

Effect of high pressure on the crystal structure and electronic properties of magnetite below 25 GPa

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ABSTRACT

We report results from high-pressure single-crystal X-ray diffraction and Mössbauer absorption experiments on magnetite. Based on high-quality diffraction data, we have obtained accurate information on the crystal structure of magnetite below 25 GPa, which enables an unambiguous interpretation of the Mössbauer data using constrained area ratios and a full transmission integral fit that avoids area distortion due to thickness effects. Based on our analysis, all aspects of the electronic and magnetic properties of magnetite reported previously below 25 GPa at ambient temperature can be explained solely by the enhanced delocalization of 3*d* electrons of iron atoms. For instance, we present evidence that the compression-induced metallization changes the sign of the charge carrier spin polarization at 15 GPa.

Keywords: Magnetite, high pressure, Mössbauer spectroscopy, single-crystal X-ray diffraction

INTRODUCTION

Magnetite is one of the most fascinating and important iron-containing minerals. In nature, simple life forms such as bacteria and more evolved species such as birds use magnetite crystals as magneto receptors to orient themselves in the Earth's magnetic field (Gould 2008). Magnetite is also widely used commercially as a pigment for paints and in construction as an aggregate for high-density concrete, as well as in many other forms for diverse purposes (e.g., Hiergeist et al. 1999; Mayo et al. 2006). Away from ambient conditions, extreme temperatures or pressures have revealed the complex physics of this material.

The crystal structure of magnetite is an inverse spinel type with tetrahedral (T) sites occupied by Fe³⁺ and octahedral (O) sites occupied by both Fe²⁺ and Fe³⁺. The antiferromagnetic exchange between T- and O-sites align magnetic moments of iron along the [111] direction. Electron hopping between octahedra occupied by iron ions in different valence states determines the transport properties of magnetite. Magnetite is a half metal at ambient conditions with high polarization of charge carriers (Dedkov et al. 2002). The application of moderate pressures (<25 GPa) induces profound changes to its electronic properties (Morris and Williams 1997), leaving the crystal structure almost unaffected (Haavik et al. 2000), although some peculiarities were reported in a powder X-ray diffraction study (Rozenberg et al. 2007). It is worth noting here, however, that powder X-ray

diffraction analysis at high pressure of subtle features such as element coordination can give ambiguous and sometimes unrealistic results. This is mostly due to the small amount of sample that limits the signal quality, the limited resolution and 2θ range, as well as evolution of texture effects arising from uniaxial stress. Based on existing information of the crystal structure of magnetite below 25 GPa, two possible scenarios have been heavily discussed in the literature to explain the high-pressure behavior of magnetite.

The first hypothesis is a transition from the inverse type (IT) of spinel to the normal type (NT) at pressures 10–20 GPa (Rozenberg et al. 2007; Pasternak et al. 2003). Analysis of powder X-ray diffraction data suggested a pressure-induced anomaly of the unit-cell oxygen coordinate (*u*), indicating a decrease of the relative volumes of O-sites (V_O/V_{cell}) and an increase for T-sites (V_T/V_{cell}). The reported effect was extremely large: on average there was a ~10% volume change of O- and T-sites, which was interpreted to indicate that the large Fe²⁺ ion changed its position from the O- to the T-site due to a compression induced redistribution of electronic charge.

The second hypothesis is a spin state transition of Fe²⁺ (O-sites) from high spin (HS) to intermediate spin (IS) (Ding et al. 2008). Combined X-ray magnetic circular dichroism and X-ray emission spectroscopy studies revealed a reduction of the net magnetic moment of magnetite. It was proposed that the competition between the crystal field splitting, Hund exchange integral and covalence effects induced the change of spin state.

The physics behind the HS-LS transition differs from the

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IT-NT model. It is important to note that these two scenarios of high-pressure behavior are incompatible, and that IT-NT and HS-IS transitions cannot occur within the same pressure range (10–20 GPa).

To seek a deeper insight into the complex physics of magnetite below 25 GPa, we performed a combined single-crystal X-ray diffraction and Mössbauer study. The different crystallographic environments and valence states of iron in magnetite constrain the assignment of absorption features of the Mössbauer spectra. Thus before fitting the Mössbauer spectra, we obtained accurate information on the crystal structure of magnetite and directly tested the IT-NT model. The results of the single-crystal study enabled an unambiguous fitting of Mössbauer data (powder samples). Mössbauer parameters obtained in the experiment allowed a rigorous testing of the HS-IS model through tracking of pressure-induced changes of the electronic structure, crystallographic site valence states (isomer shift), distortions of the O- and T-sites (quadrupole splitting), and magnetic moments of iron atoms in different crystallographic sites (hyperfine magnetic field).

EXPERIMENTAL METHODS

The magnetite powders for the Mössbauer experiment were prepared in a gas mixing furnace from 99.99% Fe₂O₃ enriched with ⁵⁷Fe (>90%). The hematite starting material was compressed into pellets, heated for 12 h at 1200 °C in a CO/CO₂ mixture [$\log(pO_2) = -6.4$] and subsequently quenched. Based on the results of Mössbauer and X-ray powder diffraction experiments, we confirmed that the prepared material contained single-phase magnetite. No traces of other iron oxides were found. The deviation from nonstoichiometric composition (Fe₃O_{4- δ}) for the powder material was estimated to be $0.0001 < \delta < 0.001$ based on the preparation conditions (Aragón et al. 1985). For the single-crystal X-ray diffraction experiments, we selected several small chips of natural magnetite (~3 × 10 × 20 μm) originating from the Bijiki iron formation, upper peninsula of Michigan, U.S.A. The analysis of impurities (Table 1) of the natural sample was done using a Jeol JXA-8200 electron microprobe equipped with five wavelength-dispersive spectrometers. An accelerating voltage of 15 kV and a beam current of 15 nA were employed. The beam size was 1–2 μm.

The natural single-crystal samples are expected to have a lower degree of stoichiometry (higher δ values) than the synthesized powder material used in this work (Shepherd et al. 1985). Nevertheless, we believe that it is valid to use the single-crystal structural data of magnetite to interpret the Mössbauer data of the powder material. Our reasoning comes from the observation of the behavior of the material in the vicinity of the Verwey transition (VT). On one hand, VT in magnetite can be affected by a deviation of δ from zero. For example for a material with $\delta > 0.0036$, the VT changes from first to second order (Kakol and Honig 1989). On the other hand, the high-pressure resistivity data provide evidence that the driving force for the VT remains the same for different values of δ [13], and that the difference of VT critical pressures is small (Móri et al. 2002; 1–4 GPa, measured in a highly nonhydrostatic pressure medium). In this work, we employ a significantly more hydrostatic pressure medium (Ne), and we believe that the difference between high-pressure transitions at ambient temperature of magnetite with low and high degrees of stoichiometry should be negligible.

High-pressure Mössbauer experiments were conducted using a modified Merrill-Bassett diamond-anvil cells (DACs). For single-crystal X-ray diffraction experiments, we used a different DAC (60° diffraction cone opening) equipped with two Boehler-Almax diamonds. The diamond culet size was 300 μm. The samples were loaded into 150 μm holes drilled in 30–40 μm preindented rhenium gaskets along with ruby chips for pressure calibration (Mao et al. 1986). Neon was used as a pressure-transmitting medium for all experiments.

The ⁵⁷Fe Mössbauer spectra were collected at Bayerisches Geoinstitut, Bayreuth, Germany. Spectra were obtained at room temperature in transmission mode on a constant acceleration Mössbauer spectrometer using a nominal 370 MBq ⁵⁷Co high specific activity source in a 12 μm Rh matrix (point source). The velocity scale was calibrated relative to 25 μm thick α -Fe foil. The collection time for each spectrum varied from 24 to 30 h. Mössbauer absorption varied from 7 to 9%, depending on the sample loading. The spectra were fitted using the full transmission integral procedure implemented in the commercially available fitting program NORMOS written by R.A. Brand (distributed by Wissenschaftliche Elektronik GmbH, Germany).

Single-crystal X-ray diffraction data were collected at room temperature using a MAR555 flat panel detector at ID09a, European Synchrotron Radiation Facility, Grenoble. We used 60° ω scans with a 0.5° step at 0.41520 Å wavelength. Oxford Diffraction CrysAlis and JANA2006 (Petricek et al. 2006) software were used for data analysis and refinement of the lattice parameter and crystal structure of magnetite. Typical values of the R-factor were 3–7% (JANA2006). The data on pressure induced variation of crystallographic parameters can be found in Table 2.

RESULTS AND DISCUSSION

We collected single-crystal diffraction at pressures from 0 to 21 GPa. Our data on unit-cell volumes (Fig. 1, inset) are in good agreement with previous powder diffraction experiments (Rozenberg et al. 2007). However, we find a different pressure-induced behavior of the u parameter from that reported previously (Fig. 1a). Our single-crystal diffraction data provide unambiguous evidence that the value of u remains essentially constant within experimental uncertainty at all studied pressures. This observation proves that there is no change in the relative volumes of T- and O-sites (Fig. 1b). Thus, we conclude that there is no IT-NT transition in single-crystal magnetite at pressures of 10–21 GPa.

In the case of the HS-IS transition model the following considerations apply. Fe²⁺ occupies only O-sites and has a larger ionic radius in the high spin state than in the intermediate spin state. However, due to charge hopping between the O-sites the volume

TABLE 2. Lattice and crystallographic parameters, volume, and R -factors of the data evaluation determined on natural single crystal of magnetite at 300 K

P (GPa)	a (Å)	V (Å ³)	U	R_{int} (%)	R_1 (%)
0.0001	8.394(3)	591.5(6)	0.2549(4)	6.9	4.2
2.9(1)	8.350(3)	582.1(6)	0.2554(5)	4.3	4.3
4.4(1)	8.328(3)	577.6(6)	0.2551(4)	3.4	3.4
6.3(1)	8.304(3)	572.5(6)	0.2547(3)	3.5	3.5
8.6(1)	8.272(3)	566.1(6)	0.2555(7)	6.6	6.6
10.0(1)	8.261(3)	563.8(6)	0.2550(5)	5.2	5.2
11.0(1)	8.249(3)	561.3(6)	0.2553(7)	5.7	4.5
12.1(1)	8.236(3)	558.7(6)	0.2554(6)	5.0	4.3
12.9(1)	8.225(3)	556.4(6)	0.2554(8)	5.3	4.4
14.4(1)	8.207(3)	552.7(6)	0.2552(5)	3.5	3.6
15.1(1)	8.198(3)	550.9(6)	0.2554(4)	3.4	3.3
16.0(1)	8.184(3)	548.1(6)	0.2551(6)	3.7	3.9
17.0(1)	8.174(4)	546.2(8)	0.2543(11)	8.4	7.4
18.1(1)	8.158(3)	543.0(6)	0.2547(4)	4.6	3.9
19.1(1)	8.149(3)	541.1(6)	0.2548(4)	4.7	3.7
20.0(1)	8.138(3)	539.0(6)	0.2543(7)	5.2	6.0
21.1(1)	8.125(3)	536.4(6)	0.2542(10)	5.9	5.6

Notes: The fractional coordinates of Fe¹ and Fe² are (0.5 0.5 0.5) and (0.125 0.125 0.125). The R factors R_1 and R_{int} are defined as $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_{\text{int}} = \sum |F_o - F_c(\text{mean})| / \sum F_o$, where F_o and F_c are the observed and the calculated intensities, respectively. The number of observed unique reflections of the sample loaded in the diamond-anvil cell is 28–35 in the high-pressure experiment (depending on loading and pressure).

TABLE 1. Impurity element fractions in mole percent determined by microprobe on natural single crystal of magnetite (locality Bijiki iron formation, upper peninsula of Michigan, U.S.A.)

Na	Si	Ti	Ni	Fe	Al	Mg	Co	Cr	Mn
0.02(1)%	0.08(1)%	0.19(4)%	0.01(1)%	99.22(20)%	0.40(4)%	0.04(2)%	0.00(0)%	0.03(1)%	0.02(5)%

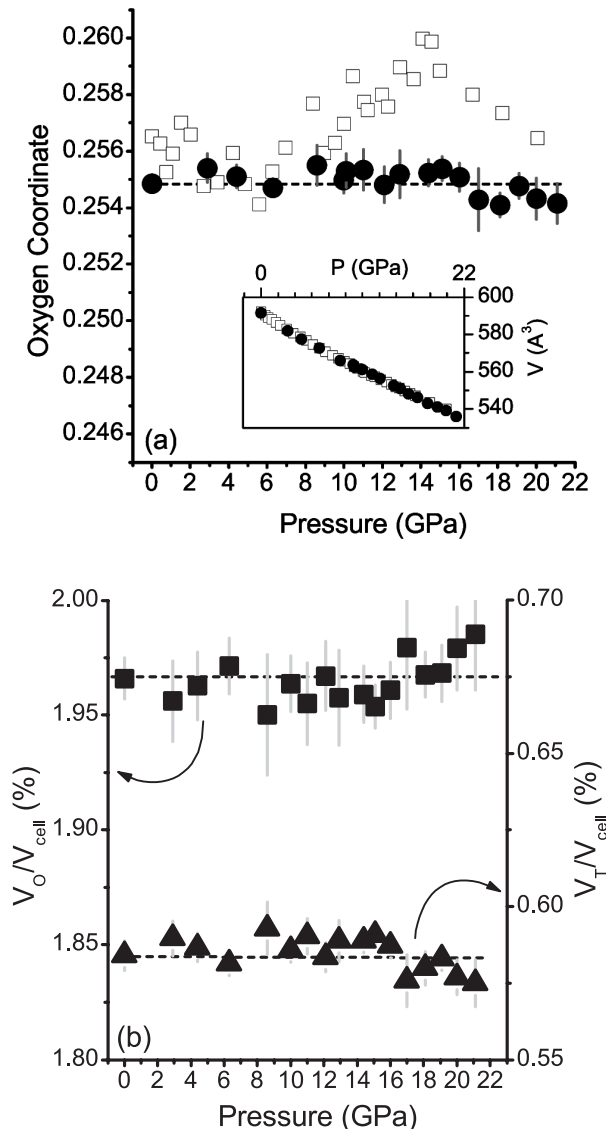


FIGURE 1. Pressure dependence of the magnetite (a) unit-cell oxygen coordinate u and (b) ratios of specific crystallographic site volumes ($T-V_T$ and $O-V_O$) to volume of the unit cell (V_{cell}). The solid circles in **a** represent current data; open squares = data from Rozenberg et al. (2007). The inset in **a** shows the unit-cell volume as a function of pressure. The closed triangles and squares in **b** mark T- and O-sites, respectively. Dashed lines are guides for the eye.

effect could be small. It is therefore possible that we are not able to resolve changes of this magnitude in the single-crystal X-ray diffraction experiment. To more accurately investigate the possibility of a HS-IS transition, we have approached this problem independently using Mössbauer spectroscopy as described below.

The Mössbauer spectrum of magnetite consists of two subspectra at ambient conditions. One corresponds to $\text{Fe}^{2.5+}$ in O-sites while the second corresponds to Fe^{3+} in T-sites. The observation of $\text{Fe}^{2.5+}$ is due to the mean lifetime of the excited

^{57}Fe nucleus ($\sim 10^{-7}$ s) being much longer than charge fluctuation between the Fe^{2+} and Fe^{3+} ions ($< 10^{-16}$ s, according to results of García et al. 2000). Consequently, O-site Fe^{2+} and Fe^{3+} should be indistinguishable in Mössbauer absorption spectra.

Based on our single-crystal X-ray diffraction studies, we fitted Mössbauer absorption spectra using the inverse spinel-type structure model. Because overlapping peaks do not enable a unique set of hyperfine parameters to be obtained from an unconstrained fit of the data, we applied constraints based on results from the single-crystal structural data. We fixed the area ratio between O- and T-subspectra to be 2:1, which is justified because we used the full transmission integral to fit the data, which corrects for distortion of the areas due to thickness effects. We assumed zero quadrupole splitting of the T-sites (no electrical field gradient) based on the cubic environment of the site and the absence of charge hopping from O- to T-sites (T-sites are not observed to participate in charge transfer at ambient conditions, and according to theoretical studies, T-sites do not affect conductivity up to 20 GPa (Friák et al. 2007). On the other hand, the iron ions at the O-sites act as electron donors to the conductivity band; thus we allowed distortions of the O-site and hence non zero values of quadrupole splitting. The results of the fitting of Mössbauer absorption spectra are shown on Figure 2.

The pressure dependence of the parameters derived from the fits, namely isomer shift (IS), quadrupole splitting (QS), and the hyperfine magnetic field (HMF), for different crystallographic sites are shown in Figure 3. Our data on hyperfine magnetic splitting and isomer shift are in good agreement with data reported by Kobayashi et al. (2006), although we do not see an additional O-site component. This discrepancy can be related to the more hydrostatic conditions in our experiments due to the Ne pressure-transmitting medium.

Before advancing to more detailed analysis, we address the question of the HS-IS transition in magnetite (Ding et al. 2008). The isomer shift data do not support presence of this transition. We consider the following simple reasoning. In the case of a spin-state transition in Fe^{2+} ions, the charge distribution on the iron nucleus would become more spherical ($t_{2g}^4 e_g^2 \rightarrow t_{2g}^5 e_g^1$), and the slope of isomer shift would change significantly, reflecting the higher polarization of s -electrons. No such changes are observed in the isomer shift data. In addition, it is important to add that the transport properties of magnetite are controlled by the t_{2g} electron minority band. In the case of a HS-IS transition, an additional electron is effectively added to the conduction band ($t_{2g}^3 \uparrow t_{2g} \downarrow e_g^2 \uparrow \rightarrow t_{2g}^3 \uparrow t_{2g}^{1+2} \downarrow e_g^1 \uparrow$); thus the resistivity of the material should drop significantly. There is no experimental observation of any electrical resistivity anomaly of magnetite in the pressure range of interest, 10–20 GPa (e.g., Morris and Williams 1997; Ovsyannikov et al. 2008). We therefore conclude that there is no HS-IS transition in magnetite at pressures of 10–20 GPa.

Based on the current data and information available in the literature, we suggest the following model for the high-pressure behavior of magnetite. At ambient conditions magnetite is a half metal, and the O-site $t_{2g} \downarrow$ minority band electrons are responsible for conductivity. However, the polarization of charge carriers is less than 100%; thus the majority spin electrons $t_{2g} \uparrow$ also participate in charge transport.

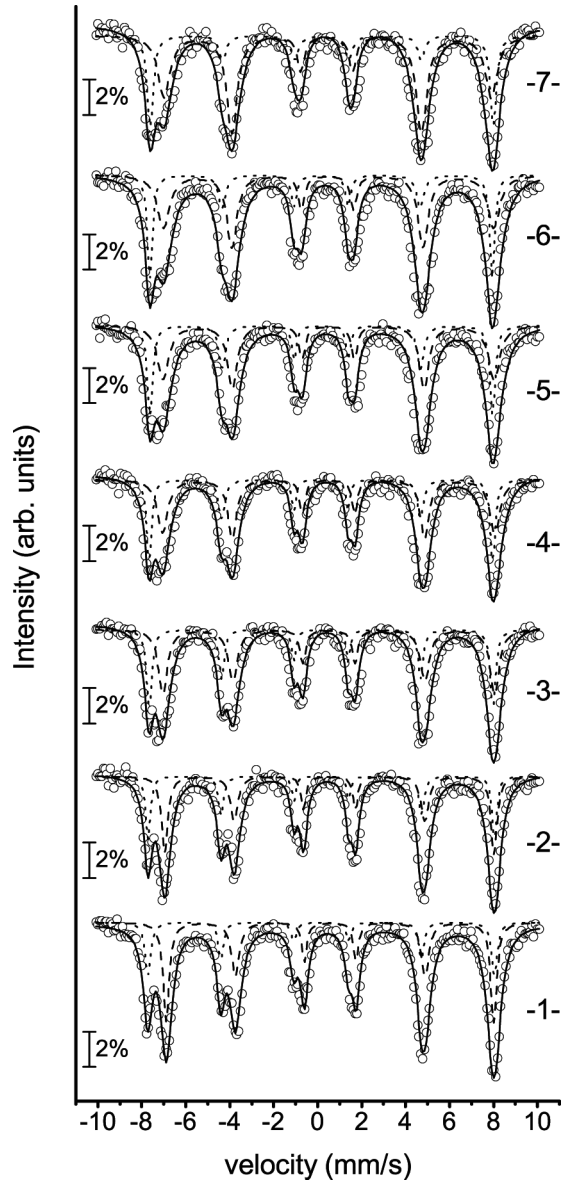


FIGURE 2. Mössbauer spectra of magnetite at different pressures: (1) 0 GPa, (2) 4.2 GPa, (3) 12.2 GPa, (4) 16.3 GPa, (5) 19.19 GPa, (6) 20.7 GPa, (7) 24.9 GPa. Fitting was performed using the full transmission integral procedure.

Pressure induces changes in the electronic and magnetic properties of magnetite

First, pressure-enhanced hybridization of charge carriers induces a drop of resistivity (Morris and Williams 1997). Analysis of isomer shift pressure dependence provides insight into the different roles of the T- and O-sites on the transport properties. By definition, the value of the isomer shift is related to the density of *s*-electrons at the nucleus; however shielding by *d*- and *p*-electrons also affects this value. For example, an increased hybridization of *d*-electrons with the conduction band would result in a larger density of *s*-electrons at the nucleus; hence the isomer shift would decrease. While the T-site isomer shift is

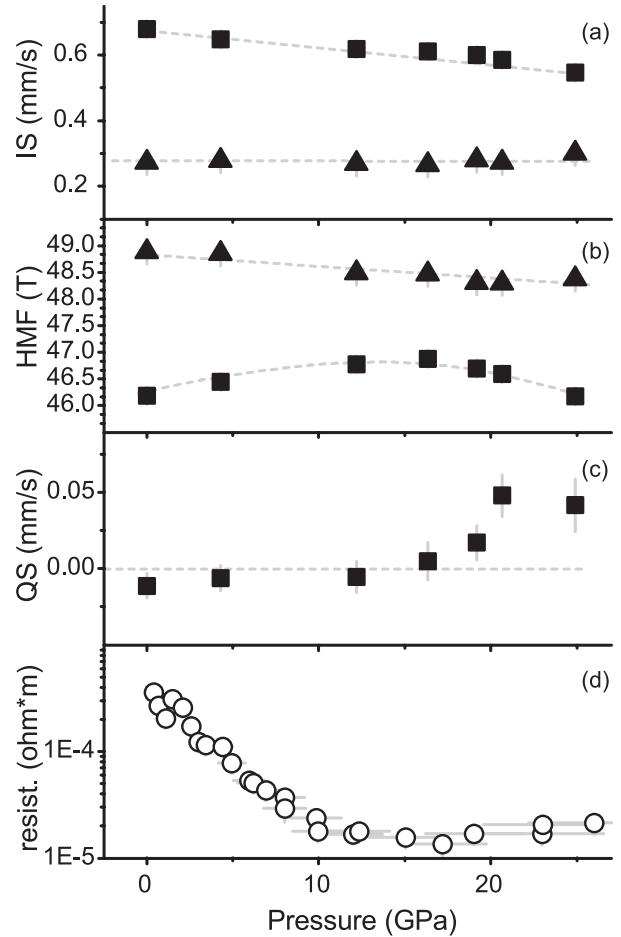


FIGURE 3. Pressure dependencies of (a) IS = isomer shift; (b) HMF = hyperfine magnetic field; (c) QS = quadrupole splitting; (d) bulk resistivity from Morris and Williams (1997). The O- and T-sites are marked by squares and triangles, respectively. The lines are guides for the eye.

almost constant at the pressures of our experiment, the value for O-site isomer shift constantly decreases with pressure. Thus at the pressures of this study, only O-sites provide charge carriers.

The higher the pressure, the greater is the number of *3d* electrons that become delocalized. At some critical pressure, delocalization of electrons leads to distortions of the crystal lattice, which is strongly coupled to the electronic and magnetic properties of magnetite. Thus, the resistivity of the material will be significantly affected by electronic or crystal structure distortions. According to data of Morris and Williams (1997), the resistivity decreases and then probably saturates at pressures below 25 GPa. Our single-crystal study showed that structural distortions are small and cannot be resolved by X-ray diffraction data, but we can detect them through the quadrupole splitting (QS) Mössbauer parameter. QS is very sensitive and is nearly zero for the O-site at pressures below 15 GPa, but its value slightly increases at higher pressures. Based on the combined evidence above, we suggest that at 15 GPa the delocalization of *3d* electrons could lead to dynamical distortions of the structure (dynamic Jahn-Teller effect). However, the explanation could

be more complex, since there are three contributions to QS: effects of bonding and nonbonding electrons as well as the effect of lattice distortions (Parish 1986).

We can extract further information from the high-pressure behavior of hyperfine magnetic fields (HMF) of T- and O-sites. In the case of iron ions, the total hyperfine magnetic field can be written as:

$$\text{HMF} = B_c + B_{\text{orb}} + B_{\text{dip}} \quad (1)$$

where the terms are as follows: B_c is contact interaction (describes polarization of s -electrons by unpaired $3d$ electrons); B_{orb} is magnetic field produced at the nucleus by orbital motion of unpaired $3d$ electrons; and B_{dip} is hyperfine interaction produced by dipolar field of the spins of $3d$ electrons. The major contribution to the total hyperfine field is the contact interaction (B_c). By definition, B_c is a function of the effective value of the magnetic spin ($\langle S \rangle$) multiplied by a parameter describing the polarization of the s -electrons (k) (Thomas and Johnson 1986).

T- and O-sites show different pressure dependences of HMF. There is a gradual decrease of HMF for the T-site. For Fe^{3+} in the T-site, the spherical charge distribution results in zero contribution from the B_{orb} and B_{dip} terms. Thus, we argue that the pressure induced decrease of HMF (T-sites) is related to the decrease of the effective value of the magnetic spin/magnetic moment ($\langle S \rangle$) at the T-site. Additionally, compression could induce weakening of the magnetic interaction between T-/O-sites.

The analysis of hyperfine magnetic interactions for the O-sites is challenging, as we expect non-zero values of B_{orb} and B_{dip} at higher hybridization or non zero values of quadrupole splitting. The magnetic moment on the O-site also decreases with pressure (Klotz et al. 2008). This observation is important because O-sites are occupied by Fe^{2+} ions ($3d^6 \uparrow; 3t_{2g} \uparrow + 2e_g \uparrow - 1t_{2g} \downarrow = 4 \uparrow$) as well as Fe^{3+} ($3d^5; 3t_{2g} \uparrow + 2e_g \uparrow = 5 \uparrow$). We believe that both majority- and minority-spins are hybridized, otherwise the magnetic moment on the O-site would increase with pressure. At low pressures the distortions of O-sites are small, and the t_{2g} energy levels are degenerate. Thus $t_{2g} \uparrow$ electrons are equally delocalized until at some critical pressure (P_c), the spin polarization of the charge carriers will become zero and will then change sign with compression.

At pressures higher than P_c , the magnetic moment of O-sites will suddenly decrease, because the effective number of spin-up states (\uparrow) will exceed the number of those with spin down (\downarrow). A recent XMCD study by Baudelet et al. (2010) has shown that the total magnetization of magnetite starts to decrease at pressures considerably higher than 15 GPa. Comparing the experimental observations, we conclude that at 15 GPa there is a change of charge carrier polarization.

In summary, the effective magnetic moment of the O-site decreases with pressure as a consequence of the weaker magnetic interaction between T- and O-sites and the ongoing hybridization. At first glance, the behavior of the O-site HMF appears to contradict our model below 15 GPa, because we observe an increase of HMF with compression (Fig. 3). However this observation can be easily explained by pressure-induced changes of the contact field (B_c), the major component of HMF.

As mentioned above, B_c is a function of $\langle S \rangle \cdot k$. For the O-sites,

higher polarization of s -electrons (k) implies a lower number of d -electrons in the $3d$ shell and hence a lower value of the isomer shift. Thus in a first-order approximation, if paired t_{2g} electrons are first hybridized, the magnetic moment of the O-site will not decrease; however the polarization of s -electrons at the iron nucleus will increase considerably.

Next, if the increase in k overcompensates the decrease of $\langle S \rangle$, there will be a positive change of B_c . We can neglect the $B_{\text{orb}} + B_{\text{dip}}$ contributions at pressures below 15 GPa (small quadrupole interaction at the O-site; small value of B_{orb}). Thus, HMF at O-sites will increase with compression below some critical pressure near 15 GPa. At higher pressures, the polarization of charge carriers changes, and we argue that the behavior of B_c and HMF is dominated by decreasing $\langle S \rangle$. The total HMF of the O-site then decreases at pressures above 15 GPa.

Although we cannot separate the contributions of t_{2g} and e_g electrons, the non-zero quadrupole splitting at O-sites at pressures higher than 15 GPa is evidence for small distortions from cubic symmetry. In this case, e_g electrons should be more separated from t_{2g} electrons by a potential energy barrier and should contribute much less to the conductivity.

In conclusion, we have shown that there is no IT-NT spinel transition in magnetite at pressures up to 21 GPa. We argue that there is also no HS-IS transition in magnetite in the same pressure range. Based on the analysis of our Mössbauer data and data available in the literature, we propose a consistent model of the delocalization of $3d$ electrons. Within the framework of this model we distinguish two regions: one below 15 GPa and the other above. We suggest that below 15 GPa the hybridization of majority spin electrons slowly increases with pressure. At 15 GPa, the spin polarization of charge carriers becomes zero and slowly changes sign with further compression, resulting in a decrease of the magnetic moment at the O-site and a decrease in the bulk magnetization of magnetite.

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