Absence of abrupt pressure-induced magnetic transitions in magnetite

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The structural properties of magnetite Fe_3O_4 under pressure have been extensively studied and are well established. This is not the case for its electronic and magnetic properties. We report a high-pressure x-ray magnetic circular dichroism study of magnetite up to 41 GPa. We observe a continuous evolution of the magnetic moment in the whole pressure range, in agreement with a band-structure description of the electronic state of magnetite. We highlight distinct regimes of magnetism. The x-ray absorption spectra do not suggest any major modification in the local structure in this pressure range.

I. INTRODUCTION

Magnetite Fe_3O_4 is the most magnetic of all the natural minerals and this property did allow using it as an early form of magnetic compass. It carries the dominant magnetic signature in rocks, and so has been a major tool in paleomagnetism, especially in discovering and understanding plate tectonics. It crystallizes at room temperature in the cubic inverse spinel structure ($Fd\bar{3}m$), formally written $[Fe]_A[Fe_2]_BO_4$. The A-type ions are tetrahedrally coordinated and nominally in a Fe^{3+} ($S \sim -5$ μ_B) configuration, while B-type ions are octahedrally coordinated with equally distributed Fe^{3+} ($S \sim +5$ μ_B), and Fe^{2+} ($S \sim +4$ μ_B) configurations. The Fe ions on A and B sites have opposite spins leading to a ferrimagnetic ordering.

At ambient pressure with decreasing temperature magnetite undergoes an abrupt increase in the electrical resistivity at $T_V = 125$ K, the so-called Vervey transition. This electronic transition has been associated to a structural phase transition to a monoclinic phase[1,2] and more recently to a first-order structural transition from a cubic metallic phase to a distorted cubic insulating phase,[3] characterized by a gap opening in the electronic band structure due to the lower symmetry.

Much experimental work has been performed to understand the behavior of magnetite under compression. The Vervey temperature $T_V(P)$ decreases with increasing pressure and falls off very rapidly above 6 GPa. Between 6 and 8 GPa the first-order Verwey transition disappears.[3–5] Above 25 GPa, magnetite undergoes a structural transformation to a high-pressure phase[6,7] and above 50 GPa an incipient metallic behavior coupled to a magnetic moment collapse has been observed.[8]

A coordination crossover, whereby the spinel structure changes from inverse to normal with increasing pressure has also been reported.[9,10] At ambient pressure this crossover occurs at temperatures close to the Vervey transition: $T_{cc}(P = \text{ambient}) \sim T_V(P = \text{ambient})$ but with increasing pressure $T_{cc}(P)$ increases rapidly, whereas $T_V(P)$ decreases.[3,9]

In a crude atomic description, the change in the total magnetic moment between the inverse and the direct spinel structure is expected to be on the order of +50%,

$$[Fe^{3+}]_A[Fe^{2+}Fe^{3+}]_B \rightarrow [Fe^{2+}]_A[Fe^{3+}Fe^{3+}]_B,$$
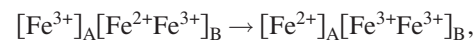
$$\text{Inverse spinel}(S = +4) \rightarrow \text{direct spinel}(S = +6).$$

Such an important variation in the magnetic moment on Fe should be easily detectable by Fe K-edge x-ray magnetic circular dichroism (XMCD) measurements but up to now has never been reported.[11,12] In Ref. 11, a sharp decrease ($\sim 50\%$) in the amplitude of the XMCD signal is observed between 12 and 16 GPa, almost independent of temperature in a wide range from 40 to 300 K. This abrupt change is interpreted as a high-spin to intermediate-spin transition of Fe^{2+} ions in octahedral sites. In Ref. 12, the amplitude of the XMCD signal at ambient temperature is seen to decrease with pressure of about 50% from ambient to 25 GPa, the highest pressure reached in this study.

Hence, there has been an enormous controversy in the recent years on the magnetic behavior of magnetite with pressure. In the present Rapid Communication, we present results obtained by XMCD up to 41 GPa, enabling to give a comprehensive view of the effects of compressing magnetite and providing clear answers to fundamental questions that have recently been posed in the literature: is there an inverse-direct spinel crossover in magnetite? Is there a high-spin $\rightarrow$ intermediate-spin transition? In both cases the answer is negative. Moreover, at 25 GPa we report a change in magnetism, which can be related to the previously observed structural modification[6,7] and to the onset of a semiconducting phase.[8]

II. RESULTS

High-pressure room-temperature x-ray absorption spectroscopy (XAS) and XMCD measurements at the Fe K edge have been performed on the ODE dispersive XAS beamline at SOLEIL 'Gif sur Yvette, France.

The sample, a micrometer-sized magnetite "Aldrich" commercial powder, was subject to high pressure (up to 41 GPa) using a 250 μm perforated diamond-anvil cell. The sample quality was checked by careful heat-capacity measurements, which exhibit the presence of a broad Verwey transition at 120 K.[13] The pressure-transmitting medium is silicone oil.
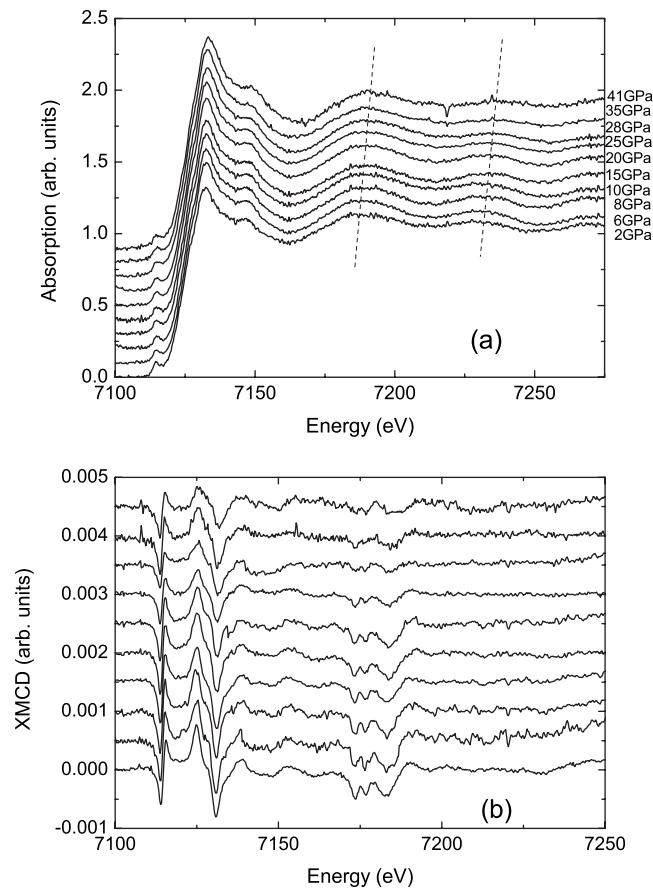
FIG. 1. (a) Magnetite Fe *K*-edge XAS spectra at various pressures indicated at the right-hand side of the figure. The dashed lines show the maximum of EXAFS oscillations. (b) XMCD spectra taken at the same pressures as the XAS spectra.
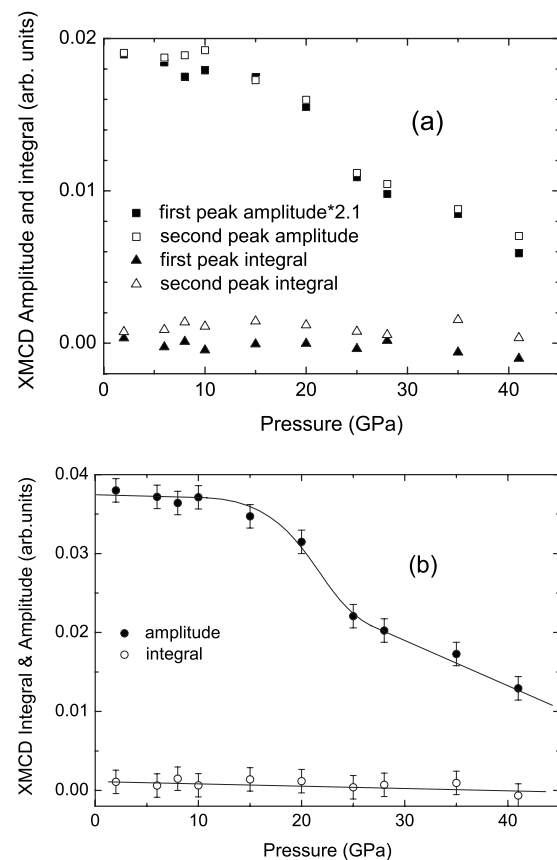

FIG. 2. (a) First and second XMCD double-peak integral (triangles) and amplitude (squares) pressure variation. (b) complete XMCD integral (open circles) and amplitude (full circles) pressure variation (the lines are guide for the eyes).

The XAS spectra [Fig. 1(a)] do not show any visible structural or electronic change under pressure, except for a shift to higher energies of the extended x-ray-absorption fine structure (EXAFS) oscillation due to the compression effect, and a slight increase in the intensity of the white line region, in agreement with previous work.[12] At the highest pressure values, a slight prepeak decrease is possibly seen but must be confirmed by more resolved measurements.

The corresponding XMCD spectra [Fig. 1(b)] exhibit two double peaks in the absorption edge region. The first one at around 7115 eV corresponds to the pre-edge peak of the XAS, where the dipolar contribution from tetrahedral sites is dominant.[14,15]

The second one at around 7130 eV corresponds to the absorption edge where all Fe atoms (in tetrahedral and octahedral sites) contribute. Since there are twice as many octahedral sites than tetrahedral sites, this double peak reflects mostly the octahedral sites.

The sign of the XMCD signal indicates the direction of the absorber magnetic moment with respect to the axis of propagation of the circularly polarized x ray: the signs of the two double peaks at ~7115 eV and at ~7130 eV are inverted, reflecting the antiferromagnetic coupling between the octahedral and the tetrahedral sites.

A spin-polarized multiple excitation is seen at 7175 eV in the XMCD signal, although it is not visible in the absorption spectra. This excitation is due to monopole transitions.[16] The excitation energy position is pressure independent, confirming its link to the edge energy position which does not vary with pressure. Its amplitude follows roughly the global magnetic moment.

We report in Fig. 2 the pressure variation in the "absolute value integrals," which is proportional to the peak-peak amplitudes and the integral values of both double peaks. Figures 2(a) and 2(b) report them separately and averaged, respectively, to avoid artifacts induced by the arbitrary choice for the energy value separation. In the following we call "amplitude" the absolute value integrals for simplicity.

III. DISCUSSION

We will first discuss our x-ray appearance near-edge structure (XANES) spectra shown in Fig. 1(a) and then the XMCD data [Fig. 1(b)] and their pressure dependence (Fig. 2). The position of the XANES pre-edge peak is expected to be sensitive to the coordination crossover,[9] where a macroscopic charge is transferred from the octahedral B sites to the tetrahedral A sites. The intensity of the lower energy part of the pre-edge peak, corresponding to the Fe^{2+} atoms contribution is expected to increase slightly when the Fe^{2+} moves to the tetrahedral site.[15] The Fe^{2+} and Fe^{3+} contributions to the

XANES are separated only by $\sim$2 eV. Nevertheless this small variation is within the experimental resolution of the XAS experiment and is sufficient to detect a small variation in the lower energy part of the XANES pre-edge peak but no change has been observed. This is an indication that we do not observe any coordination crossover in the pressure range examined.

Within the simple two-step model,[17] the excited photoelectron in K-edge spectroscopy has a pure orbital polarization and no spin polarization because of the absence of spin-orbit coupling in the 1s core state. The K-edge XMCD signal therefore derives from the spin-orbit coupling in the empty p level and its interaction with the magnetism of neighboring atoms. As mentioned previously, both octahedral and tetrahedral sites contribute to the second double peak, so its variation reflects that of the total magnetic moment, while the contributions to the first double peak are less clear and are dominated by the dipolar transition on the tetrahedral site.[15]

The integral of the K-edge XMCD yields a direct measurement of the expectation value of the 4p orbital angular momentum.[18] When this integral is zero, the 4p orbital moment is quenched. Our measurements indicate that the integrals of the two XMCD features remain close to zero in the entire pressure domain. Within the experimental error we therefore see a negligible orbital moment in this pressure range, in agreement with Refs. [19] and [20]. Although the signal integral may be zero, its amplitude may provide useful physical information. When no p orbital moment is present on the absorber, the amplitude of the XMCD reflects the mean neighborhood magnetic moment. The spatial extension of this neighborhood is evidently large enough to yield similar average magnetic moments on both the tetrahedral and octahedral sites since Fig. 2 shows that pressure dependence of the amplitudes of both double peaks are the same.

To conclude, we derive the following physical information from the two double peaks in the measured XMCD signal: the opposite signs reflect the ferrimagnetic order between the tetrahedral and octahedral sites, the null integral reflects the quenched 4p orbital moment, and the amplitudes are both proportional to the mean magnetic moment around the absorbers with different coefficients.

At first sight one could distinguish three pressure regimes in the pressure dependence of the amplitude [Fig. 2(b)]. Initially the decrease is very weak up to 10–15 GPa, then it speeds up between 20 and 25 GPa, and then it slows down again after 25 GPa up to 41 GPa, the highest pressure reached in this study. This evolution is compatible with the data shown in Ref. [12] within the error bars cited there. However, it is in full contradiction with the data shown in Ref. [11], where a 30–40 % decrease is observed at ambient temperature between 12 and 16 GPa, whereas our data shows a much weaker decrease ($\sim$10%) in this pressure range. The separation between the first two pressure regimes at 10–15 GPa is rather arbitrary: the amplitude starts decreasing more rapidly after this pressure, reaching the fastest attenuation rate between 20 and 25 GPa. This choice is nevertheless helpful to compare our results to those expected from Refs. [9] and [11], where abrupt changes around $\sim$8 GPa and 12–16 GPa are seen, respectively. Also, the observation of a continuous decrease in magnetic moment in the whole pressure range is incompatible with the occurrence of a coordination crossover as suggested in Ref. [9] because in that case an increase of $\sim$50% of the magnetic moment, i.e., of the amplitude of the XMCD signal, should be observed.

The conduction of magnetite at ambient pressure has been described in terms of different contributions from band and hopping conductivity as a function of temperature.[21] At ambient temperature, the change in the evolution of electrical resistance with pressure observed close to 6 GPa has been interpreted as the onset of a nearly metallic hopping conductivity via the octahedral network.[22] Above 8 GPa, the temperature dependence of the resistivity exhibits metallic behavior.[4]

Magnetite has also been reported as half metal where the conductivity is due to minority-spin electrons.[23] density-functional theory calculations[24] show that the majority-spin channel becomes metallic under hydrostatic compression when the volume is reduced beyond 0.91V_0. In particular, the transition is seen to be driven by the compression of the $[Fe]_B$-O distance. Onset of metallic behavior occurs for a $\sim$3% compression of this bond. Magnetite is therefore expected to undergo a half-metal to metal transition under pressure. When this occurs, majority-spin valence-band states near the Fermi level are depopulated in favor of the minority ones, inducing a small ($\sim$1%) magnetic moment reduction.[24] High-precision x-ray diffraction[10] results up to 20 GPa at ambient temperature are compatible with a compression and an expansion of the $[Fe]_B$ and $[Fe]_A$ site volumes, respectively. This "volume anomaly" starts around 8–10 GPa and is maximum at around 15 GPa. Here the octahedral (tetrahedral) sites are compressed (expanded) by 7% (17%). This behavior, combined to Mössbauer spectroscopy results, had been interpreted as the evidence of the inverse, normal spinel transition. But within this picture, an increase in magnetic moment should have been observed between 10 and 15 GPa, in total contradiction with the present XMCD data. Rather, the observed compression of the octahedral site volume, could be associated to a half-metal$\rightarrow$metal transition, in agreement with Ref. [24] and therefore to a decrease in the magnetic moment, in qualitative agreement with our XMCD data. This result is then in favor of a band-structure description of the electronic state of magnetite in contrast to the ionic model of presence of Fe^{2+} and Fe^{3+} ions. Magnetite seems not anymore the archetype for an ionic charge ordering which is still largely debated.

Within the present error bars, a monotonous (even linear) decrease between 15 and 41 GPa could also explain our data, simply reflecting a magnetic moment decrease due to a band broadening of iron. Nevertheless, as can be seen in Fig. 2, the slope of the magnetic moment decrease seems to become weaker above 25 GPa. From an extrapolation of the trend above 25 GPa, the loss of the ferromagnetic moment occurs around 70 GPa. In this pressure domain, magnetite is reported to transform into a high-pressure polymorph[6,7,25,26] around 25 GPa with an important increase in resistivity. The high-pressure polymorph transformation above 25 GPa tends to form octahedral sites only. The XAS prepeak in Fig. 1 is then expected to disappear. A very small decrease in the XAS prepeak does seem to occur at the highest pressures. Incipi-

ent metallic behavior starts above 50 GPa (Refs. 8 and 26) with a progressive loss of the Mössbauer magnetic components, even at low temperature.[8] A clear metallic behavior in the 120–300 K range is observed above 70 GPa.[8] We can therefore associate our extrapolated value of 70 GPa for the total loss of magnetism with the onset of full metallic behavior.

IV. CONCLUSIONS

Magnetite under pressure carries a magnetic moment of pure spin origin. Its pressure dependence can be divided into three domains: the first between ambient and 10–15 GPa where the magnetic moment is almost constant. Above 15 GPa the magnetic moment starts decreasing rapidly up to 25 GPa. We interpret this fast decrease as a result of the widening of the majority-spin valence band until it crosses the Fermi level at the octahedral site, in agreement with the observed decrease in the resistivity. These observations are in total contradiction with an inverse to direct spinel transition or with an abrupt transition toward an intermediate spin state. Above 25 GPa, the magnetic moment decreases more gradually as magnetite transforms progressively into an orthorhombic nonmagnetic phase. We extrapolate that magnetism is lost at ∼70 GPa. Our work plaids for the band-structure description of the electronic state of magnetite in contrast to the ionic model. Within this description, the debate concerning charge ordering is no more justified.

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