MS15-O5 Ordering phenomena in minerals: the Verwey phase of natural magnetite

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Transition metal oxides can feature mixed valence cations, spin ordering and direct interactions between *d*-orbitals. This makes them intrinsically susceptible to the formation of atomic clusters with direct metal-metal interactions (*orbital molecules*).

The most significant example of orbital molecule behaviour is in the Verwey phase of magnetite (Fe_3O_4). Cooling magnetite below ~125 K causes remarkable changes to its conductivity, magnetisation and heat capacity; this is called the Verwey transition, commonly used for detection and quantification of magnetite in minerals. The transition is also accompanied by a structural change, whose specifics were only determined in 2012: the *Fd-3m* high-temperature structure distorts to a monoclinic *Cc* supercell; the change of physical properties is due to a cooperative bond distortion that brings together three neighbouring Fe sites in a linear Fe^{3+}-Fe^{2+}-Fe^{3+} arrangement, delocalizing the extra electron provided by Fe^{2+}. This bonded cluster is a three-atom orbital molecule, called a '*trimeron*' (Fig.1). [1] The trimeron formation is one of the most complex electronically ordered ground states known, and as such is notoriously susceptible to the effects of non-stoichiometry, through both oxidation effects and cation substitution. [2]

We investigated the low-temperature behaviour of a sample of natural magnetite from Ouro Preto, Brazil, crushed to provide a microcrystal of 60 × 50 × 25 μm from the bulk of the rock. Electron Probe Microanalysis showed a relatively low dopant content (< 0.5% total impurities, mainly Al and Si). SQUID magnetization measurements identified a lowering of the transition temperature to T_V = 119 K. The structural transition was studied with single crystal synchrotron XRD at the ESRF, and we were able to apply the established trimeron model to the data, with some relevant variations that show us an influence of the stoichiometry also on the structural arrangement.

On this basis, we claim evidence of long-range electronic order as a natural occurrence in the magnetite system. Therefore, we suggest that the Verwey transition may contribute to geophysical processes in rocky bodies that can easily cycle above and below ~125 K (i.e.: meteorites, iron-rich planets, etc.). [3]

References: [1] M.S. Senn, J.P. Wright and J.P. Attfield, *Nature* 481, 173 (2012); [2] J. M. Honig, *J Alloy Compd* 229, 24 (1995); [3] G. Perversi, J. Cumby, E. Pachoud, J. P. Wright and J.P Attfield, *Chem. Comm.* 52, 4864 (2016)

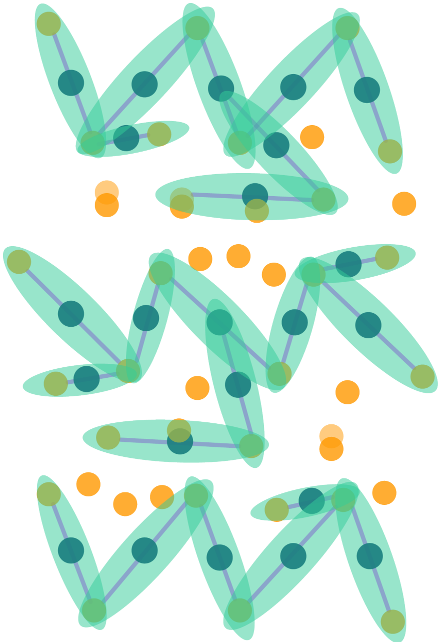

Figure 1. Trimeron arrangement in the low-temperature *Cc* structure. Fe^{2+} in blue, Fe^{3+} in yellow, delocalization region is indicated in green. Only octahedral cations are displayed.

Keywords: Single crystal XRD, low-temperature, phase transition, Verwey transition, ordering, distortions, minerals, magnetite