

Keynote Lectures

[KN12] The Verwey structure of magnetite -from crystals to powders to microcrystals

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Magnetite (Fe_3O_4) is the original magnetic material and remains fundamental to understanding of magnetism. On cooling below 125 K, magnetite undergoes a complex structural distortion and becomes electrically insulating. Verwey proposed in 1939 that this transition is driven by a charge ordering of Fe^{2+} and Fe^{3+} ions ordering of Fe and Fe ions [1], but the low temperature state remained uncertain and has been a contentious problem for over 70 years. Attempts to solve the low temperature Verwey structure from single crystal data in the 1970's and 80's were frustrated by the combination of structural complexity (the monoclinic Cc supercell contains 24 distinct Fe sites) and extensive microtwinning of the Verwey domains [2]. Partial structure refinements against high resolution neutron and synchrotron X-ray powder data provided direct evidence for $\text{Fe}^{2+}/\text{Fe}^{3+}$ charge order [3,4], and this was corroborated by subsequent Fe K-edge resonant X-ray analyses [5-7]. The full low temperature superstructure of magnetite was recently determined by high energy x-ray diffraction from an almost single domain 40 μm grain, enabling the electronic order to be identified [8]. Verwey's $\text{Fe}^{2+}/\text{Fe}^{3+}$ charge order hypothesis was found to be approximately correct, with a pronounced orbital ordering of tetragonally compressed Fe^{2+} states, but an unexpected localization of electrons in linear, three-Fe 'trimeron' units was discovered. This description is supported by band structure calculations [9]. Trimerons are examples of 'orbital molecules' which may be important quasiparticles in magnetic oxides.

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