Pressure-induced magnetic transition in Fe$_3$O$_4$ and CoFe$_2$O$_4$ spinels

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Abstract. The pressure dependence of the x-ray magnetic circular dichroism (XMCD) has been measured in spinel ferrites (Fe$_3$O$_4$ and CoFe$_2$O$_4$). Room temperature XMCD spectra have been collected at the Fe K-edge measuring the difference in absorption between two helicity states of the photon. We measured from ambient pressure up to almost 23 GPa in the case of Fe$_3$O$_4$ and to 27 GPa in case of CoFe$_2$O$_4$. The XMCD spectra of Fe$_3$O$_4$ decrease monotonically as the pressure increases being the dichroic signal at 23 GPa half of that observed at ambient pressure. On the other hand, the dichroic signal almost disappears at 27 GPa in CoFe$_2$O$_4$. This result evidences a pressure-induced phase transition from a ferromagnetic state to a non-magnetic state. We note that the two signals, one from the tetrahedral and the other from the octahedral Fe atoms, disappear simultaneously indicating a strong reduction of the ferromagnetic order of the two sub-lattices. In addition to this phenomenology, a clear variation of the XANES spectra at the same pressure indicates that this transition comes from a structural change. Moreover, when releasing the pressure, the dichroic signal is not recovered, even in new measurements at ambient pressure.

1. Introduction
Applying high pressure to magnetic materials is appropriate for studying the correlation between the magnetic order and cell volume. Recently, magnetism under high pressure has been actively studied using x-ray magnetic circular dichroism (XMCD) with synchrotron radiation [1]. In particular, XMCD is useful for probing magnetically polarized states of ferromagnetic and ferrimagnetic materials. Among the magnetic materials, particular interest has the spinel ferrites due to their significant technological potential applications in high frequency and magnetic recording. It is well established that the magnetic behaviour of these ferrites is closely tied to their structural properties. Spinel ferrites have a basic AB$_2$O$_4$ structure with the space group $Fd-3m$. The crystal structure involves two crystallographic distinct sites designed as “tetrahedral (A)” sites and “octahedral (B)” sites. Depending on the arrangement of metal-ions between A and B sites, the structure can cover different spinel configurations between the two extremes of normal spinel [M$^{2+}$]$^2$[Fe$^{3+}$Fe$^{3+}$]$^1$O$_4$ and inverse spinel [Fe$^{3+}$]$^3$[Fe$^{3+}$M$^{2+}$]$^1$O$_4$ where M$^{2+}$ is a divalent metal-ion. With the possible exception of magnetite showing a purely inverse character at ambient conditions, spinels generally exist as intermediate configurations between the two theoretical edges. Recent diffraction studies aim to investigate the effect of pressure upon the degree of inversion in various cubic spinels. For Fe$_3$O$_4$, x-ray diffraction measurements at room temperature proposed an inverse to normal transition at P about 15 GPa.
whereas an intermediate region is designated in the pressure range from 7 GPa up to 15 GPa, perhaps corresponding to a mixture of inverse and normal phases [2].

For inverse Fe$_3$O$_4$, the magnetic moments of tetrahedral and octahedral sites couple antiferromagnetically resulting in a ferrimagnet with a net magnetic moment of 4 $\mu_B$ per formula unit. The proposed inverse to normal transition should result in a 50% increase in net magnetic moment of ferrimagnetic Fe$_3$O$_4$. A very recent experiment reports on XMCD measurements of Fe$_3$O$_4$ at the Fe K-edge under variable pressure and temperature conditions [3]. The authors reveal a pressure-induced magnetic transition at 12-16 GPa that they interpret as a high-spin to intermediate-spin transition of Fe$^{2+}$ in the octahedral sites. However, previous x-ray absorption spectroscopy (XAS) [4] and resonant x-ray scattering (RXS) [5] experiments indicate that octahedral atoms are electronically equivalent in a time scale lower than $10^{-16}$ s.

In this contribution we re-visited the nature of the magnetic transition in Fe$_3$O$_4$ occurring in the pressure range from 7 GPa up to 15 GPa. We measured the pressure dependence of the XMCD and XANES spectra of Fe$_3$O$_4$ at the Fe K edge. We show that the XMCD spectra of Fe$_3$O$_4$ decrease monotonically as the pressure increases. The dichroic signal at high pressure (23 GPa) is found to be half of that observed at ambient pressure, challenging the recent reported sharp discontinuity [2]. On the other hand, CoFe$_2$O$_4$ has an inverse spinel structure too, in which Co$^{2+}$ atoms substitute for Fe$^{2+}$ in Fe$_3$O$_4$. Therefore, we also observe the two features in the XMCD spectrum, corresponding to the tetrahedral and octahedral Fe atoms. Surprisingly, and opposite to Fe$_3$O$_4$, there is a sharp discontinuity in the pressure dependence of XMCD between 24 and 27 GPa and we observe that the dichroic signal almost disappears at 27 GPa in CoFe$_2$O$_4$.

2. Experimental section
Polycrystalline samples of Fe$_3$O$_4$ and CoFe$_2$O$_4$ were obtained from crushing a piece of the respective high-quality single crystals grown by floating zone method [6]. The samples were characterized by x-ray diffraction and magnetic measurements ensuring the right oxygen stoichiometry. All samples were single phase at room temperature.

XANES and XMCD experiments at the Fe K edge under high pressure were carried out using the helicity-reversal method on the energy dispersive beam line ID24 [7] at the European Synchrotron Radiation Facility (ESRF) in Grenoble. The magnetic field on the sample was ~0.7 T, sufficient to magnetically saturate all samples at ambient pressure. The powders, mixed with silicone oil as pressure transmitting medium, were loaded into a non-magnetic cube Diamond-Anvil Cell (DAC) equipped with a pair of 1.2 mm thick diamond anvils. Ruby chips were used as pressure markers. Room temperature XANES and XMCD spectra have been collected from atmospheric pressure (AP) to almost 23 GPa in the case of Fe$_3$O$_4$ and to 27 GPa in case of CoFe$_2$O$_4$, applied to the powder samples.

3. Results and discussion
Normalized XANES spectra Fe K-edge of Fe$_3$O$_4$ as a function of pressure are compared in figure 1. We have made the pixel-to-energy equivalence comparing the XANES spectrum measured at 0.4 GPa with a XANES measurement recorded in a pellet of Fe$_3$O$_4$ in transmission mode in the beam line BM29. We notice an increase of the white line with increasing pressure joined to the monotonic energy shift of the first resonance (labelled as peak A in figure 1) in the extended region. This energy shift correlates with the uniform decreasing of interatomic distances as the pressure is increased. The XMCD spectra for different pressures at the Fe K edge in magnetite are shown in figure 2 (upper panel). Two different dichroic signals can be identified, the first one between 7110 to 7115 eV that coincides with prepeak in the XANES spectrum and the second one between 7120 to 7135 eV that corresponds to the main rising edge. Since the pre-peak mainly comes from the tetrahedral Fe atoms, it follows that the first dichroic signal is related to the ferromagnetic order of the tetrahedral atoms (i.e. the magnetic moment on the A atoms). On the other hand, the dichroic signal in the edge region originates from both tetrahedral and octahedral Fe atoms. Because of the statistical weight (2 B atoms
and one A atom), we can deduce that this energy region gives mainly information on the ferromagnetic order of the octahedral B atoms.

As it is demonstrated in figure 2, the dichroic signal decreases monotonically with increasing the pressure. This result challenges previous findings where a sharp discontinuity was observed at about 12 to 16 GPa [3]. The lower panel in figure 2 shows the integrated area of the marked peaks as a function of pressure showing that the decrease of the XMCD signal occurs simultaneously in the two crystallographic sites.

**Figure 1.** XANES spectra at the Fe K edge as a function of pressure in Fe$_3$O$_4$. Inset: zoom of the extended region (peak A).

**Figure 2.** Upper panel, XMCD spectra as a function of pressure in Fe$_3$O$_4$. Lower panel, Pressure dependence of the integrated dichroic signals.

The study of the CoFe$_2$O$_4$ ferrite as a function of pressure resulted in a completely different behaviour. Figure 3 and figure 4 reports the pressure dependence of the XANES and XMCD spectra, respectively. The dichroic feature at 7110 eV (A) is almost identical in the spectral shape and intensity to the one observed in Fe$_3$O$_4$. This suggests that tetrahedral Fe$^{3+}$ ions have a similar electronic state regarding 3d and 4p states in Fe$_3$O$_4$ and CoFe$_2$O$_4$. It also implies that octahedral Fe ions do not affect the pre-edge structures at the K edge. On the other hand, the XMCD signal at the main edge (B) changes significantly, being broader and less intense than for Fe$_3$O$_4$. Since Co$^{2+}$ ions enter into the octahedral sites in the Co ferrite, only octahedral Fe$^{3+}$ ions are present. This can explain that the main edge peaks are less structured and their height decreases due to the lack of contribution of Fe$^{2+}$ ions. As it is observed in figure 4, the dichroic signal is drastically reduced at about 27 GPa. Our results show an evidence of a transition from a ferrimagnetic state (low-pressure) to a non-magnetic (high-pressure) state; the ferromagnetic ordering of the two sublattices nearly disappears. Moreover, the XMCD signal is not recovered after releasing the pressure. This magnetic phase transition is correlated to a structural one. In fact, some features in the XANES spectra change in coincidence with the loss of the XMCD signal indicating that a distortion of the local structure is simultaneously induced. These changes in the XANES spectra that are clearly shown by asterisk in figure 3 mainly affect the main edge region of energies (B), keeping the pre-edge peak almost unchanged.
4. Conclusions
Several conclusions can be derived from the present study. Similar to metallic magnets [8,9], pressure tends to decrease the magnetization in spinel ferrites. In the case of Fe₂O₃, the decreasing of the magnetic moment is monotonous and occurs simultaneously in the two crystallographic sites. On the other hand, the achievement to a non-magnetic state occurs through a structural phase transition for CoFe₂O₄. In this case, the suppression of the dichroic signal also occurs homogeneously and at 27 GPa the XMCD signal for the two ferrimagnetic sublattices almost vanishes. The surprising point is that this new non-magnetic phase obtained at high pressures is maintained after releasing the pressure since the XMCD signal is not recovered at ambient pressure.

Acknowledgements
The authors acknowledge financial support from CICyT FIS08-03951 and DGA (CAMRADS) projects. VC thanks the research grant from MICINN. The authors also thank ESRF for granting beam time.

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