ESRF	**Experiment title:** Study of forbidden reflections of magnetite above the Neel temperature	**Experiment number:** HS1249
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Report:

Magnetite (Fe3O4), a mixed-valence 3d transition-metal oxide, was the first material for which a charge ordering transition was proposed to explain the insulator behavior at low temperatures. It crystallizes in the inverted spinel structure in which tetrahedral sites (A) contain one-third of the Fe ions as Fe3+, while octahedral sites (B) contain the remaining Fe ions, with equal numbers of Fe2+ and Fe3+ in B1 and B2 sites, respectively. Below T 860 K, magnetite is ferrimagnetic with A-site magnetic moments aligned antiparallel to B-site ones. In 1939, Verwey reported about a metal-insulator transition at Tv=120 K that now bears his name. He proposed that below the transition temperature, the distribution of Fe2+ and Fe3+ ions in B-sites changes from a dynamical disorder to a long-range order, in which Fe2+ and Fe3+ layers laminate alternately along the c-axis. Electron and neutron diffraction studies and nuclear magnetic resonance experiments show that, below Tv, the B1 and B2 sites are structurally distinguishable in a distorted crystal structure. In spite of the extensive work carried out, this phase transition is still not completely understood. Up to now, two models are proposed to describe the charge ordering in magnetite below the Verwey transition: Mizoguchi and Zuo models. We have studied, in previous experiment at D2AM, the charge/orbital ordering mechanism in Fe3O4, by means of DAFS measurements of forbidden (004n+2) reflections. The main goal of our research was the investigation of the different proposed charge ordering models. We obtained very interesting and unexpected reults, showing the lack of charge fluctuations in the high temperature phase and the absence of charge ordering in in the low temperature phase of magnetite. They have been object of several publications(please,see references on the new proposal form) and talks at International Conferences.

In this experiment we have studied the behavior of the observed (0,0,4n+2) forbidden reflections upon increasing the temperature across the Neel temperature. This point is of fundamental interest in order to know if the anisotropy of the scattering factor is correlated with the magnetic ordering. X-ray resonant scattering experiments, at the Fe K-edge, at high temperatures, were carried out using a furnace working in vacuum environment. No remarkable changes were showed when increasing the temperature, apart from a continuous decrease of the main resonance intensity, as shown in fig.1. This result shows that the the anisotropy of the octahedral irons is not correlated with the magnetic ordering. We also performed preliminary resonant scattering measurements at the Fe and Mn K-edge at room temperature of a MnFe2O4 single crystal. In this system, Mn atoms substitute Fe atoms preferentially at the tetrahedral sites. The Neel temperature lowers at about 600 K, suggesting that the magnetic coupling mechanism changes. The ferrite DAFS spectrum of the (002) forbidden reflection, at the Fe K-edge, is shown in fig.2. We showed in our previous work that the prepeak feature in the DAFS of magnetite comes from the tetrahedral Fe sites. The lack of preapeak in the ferrite spectrum confirms our previous results.

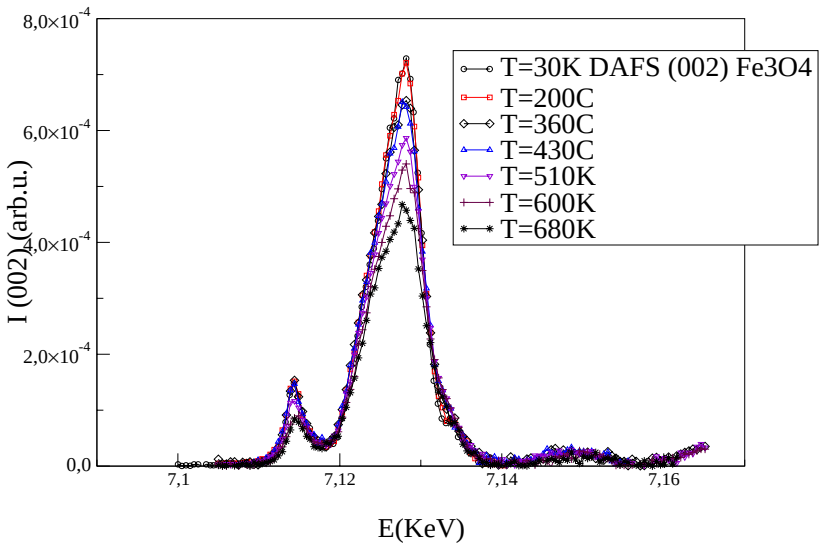

Figure 1: DAFS spectra of magnetite (002) Bragg reflection

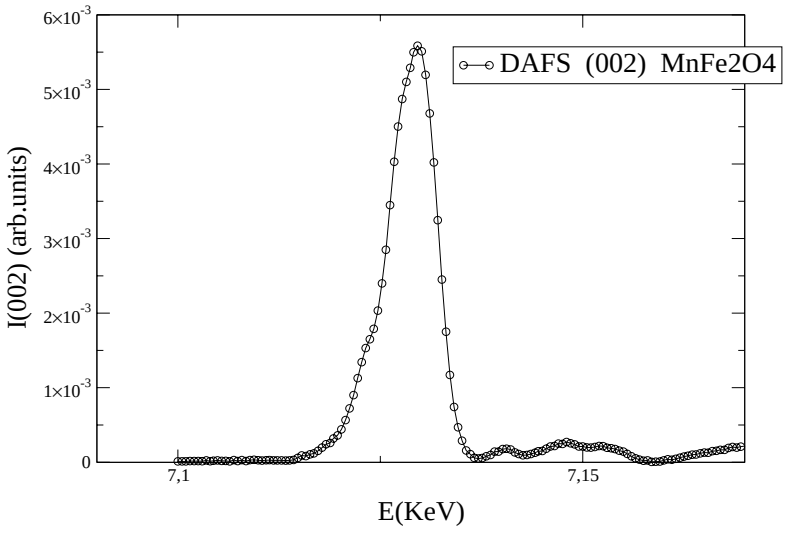

Figure 2: DAFS spectra of MnFe2O4 (002) Bragg reflection