Verwey Transition in a Perovskite-Type Structure

Pavel Karen, *Department of Chemistry, University of Oslo, POB 1033 Blindern, 0315 Oslo, Norway*. E-mail: pavel.karen@kjemi.uio.no

Above Verwey transition at 120 K, magnetite (Fe_3O_4) is a spin-polarized conductor, feasible for applications in spin computing. Owing to continuing controversy about charge order in the complex low-temperature phase, Verwey transition in magnetite remains a mystery. Double-cell perovskites of the $YBaFe_2O_5$ type contain iron in the average oxidation state +2.5 and exhibit all symptoms of the Verwey transition. The charge-ordered superstructures are simple and the refined iron–oxygen bond distances suggest a 70 to 80% of long-range charge separation into di- and trivalent iron, likely to mean a 100% charge separation on the local scale. The charge order violates Coulombic minimization of point charges, implying orbital ordering. The associated orthorhombic distortion identifies the doubly-occupied d_{xz} orbital of Fe^{2+}. Magnetic interactions define the orientation of the orthorhombic distortion, but the charge order occurs independently of any specific spin coupling. Magnetostriction opens for an incipient partial charge ordering that occurs before the Verwey transition itself distorts the structure under continued cooling. Replacing Y with Sm and Nd shows that when the size of this seemingly uninvolved atom becomes unfavorable (a large projected ΔV at the transition), orbital ordering continues at a cost of symmetry lowering. Oxygen nonstoichiometry decreases Verwey-transition entropies ΔS and transition temperatures T_V in a manner that corresponds to an ideal solution of $YBaFe_2O_6$ in the $YBaFe_2O_5$ solvent. Verwey transition is a klassengleich switch from a valence-mixed halfmetal into a valence-ordered semiconductor, achieved via orbital ordering of one single, singly or doubly occupied *d* orbital of t_{2g} symmetry.

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