![ESRF]	**Experiment title:** Study of the evolution of (0,0,4n+2) forbidden reflections in magnetite across the Néel temperature	**Experiment number**: 02-02-195
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Report:

We have investigated the interplay between the onset of ferrimagnetism and the anisotropy associated with the forbidden (0 0 4l+2) reflections in magnetite (Fe$_3$O$_4$) [1] via x-ray resonant scattering (XRS) at the Fe K-edge in a single crystal cut and polished to a flat (001) surface, which shows the Verwey transition at T_V=121 K.

Fe$_3$O$_4$ is the oldest known magnetic material and the original Néel ferrimagnet (T_N=851 K). It crystallizes in the inverse spinel AB$_2$O$_4$ structure at room temperature (space group *Fd-3m*), where A and B sites are occupied by the tetrahedral and octahedral Fe atoms, respectively. This cubic symmetry makes the (0kl) reflections with k+l=4n+2 extinguished due to the diamond glide plane rule. The Verwey ionic Fe^{2+}-Fe^{3+} ordering scheme is characterized by the appearance of these reflections near the Fe K edge. However, the point group symmetry of the octahedral B sites is *–3m* (trigonal) and consequently, the atomic scattering factor of the octahedral Fe atoms is anisotropic, i.e. it is a tensor with two principal components, parallel and perpendicular to the trigonal axis. A complete XRS study of these forbidden (0 0 4l+2) reflections in several spinel ferrites in the temperature range from 20 K up to room temperature [1,2] showed that the reported resonances at the absorption edge can be perfectly explained as due to the anisotropy of the x-ray susceptibility caused by the trigonal distortion of the octahedral B sites, i.e. they have mainly a structural origin. Although charge and orbital ordering of the atomic d states of the Fe atoms cannot be considered as origin for these resonant refelctions, further contributions coming from the magnetic order can not be completely discarded. Actually, the interplay between orbital and spin degrees of freedom is becoming a subject of intense investigation in the physics of various transition-metal oxides, for instance the manganites.

The temperature evolution of the energy-dependent XRS spectra of the (002) reflection in Fe_3O_4 is reported across the Néel temperature in Figure 1. Integrated intensity, collected using a ω-scan mode at fixed energy (maximum of the main-edge resonance), is shown as a function of temperature in the inset. High-temperature measurements were carried out on the Fe_3O_4 single-crystal heated by means of an electric resistance heater working under vacuum conditions. The accuracy in the temperature value was of ±5 K. Measured intensity at room temperature does not show any significant change after the heating-and-cooling process, indicating that no sample degradation occurs.
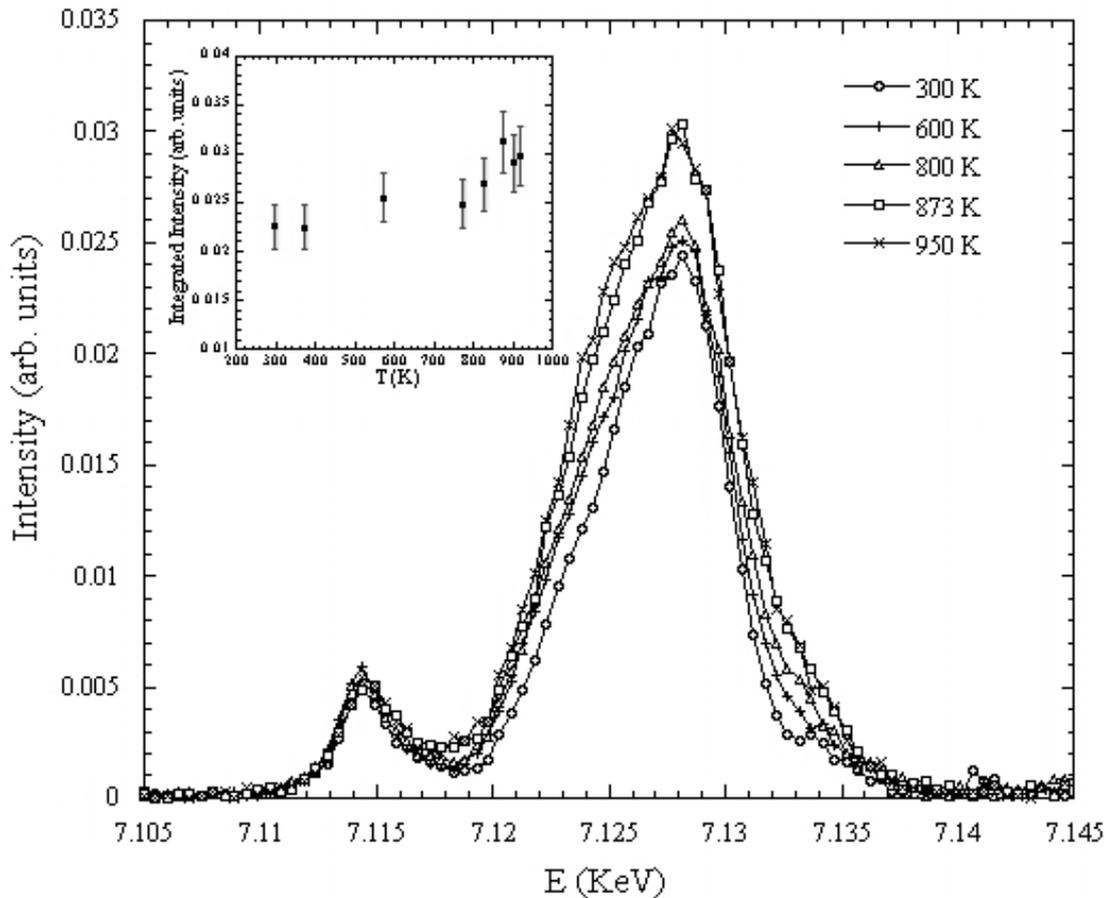

Figure 1.XRS spectra of the (002) reflection at the Fe K edge in Fe_3O_4 across the Néel temperature (T_N=851 K). Inset: Temperature dependence of the integrated intensity (θ-2θ scan) at E=7128 eV.

First, the energy line shape remains nearly alike in the whole temperature range from 300 K up to 950 K. Second, the temperature dependence of the integrated intensity is almost constant with a slight increase at temperatures above 800 K. We note that these changes in the integrated intensity are within the experimental error.

Summing up, the ferrimagnetic ordering in magnetite has no effect on the different features of the XRS spectra at the forbidden (0 0 4l+2) reflections. This result discards any additional contribution to the resonant signal coming from the magnetic ordering, giving further support for the structural origin.

[1] G. Subías *et al*., *Phys. Rev. B* **70**, 155105 (2004)
[2] J. García *et al*., *Phys. Rev. Lett*. **85**, 578 (2000); J. García *et al*., *Phys. Rev. B* **63,** 054110 (2001)