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Spin state of iron in Fe$_3$O$_4$ magnetite and h-Fe$_3$O$_4$

Amelia Bengtson, Dane Morgan, and Udo Becker

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Title: Spin state of iron in Fe₃O₄ magnetite and h-Fe₃O₄

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Abstract

The high-pressure behavior of magnetite has been widely debated in the literature. Experimental measurements have found conflicting high-pressure transitions: a charge reordering in magnetite from inverse to normal spinel [Pasternak, M.P., et al. J. Phys. Chem. Solids 65, 1531 (2004); Rozenberg, G.K., et al. PRB. 75 (2007)], iron high- to intermediate-spin transition in magnetite [Ding, Y., et al. PRL 100 (2008)], electron delocalization in magnetite [Baudelet, F., et al. PRB 82 (2010); Glazyrin, K., et al. Am. Min. 97, 128], and a structural phase transition from magnetite to h-Fe3O4 [Dubrovinsky, L.S., J. Phys.: Condens. Matter 15, 7697 (2003); Fei, Y.W., Am. Min. 84, 203 (1999); Haavik, C., Am. Min. 85, 514 (2000)]. We present the first ab initio calculations of iron’s spin state in magnetite and h-Fe3O4, which helps resolve the high-pressure debate. The results of the calculations find that iron remains high spin in both magnetite and h-Fe3O4; intermediate-spin Fe is not stable. In addition, magnetite remains inverse spinel but undergoes a phase transition to h-Fe3O4 near 10 GPa. Magnetite has a complex magnetic ordering, multiple valence states (Fe2+ and Fe3+), charge ordering, and different local Fe site environments, all of which were accounted for in the calculations. The lack of intermediate-spin iron in magnetite helps resolve the spin state of Fe in perovskite, the major mineral in the lower mantle. In both magnetite and perovskite, XES measurements in the literature show a drop in satellite peak intensity by approximately half, which is interpreted as intermediate-spin Fe. In both minerals, calculations give no indication of intermediate-spin iron and predict high-spin iron to be stable for defect-free crystals. The results question the interpretation of a non-zero drop in XES satellite peak intensities as intermediate-spin Fe.
I. INTRODUCTION

Magnetite (Fe$_3$O$_4$) has been of interest throughout history because it is one of the most magnetic naturally-occurring minerals and is important for paleomagnetic measurements and past continent reconstruction$^1$. Magnetite can also be found at higher pressures in the mantle wedge of subduction zones$^2$ formed as a by-product of serpentinization of olivine$^3$. In addition, electrical resistivity measurements in magnetite are useful for interpreting magnetotelluric measurements of the mantle$^4$.

The high-pressure structural, electronic, and magnetic properties of Fe$_3$O$_4$ are not well characterized and the complex coupling of Fe spins contributes to these properties. Changes in magnetic, spin, and structural states will alter density, elasticity, and electrical conductivity$^5$ and thus have an influence on interpretation of magnetotelluric measurements. In addition, changes that occur in the electronic or magnetic structure of Fe$_3$O$_4$ at high-pressure could reset magnetic ordering in meteorites that collide at high-pressure, therefore complicating the interpretation of paleomagnetic data$^6$.

Fe$_3$O$_4$ has recently been suggested to undergo a transition to an intermediate-spin state on some of the Fe atoms$^7$. The nature of the possible intermediate-spin transition in magnetite is important both for understanding Fe$_3$O$_4$ and for a more general understanding of the spin state of Fe in the Earth’s lower mantle. Despite numerous experimental measurements and theoretical calculations, the spin state of Fe in perovskite, the dominant mineral in the lower mantle, is still under debate. X-ray emission spectroscopy (XES) measurements find the satellite peak intensity of Fe in perovskite drops to a non-zero value with increasing pressure, which is interpreted as a transition from high- to intermediate-spin Fe$^8$. However, theoretical calculations do not support intermediate-spin Fe in perovskite$^{9,10-13}$. XES measurements in magnetite show a similar drop in satellite peak intensity to perovskite, suggesting the spin state of Fe in magnetite is also intermediate-spin$^7$. Calculations of the spin state of Fe in magnetite will therefore provide additional evidence to help settle the more general debate over whether intermediate-spin Fe is occurring in high-pressure Fe compounds.

At ambient pressure and temperature, magnetite has an inverse spinel structure
with a random distribution of Fe$^{2+}$ and Fe$^{3+}$ on the octahedral site. The charges average to an effective valence state of Fe$^{2.5+}$ on the octahedral sites. In the literature, agreement exists that a transition occurs in Fe$_3$O$_4$ between 10-20 GPa, but there is lack of agreement as to the type of transition. $^{57}$Fe Mössbauer spectroscopy measurements suggest the high-pressure phase goes through an inverse- $\left[Fe^{3+}\right]_{\text{TET}}$ to normal- $\left[Fe^{2+}\right]_{\text{TET}}$ spinel transition with increasing pressure (8-15 GPa at room temperature). However, K-edge x-ray magnetic circular dichroism and x-ray emission spectroscopy measurements are interpreted as an Fe$^{2+}$ transition on the octahedral site from high- to intermediate-spin at 12-16 GPa. An additional hypothesis, based on X-ray diffraction measurements, is that Fe$_3$O$_4$ has a phase transition from magnetite ($Fd\overline{3}m$ symmetry, $\left[Fe^{3+}\right]_{\text{TET}}$ inverse spinel) to a new high-pressure phase, h-Fe$_3$O$_4$ ($Pbcm$ symmetry, $\left[Fe^{2+}\right]_{\text{TET}}$ normal spinel) between 10-20 GPa (300 K). The h-Fe$_3$O$_4$ crystal structure is a CaMn$_2$O$_4$-type structure (Fig. 1). No studies have yet been done on the spin-state of Fe in h-Fe$_3$O$_4$. More recent X-ray diffraction measurements and Mössbauer spectroscopy experiments as well as x-ray absorption spectroscopy and Fe K-edge x-ray magnetic circular dichroism measurements find magnetite remains inverse spinel up to 25 GPa. Above 15 GPa, the measurements suggest the Fe electrons delocalize, exhibiting a continuous decrease in moment rather than undergoing a spin transition. The measurements just discussed suggest four possible and quite different transitions with pressure: charge reordering in magnetite (inverse to normal spinel), spin transition in magnetite (high- to intermediate spin), electron delocalization in magnetite, or a structural transition to a new phase (magnetite to h-Fe$_3$O$_4$). The goal of this paper is to calculate, using quantum-mechanical ab initio methods, the spin state of Fe as a function of pressure in Fe$_3$O$_4$ magnetite and h-Fe$_3$O$_4$. Because spin is linked to valence and site occupancy (and possibly magnetic ordering), multiple combinations of spin and ordering in both magnetite and h-Fe$_3$O$_4$ need to be explored. This work will both help elucidate the proposed pressure transitions that are actually occurring and the possibility of intermediate spin Fe in
magnetite. Section II describes the computational methods, including the \textit{ab initio} details and the different magnetic and spin states considered. Section III gives the results for magnetic and spin state behavior of each structure of interest, including inverse spinel (section III A), normal spinel (section III B), and h-Fe$_3$O$_4$ (section III C). The implications of these results for the stable phase as a function of pressure are given in section III D and section III D provides useful elastic constant data.
II. METHODS

In this study we used density functional theory (DFT) methods as implemented in the Vienna Ab
Initio Simulation Package (VASP)\textsuperscript{21}. VASP calculations were performed with the projector-augmented wave method (electronic configuration: 2s\(^2\) 2p\(^4\) for oxygen, 3p\(^6\) 3d\(^7\) 4s\(^1\) for Fe)\textsuperscript{22} using the Generalized Gradient Approximation (GGA) exchange-correlation with the Perdew-Burke-Ernzerhof (PBE) parameterization\textsuperscript{21} and a cutoff energy for the planewave basis functions of 600 eV. A 2 \times 2 \times 2 Monkhorst-Pack \(k\)-point mesh was used for sampling the Brillouin zone of the reciprocal space for all structures. All \(k\)-point meshes and energy cutoffs were chosen to have a convergence of less than 0.005 eV in energies and 0.02 Å\(^3\)/atom in volume. A Hubbard U parameter\textsuperscript{10} was applied to provide more accurate electronic structure for the localized d-orbitals, and is necessary to stabilize distinct Fe\(^{2+}\) and Fe\(^{3+}\) atoms\textsuperscript{24}. The invariant spin-polarized GGA+U scheme is used\textsuperscript{25} and U is added to Fe atoms only. We used U, the on-site Coulomb interaction parameter, equal to 4.6 eV and J, the effective on-site exchange interaction parameter, equal to 0.544 eV, consistent with previous work on Fe\(_3\)O\(_4\)\textsuperscript{24}.

All calculations were performed as spin polarized. Individual moments were allowed to relax and the total net moment of the cell was fixed. The spin and magnetic arrangements were created by setting initial magnetic moments on each atom and fixing the total net moment of the cell. Spins on the individual atoms were allowed to fully relax in the calculations. In some cases, a desired spin state with a given fixed total moment may relax to another spin state with the same total net moment. Details on fixed total net moments, initial moments, and final relaxed moments are given below.

A. Computational structural details

A central goal of this study is to calculate the spin state of Fe as a function of pressure in magnetite. The structure of magnetite may change with pressure and therefore three structures will be considered in the calculations in order to map the entire pressure space: inverse-spinel magnetite, normal-spinel magnetite, and h-Fe\(_3\)O\(_4\) (Table I).

In the remainder of the paper, the following notation will be used:
\[ \left[ (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} \right]_{\text{TET}} \left[ (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} \right]_{\text{OCT}} \]

\[ \left[ (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} \right]_{\text{TET}} \left[ (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} \right]_{\text{OCT}} \]

\[ \left[ (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} \right]_{\text{TET}} \left[ (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} (-)Fe_{\text{spin}}^{\text{valence}} \right]_{\text{OCT}} \]

[Fig. 1(a)]

Table I: Three structures are explored in the calculations. Magnetite may undergo an inverse to normal spinel transition with pressure. Magnetite may also undergo a phase transition to h-Fe3O4 with pressure. The spin state of Fe within all three structures is necessary to gain a complete understanding of the high-pressure spin states.

<table>
<thead>
<tr>
<th>Low-pressure</th>
<th>High-pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>magnetite, inverse spinel</td>
<td>magnetite, normal spinel</td>
</tr>
<tr>
<td>[ Fe^{3+} ]<em>{TET} \left[ Fe^{2+} \right]</em>{TET} Fe^{3+} \right]_{OCT}</td>
<td>magnetite, normal spinel</td>
</tr>
<tr>
<td>Imma symmetry</td>
<td>h-Fe3O4, normal spinel</td>
</tr>
<tr>
<td>[ Fe^{2+} ]<em>{TET} \left[ Fe^{3+} \right]</em>{TET} Fe^{3+} ]_{OCT}</td>
<td>[ Fe^{2+} ]<em>{TET} \left[ Fe^{3+} \right]</em>{TET} Fe^{3+} ]_{OCT}</td>
</tr>
<tr>
<td>Fig. 1(a)</td>
<td>[ Fd\bar{3}m ] symmetry</td>
</tr>
<tr>
<td>[ Fd\bar{3}m ] symmetry</td>
<td>[ Pbcm ] symmetry</td>
</tr>
<tr>
<td>Random distribution of Fe^{2+} and Fe^{3+} on the OCT site. Fig. 1(a)</td>
<td>High-pressure phase.</td>
</tr>
<tr>
<td>Fig. 1(a)</td>
<td>Fig. 1(b)</td>
</tr>
</tbody>
</table>

Table II: Total number of unpaired electrons and magnetic moment (\(\mu_B\)) for each spin state and valence state (Fe^{2+} and Fe^{3+}).

<table>
<thead>
<tr>
<th>valence</th>
<th>HS high-spin</th>
<th>IS intermediate-spin</th>
<th>LS low-spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe^{2+}</td>
<td>4</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Fe^{3+}</td>
<td>5</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>
1. Magnetite at ambient conditions: inverse spinel

Fe occupies both tetrahedral (TET) and octahedral (OCT) sites in magnetite (Fig. 1) at ambient conditions. The magnetism in magnetite is due to the ferrimagnetic ordering of Fe spins between the TET and OCT sites (Fig. 1). The known phases for the magnetite at lower pressure include both a low-temperature monoclinic phase with ordered Fe\(^{2+}\) and Fe\(^{3+}\) and a disordered Fd-3m symmetry structure. At 120 K (T\(_V\)) magnetite undergoes an electronic transition, the Verwey transition, which corresponds to a change in electrical conductivity due to the transition:

\[
\left[\text{Fe}^{3+}\right]_{\text{TET}} \left[\text{Fe}^{3+}\text{Fe}^{2+}\right]_{\text{OCT}} \xrightarrow{T<T_V}\ \left[\text{Fe}^{3+}\right]_{\text{TET}} \left[\text{Fe}^{2+}\text{Fe}^{2+}\right]_{\text{OCT}}
\]

When T > T\(_V\), there is a statistical distribution of Fe\(^{2+}\) and Fe\(^{3+}\) with an average charge of Fe\(^{2.5+}\) on the octahedral sites leading to high electrical conductivity. For T < T\(_V\), Fe\(^{2+}\) and Fe\(^{3+}\) become ordered on the OCT site and, as a consequence, conductivity is lost. Charge ordering has been confirmed by resonant x-ray diffraction experiments. DFT calculations are technically at absolute zero, since the energy solution corresponds to the ground state energy.

The focus of this study is on pressure-induced spin transitions in magnetite at room temperature for direct comparison with the experimental spin-transition study by Ding et al. Ideally, both phases would be included for a complete study of the spin state with and without the effect of charge-ordering. Instead, a single phase, the charge-ordered structure \(\left[\text{Fe}^{3+}\right]_{\text{TET}} \left[\text{Fe}^{3+}\text{Fe}^{2+}\right]_{\text{OCT}}\) was used as an approximation of the true statistical distribution. This is a necessary approximation to make the calculations practical and an acceptable approximation given the goal of the work to study the spin transition. Representing the random distribution of Fe\(^{2+}\) and Fe\(^{3+}\) atoms in the T > T\(_V\) charge-disordered structure \(\left[\text{Fe}^{3+}\right]_{\text{TET}} \left[\text{Fe}^{2+}\text{Fe}^{2+}\right]_{\text{OCT}}\) would require a large cell that is computationally impractical for this work. Furthermore, the pressure-dependence of T\(_V\) is not yet clear and at the higher pressures of the mantle the charge-ordered structure may in fact be the most stable structure at temperatures of interest.

In terms of the accuracy of the approximation, both the monoclinic (charge-ordered) and Fd-3m (charge-averaged) structures are clearly quite similar in energy, as the Verwey transition occurs at
$T_{\text{Verwey}}=120\text{K}$. This generally argues for charge ordering being a small contribution to the energy, on the order of just $kT_{\text{Verwey}} \sim 10\text{ meV/Fe atom}$. The results of this study will show the energy scale of the high-to intermediate-spin transition in magnetite is $1.01\text{ eV/f.u.} (\sim 340\text{ meV/Fe})$. Therefore, the energy change due to charge ordering differences should not change the energetics of the spin transition enough to stabilize intermediate-spin and in general would have negligible effects on the transitions of interest.

The charge-ordered inverse-spinel magnetite structure was created by starting with $Fd\bar{3}m$ symmetry and the experimental atomic positions (Fe(tet) 0.125 0.125 0.125, Fe(oct) 0.5 0.5 0.5, O .2549 .2549 .2549, $a=b=c=8.3965$, $\alpha=\beta=\gamma=90^\circ$)\textsuperscript{17,28}. To allow for ordering of Fe$^{2+}$ and Fe$^{3+}$, a 14-atom unit cell was created\textsuperscript{29} and the symmetry on the OCT site was reduced to $Imma$ by making the 4th and 5th Fe atoms Fe$^{2+}$, consistent with Wenzel and Steinle-Neumann (2007). The choice of the $Imma$ charge-ordered inverse-spinel magnetite structure is a practical approximation that has allowed us to elucidate the magnetite spin behavior with minimal loss of accuracy.

2. Magnetite at high pressure: normal spinel

Magnetite may undergo an inverse to normal spinel transition near 8 GPa\textsuperscript{15,16}. 8 GPa is near the possible spin-transition region, therefore spin transitions should also be considered in normal spinel. The normal-spinel structure was created from the experimentally identified atom positions for this structure in a 14-atom unit cell with $Fd\bar{3}m$ symmetry\textsuperscript{17}. In the input file all TET atoms were specified as Fe$^{2+}$ and all OCT atoms were specified as Fe$^{3+}$ by setting their respective initial magnetic moments.

3. Phase change in magnetite at high-pressure: $h$-Fe$_3$O$_4$

The high-pressure magnetite phase, h-Fe$_3$O$_4$ has a CaMn$_2$O$_4$-type structure with $Pbcm$ space group\textsuperscript{18}, with the magnetic ordering of Fe$^{2+}$ on the tetrahedral site and Fe$^{3+}$ on the octahedral site $[Fe^{2+}]_{\text{TET}}[Fe^{3+}Fe^{3+}]_{\text{OCT}}$ (Fig. 1b). Within the calculations, the $Pbcm$ symmetry relaxes to CaTi$_2$O$_4$-type $Bbmm$\textsuperscript{29}, consistent with\textsuperscript{19} and\textsuperscript{17}. A 28-atom unit cell was used.
A. Calculations under pressure

High-pressure behavior of magnetite (inverse spinel and normal spinel) and h-Fe₃O₄ was studied by performing fixed volume calculations. The ions were allowed to relax but cell shape and volume were fixed – this corresponds to ISIF=2 in the VASP INCAR file. In the magnetite 14-atom unit cell, the volume space grid was 155, 150, 145, 140, 135, 130, 125, and 120 Å³. In the 28-atom h-Fe₃O₄ unit cell the volume space grid was 290, 285, 280, 275, 270, 265, 260, 250, 240, 230 and 220 Å³. For each structure and spin state, energy as a function of volume, E(V), was fit to a 3rd-order Birch-Murnaghan equation of state to determine the energy and volume as a function of pressure. From E(P) and V(P), enthalpy as a function of pressure, H(P)=E(P)+P·V(P), and the equation of state parameters were found.

B. Calculating the spin state

Our goal is to understand the spin state of Fe in Fe₃O₄. Since the spin state of Fe could be linked to site coordination (TET vs. OCT), magnetic ordering, charge ordering, and charge coordination (valence), all these factors must be studied in order to have a full understanding of the spin state of Fe in Fe₃O₄. In this section, the spin calculations are laid out in detail.

To motivate the spin states studied, we first consider the spin related changes measured as a function of pressure by Ding et al., 2008. Their K-edge x-ray magnetic circular dichroism measurements show a drop in total magnetic moment by half (a decrease of 4μB to 2μB/formula unit, which would be 8μB to 4μB in our fourteen-atom computational unit cell) and their X-ray emission-spectroscopy measurements find a drop of peak intensity by ~15%, meaning ~15% of unpaired electrons have reduced their spins. In the formula unit of inverse-spinel magnetite (3 Fe atoms) \([-Fe^{3+}]_{TET}[Fe^{3+}Fe^{2+}]_{OCT}\), there are two Fe³⁺ atoms (five unpaired electrons each, Table II) and one Fe²⁺ atom (four unpaired electrons, Table II), with a total of fourteen unpaired electrons. If Fe²⁺ goes from HS to IS (drop from four to two unpaired electrons), the reduction in unpaired electrons is 14%, consistent with measurements. Another spin transition that would be consistent with measurements but not considered by Ding et al. (2008), is...
one Fe\textsuperscript{3+} atom (either on the TET or OCT site, but not both) going through a HS to IS transition, corresponding to a drop in unpaired electrons by 2 (14\%). Therefore both intermediate-spin Fe\textsuperscript{2+} and Fe\textsuperscript{3+} are considered in this study. Even though transitions from HS to LS Fe\textsuperscript{2+} or Fe\textsuperscript{3+} are too high of a drop in unpaired electrons to match the experimental measurements of Ding, et al., these larger spin state changes are also considered in order to map out the entire spin space.

1. Calculating the spin state of inverse spinel

All calculations started with \textit{Imma} symmetry (see section II A), which allowed for ordering of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} on the OCT sites. In VASP, the initial magnetic moments and moment directions on each Fe atom can be specified but only the total net magnetic moment (NMM) in the 14-atom unit cell can be fixed throughout the calculation. Therefore the direction of the moments on individual atoms can relax to different orderings as long as the NMM remains fixed. For inverse spinel,

\[ \left[ -\text{Fe}_{\text{HS}}^{3+} - \text{Fe}_{\text{HS}}^{3+} \right]_{\text{TET}} \left[ \text{Fe}_{\text{HS}}^{3+} \text{Fe}_{\text{HS}}^{2+} \text{Fe}_{\text{HS}}^{2+} \text{Fe}_{\text{HS}}^{3+} \right]_{\text{OCT}} \]

the net moment is 8 \( \mu_B \) because the individual magnetic moments (in \( \mu_B \)) are -5 -5 + 5 +4 +4 +5, which sum to 8 (see Table II, Table III, Table IV).

The magnetic ordering schemes considered for HS are given in Table III. These are all possible distinct (i.e., symmetrically inequivalent) magnetic orderings in the 14-atom unit cell. Besides the ferromagnetic arrangement, all magnetic orderings are ferrimagnetic except one with a net moment of 0, which is antiferromagnetic.

Table III: All possible magnetic arrangements in 14-atom inverse-spinel magnetite cell. If the arrangement/spin is metastable, then the initial moments specified in calculation are \textit{locally} meta-stable after the final relaxations. Otherwise the initial moments are \textit{not locally} meta-stable and relaxed to different individual moments with the same total net moment. Italicized abbreviations in the left column match those in Fig. 2.

<table>
<thead>
<tr>
<th>TET</th>
<th>OCT</th>
<th>Net Moment</th>
<th>Locally meta-stable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>Fe2</td>
<td>Fe3</td>
<td>Fe4</td>
</tr>
</tbody>
</table>

Magnetic orderings, all high-spin

Ferrimagnetic (\textit{mag I})

\[ \left[ -\text{Fe}_{\text{HS}}^{3+} - \text{Fe}_{\text{HS}}^{3+} \right]_{\text{TET}} \left[ \text{Fe}_{\text{HS}}^{3+} \text{Fe}_{\text{HS}}^{2+} \text{Fe}_{\text{HS}}^{2+} \text{Fe}_{\text{HS}}^{3+} \right]_{\text{OCT}} \]
Energies for all these magnetic orderings as a function of pressure have been calculated and are discussed in section 3.1. The most stable magnetic ordering was used as the starting configuration for all spin-transition calculations. The atomic positions and individual moments were then allowed to relax. There are two measures of spin stability. The first measure is that individual moments for a fixed NMM must retain their starting spin state after relaxation. If the spin state on the individual Fe atoms relaxes to different moments for a given initial NMM, the initial spin arrangement is not stable. If the individual spin states are the same after relaxation, then the spin state is considered locally stable. For each locally stable spin state we explore a second measure to determine if the spin state is stable globally. Global stability is determined by plotting the enthalpy curves for different spin states as a function of pressure and determining the most stable spin state of all the spin arrangements considered at each pressure.

In the 14-atom computational cell (six Fe atoms) HS inverse-spinel magnetite has a net moment of 8. Calculations with all intermediate-spin (net moment 4) were not locally stable; the cell relaxed to high-spin Fe$^{3+}$ on the TET and OCT sites and intermediate-spin Fe$^{2+}$ on the OCT (net moment 4). Calculations with all low-spin (net moment 0) were also not locally stable. The calculation relaxed to
high-spin Fe$^{3+}$ on the TET and OCT and low-spin Fe$^{2+}$ on the OCT (net moment of 0). Decreasing the moment of Fe$^{3+}$ on TET without reducing the moment on the OCT increases the total net moment (12 for IS Fe$^{3+}$, 16 for LS Fe$^{3+}$) and is not locally stable. IS Fe$^{3+}$ on TET relaxed to all high-spin normal spinel, or

$$[-Fe_{HS}^{2+} - Fe_{HS}^{2+}]_{TET} \left[Fe_{HS}^{3+}Fe_{HS}^{3+}Fe_{HS}^{3+}Fe_{HS}^{3+}\right]_{OCT}.$$  

LS Fe$^{3+}$ on TET relaxed to normal spinel with IS Fe$^{2+}$ on the TET site, or

$$[-Fe_{IS}^{2+} - Fe_{IS}^{2+}]_{TET} \left[Fe_{HS}^{3+}Fe_{HS}^{3+}Fe_{HS}^{3+}Fe_{HS}^{3+}\right]_{OCT}.$$  

Unlike spin transitions on the TET site, decreasing the moment of Fe$^{2+}$ or Fe$^{3+}$ on the OCT site decreases the total net moment (4 for IS Fe$^{2+}$ and Fe$^{3+}$, 0 for LS Fe$^{2+}$ and Fe$^{3+}$). Magnetite with intermediate-spin Fe$^{3+}$ on the OCT site has the same total net magnetic moment as magnetite with Fe$^{2+}$ on the OCT site. During relaxation, intermediate-spin Fe$^{3+}$ was only locally stable in the calculation for very low-pressures and never globally more stable than high-spin. For higher pressures, Fe$^{3+}$ on the OCT site changed to high-spin and Fe$^{2+}$ relaxed to intermediate-spin. For a total net moment of 4, it is more energetically favorable for Fe$^{2+}$ to change from high- to intermediate-spin than for Fe$^{3+}$. Likewise, low-spin Fe$^{3+}$ was not stable in the calculation. For a fixed total moment of 0, the calculations relaxed to LS Fe$^{2+}$ instead of Fe$^{3+}$, suggesting Fe$^{3+}$ in inverse-spinel magnetite is only stable as high-spin.

2. Calculating the spin state of normal spinel

Since there may be an inverse to normal spinel transition in magnetite, spin transition calculations were also conducted in the normal spinel structure as a function of pressure (Fig. 3). All possible spin states (HS, IS, LS) on the TET and OCT sites were explored (Table V). Spin transitions were considered on both TET and OCT sites as well as individually on the TET or OCT site (Table V).

A number of the normal-spinel spin configuration calculations were not locally stable. Calculations of all intermediate-spin Fe relaxed to inverse-spinel HS. Calculations of all low-spin Fe relaxed to Fe with moments slightly reduced from HS, maintaining a net moment of 4. Reducing the spin of Fe$^{3+}$ to LS or IS on the OCT site was not energetically favorable. To maintain the net magnetic moment,
the system preferred to change the TET site to HS Fe$^{3+}$ (inverse spinel), and reduce the total moment on every Fe atom on the OCT site.

3. Calculating the spin state of h-$\text{Fe}_3\text{O}_4$

The correct magnetic ordering also needs to be determined in the high-pressure phase, h-$\text{Fe}_3\text{O}_4$. The experimentally determined h-$\text{Fe}_3\text{O}_4$ unit cell is twice that of magnetite, therefore spins and magnetic ordering are given for the 12 Fe atoms in the unit cell (out of 28 total atoms). Only magnetic orderings that fit within the crystallographic unit cell are considered (Table VI). Trying every possible magnetic arrangement in the 28-atom cell would be computationally impractical. Therefore, only a few representative magnetic orderings were chosen based on the results in magnetite (Fig. 2): the same magnetic ordering as magnetite, magnetic ordering yielding a net magnetic moment of 0, and ferromagnetic. Energetics and details of the different magnetic arrangements for h-$\text{Fe}_3\text{O}_4$ are discussed in section 3.3.

Calculations starting with all intermediate-spin or all low-spin Fe on the OCT and TET sites were not locally stable and relaxed to a combination of high-, low-, and reduced-spin Fe$^{2+}$ and Fe$^{3+}$ with a net moment of 16 (8 for all low-spin). Calculations that started with intermediate-spin Fe$^{3+}$ on the OCT site were not locally stable and relaxed to a combination of high- and low-spin Fe atoms and the TET site became Fe$^{2+}$. 
III. RESULTS

This section is organized as follows. First, magnetic ordering and spin transitions within inverse-spinel magnetite are presented (section A). Then results on magnetic ordering and spin transitions in normal-spinel magnetite are given (section B). The stable magnetic arrangements and spin states in h-Fe$_3$O$_4$ are presented in section C. Section D discusses the impact of magnetic order, spin and normal/inverse spinel on the pressure-induced phase transition of inverse-spinel magnetite to h-Fe$_3$O$_4$. Finally, section E gives the equations of state of the key phases as a function of pressure.

A. Magnetic ordering and spin transitions in inverse-spinel magnetite

The strong magnetic moment in inverse-spinel magnetite occurs due to ferrimagnetic

\[
\left[ -Fe^{3+}_{HS} - Fe^{3+}_{HS} \right]_{TET} \left[ Fe^{3+}_{HS} Fe^{2+}_{HS} Fe^{2+}_{HS} Fe^{3+}_{HS} \right]_{OCT}
\]

ordering between the TET and OCT sites. We test that this is the correct magnetic ordering in inverse-spinel magnetite by comparing the enthalpies as a function of pressure for multiple magnetic arrangements in the charge-ordered structure. The relative enthalpies of the different magnetic orderings are plotted in Fig. 2(a). The figure clearly shows that ferrimagnetic ordering between the TET and OCT sites \([ -Fe^{3+}_{HS} - Fe^{3+}_{HS} ]_{TET} [ Fe^{3+}_{HS} Fe^{2+}_{HS} Fe^{2+}_{HS} Fe^{3+}_{HS} ]_{OCT} (mag1)\) is the most stable for all pressures by more than 140 meV/f.u. and is used for the remainder of the inverse-spinel magnetite spin studies. There is no magnetic ordering transition under pressure in magnetite.

Ferromagnetic ordering (FM) is over 0.8 eV/f.u. less stable than ferromagnetic mag1.

The spin transition pressure of Fe is considered on both TET and OCT sites (Fig. 2(b)). Table IV lists the spin states considered, the initial individual moments specified on each atom, and the total magnetic moment. Fe$^{3+}$ on the TET site in inverse-spinel magnetite remains HS for all pressures. Neither all intermediate- nor low-spin Fe on the TET site are locally stable in the calculations (Table IV).

The relative enthalpies of high-, intermediate-, and low-spin Fe$^{2+}$ on the OCT site are plotted in Fig. 2(b). Intermediate-spin Fe$^{2+}$ is 1 eV/f.u. less stable at ambient pressure than high-spin Fe. Low-spin
Fe$^{2+}$ is 1.2 eV/f.u. less stable than high-spin. For all pressures up to 45 GPa (the highest considered), Fe$^{2+}$ and Fe$^{3+}$ in inverse-spinel magnetite will remain high-spin. To be sure that the instability of the intermediate-spin state was not due to our specific value of $U$, a range of $U$ values were explored. Increasing $U$ stabilizes high-spin magnetite with respect to intermediate-spin and decreases the h-Fe$_3$O$_4$ to magnetite phase transition pressure$^{29}$. The experimentally observed phases involve unit cells significantly larger than 14-atom unit cell. Pursuing larger cells with more complex charge ordering would greatly complicate and slow the calculations. In fact, in addition to the 14-atom charge-ordered structure with *Imma* symmetry, the 56-atom structure charge-ordered structure with *P2/c* monoclinic symmetry (*Pmca* pseudosymmetry) was also used. The larger unit cell was calculated with intermediate-spin Fe$^{2+}$ on the octahedral site. Intermediate spin was not metastable in the calculations; the Fe spins relaxed to a mixture of high- and low-spin Fe$^{2+}$ and Fe$^{3+}$. In VASP, only the total moment can be fixed; moments on individual atoms cannot be fixed. The larger unit cell made controlling the individual spins on the Fe atoms computationally impossible; therefore the simpler *Imma* symmetry was chosen for easier control of Fe’s spin state.

**Table IV:** Summary of all inverse-spinel magnetite spin states considered in this study, organized by site. Initial moments for each spin state and total fixed net moment for cell in the 14-atom cell. Italicized abbreviations in the left column match those in Fig. 2(b). When a calculation is not locally meta-stable, the final spin state after relaxation is noted and explained in the text.

<table>
<thead>
<tr>
<th>Spin-transitions (mag/l)</th>
<th>TET</th>
<th>OCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>All high-spin (mag)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[-Fe^{3+}<em>{HS} - Fe^{3+}</em>{HS}]<em>{TET} [Fe^{3+}</em>{HS}Fe^{2+}<em>{HS}Fe^{2+}</em>{HS}Fe^{3+}<em>{HS}]</em>{OCT}$</td>
<td>-5</td>
<td>-5</td>
</tr>
<tr>
<td>All intermediate-spin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[-Fe^{3+}<em>{IS} - Fe^{3+}</em>{IS}]<em>{TET} [Fe^{3+}</em>{IS}Fe^{2+}<em>{IS}Fe^{2+}</em>{IS}Fe^{3+}<em>{IS}]</em>{OCT}$</td>
<td>-3</td>
<td>-3</td>
</tr>
<tr>
<td>All low-spin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[-Fe^{3+}<em>{LS} - Fe^{3+}</em>{LS}]<em>{TET} [Fe^{3+}</em>{LS}Fe^{2+}<em>{LS}Fe^{2+}</em>{LS}Fe^{3+}<em>{LS}]</em>{OCT}$</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

$\Rightarrow IS^{2+} OCT$

$\Rightarrow LS^{2+} OCT$
### Tetrahedral (TET) site spin-transitions

<table>
<thead>
<tr>
<th>Spin State</th>
<th>符号</th>
<th>TET</th>
<th>OCT</th>
<th>TET</th>
<th>OCT</th>
<th>TET</th>
<th>OCT</th>
<th>TET</th>
<th>OCT</th>
<th>TET</th>
<th>OCT</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermediate-spin Fe$^{3+}$</td>
<td>$[\text{Fe}^{3+}<em>{\text{TET}} \text{Fe}^{3+}</em>{\text{OCT}}]$</td>
<td>-3</td>
<td>-3</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>12</td>
<td>no</td>
<td>normal spinel $\text{HS TET, OCT}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low-spin Fe$^{2+}$</td>
<td>$[\text{Fe}^{2+}<em>{\text{TET}} \text{Fe}^{2+}</em>{\text{OCT}}]$</td>
<td>-1</td>
<td>-1</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>16</td>
<td>no</td>
<td>normal spinel $\text{ IS 2+ TET}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Octahedral (OCT) site spin-transitions

<table>
<thead>
<tr>
<th>Spin State</th>
<th>符号</th>
<th>TET</th>
<th>OCT</th>
<th>TET</th>
<th>OCT</th>
<th>TET</th>
<th>OCT</th>
<th>TET</th>
<th>OCT</th>
<th>TET</th>
<th>OCT</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermediate-spin Fe$^{2+}$ (IS 2+ OCT)</td>
<td>$[\text{Fe}^{3+}<em>{\text{TET}} \text{Fe}^{3+}</em>{\text{OCT}}]$</td>
<td>-5</td>
<td>-5</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>4</td>
<td>yes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intermediate-spin Fe$^{3+}$</td>
<td>$[\text{Fe}^{3+}<em>{\text{TET}} \text{Fe}^{3+}</em>{\text{OCT}}]$</td>
<td>-5</td>
<td>-5</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>4</td>
<td>Low pressure only $\Rightarrow$ IS 2+ OCT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low-spin Fe$^{2+}$ (LS 2+ OCT)</td>
<td>$[\text{Fe}^{3+}<em>{\text{TET}} \text{Fe}^{3+}</em>{\text{OCT}}]$</td>
<td>-5</td>
<td>-5</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>yes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low-spin Fe$^{2+}$</td>
<td>$[\text{Fe}^{3+}<em>{\text{TET}} \text{Fe}^{3+}</em>{\text{OCT}}]$</td>
<td>-5</td>
<td>-5</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>no $\Rightarrow$ LS 2+ OCT</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. Magnetic ordering and spin transitions in normal-spinel magnetite

Normal spinel is less stable than inverse spinel (mag1) by over 0.77 eV/f.u. for all pressures (Fig. 3). As in the case of inverse spinel, intermediate- and low-spin Fe$^{2+}$ on the TET site in normal spinel are energetically unfavorable with respect to high-spin iron. Spin transitions on the OCT site were considered (Table V), especially intermediate-spin Fe$^{3+}$, which has a net moment of four. However, changing to intermediate-spin on the OCT site was not locally stable and upon relaxation the system formed inverse spinel (Fe$^{3+}$ on the TET site) and reduced the moment of Fe$^{2+}$ on the OCT site (without actually flipping an electron spin to fully form the intermediate-spin state).

Table V: Spin states considered in the fourteen-atom normal-spinel magnetite unit cell. Italicized abbreviations in the left column match those in Fig. 3. When a given spin or magnetic arrangement is not locally meta-stable, the final spin state after relaxation is noted and explained in the text.
C. Magnetic ordering and spin transitions in h-Fe₃O₄

The most stable magnetic ordering in h-Fe₃O₄ is antiferromagnetic ordering (h-NMM0) with a total net moment of 0 (Fig. 4(a)). Ferrimagnetic ordering between TET and OCT (h-NMM24) with a net moment of 24 has very similar energetics to the antiferromagnetic ordering, differing by ~ 20 meV/f.u..

There is an approximately 140 meV/f.u. difference between ferrimagnetic and ferromagnetic ordering in h-Fe₃O₄.

Intermediate-spin Fe²⁺ on the TET site is more than 0.84 eV/f.u. less stable than HS (Fig. 4b).

Low-spin Fe²⁺ on the TET site is more than 1.26 eV/f.u. less stable than HS Fe²⁺. Ferrimagnetic LS Fe³⁺ on
the OCT site and ferromagnetic Fe$^{3+}$ on the OCT site have similar enthalpies (to within 140 meV/f.u.), but both are more than 2.1 eV/f.u. less stable than HS h-Fe$_3$O$_4$. Therefore high-spin Fe remains stable in both TET and OCT sites for all pressures considered in this study (up to 70 GPa).

It is worth noting that in both magnetite and h-Fe$_3$O$_4$, spin lowering in Fe$^{2+}$ was more stable than spin lowering in Fe$^{3+}$. If the initial moments were set such that Fe$^{3+}$ had a lower moment, the relaxations tended to favor flipping the spin on the Fe$^{2+}$ rather than on the Fe$^{3+}$. This demonstrates a clear coupling of valence and spin state, with Fe$^{3+}$ favoring high-spin more than Fe$^{2+}$ in the magnetite structure. This result might be expected due to the half-filled d-shell providing additional stabilization in the Fe$^{3+}$ HS state.
Table VI: Magnetic orderings and spin arrangements considered in 28-atom h-Fe₃O₄. Italicized abbreviations in the left column match those in Fig. 4. To conserve space, individual moments are not listed. When a calculation is not locally stable, the final spin state after relaxation is noted and explained in the text.

Magnetic ordering arrangements, all high-spin

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Net moment</th>
<th>Locally meta-stable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inverse spinel, ferrimagnetic (<em>magl</em>)</td>
<td>16</td>
<td>Yes</td>
</tr>
<tr>
<td>([-Fe^{3+}<em>{HS} - Fe^{3+}</em>{HS} - Fe^{3+}<em>{HS} - Fe^{3+}</em>{HS}]<em>{TET}[Fe^{3+}</em>{HS}Fe^{3+}<em>{HS}Fe^{2+}</em>{HS}Fe^{2+}<em>{HS}Fe^{2+}</em>{HS}Fe^{3+}<em>{HS}Fe^{3+}</em>{HS}Fe^{3+}<em>{HS}]</em>{OCT})</td>
<td>0</td>
<td>Yes</td>
</tr>
<tr>
<td>h-Fe₃O₄, anti-ferromagnetic (h-NMM0)</td>
<td>24</td>
<td>Yes</td>
</tr>
<tr>
<td>([-Fe^{2+}<em>{HS} - Fe^{2+}</em>{HS} - Fe^{2+}<em>{HS} - Fe^{2+}</em>{HS}]<em>{TET}[Fe^{3+}</em>{HS}Fe^{3+}<em>{HS}Fe^{3+}</em>{HS}Fe^{3+}<em>{HS}Fe^{3+}</em>{HS}Fe^{3+}<em>{HS}Fe^{3+}</em>{HS}Fe^{3+}<em>{HS}]</em>{OCT})</td>
<td>56</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Spin-transitions on both sites

<table>
<thead>
<tr>
<th>Spin-transition</th>
<th>Net moment</th>
<th>Locally meta-stable</th>
</tr>
</thead>
<tbody>
<tr>
<td>All intermediate-spin</td>
<td>16</td>
<td>no ➔ reduced moments</td>
</tr>
<tr>
<td>([-Fe^{3+}<em>{LS} - Fe^{3+}</em>{LS} - Fe^{3+}<em>{LS} - Fe^{3+}</em>{LS}]<em>{TET}[Fe^{3+}</em>{LS}Fe^{3+}<em>{LS}Fe^{3+}</em>{LS}Fe^{3+}<em>{LS}Fe^{3+}</em>{LS}Fe^{3+}<em>{LS}Fe^{3+}</em>{LS}Fe^{3+}<em>{LS}]</em>{OCT})</td>
<td>8</td>
<td>no ➔ reduced moments</td>
</tr>
</tbody>
</table>

Tetrahedral (TET) site spin-transitions

<table>
<thead>
<tr>
<th>Spin-transition</th>
<th>Net moment</th>
<th>Locally meta-stable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermediate-spin Fe⁷⁺ (LS ²⁺ TET)</td>
<td>32</td>
<td>Yes</td>
</tr>
<tr>
<td>([-Fe^{2+}<em>{LS} - Fe^{2+}</em>{LS} - Fe^{2+}<em>{LS} - Fe^{2+}</em>{LS}]<em>{TET}[Fe^{3+}</em>{LS}Fe^{3+}<em>{LS}Fe^{3+}</em>{LS}Fe^{3+}<em>{LS}Fe^{3+}</em>{LS}Fe^{3+}<em>{LS}Fe^{3+}</em>{LS}Fe^{3+}<em>{LS}]</em>{OCT})</td>
<td>40</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Octahedral (OCT) site spin-transitions

<table>
<thead>
<tr>
<th>Spin-transition</th>
<th>Net moment</th>
<th>Locally meta-stable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermediate-spin Fe⁷⁺</td>
<td>8</td>
<td>no ➔ reduced moments</td>
</tr>
<tr>
<td>([-Fe^{2+}<em>{HS} - Fe^{2+}</em>{HS} - Fe^{2+}<em>{HS} - Fe^{2+}</em>{HS}]<em>{TET}[Fe^{3+}</em>{HS}Fe^{3+}<em>{HS}Fe^{3+}</em>{HS}Fe^{3+}<em>{HS}Fe^{3+}</em>{HS}Fe^{3+}<em>{HS}Fe^{3+}</em>{HS}Fe^{3+}<em>{HS}]</em>{OCT})</td>
<td>24</td>
<td>Yes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spin-transition</th>
<th>Net moment</th>
<th>Locally meta-stable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low spin Fe⁷⁺, ferromagnetic (LS ³⁺ OCT)</td>
<td>-8</td>
<td>Yes</td>
</tr>
</tbody>
</table>
D. Phase transitions under pressure: inverse-spinel magnetite to h-Fe$_3$O$_4$ structure.

Based on the most stable spin states vs. pressure for inverse-spinel magnetite, normal-spinel magnetite, and h-Fe$_3$O$_4$ there is a predicted phase transition from the inverse-spinel magnetite to h-Fe$_3$O$_4$ at 10 GPa. Below 10 GPa the most stable state is the inverse-spinel magnetite structure (mag1) with high-spin Fe and ferrimagnetic ordering between the OCT and TET sites (Fig. 4). Above 10 GPa, the most stable state is the normal-spinel high-pressure magnetite structure h-Fe$_3$O$_4$ with high-spin Fe. This corresponds to an inverse to normal spinel transition due to the phase transition. Within magnetite (mag1), there is no inverse to normal spinel transition. The proposed inverse- $\left[Fe^{3+}\right]_{TET}[Fe^{2+/3+}Fe^{2+/3+}]_{OCT}$ spinel transition in magnetite around 8-15 GPa $^{15,16}$ was not supported by the calculations (Fig. 3). As illustrated in the previous figures, there are no spin transitions in inverse-spinel or normal-spinel magnetite or h-Fe$_3$O$_4$ as a function of pressure. Across the phase transition the volume decreases by 7-8%, consistent with experimentally measured volume changes (Fig. 5). In magnetite, the calculated volume is almost 4% higher than the experimental values at all pressures (Fig. 5). The discrepancy is consistent with typical volume overestimation of a few percent from GGA vs. experiment. However, some of the error may come from comparing the Imma structure of this study, which has charge ordering on the octahedral site, to the $Fd\bar{3}m$ structure$^{17}$, which is charge-averaged. The ordering on the octahedral site of Imma may expand the lattice relative to the charge-averaged structure ($Fd\bar{3}m$). In h-Fe$_3$O$_4$, the computational volume is less than 3% larger the experimental volume (Fig. 5), also consistent with GGA simulations overestimating the volume. A full structural comparison between this study and literature values is given in the supplemental materials$^{29}$.

The system also undergoes an insulating to metal transition, which can be seen in the electronic density of states (DOS) show in Figure 6. Magnetite (charge ordered, Imma) is insulating at the ground state with a band gap of just under 0.2 eV at 0 GPa, consistent with previous computational and
experimental studies. Magnetite remains insulating up to 21 GPa. However h-Fe$_3$O$_4$ exhibits metallic behavior, with a significant DOS at the Fermi level at 20 GPa.

E. Bulk elastic properties as a function of pressure

The equation of state parameters were calculated for Fe$_3$O$_4$ (Table VII). The calculated bulk modulus, $B_0$, of inverse- and normal-spinel magnetite vary by less than 5 GPa, and are more compressible than h-Fe$_3$O$_4$ by over 15 GPa. Likewise, the volumes of inverse and normal spinel are similar to each other and larger than $V_0$ of h-Fe$_3$O$_4$ by almost 0.9 Å$^3$/atom. For all cases, lowering the spin state from high-spin to intermediate- and low-spin raises $E_0$ and lowers $V_0$. $B'$ remains almost unchanged for lower-spin states. In magnetite, $B_0$ and $B'$ are in the same range as other experimental and computational values (Table VII). As explained above, the calculated $V_0$ is ~ 4% larger than the one obtained from experiments.

**Table VII**: Equation of state parameters for Fe$_3$O$_4$ at ambient pressure. Energy, $E_0$, bulk modulus, $B_0$, the pressure derivative of the bulk modulus, $B'$, and the ground state volume, $V_0$, come from fits to a 3rd order Birch-Murnaghan equation of state. Parameters are given for high-spin (HS), intermediate-spin (IS) and low-spin (LS) Fe.

<table>
<thead>
<tr>
<th>Magnetite: inverse-spinel</th>
<th>HS</th>
<th>Literature (HS)</th>
<th>IS 2+ OCT</th>
<th>LS 2+ OCT</th>
<th>Magnetite: normal spinel</th>
<th>h-Fe$_3$O$_4$</th>
<th>IS 2+ TET</th>
<th>LS 2+ TET</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$ (eV/atom)</td>
<td>-6.946</td>
<td>-6.802</td>
<td>-6.774</td>
<td></td>
<td>h-Fe$_3$O$_4$</td>
<td>-6.888</td>
<td>-6.7506</td>
<td>-</td>
</tr>
<tr>
<td>$B_0$ (GPa)</td>
<td>173</td>
<td>141-222$^{17}$, 180.6$^{16}$</td>
<td>188</td>
<td>172</td>
<td>189</td>
<td>187</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$B'$</td>
<td>3.97</td>
<td>4-7.5$^{17}$, 4.33$^{16}$</td>
<td>3.98</td>
<td>3.92</td>
<td>4.02</td>
<td>3.9974</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$V_0$ (Å$^3$/atom)</td>
<td>11.07</td>
<td>10.57$^{16}$</td>
<td>10.78</td>
<td>10.76</td>
<td>10.19</td>
<td>10.1516</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
IV. DISCUSSION

The calculations of the magnetic ordering in inverse-spinel magnetite indicate that there is ferrimagnetic ordering between the TET and OCT sites \([-\text{Fe}^{3+}_\text{HS} - \text{Fe}^{3+}_\text{HS}]_{\text{TET}} [\text{Fe}^{3+}_\text{HS} \text{Fe}^{2+}_\text{HS} \text{Fe}^{2+}_\text{HS} \text{Fe}^{3+}_\text{HS}]_{\text{OCT}}\] with a residual moment of 8\(\mu_B\)/14-atom unit cell (4\(\mu_B\)/formula unit). All possible magnetic ordering arrangements in the 14-atom cell were calculated. We confirm that the inverse spinel ordering, \([-\text{Fe}^{3+}_\text{HS} - \text{Fe}^{3+}_\text{HS}]_{\text{TET}} [\text{Fe}^{3+}_\text{HS} \text{Fe}^{2+}_\text{HS} \text{Fe}^{2+}_\text{HS} \text{Fe}^{3+}_\text{HS}]_{\text{OCT}}\), is still the most stable magnetic ordering configuration up to 45 GPa. The computational results therefore suggest that the reduction of total moment by one half observed experimentally\(^7\) cannot be attributed to a change of magnetic ordering arrangements.

Having the correct magnetic arrangement at ambient pressure allowed for studying the spin in the correct structure. In our study, we accounted for Fe in different sites (TET and OCT), Fe with different valence (Fe\(^{2+}\) and Fe\(^{3+}\)), and different charge coordination (inverse spinel and normal spinel). Iron remained high-spin for all charge sets, site occupations, pressures and structures considered. In the calculations, there is no pressure-induced transition from inverse-spinel magnetite to normal-spinel magnetite. The calculations predict a pressure-induced phase transition from inverse-spinel magnetite to normal-spinel h-Fe\(_3\)O\(_4\) at 10 GPa, in agreement with some older experimental measurements\(^{17-19}\) but contradictory to more recent experiments\(^4,20\). Instead of finding a phase transition, Baudelet et al (2010) and Glazyrin et al (2012) found the magnetic moment decreases with increasing pressure.

The high-pressure h-Fe\(_3\)O\(_4\) phase is predicted to be antiferromagnetic, but the enthalpies of all magnetic ordering arrangements considered are within 0.175 eV/f.u. of each other. The close energetics are in contrast with inverse-spinel magnetite where magnetic orderings vary by over 0.875 eV/f.u.. Therefore, magnetic ordering has a much greater stabilizing effect in inverse-spinel magnetite than in h-Fe\(_3\)O\(_4\). The small energy difference between different magnetic arrangements in h-Fe\(_3\)O\(_4\) may explain why it has been measured as being paramagnetic at room temperature\(^7\). The h-Fe\(_3\)O\(_4\) phase also remains high-
spin for pressures up to 45 GPa (the highest of this study). Therefore, the calculations predict that Fe$_3$O$_4$

will undergo a phase transition at 10 GPa but the spin state of Fe will remain high-spin for all pressures.

Table VIII: The magnitudes of the magnetic, $\Sigma_{\text{magnetic}}=kT \ln (2S+1)$, and electronic, $\Sigma_{\text{electronic}}=kT \ln (D)$, entropy contributions to the free energy for high-spin ($3t_{2g} \uparrow 2e_g \uparrow 1t_{2g} \downarrow$), intermediate-spin ($3t_{2g} \uparrow 1e_g \uparrow 2t_{2g} \downarrow$) and low-spin ($3t_{2g} \uparrow 3t_{2g} \downarrow$) Fe$^{3+}$. $S_{\sigma}$ is the spin number and $D$ is the electron degeneracy in $t_{2g}$ and $e_g$. At room temperature, $kT$ is

approximately 0.026 eV. There are 3 Fe atoms in a formula unit of Fe$_3$O$_4$, therefore $\Sigma_{\text{magnetic}} + \Sigma_{\text{electronic}}$ is reported for 3 Fe atoms. The expression for $\Sigma_{\text{magnetic}}$ above is only applicable to paramagnets. If magnetite (high-spin Fe) has strong magnetic ordering, there will be no magnetic entropy term ($\Sigma_{\text{magnetic}}=0$). We assume the other phases are paramagnetic. Assuming magnetite with intermediate-spin Fe is paramagnetic provides an upper bound on its free energy gain associated with the magnetic degrees of freedom. The total contribution to the free energy is given by $-\Sigma_{\text{total}}$.

<table>
<thead>
<tr>
<th>$S_{\sigma}$</th>
<th>$D$</th>
<th>$\Sigma_{\text{magnetic}}$ (kT/f.u.)</th>
<th>$\Sigma_{\text{electronic}}$ (kT/f.u.)</th>
<th>$\Sigma_{\text{total}} = \Sigma_{\text{magnetic}} + \Sigma_{\text{electronic}}$ (kT/f.u.)</th>
<th>$-\Sigma_{\text{total}}$ (eV/f.u. at room temp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Spin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>2</td>
<td>3 $t_{2g}$</td>
<td>0</td>
<td>3kTln(3)</td>
<td>-0.086</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Magnetite (magnetically ordered)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Magnetite (paramagnetic)</td>
<td>3kTln(5)</td>
<td>3kTln(3)</td>
<td>-0.211</td>
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<tr>
<td></td>
<td></td>
<td>h-Fe$_3$O$_4$</td>
<td>3kTln(5)</td>
<td>3kTln(3)</td>
<td>-0.211</td>
</tr>
<tr>
<td>Intermediate</td>
<td>1</td>
<td>3 $t_{2g}$, 2 $e_g$ (total = 3×2 = 6)</td>
<td>3kTln(3)</td>
<td>3kTln(6)</td>
<td>-0.225</td>
</tr>
<tr>
<td>Spin Fe$^{3+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Magnetite</td>
<td>3kTln(3)</td>
<td>3kTln(6)</td>
<td>-0.225</td>
</tr>
<tr>
<td></td>
<td></td>
<td>h-Fe$_3$O$_4$</td>
<td>3kTln(3)</td>
<td>3kTln(6)</td>
<td>-0.225</td>
</tr>
<tr>
<td>Low Spin</td>
<td>0</td>
<td>1 $t_{2g}$</td>
<td>3kTln(1)</td>
<td>3kTln(1)</td>
<td>0</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td></td>
<td>magnetite</td>
<td>3kTln(1)</td>
<td>3kTln(1)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>h-Fe$_3$O$_4$</td>
<td>3kTln(1)</td>
<td>3kTln(1)</td>
<td>0</td>
</tr>
</tbody>
</table>

DFT calculations are effectively at absolute zero and therefore do not include temperature effects.

From the DFT calculations alone, it is not clear if increasing temperature could stabilize intermediate-spin with respect to high-spin. The effect of temperature on the spin transition can be determined from the Gibbs free energy expression ($G = H - T\Sigma$). The Gibbs free energy is the sum of the enthalpy, $H$, and entropy, $\Sigma$, (vibrational, magnetic, electronic) terms multiplied by temperature, $T$. The enthalpy was calculated from DFT (see results section). The entropic terms relevant to spin are the magnetic and electronic entropies estimated for a paramagnetic phase as:

$$\Sigma_{\text{magnetic}} = k \ln (2S_{\sigma} + 1)$$

$$\Sigma_{\text{electronic}} = k \ln (D)$$
where $S_\sigma$ is the spin quantum number, $D$ is the orbital degeneracy in $t_{2g}$ and $e_g$ states, and $k$ is the Boltzmann constant. $S_\sigma$ and $D$ values for high-, intermediate, and low-spin Fe$^{2+}$ and Fe$^{3+}$ in OCT and TET sites are shown in Table VIII, where $D$ value are estimated from crystal field arguments. The entropy contributions to the free energy in units of $kT$ ($kT = 0.026$ eV) evaluated at room temperature are given in Table VIII. These estimates assume all phases are paramagnetic except for high-spin magnetite, which is known to have strong magnetic ordering at room temperature. This approach gives the largest possible temperature dependence to the free energy estimates and therefore provides an upper bound on the magnetic and electronic contributions to the spin and phase stability. In magnetite, the sum of the magnetic and electronic contributions to the entropy are -0.086 eV/f.u. for high-spin Fe$^{2+}$, -0.225 eV/f.u. for intermediate-spin Fe$^{2+}$, and 0 eV/f.u. for low-spin Fe$^{2+}$ (at room temperature). These additional contributions to the free energy form the electronic and magnetic entropy will only reduce $\Delta H$ by 0.139 eV/f.u. at room temperature (0.463 eV/f.u. at 1000 K), which is too small to stabilize intermediate-spin (Fig. 2(b)).

The effect of temperature and the electronic and spin degrees of freedom on the phase transition from magnetite to h-Fe$_3$O$_4$ (Fig. 4b) can also be estimated using the same arguments as above. At room temperature, magnetite with high-spin Fe$^{2+}$ has strong magnetic ordering (Fig. 2a) and thus no magnetic entropy contribution; therefore the entropic and temperature contributions to Gibbs free energy due to high-spin Fe$^{2+}$ is -0.086 eV/f.u. The high-pressure phase h-Fe$_3$O$_4$ has weak magnetic ordering (Fig. 4(a)) (paramagnetic, Table VIII) leading to a total contribution to the Gibbs free energy of -0.211 eV/f.u. Thus, temperature will drive the phase transition towards lower pressures and reduce $\Delta H$ by 0.125 eV/f.u. (at 300K). If h-Fe$_3$O$_4$ retains magnetic ordering, then the entropy contributions to the Gibbs free energy will be the same for magnetite and h-Fe$_3$O$_4$ and the phase transition will remain unchanged.

It should be noted that there are also vibrational contributions to the free energies of the different phases and spin states in this study. However, we assume that the change in vibrational free energy between different spin states is small due to the general similarity of the structures involved. Furthermore, we expect that lower spin states will produce smaller volumes and correspondingly stiffer
lattices, which will reduce the stabilizing effects of vibrational degrees of freedom\textsuperscript{32}. Therefore, it is expected that a rigorous treatment of vibrational contributions will only further destabilize the intermediate- and low-spin states. The vibrational contributions to the magnetite to h-Fe\textsubscript{3}O\textsubscript{4} transition are not clear; however, because the high-pressure phase is stiffer, it is expected to be destabilized by vibrational contributions, leading to some lowering of the phase transition pressure with increasing temperature.

Magnetite is now the third system in which experimental X-ray emission spectra (XES) measurements have been interpreted as intermediate-spin Fe but theoretical calculations have not found intermediate-spin to be stable. In the other systems, (Mg,Fe)SiO\textsubscript{3} perovskite and post-perovskite, XES measurements show a drop in peak intensity to a non-zero value, which is interpreted as intermediate spin\textsuperscript{8,33}. Yet calculations in perovskite do not predict IS Fe to be stable\textsuperscript{9,13,34}. In magnetite, perovskite and post-perovskite, the satellite peak from the XES measurements did not completely disappear. In systems where XES measurements show a drop in satellite peak intensity to zero good agreement exists between theory and XES measurement interpretations. For example, both theory and XES measurements support a high- to low-spin transition in (Mg,Fe)O ferropericlase, (see \textsuperscript{35} and references within) and FeS\textsuperscript{11}.

There are two implications of this experimental-theoretical discrepancy. The first is a possible a limitation in the \textit{ab initio} methods. To test this hypothesis, two additional quantum mechanical approaches were used. DMol\textsuperscript{3}, a DFT approach with localized-basis function methods\textsuperscript{12}, was chosen to test if the localized basis functions of DMol\textsuperscript{3} better describe intermediate-spin Fe than the planewave basis functions use in VASP. VASP hybrid DFT-Hartree Fock methods\textsuperscript{36} were also explored to see if the addition of Hartree-Fock terms to the energetics changed the qualitative predictions regarding intermediate spin. The energy of magnetite was calculated with both methods for high-, intermediate- and low-spin Fe\textsuperscript{2+} on the \textit{OCT} site\textsuperscript{29}. All approaches predict that the \textit{OCT} Fe\textsuperscript{2+} will remain high-spin up to 40 GPa (Table A1). DFT using planewaves and local basis functions, as well as hybrid DFT- Hartree-Fock methods all find high-spin Fe to be stable with respect to intermediate-spin Fe. Cluster-based DFT methods with newer functionals do not find a stable intermediate-spin state in perovskite\textsuperscript{13} and other iron-
bearing complexes either. The agreement amongst these various methods suggests the calculations are
capturing the correct spin behavior of iron, however the small possibility exists that essential physics of
intermediate-spin are not accurately described.

The more plausible implication of the experimental-theoretical discrepancy is that the observed
drop of satellite peak intensity to a non-zero value in XES measurements at high-pressure is due to a
change other than a transition to intermediate-spin iron, such as electron delocalization with pressure.

If XES with a satellite peak that is reduced to a non-zero value cannot be interpreted as intermediate-spin
Fe\(^{2+}\), then Fe\(^{2+}\) in magnetite, perovskite, and post-perovskite will remain high-spin.
V. CONCLUSIONS

The ab initio calculations isolated the complex magnetic ordering, valence states, charge ordering, and different local Fe site environments in magnetite and h-Fe₃O₄ as a function of pressure. The calculations found a pressure-induced structural phase transition from inverse-spinel magnetite to normal spinel h-Fe₃O₄. The magnetic ordering of inverse-spinel magnetite does not change with pressure and iron remains high-spin for all pressures. There is no evidence from the ab initio energetics for an inverse to normal spinel transition with pressure in magnetite. However, the magnetite to high-pressure magnetite h-Fe₃O₄ phase transition corresponds to an inverse to normal spinel transition, but the normal-spinel h-Fe₃O₄ has a different symmetry and structure from magnetite.

The most stable spin state is high-spin Fe in the ferrimagnetic arrangement for both magnetite and high-pressure magnetite h-Fe₃O₄ structures up to 50 GPa (the highest pressure considered in this study). The calculations have accounted for site occupation, valence, and charge coordination. Intermediate-spin iron is not stable in magnetite, contrary to experimental measurements. The discrepancy between theoretical and experimental measurements of intermediate-spin iron only occurs when the x-ray emission spectra satellite peak intensity drops to a non-zero value, which has been seen in magnetite, perovskite, and post-perovskite. The results suggest X-ray emission spectra may need to be interpreted differently at high pressures. Failure to find intermediate spin in magnetite implies Fe²⁺ in perovskite and post perovskite will also remain high spin.
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Figure 1: (a) magnetite. As inverse spinel, the octahedral site (OCT, light grey) is a statistical distribution of Fe$^{2+}$ and Fe$^{3+}$ and the tetrahedral site (TET, black) is Fe$^{3+}$. As normal spinel, the octahedral site is Fe$^{3+}$ and the tetrahedral site is Fe$^{2+}$. (b) h-Fe$_3$O$_4$, the high-pressure magnetite phase. The octahedral site (OCT, light grey) is Fe$^{3+}$ and the tetrahedral site (TET, black) is Fe$^{2+}$. 
Figure 2: (a) stable magnetic ordering in inverse-spinel magnetite. All enthalpies are referenced to high-spin (HS) magnetite, mag1. Abbreviations are explained in Table III. (b) Spin states in inverse spinel magnetite. Enthalpies of Fe$^{2+}$ in high-, intermediate- (IS), and low-spin (LS) states on the octahedral (OCT) site referenced to high-spin magnetite. Abbreviations are explained in Table IV.
Figure 3: stable spin states in normal-spinel magnetite. All enthalpies are referenced to HS magnetite with the inverse spinel structure, \textit{mag1}. Details of the magnetic arrangements can be found in Table V.
Figure 4: (a) Stable magnetic arrangements in normal-spinel h-Fe₃O₄ referenced to high-spin magnetite, mag₁ (b) Stable spin states in h-Fe₃O₄ Pbcm. Abbreviations for spin states and magnetic orderings given in Table VI.
Figure 5: Volume change across phase transition from inverse-spinel magnetite ([Fe$^{3+}_{HS}$ − Fe$^{3+}_{HS}$]$_{TET}$ [Fe$^{3+}_{HS}$Fe$^{2+}_{HS}$Fe$^{2+}_{HS}$Fe$^{3+}_{HS}$]$_{OCT}$) to h-Fe$_3$O$_4$ ([Fe$^{2+}$]$_{TET}$ [Fe$^{3+}$Fe$^{3+}$]$_{OCT}$). The volume curves for each phase are given in orange squares (light for magnetite, dark for h-Fe$_3$O$_4$). The dashed orange line follows the stable phase as a function of pressure. Experimental volumes for magnetite and h-Fe$_3$O$_4$ (grey/black circles) are shown for comparison with the calculations. The dashed black line follows the experimental stable phase as a function of pressure.
Figure 6: Electronic structure of (a) magnetite, \([\text{Fe}^{3+}_{\text{HS}} - \text{Fe}^{3+}_{\text{HS}}]_{\text{TET}} [\text{Fe}^{3+}_{\text{HS}} \text{Fe}^{2+}_{\text{HS}} \text{Fe}^{3+}_{\text{HS}}]_{\text{OCT}}, \text{ at ambient pressure} \) (b) magnetite at 1 GPa, (c) magnetite at 21.1 GPa, and (d) h-Fe3O4, \([\text{Fe}^{2+}]_{\text{TET}} [\text{Fe}^{3+}_{\text{HS}} \text{Fe}^{3+}_{\text{HS}}]_{\text{OCT}}, \text{ at 20.8 GPa with high-spin Fe on all sites. The Fermi energy has been subtracted from all energy values. The density of state (DOS) is reported as the number of states/eV in the unit cell.}\)
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