not definitively shown that trimeron distortions are responsible for the Fe and other displacements, and one RIXS study suggests that this geometry is not dominant.²⁹ It is notable that several other mixed valent Fe oxides (Fe₂O₅) resonant and nonresonant IXS,³¹-³⁴ with the majority of these experiments performed at the ESRF. Coherent light sources have also been important for pump–probe studies of lattice dynamics.²⁹,³¹ Improved DFT codes have supported many of these investigations, also enabling accurate NMR and Mössbauer spectra to be simulated.²⁴-²⁶,³² Developments in nanoparticle chemistry have enabled influences of particle size and oxygen content on the Verwey transition to be determined in exquisite detail.³³,³⁴ High pressure discoveries of new mixed-valent binary iron oxides have broadened insights into magnetite.³⁵-³⁶

The SWA model for the Cc crystal structure of magnetite below the Verwey transition has been corroborated by subsequent microcrystal diffraction studies showing only small changes with temperature or doping, although the selective destruction of one trimeron in Fe₀.⁹⁸Zn₀.₀₂O₄ is a notable structural variation.³³ The Fe²⁺/Fe³⁺ charge ordering and Fe²⁺/Fe³⁺ orbital ordering deduced from the SWA model have been confirmed by many other techniques, notably through spectroscopic assignment of all 24 ⁵⁷Fe NMR signals and the four classes of Mössbauer resonances.³⁵-³⁶ The long-running hypothesis that magnetite has a charge ordered ground state, originally proposed by Verwey in 1939, has thus been comprehensively confirmed over the past decade. The origin of the change from first to second order Verwey transitions in doped magnetites has also been revealed by a nanoparticle oxidation study.³²
Fe₂O₄,⁶⁰ and Fe₂OBO₃,⁶²,⁶³ show ordering of two-site dimers or a mix of trimer and dimer units, at ambient or high pressure. Hence, the cubic phase of magnetite might contain mixtures of one-site (single Fe²⁺ ions), two-site (dimer), three-site (trimer), and perhaps other orbital molecule fluctuations that are likely to change their populations with temperature. The nature of magnetite at ambient temperature (above Tᵥ) thus remains a continuing topic for human inquiry, as it has for around 3000 years.

■ CONCLUSIONS
Discoveries over the past decade have led to great progress in understanding of the Verwey transition at Tᵥ ≈ 125 K in magnetite. Long range Fe²⁺/Fe³⁺ charge ordering below the transition is confirmed from full refinement of the acentric Cc crystal structure, and Fe²⁺ orbital ordering and formation of trimers through weak bonding of Fe²⁺ states to two Fe neighbors have been discovered. This model has accounted for many spectroscopic observations such as the ⁵⁷Fe NMR frequencies. The trimer lifetime has been measured, and trimer soft modes have been observed. The origin of the first to second order crossover of Verwey transitions in doped magnetites has also been revealed by a nanoparticle oxidation study. Studies of the cubic phase of magnetite have shown that electronic and structural fluctuations persist to temperatures far above Tᵥ and local structural distortions track the bulk magnetization, disappearing at the Curie transition at Tᵥ ≈ 850 K. However, whether the high-temperature structural fluctuations are trimer-like remains to be determined. New binary mixed-valent iron oxides discovered at high pressure are found to have similar electronic transitions and orbital molecule ground states, establishing a broader context for the electronic properties of magnetite.

■ AUTHOR INFORMATION

Corresponding Author
J. Paul Attfield — Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom; orcid.org/0000-0001-9763-3987; Email: j.p.attfield@ed.ac.uk

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chemmater.2c00275

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