

Magnetism and the Verwey transition in Fe₃O₄ under pressure

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We have used high precision neutron diffraction and *ab initio* calculations to investigate the behavior of the magnetism of spinel magnetite (Fe₃O₄) under pressure in the 0–10 GPa range and at temperatures of 130–300 K. We find a significant but continuous decrease of the magnetic moments at both the *A* and *B* sites to at least 10 GPa, as well as an absence of any detectable pressure dependence of the oxygen atomic parameter. The data indicate a very weak dependence of the saturation moment on pressure and temperature and rule out unambiguously a transition from inverse to normal spinel in the *P/T* range investigated. Consequently, charge ordering cannot be precluded as the origin of the Verwey transition under pressure.

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Magnetite is the oldest magnetic material known.¹ Due to its fascinating electronic properties related to the Verwey transition, its abundant occurrence on Earth and Mars, its relevance in biology as magnetoreceptors, as well as its potential applications for magnetic nanocomposites, magnetite has been subject of numerous investigations. It has been extensively investigated under high pressure not only for evident geophysical reasons but also because high pressure experiments are thought to improve our understanding of its unusual electronic and magnetic ground state properties.

Fe₃O₄ crystallizes at ambient conditions in the cubic spinel structure of space group $Fd\bar{3}m$ with 8 f.u. in the conventional unit cell. The spinel type is inverse, i.e., the tetrahedral (*A*) sites are occupied by Fe³⁺, whereas the twice as abundant octahedral *B* sites are randomly occupied by Fe²⁺ and Fe³⁺. Magnetite is ferrimagnetic ($T_N=851$ K) since the moments at the *A* and *B* sites point in opposite directions, giving a net magnetic moment corresponding to one Fe²⁺, i.e., formally $4\mu_B$ /f.u. The inverse spinel structure manifests itself in the Fe–O bond lengths d_A and d_B through the well established valence sum rules,² and hence in the fractional atomic *z* position of the oxygen atom $u(O)$, to which they are related by $d_A=\sqrt{3}a(u-1/8)$ and $d_B=a(1/2-u)$. For inverse spinel Fe₃O₄, $u=0.255$,³ whereas one would expect $u=0.260$ if magnetite were in a normal spinel state in which the *A* and *B* sites are occupied by Fe²⁺ and Fe³⁺, respectively. The pressure dependence of the u parameter hence monitors the magnetic state. For this reason, the variation of u with pressure and temperature has attracted considerable interest over the last 4 decades, without, however, reaching a conclusion so far. From the measured pressure dependence of the Néel temperature ($dT_N/dp=+20.5$ K/GPa) and empirical relations between bond lengths and magnetic exchange parameters, Samara and Giardini⁴ predicted an increase of u with pressure at a rate of 5.8×10^{-4} GPa⁻¹ and suggested that it would be very desirable to do a detailed x-ray and/or neutron study to check this. Subsequent single crystal x-ray work^{5,6} did not

show any significant variation of u at least up to 4.5 GPa. This contrasts with more recent powder x-ray data^{7,8} to 20 GPa (obtained at 300 K), which report either a decrease⁷ or an increase⁸ of u above 4 GPa. The most recent work, a single crystal x-ray study to 8 GPa by Gatta *et al.*⁹ and our own neutron powder work to 5 GPa (Ref. 10) find no significant change of u and hence confirm the earlier x-ray results.^{5,6} A difference as small as $\sim 2\%$ in u could be considered as irrelevant if it did not entail two important consequences. First, if the *A* sites were occupied by Fe²⁺ (normal spinel), the net magnetic moment would be $(5+5-4)\mu_B=6\mu_B$, i.e., a 50% increase in normal compared to inverse spinel Fe₃O₄. Second, in normal spinel Fe₃O₄, the *B* sites are occupied by Fe³⁺ only. This means that if magnetite is a normal spinel at 130 K under pressure, as suggested^{11,12} (see Fig. 1), charge ordering can no longer be invoked to explain the metal-insulator Verwey transition¹³ which occurs at lower temperatures between 0 and 8 GPa.¹⁴ Such a situation would obviously be of significance for band structure computations that investigate charge ordering at the Verwey transition (Refs. 15–18 and references therein).

We have investigated the problem of magnetism in Fe₃O₄ in more detail, both experimentally as well as by first-principles calculations. We have applied the most direct experimental method to probe magnetism, i.e., *in situ* high pressure neutron scattering. X-ray diffraction suffers from the weak scattering power of oxygen compared to iron which makes the precise measurements of $u(O)$ difficult, in particular, in the presence of nonhydrostatic pressure conditions.⁹ The interpretation of changes in the Mössbauer spectra under pressure is far from being unambiguous and remained inconclusive.^{11,12,19} In contrast, neutron diffraction determines directly the magnetic structure and its pressure dependence, without the need to deduce it indirectly from the oxygen position.

A sample of Fe₃O₄ was obtained by grinding in acetone a part of a (1 cm³) perfect single crystal purchased from

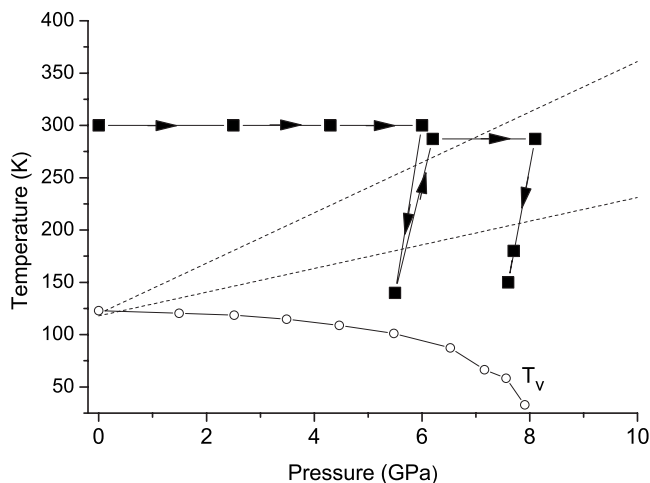


FIG. 1. Sequence of neutron measurements with P/T conditions where data have been collected (squares). The dashed lines delimitate the stability range of inverse and normal spinel magnetite, as proposed in Ref. 8 (inverse above, normal below, and intermediate between). Circles correspond to the metal-insulator Verwey transition as determined by Mori *et al.* (Ref. 14).

NEYCO. Heat capacity measurements on a small piece of sample showed a sharp Verwey temperature with an onset at 120 K which indicates²⁰ that the sample is almost perfectly stoichiometric ($\delta=0.001$) in $\text{Fe}_{3(1-\delta)}\text{O}_4$. About 50 mg of the sample was loaded into a Paris-Edinburgh press using a 4:1 deuterated methanol-ethanol mixture as the pressure transmitting medium and a setup previously described.²¹ At 300 K, this liquid provides hydrostatic conditions in the pressure range considered here (0–9 GPa).⁹ Pressures were changed only at ambient temperature (Fig. 1), and cooling was achieved by a dedicated cryocooler which enables us to stabilize the temperature to within 1 K. Measured temperature gradients across the 30 kg press were less than 2 K. All diffraction data were collected at the D20 high intensity diffractometer at the Institute Laue Langevin, Grenoble (France), using a wavelength $\lambda=1.4807$ Å and an oscillating radial collimator to avoid background signal from the cryostat. Contrary to our previous measurements to 5 GPa at ISIS,¹⁰ the D20 setup allows us to collect all low- Q reflections which carry the important magnetic intensity of interest in this study. Patterns were collected at nine different P/T points between 0 and 8.1 GPa in the temperature range of 130–300 K (Fig. 1). Rietveld refinements were carried out using FULLPROF,²² refining a minimal set of variables, i.e., the lattice parameter, the internal oxygen coordinate u , the magnitude of the magnetic moments on the A and B sites, as well as background and profile coefficients. Pressure values were obtained from the measured lattice parameter by a second order Birch-Murnaghan equation of state using a bulk modulus $B=180$ GPa as proposed by Gatta *et al.*⁹ and zero pressure volumes $V_0=592.4$ Å³ (300 K), 590.9 Å³ (180 K), 590.5 Å³ (150 K), and 590.4 Å³ (140 K).

Figure 2 shows neutron diffraction data and corresponding refinements for spectra at various pressures and temperatures, as explained in Fig. 1. It is important to note that up to

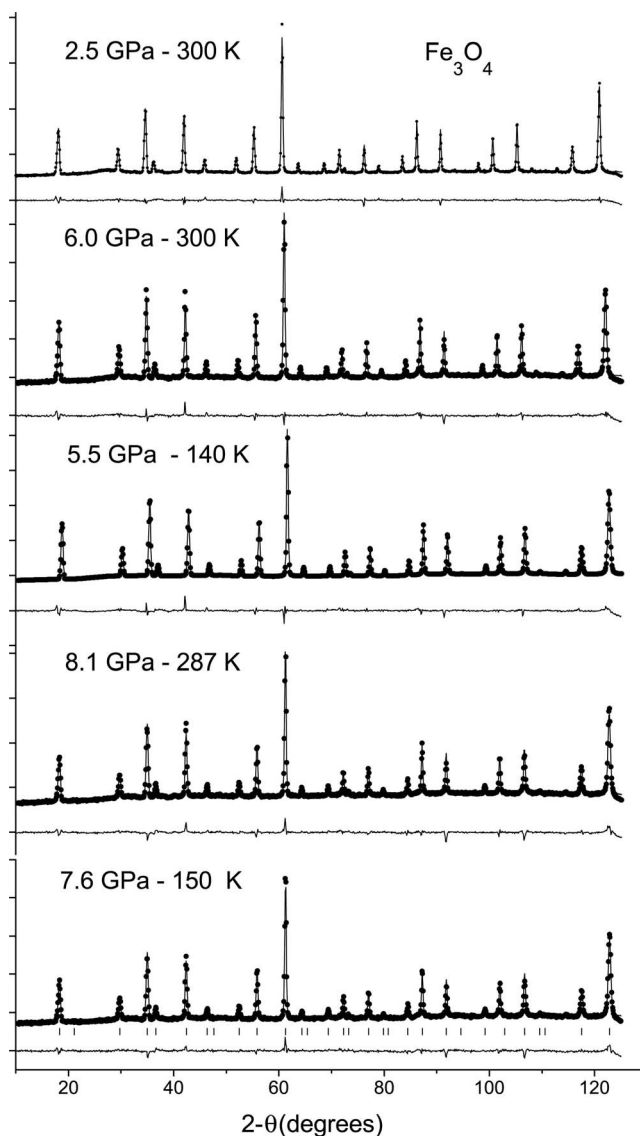


FIG. 2. Diffraction patterns of Fe_3O_4 at various P/T conditions, as explained in Fig. 1. The lines through the data (dots) are results of a Rietveld fit; difference plots are given below. Tickmarks designate positions of nuclear and magnetic reflections. Typical data accumulation times per pattern were 3–4 h.

8.1 GPa and down to 130 K, there is no detectable change in the five refined peak profile coefficients, i.e., the pressure conditions are as hydrostatic as one can tell, even at low temperatures. We focus on the evolution of the magnetic moments as a function of pressure and temperature (Fig. 3). Under pressure, both moments at the A and B sites decrease significantly in magnitude at rates of $\partial|m_A|/\partial P = -0.093\mu_B/\text{GPa}$ ($\partial \ln|m_A|/\partial \ln V = +4.1$) as well as $\partial|m_B|/\partial P = -0.041\mu_B/\text{GPa}$ ($\partial \ln|m_B|/\partial \ln V = +2.0$). There appears to be no temperature dependence, i.e., the data points at 130 K fall within the error bars on the lines valid for high temperature. This might be expected since the Néel temperature at 1 bar is 851 K and at 8 GPa, approximately 1015 K,⁴ i.e., in both cases far above the temperature of our measurements. Therefore, although m_A and m_B decrease substantially under pressure, the data clearly rule out a change in the mag-

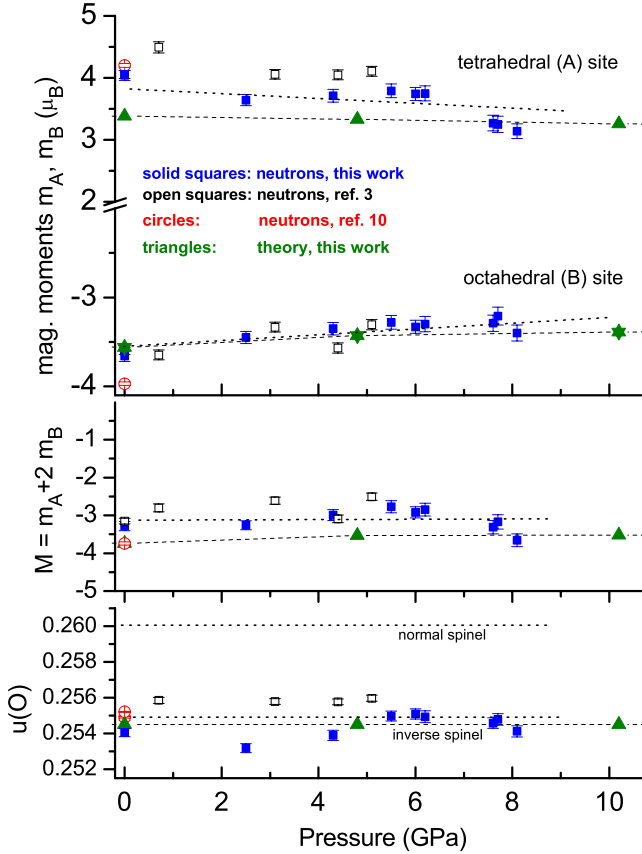


FIG. 3. (Color online) Magnetic moments (upper), total moment M (middle), and fractional atomic coordinate of oxygen (lower) of Fe_3O_4 at P/T conditions, as shown in Fig. 1. The dotted and dashed lines are guides for the eyes for the experimental and theoretical data, respectively. Ambient pressure neutron data (Ref. 3, obtained at 130 K), as well as previous neutron data to 5 GPa (Ref. 10, obtained at 300 and 130 K), are given for comparison. Note that in the calculations, the two magnetic moments on the B site (triangles up and down) in the $Imma$ setting are identical.

netic structure in the 0–9 GPa and 100–300 K ranges.

The experiments were complemented by first-principles computations using the state-of-the-art all electron linearized augmented plane wave (LAPW) method as implemented in the WIEN2K code.^{23,24} While a lot of work in recent years has focused on the local-density approximation (LDA)+ U method (e.g., Refs. 16, 17, and 25), we here chose the generalized gradient approximation (GGA) to the exchange and correlation potentials,²⁶ as even for moderate values of the Hubbard exchange parameter U computations with GGA+ U have recently been shown to generate unphysical results.²⁷ Fe is treated with an Ar core and O with a He core, and for all valence electrons, augmented plane waves are used in the basis set. We perform computations for both the cubic structure and a structure in which the B sites are split ($B1$ and $B2$) to allow for their nonequivalency as proposed at high pressure.^{8,11} This structure is orthorhombic (space group $Imma$) and described in detail in our previous work.²⁷ Changes in magnetic moments on the B sites in the $Imma$ structure have been shown to be a sensitive indicator of the electronic environment.²⁷ Reciprocal space sampling is

performed with an $8 \times 8 \times 8$ special k -point mesh for the full Brillouin zone, and we use $RK_{max}=7.0$. We carry out computations for volumes of $(0.925-1.025)V_0$, with $\Delta V/V_0=0.025$, out of which three volumes fall within the experimental pressure range of this study. We relax internal parameters in both structures until forces are below 0.5 mRy/bohr and analyze results for the $Imma$ structure in terms of the u parameter for O. Although in the $Imma$ structures the O position is split in two sites, the relaxed structures can all be described in the $Fd\bar{3}m$ cubic structure with one parameter u for the O.

The experimentally observed pressure-induced decrease of both moments is supported by the computational results (Fig. 3). In addition, they indicate that the moments of the $B1$ and $B2$ sites (up and down triangles in Fig. 3) remain the same up to the highest pressure studied and that the moments between the cubic and the orthorhombic setups are indistinguishable. The B site moments agree with the experiments, whereas the ones on the A site are slightly lower than found experimentally. The finding of a moment that is too low for the Fe^{3+} on the A site is consistent with work on Fe_2O_3 hematite,²⁸ and adding a Hubbard U can increase the magnitude of the magnetic moment both in Fe_2O_3 (Ref. 28) and Fe_3O_4 (Ref. 27) due to stronger on-site interaction.

It is worth noting that there is some ambiguity in determining the magnetic moment in the LAPW method. The moment associated with an atom is evaluated within the muffin tin radius (R_{MT}) of the respective atom, while the “ionic” size may be different, defined, e.g., by surfaces of zero-charge-gradient flux (Bader analysis²⁹). Here, we use a R_{MT} of 1.85 bohr for both Fe sites at V_0 and decrease R_{MT} uniformly under compression.

The variation of the moments is fully consistent with the behavior of $u(\text{O})$ as a function of pressure and temperature (Fig. 3), i.e., $u(\text{O})$ remains close to the value for inverse spinel ($u=0.255$). In the computations, there is a slight difference between u in the cubic (0.2541) and the orthorhombic cell (0.2546), but no changes as a function of pressure have been observed, i.e., at all volumes, the structural parameters yield a force smaller than the convergence criterion.

A pressure-induced charge transfer from $[\text{Fe}^{3+}]_A[\text{Fe}^{2.5+}\text{Fe}^{2.5+}]_B$ to $[\text{Fe}^{2+}]_A[\text{Fe}^{3+}\text{Fe}^{3+}]_B$ would, as mentioned above, decrease the magnetic moment of the A site but increase the magnitude of the one at the B site. What we find is, however, a decrease of *both* moments. This pressure-induced “squeezing out” of the moments should be compared to the pressure dependence of the conductivity,³⁰ which increases by a factor of 50 between 0 and 3 GPa (at 160 K) and at 300 K, an estimated 3–4 orders of magnitude up to 8 GPa. The straightforward conclusion is hence a pressure-induced delocalization of the $3d$ electrons, which entails a continuous quenching of the magnetic moments, as detected in our measurements. Interestingly, although the individual moments decrease by as much as 20%, the effect on the net moment, i.e., $M=(m_A+2m_B)$, is very small because of partial cancellation linked to the ferrimagnetic structure. We find experimentally that $\partial \ln|M|/\partial P=0.35\%/ \text{GPa}$. This is again consistent with macroscopic measurements of Samara and Giardini,⁴ which conclude that M increases by less than 1%/GPa.

In summary, combining neutron diffraction and first-principles computations, we have investigated the behavior of magnetism in Fe_3O_4 under pressure. To this extent, we have analyzed data in terms of magnetic moments of the different Fe sites and the fractional coordinate of oxygen (u) in the structure. We find a significant but continuous change of the magnetic moments, but no transfer between the different sites in Fe_3O_4 up to at least 10 GPa, and u remains close to the value characteristic for the inverse spinel structure. This explains the weak pressure dependence of the magnetization and rules out an inverse to normal spinel transition in

Fe_3O_4 . As a consequence, the B sites are randomly occupied by Fe^{2+} and Fe^{3+} even at high pressure. Charge ordering can therefore not be precluded to explain the Verwey transition under high pressure and low temperatures.

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