

**Experiment title:**

Investigation of the Verwey transition in magnetite by resonant inelastic X-ray scattering

Experiment number:

HE-1297

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|--------------------------|--|-------------------------------------|
| Beamline: ID26 | Date of experiment: from: 03/07/02 to: 09/07/02 | Date of report: 22/7/2002 |
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Report:

We report here on the investigation of the Verwey transition in magnetite by resonant inelastic x-ray scattering (RIXS) at the Fe-K edge. Magnetite consists of two interconnected networks of Fe^{3+} and a mixture of Fe^{2+} and Fe^{3+} occupying tetrahedral and octahedral sites respectively. At $T_V = 120$ K, magnetite undergoes a first order metal/insulator transition (the well known Verwey transition [1]), where charge ordering among octahedrally coordinated iron atoms is supposed to occur [2].

The experiment was carried out on ID26 using the beamline RIXS spectrometer. The incident energy (E_1) was tuned on the Fe K edge using the Si (220) monochromator while the x-ray emission scattering energy (E_2) was analyzed. The spectrometer consisted of a Si (531) analyzer and a Peltier-cooled Si diode detector laid down in Rowland circle geometry, yielding a total resolution of 1.3 eV at 7 keV. The sample was a 5x5 mm pellet of Fe_3O_4 cut in a naturally grown single crystal. Two different orientations were chosen so to have the [110] and the [100] directions normal to the surface. The sample orientation was verified by x-ray diffraction prior to measurements. Both samples were mounted in a close-cycle He-cryostat for temperature dependence measurements.

Only RIXS results obtained on the [100]-oriented sample will be presented in the following, for both samples show quite similar behavior. The temperature dependence of the x-ray absorption is shown on Figure 1. The spectra were recorded through the RIXS spectrometer by sweeping the incident energy across the absorption edge while monitoring the emission intensity, thus acquiring so-called "lifetime removed" x-ray absorption spectra. The spectra show well a defined pre-edge structure; mainly due to dipolar transitions here (because of the non-centro-symmetric character of the Fe^{3+} tetrahedral site), although quadrupolar $1s \rightarrow 3d$ transitions are also expected [3]. Subtle changes in the pre-peak can be observed upon temperature decrease, in particular around the 7117 ± 2 eV energy region. The resonant Fe $K\beta$ emission lines ($3p \rightarrow 1s$) were measured in both

high and low temperature phases as illustrated on figure 2 at different excitation energies across the absorption edge. For the sake of comparison, the spectrum heights were normalized to unity. The spectra mainly consist of a main peak followed by a satellite at lower emitted energy due to the $3p$ - $3d$ exchange interaction. When the incident energy is tuned below the edge clear changes of the spectral shape can be observed specially in the main peak to satellite intensity ratio. As shown on figure 2, temperature affects mainly spectra measured at E1 ranging from 7116 to 7119 eV through a decrease of the satellite intensity at low temperature. This energy region corresponds precisely to the one identified in the absorption spectrum showing the largest variation upon cooling. A third peak indicated by ticks in figure 2 clearly builds up on the high-energy side of the emission main peak as E1 approaches 7117 eV. This feature can be assigned to a reminiscence of the Raman regime (where the emission line disperses as function of E1) within the fluorescence regime (where scattered photons are emitted at fixed energy (see Fig. 1)). The transition from the Raman to fluorescence regime occurs short after the pre-edge, indicating the delocalized nature of the electrons involved, already far below the edge. This experiment demonstrates that the pre-edge in Fe_3O_4 is strongly dominated by the dipolar transitions into the $3d$ hybridized with p -like states. No quadrupolar excitations were observed here. On the contrary, RIXS experiments on Fe oxides where Fe ions occupy Oh-sites only (like andradite) should permit to confirm the still debated quadrupolar nature of the pre-edge in these systems.

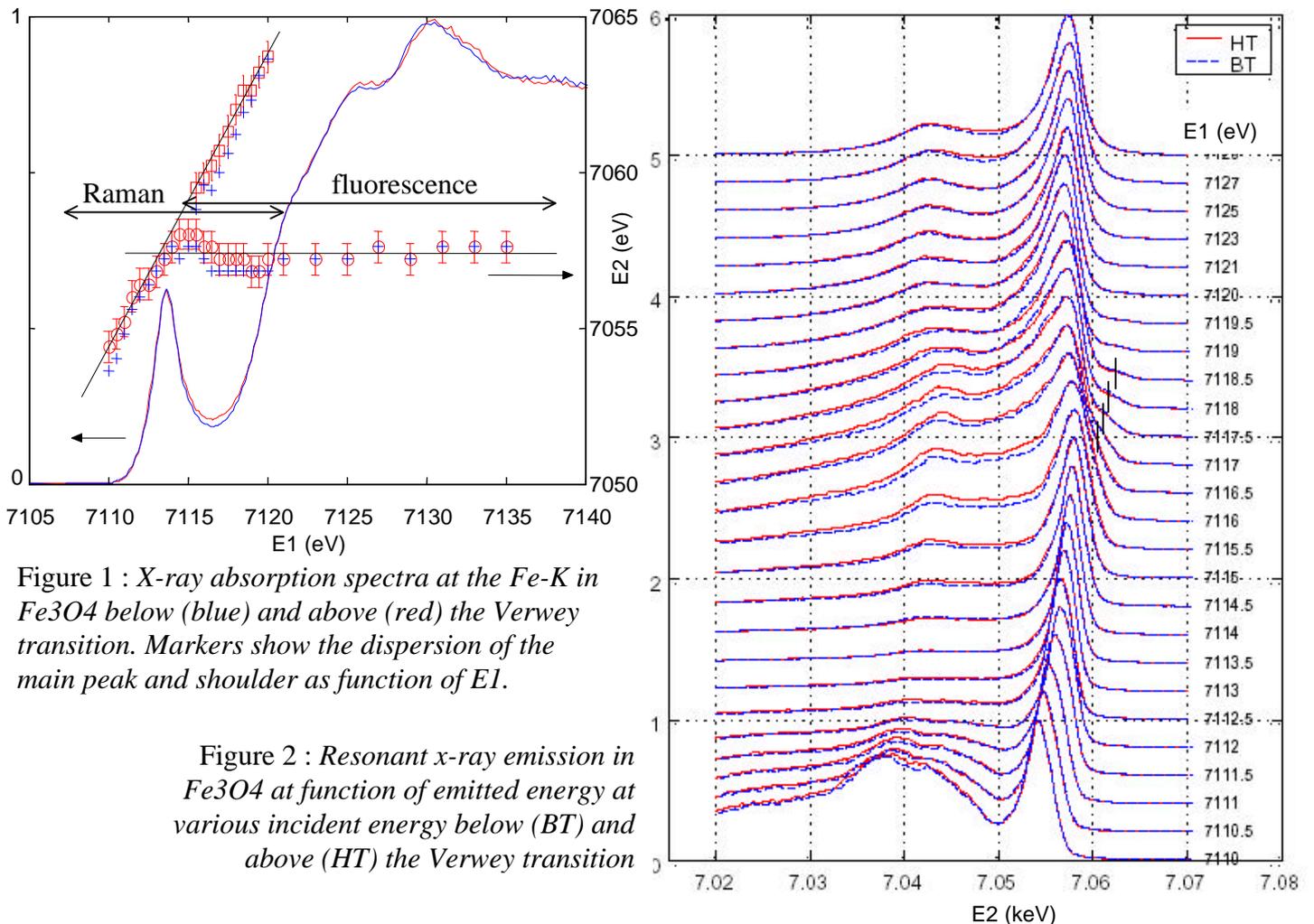


Figure 1 : X-ray absorption spectra at the Fe-K in Fe_3O_4 below (blue) and above (red) the Verwey transition. Markers show the dispersion of the main peak and shoulder as function of E1.

Figure 2 : Resonant x-ray emission in Fe_3O_4 at function of emitted energy at various incident energy below (BT) and above (HT) the Verwey transition

- [1] E. J. W. Verwey and P. W. Haayman, *Physica* **8**, 979 (1941).
- [2] J.P. Wright and J.P. Attfield and P.G. Radaelli, *Phys. Rev. Lett.* **87**, 266401 (2001)
- [3] T.E. Westre et al., *J.Am. Chem. Soc.*, 119, 6297-6314 (1997).