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Report:

We have investigated the charge-ordering (CO) problem in magnetite (Fe_3O_4) and related spinel ferrites ($MnFe_2O_4$ and $CoFe_2O_4$) across the controversial metal-insulator transition, known as Verwey transition[1]. A complete set of forbidden and superstructure reflections have been studied via x-ray resonant scattering (XRS) at the Fe K-edge in single crystals grown by floating-zone method and fully characterized for their physical properties in our home laboratory[2,3].

Fe_3O_4 crystallizes in the inverse spinel AB_2O_4 structure at room temperature (space group *Fd-3m*), where A and B sites are occupied by the tetrahedral and octahedral Fe atoms, respectively. Below the Verwey transition temperature T_V, the best structural approximation corresponds to a monoclinic cell (space group *Cc*) with the following axes $\sqrt{2}a \times \sqrt{2}a \times 2a$ (**a** being the cubic lattice parameter). The unit cell consists of a stacking of eight planes of B sites along the **c** axis. Apart from the Verwey ordering scheme, which should give rise to the appearance of forbidden (0 0 4*l*+2) reflections, the CO arrangements proposed for Fe_3O_4 correlate with the atomic displacements developing below T_V. Two main types of superstructure reflections appear: (I) half-integer (*h k l*+1/2) from the doubling of the c axis and (II) even-odd mixed-integer resulting from the loss of the *fcc* translation. Thus, CO modulations could exist along the c-axis for the periodicities given by **q**=(002), **q**=(001) or **q**=(001/2) wave vectors.

First, we have analysed the Verwey CO ordering model by XRS experiments at the forbidden (0 0 4*l*+2) reflections in several spinel ferrites[2]. Resonant effects are observed at the Fe K edge for the three studied Fe_3O_4, $MnFe_2O_4$ and $CoFe_2O_4$ samples (Fig. 1), even at room temperature above T_V. We note that no pre-edge resonance is seen for $MnFe_2O_4$, where Mn^{2+} mainly replaces Fe in the tetrahedral A sites. The energy dependence and polarization anlayses of the scattered intensities showed that the resonance line at the pre-edge originates from dipolar-quadrupolar transitions at the tetrahedral site whereas the one at the absorption edge comes from dipolar transitions at the octahedral site. The azimuthal dependence confirms that the

resonances at the absorption edge appear due to the anisotropy of the x-ray susceptibility caused by the trigonal distortion of the octahedral B sites, i.e. they have a structural origin.
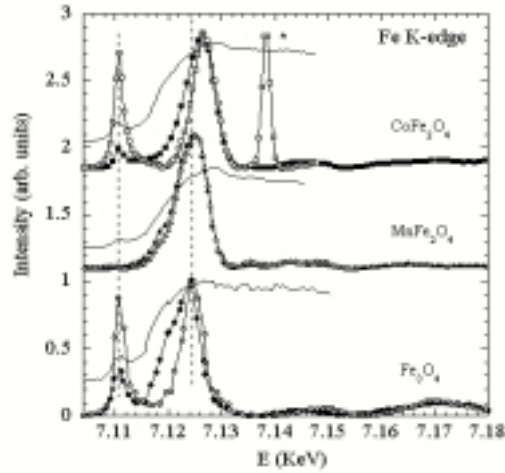

Figure 1.XRS spectra of (002) (closed symbols) and (006) (open symbols) reflections at the Fe K edge in spinel ferrites at RT.

Second, we have searched for CO modulations in Fe_3O_4 below T_V by XRS experiments at the Fe K edge at several superstructure reflections[3], related to either $\mathbf{q}$=(001) or $\mathbf{q}$=(001/2) periodicities (Fig. 2). Resonant and non-resonant contributions were not observed at the (*0 0 half-integer*) reflections while only non-resonant intensity was detected for (*h k l*+1/2) *h,k*=4n and *h* ó *k*≠0. This implies the absence of CO modulations with $\mathbf{q}$=(001/2) periodicity. No resonant enhancement was seen near the Fe K edge for either (003) or (210) reflections. A theoretical simulation allow us to conclude that any CO modulation following the $\mathbf{q}$=(001) periodicity has to be smaller than 0.1 electron.
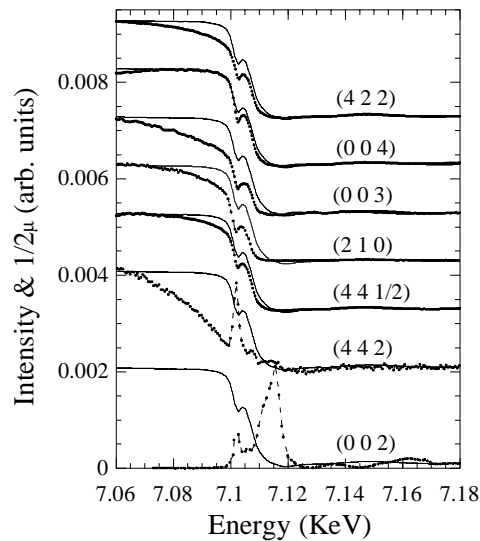

Figure 2.XRS spectra of Bragg-allowed [(004), (422)-T_D and (442)], low-temperature superstructure [(003), (210) and (441/2)] and forbidden (002) reflections at the Fe K edge in Fe_3O_4 at T=20 K compared to the self-absorption contribution (1/2μ).

Summing up, these XRS works at the Fe K edge on a wide set of superstructure reflections strongly conclude the absence of ionic (Fe^{3+} ($3d^5$) and Fe^{2+} ($3d^6$) configurations) ordering in magnetite. Thus, the main effect at the Verwey transition is the structural change and a conduction mechanism assisted by phonons would be a more reliable origin for the metal-insulator transition.

[1] J. García and G. Subías, *J. Phys.: Condens. Matter* **16,** R145 (2004)
[2] G. Subías *et al*., *Phys. Rev. B* **70**, 155105 (2004)
[3] G. Subías *et al*., *Phys. Rev. Lett*. **93**, 156408 (2004)