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Names and affiliations of applicants (* indicates experimentalists):

G. Subías[1*], J. García[1*], V. Cuartero[1*], J. Blasco[1], M.C. Sánchez[1] and J. Herrero-Martín[2]

[1]Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, 50009-Zaragoza, Spain
[2]European Synchrotron Facility, B.P. 220, 38043 Grenoble, France

Report:

The Verwey transition in magnetite is still nowadays a matter of hot debate regarding the mechanisms of the metal-insulator transition. Since pioneering resonant x-ray scattering experiments at the Fe K-edge, which showed the lack of ionic charge order (the charge disproportion is about 0.2 electrons) below the Verwey transition temperature [1,2], a wide range of other charge-order (CO) models have been proposed to describe the low temperature electronic state. The most recent theoretical models predict an orbital ordered insulator, where there is t_{2g} orbital order on the octahedral site Fe^{2+} [3].

We have investigated this proposed low temperature orbital ordered state in a highly stoichiometric single crystal of magnetite (Verwey transition at T_V= 123.5 K) by means of soft resonant x-ray scattering (SRXS) experiments [4]. Resonant intensity was observed at the Fe $L_{2,3}$ and the O K edges for the (0,0,1/2) reflection and at the Fe L_1-edge for the (001) reflection at T=30 K. The energy, azimuthal angle and temperature dependence was explored using either σ- or π-incidence.

In figure 1a, the energy dependence of the resonant intensity at the (0,0,1/2) reflection shows a sharp resonance at 708.4 eV with a shoulder (706.8 eV) at the L_3 threshold and two maxima at 720 and 721.4 eV at the L_2 one. This behavior agrees with that found on a magnetite thin film measured by Schlappa et al. [5], except for the relative intensity between the two peaks. The self-absorption effect in the bulk single crystal strongly reduces the intensity of the peak at 708.4 eV. The absorption spectrum is also plotted as reference for the energy scale. No scattered intensity was observed at energies out of the absorption edge, showing the absence of Thomson scattering. Figure 1b compares the intensity at 706.8 eV for different azimuth angles between σ– and π-incidence. Neither different intensity nor different spectral line shape are obtained (we note that the measured intensity is σ-σ + σ-π for σ-incidence and π–π + π–σ for π-incidence). Therefore, we conclude that the only active polarization channel is the σ-π one.

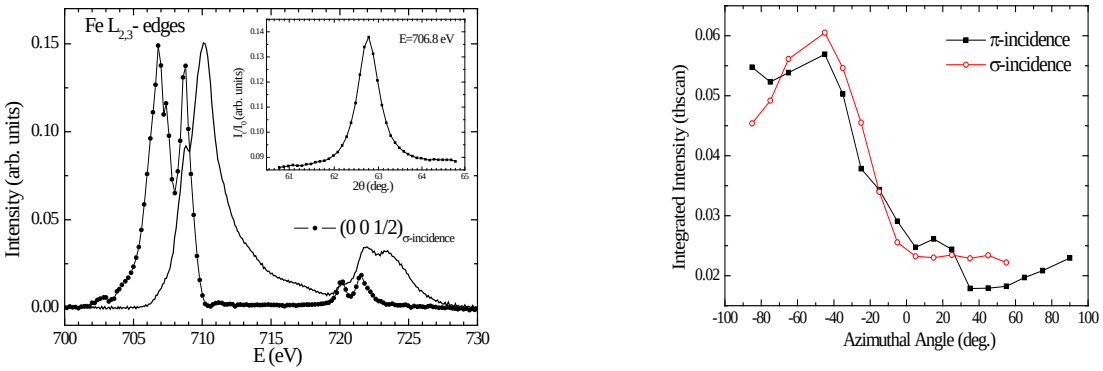

Figure 1. **(a)** Energy dependence of the (001/2) reflection (σ-incidence) recorded over the Fe L2,3 edges at 30 K. The total electron yield absorption spectrum is compared in the same energy scale. The inset shows a scan in the θ-2θ direction. **(b)** Comparison of the resonant scattered intensity of the (0,0,1/2) reflection for σ- and π-incidence at 706.8 eV *versus* the azimuth angle.

A sharp resonance was also observed at the (0,0,1/2) reflection corresponding with the rising edge of the pre-peak structures of the O K-edge, in agreement with previous works [6,7]. The intensity of the reflection and the spectral shape is independent of the incident photon polarization, as shown in fig. 2a. This result guarantees that the (0,0,1/2) reflection appears only in the σ-π polarization channel and the absence of scattering below the O K-edge confirms that it is forbidden by symmetry.

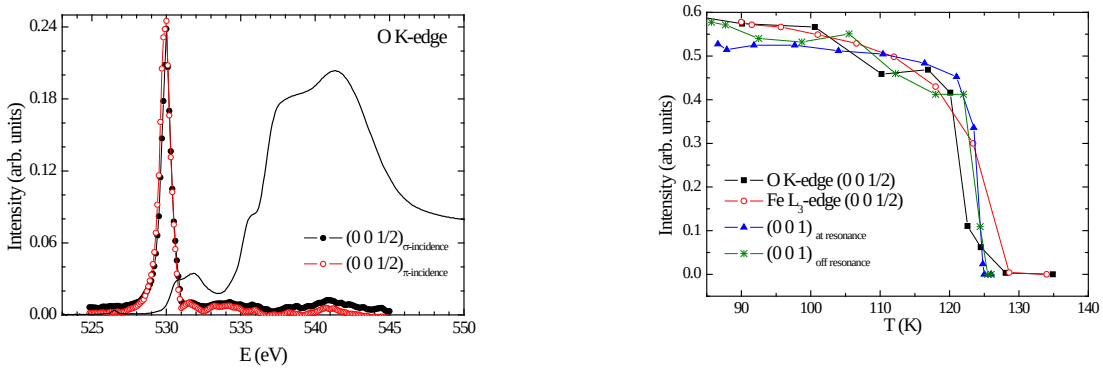

Figure 2. **(a)** Energy dependence of the (0,0,1/2) reflection at the O K-edge for σ– and π– polarization incidence. The O K-edge absorption spectrum is also shown. **(b)** Temperature dependence of the integrated intensities of the low-temperature reflections.

We have also measured the (0,0,1) reflection at the Fe L_1 edge. This reflection is active in the σ–σ´ polarization channel and it is observed at energies below the Fe L_1-edge. This behavior confirms that this reflection is permitted by the crystal symmetry of the low temperature phase.

The resonant and non-resonant scattered intensities simultaneously disappear at T_V (±0.5 K) for all the studied reflections showing that the origin of the resonances is the structural change (Fig. 2b) [8].

The observation of SRXS at these two reflections agrees with the *Pmca* structure, as described by Wright et al [9]. We conclude that the (0,0,1) periodicity comes from the existence of different crystallographic B sites and the (0,0,1/2) periodicity originates from the existence of a glide plane. The (0,0,1/2) reflection arises from local displacements of both, O and Fe atoms [7] and probes the electronic anisotropy and the ordering of their respective 2p and 3d states whereas the (0,0,1) reflection reflects the existence of a charge-density-wave.

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