Presence of an Ionic Charge ordering at the Verwey Transition in Fe₃O₄: A Resonant X-ray Diffraction Study

<u>J. Emilio Lorenzo</u>^a, E. Nazarenko^a, Y. Joly^a, J.L. Hodeau^a, D. Mannix^b, C. Marin^c. ^a*Lab. Cristallographie, CNRS, Grenoble, France.* ^b*XmaS, ESRF, Grenoble.* ^c*DRFMC-SPSMS, CEA-Grenoble, France.* E-mail: emilio.lorenzo@grenoble.cnrs.fr

Magnetite, Fe₃O₄, is a mixed valence system that exhibits many interesting properties, some of them known since the early times. Moreover, magnetite is also on the spot of physicists because of the lack of consensus as to the nature of the metal-insulator transition occurring at T_v=120K (Verwey transition). The real question that remains largely open is the amount of charge, δ , that is going to localize at the octahedral metal sites giving rise to iron charge states of the type $Fe^{2.5\pm\delta}$. To this end we have carried out a series of resonant X-ray diffraction (RXD) experiments in the neighborhood of the Fe K-edge that have revealed distinct signatures of a small charge ordering (CO) compatible with the symmetry of the low temperature structure. The magnitude of the charges, $\delta \approx 0.15$ e⁻, has been determined through a refinement of the energy dependence around the of the Fe K-edge of the line shape of 30 selected reflections of the low temperature structure. Our results, in agreement with bond valence sums calculations, are in striking contradiction with previous RXD experiments that have concluded on the absence of any CO in magnetite. This small value of the charge is of fundamental importance and strengthen the argument that covalency effects play a major role in the physics of these strongly correlated compounds. In this paper the strength and limitations of RXD will be discussed as well as, hinting why CO was not observed in previous experiments. Keywords: charge transfer, iron oxides, DAFS