

**Experiment title:**

Study of the Verwey transition by DAFS and X-Ray Anomalous Scattering.

**Experiment****number:**

HC353

**Beamline:**

BL15/D2AM

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12

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**Report:**

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is a mixed-valence 3d transition-metal compound which crystallizes in the inverted spinel structure with tetrahedral sites, A, occupied by one third of the iron  $\text{Fe}^{3+}$  ions, and octahedral sites. B1 and B2, containing equal number of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions respectively, It presents a metal-insulator transition close to  $T_v=120$  K [Verwey transition: Nature 144, 327 (1939)] associated to a change in the lattice symmetry from cubic to monoclinic/orthorhombic. Below the transition temperature the distribution of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the octahedral sites changes from dynamic disorder to a long range order. Different models have been proposed to describe this ordered structure (Rennet et al. Phys. Rev. B 53. 14262 (1996)).

In order to discriminate among the different ordering schemes, we have performed DAFS and X-Ray anomalous Diffraction experiments in powder samples of  $\text{Fe}_3\text{O}_4$ . DAFS spectra were recorded at room temperature in the (220) and (620) directions for the tetrahedral Fe site, and in the (222) and (622) for the octahedral one. DAFS spectra of the (311) Bragg peak was also measured. Powder diffraction spectra were measured at RT and at 60 K (below T,) at phonon energies of 6.9 KeV and 7.115 KeV, below and close to the absorption K-edge of iron.

The preliminary results can be summarized as follows. The DAFS spectra for (220) and (222) diffraction peaks after removal of bulk absorption are shown in Figure 1. It is clearly noticed that a better statistic is needed in order to extract XAFS data for the tetrahedral and octahedral iron sites, or to determine the chemical shift between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . At room temperature,  $\text{Fe}_3\text{O}_4$  crystallizes in the cubic space group  $\text{Fd-}3\text{m}$  ( $z=8$ ). The anomalous effect can be nicely reproduced by a Rietveld refinement of the powder diffraction data, using theoretical  $f'$  and  $f''$  values calculated at each energy with the program FPRIME. We want to note that it is particularly large for the (222) octahedral diffraction peak as it is shown in Figure 2. This peak has almost zero intensity at 7115 eV, close to the Fe K-edge. A splitting of some reflections is observed lowering the temperature below  $T_v$ , as it is expected due to the structural transition of the system to a lower symmetry. The characterization of the structure and the analysis of anomalous effect for the low temperature phase is in progress.

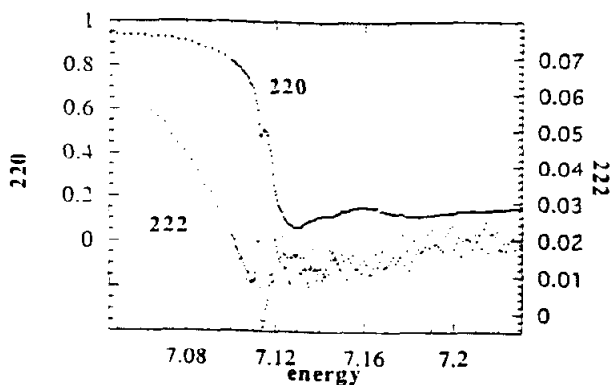


Figure 1. DAFS spectra after removal of bulk absorption for the (220) and (222) diffraction peaks of  $\text{Fe}_3\text{O}_4$ , corresponding to the tetrahedral and octahedral iron respectively, at RT.

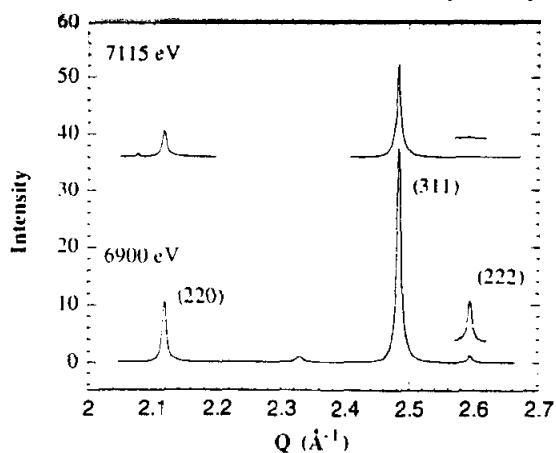


Figure 2. Powder diffraction patterns recorded for  $\text{Fe}_3\text{O}_4$  at RT and at two different energies, showing the large anomalous effect for the (222) diffraction peak close to the absorption edge of iron