



	<b>Experiment title:</b> Site and valence-selective study on the origin of the pressure-induced magnetic transition in magnetite by XMCD on Co ferrites.	<b>Experiment number:</b> HE 2933
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## Report:

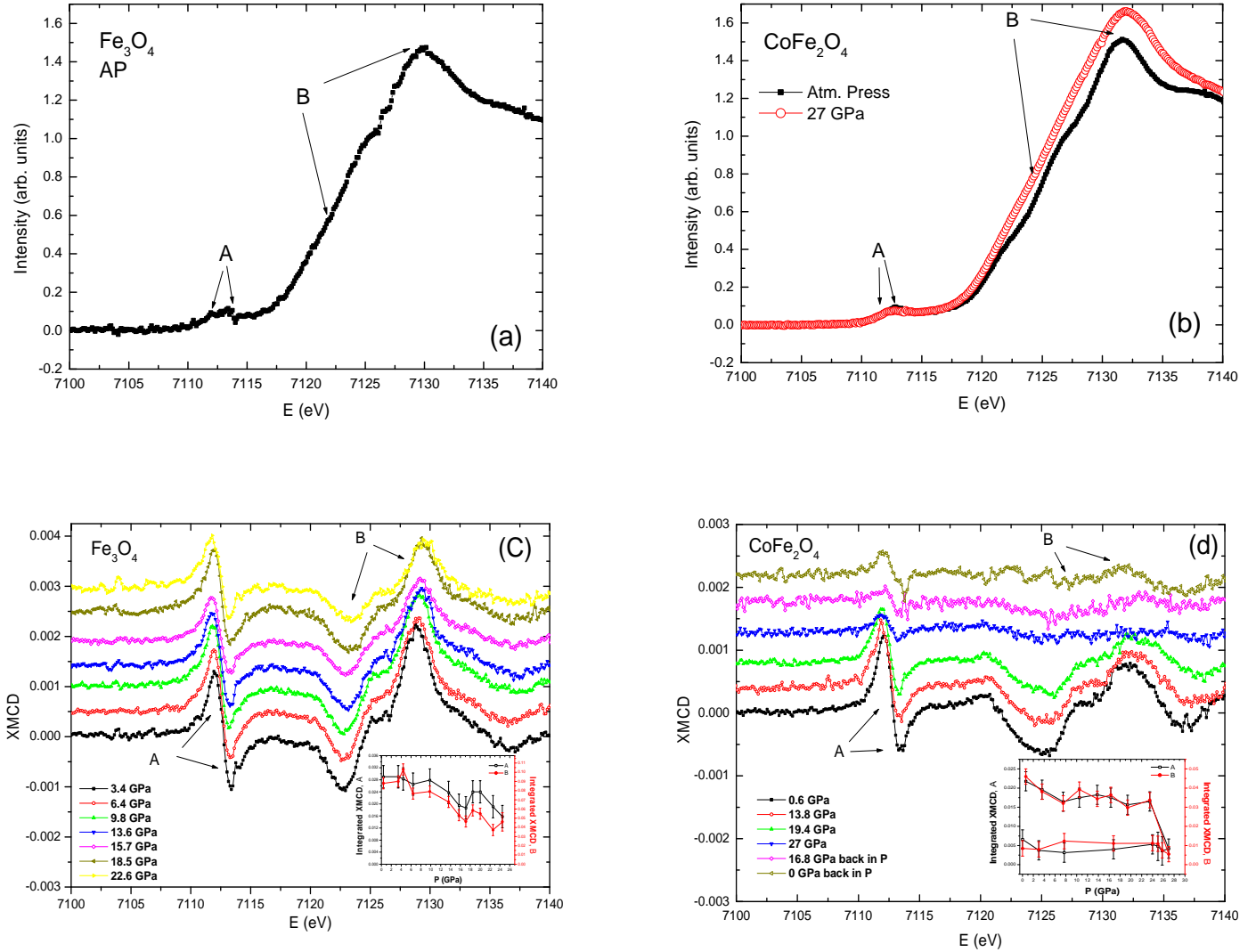
A x-ray magnetic circular dichroism (XMCD) experiment has been performed in order to investigate the correlation between magnetic behaviour and structural properties in spinel ferrites ( $\text{Fe}_3\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$ ). These compounds have attracted considerable attention due to their several applications in high-frequency and magnetic recording, and both materials have an inverse spinel structure,  $Fd-3m$ , at room temperature, with a crystallographic configuration  $[\text{Fe}^{3+}]^A[\text{Fe}^{3+}\text{M}^{2+}]^B\text{O}_4$ , where  $\text{M}^{2+}$  is the transition metal ion (being A and B tetrahedral and octahedral sites respectively). For  $\text{Fe}_3\text{O}_4$ , 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 7-15 GPa, perhaps corresponding to a mixture of inverse and normal phases<sup>[1]</sup>. The proposed inverse to normal transition should result in a 50% increase in net magnetic moment. A recent experiment reveal a pressure induced magnetic transition at 12-16 GPa interpreted as a high-spin to intermediate-spin transition of octahedral  $\text{Fe}^{2+}$ .<sup>[2]</sup>

Room temperature XMCD spectra has been collected, at the Fe K-edge (7.1 keV), measuring the difference in absorption between two helicity states of the photon. We measured from atmospheric pressure (AP) to almost 23 GPa in the case of magnetite and to 27 GPa in case of  $\text{CoFe}_2\text{O}_4$ , applied to the powder samples using a non-magnetic cube Diamond-Anvil Cell equipped with a pair of 1.2 mm thick diamond anvils.

Figures 1 (a) and (b) show the x-ray absorption near edge structure (XANES) spectra at atmospheric pressure and at 27 GPa in the case of  $\text{CoFe}_2\text{O}_4$ . The jump is normalized to 1 in all cases. We have made the pixel-to-energy equivalence comparing the spectra of the measurement at AP with a XANES measurement performed in magnetite pellets in transmission, in the beamline BM29. Labels A and B correspond to E (A) =7112-7113 eV and E (B) =7122-7130 eV.

We can see in figures 1 (c) and (d) the XMCD spectra at different pressures, for magnetite and  $\text{CoFe}_2\text{O}_4$  respectively. All of them have been normalized to the edge jump in XANES spectra. The inset show the integrated area of the marked peaks as a function of pressure. The dichroic signal in magnetite does

not disappear abruptly as a function of pressure. In fact, the integral of the XMCD decreases continuously as the pressure is increased, at least until 22.6 GPa. However, that is not the case of  $\text{CoFe}_2\text{O}_4$ , where the dichroic signal almost disappear at 27 GPa. Moreover, when releasing the pressure, the dichroic signal is not recovered, even when measuring at atmospheric pressure again.



**Figure 1.** (a) and (b) XANES spectra of  $\text{Fe}_3\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  measured at ambient pressure. In the case of the cobalt spinel, XANES at 27 GPa is also plotted. (c) and (d) XMCD moved 0.0005 units when pressure is increased. In both insets it's represented the area of the XMCD peaks marked out as A and B, as a function of pressure.

Looking at the difference between XANES spectra in the cobalt spinel at atmospheric pressure and at 27GPa (figure 1(b)), we are tempted to believe that a structural phase transition occurs when pressure is increased about 27 GPa. The structural change could cause the lost of the dichroic signal at high pressures; that is of the ferrimagnetic interaction. To determine the new magnetic and structural phase, we will pretend to perform x-ray diffraction and magnetic measurements at high pressures in further studies.

- [1] G. Kh. Rozenberg *et al.* Phys. Rev. B **75**, 020102 (2007).  
 [2] Y. Ding *et al.* Phys. Rev. Lett. **100**, 045508 (2008).