



	Experiment title: X-ray emission spectroscopy study of pressure-induced magnetic transitions in magnetite (Fe ₃ O ₄)	Experiment number: HC-3170
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Report:

The behavior of magnetite (Fe₃O₄) at high pressure is fundamentally important for understanding the magnetism in the Earth's interior. Despite a constantly high publication rate on Fe₃O₄ its high-pressure behavior is still far from being clarified. Fe₃O₄ is in a mixed valence state described as Fe_A³⁺ [Fe²⁺ Fe³⁺]_BO₄. At room temperature, it has a cubic inverted spinel structure with tetrahedral A sites occupied by Fe³⁺ ions, and octahedral B sites occupied by equal amounts of Fe²⁺ and Fe³⁺ ions. X-ray Magnetic Circular Dichroism (XMCD) measurements at the Fe-K edge revealed a drop of magnetic dichroism by 50% under high pressure between 12 and 16 GPa, which is independent of temperature from 40 K to 300 K [1]. This result was assigned to a high-spin (HS) S=2 to intermediate spin (IS) S=1 state transition of Fe²⁺ in the octahedral B sites, while Fe³⁺_A and Fe³⁺_B remain in a stable HS state. This interpretation of high-pressure Fe-K XMCD experimental data was supported by high-pressure Fe-K β X-ray Emission Spectroscopy (XES) measurements at room temperature [1]. However, such spin state transition was soon disputed using results obtained from the same XMCD technique [2]. Moreover, the interpretation of the Fe-K β XES data was based only on the decrease in the intensity of the satellite peak K β' , without any analysis of the changes in the spectral shape [1].

For the approved beamtime proposal at the ID20 beamline of ESRF we proposed a XES study at the Fe-K β emission line of Fe₃O₄, with the goal of obtaining direct information about the local spin state of the Fe²⁺ ion at the different pressures in the range between 0 and 40 GPa. The high sensitivity of K β XES to the spin state originates from the presence of a satellite peak K β' in the spectrum besides the main line K $\beta_{1,3}$ (see figure 1). The intensity of this K β' peak is directly related to the magnitude of a spin moment in the 3d ground state [3]. Furthermore, XES can become an even more powerful tool if a high energy resolution is employed, because the spectral features of the satellite K β' can be used as finger print of the spin state of 3d transition metal ions [4].

For the present investigation we used micrometer-sized powder obtained by grinding high-quality and highly stoichiometric Fe₃O₄ single crystal grown in our institute. The XES measurements, carried out successfully till a pressure as high as 49 GPa, are reported in the Figure 1. The spectrum of FeS₂ as Fe²⁺ low spin (LS) S=0 reference is also reported as dashed line. To compare the intensity ratio of the K $\beta_{1,3}$ line and the K β' line, the data are aligned to the K $\beta_{1,3}$ line and normalized to the integrated area. A zoom of the spectra reported in Figure 2 shows that the satellite K β' does not exhibit the drop in intensity expected for the reduction of the spin moment as proposed in literature. Instead the data display a smooth spectral broadening with increasing pressure without a clear evidence of a change in intensity. A spectral broadening of a

satellite peak can be misinterpreted as an apparent reduction in intensity [4]. In order to be quantitative, we have analysed the XES data using the so-called integrated relative difference (IRD) method [4].

In the IRD method one evaluates the relative intensity difference between the spectra measured on the Fe_3O_4 sample and the spectrum of the LS reference from the lowest energy to the energy at ~ 7053.5 eV where the spectral difference is zero near the left shoulder of the K main peak (yellow area in Fig. 1). This method allows us to directly integrate the difference in the satellite $K\beta'$ peak region that is most sensitive to the $3d$ electronic spin transition while avoiding the broadening effect of the dominant, intense main peak in the XES spectra. The evolution of the IRD versus pressure is plotted in Figure 3. The IRD does not exhibit any evident sign of reduction in intensity for all investigated pressure range. These results clearly rule out the spin state transition proposed in ref [1] and shows that the Fe^{2+} ion actually remains in the HS state at least till $P = 49$ GPa. Our XES results are consistent with the XMCD results of Baudelet et al. [2].

It would be very interesting to extend our XES investigation of the phase diagram of Fe_3O_4 to even higher pressure values. Recently, a post-spinel structure phase of Fe_3O_4 has been reported to occur for pressures higher than 70 GPa [5]. According to the x-ray diffraction results, the onset of the post-spinel phase at 70 GPa is characterized by a 6 % drop in volume size, which was interpreted as a sign of a transition to a lower spin state, $S=1$ or $S=0$, of Fe^{2+} [5]. A continuation of the beamtime would allow to determine the spin state of the Fe^{2+} ions in the post-spinel structure phase of Fe_3O_4 and provide more insites on the magnetic properties of the interior of the Earth.

References

- [1] Yang Ding, et al. Phys. Rev. Lett. 100, 045508 (2008).
- [2] Baudelet, F. et al., Phys. Rev. B 82, 140412(R) (2010).
- [3] J. P. Rueff et al., Phys. Rev. B 63, 132409 (2001).
- [4] Z. Mao et al., Am Miner 99, 415-423 (2014).
- [5] A. Ricolleau, Y. Fei, Am. Mineral. 101, 719 (2016).

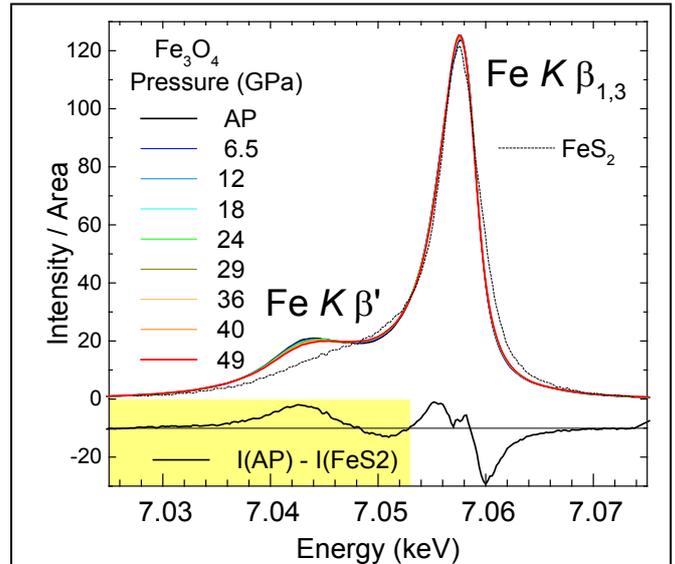


Fig.1. Fe- $K\beta$ XES spectra of Fe_3O_4 measured at various pressures on ID20 at $T=300$ K. FeS_2 (dotted line) is used as the spectral reference for the low-spin state ($S=0$).

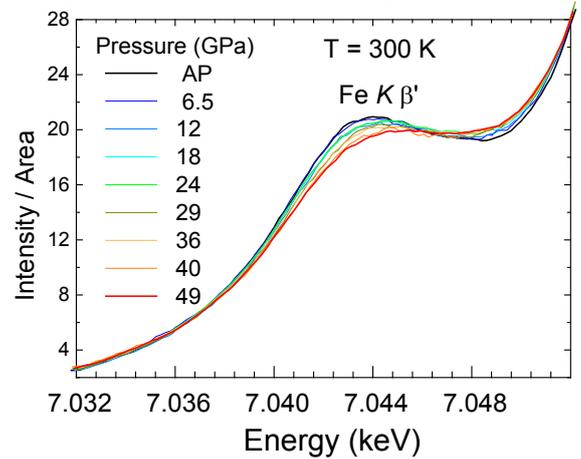


Fig.2. Zoom of the $K\beta'$ satellite in the XES spectra of Fe_3O_4 .

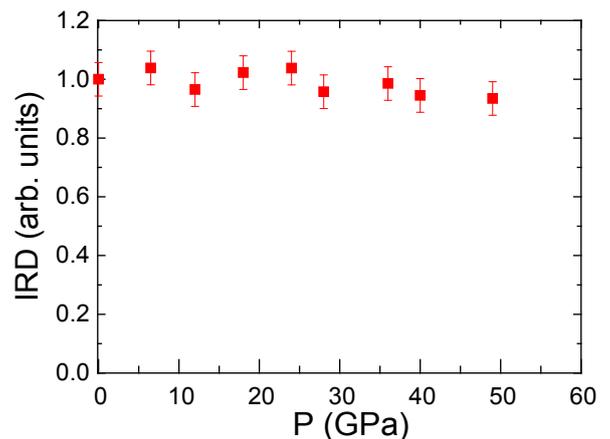


Fig.3. Integrated relative difference (IRD) of the yellow area, shown in Figure 1, of XES of Fe_3O_4 as a function of pressure .