

On the Verwey charge ordering in magnetite

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 021001

(<http://iopscience.iop.org/0953-8984/19/2/021001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 15:19

Please note that [terms and conditions apply](#).

VIEWPOINT

On the Verwey charge ordering in magnetite

I Leonov^{1,2} and A N Yaresko³

¹ The Abdus Salam International Center for Theoretical Physics, Trieste 34014, Italy

² Theoretical Physics III, Center for Electronic Correlations and Magnetism, Institute for Physics, University of Augsburg, Germany

³ Max-Planck Institute for the Physics of Complex Systems, Dresden, Germany

E-mail: ileonov@ictp.it

Received 3 November 2006

Published 15 December 2006

Online at stacks.iop.org/JPhysCM/19/021001

Magnetite, a famous permanent natural magnet, is probably the oldest magnetic material known to humans [1]. Fe_3O_4 is a ferrimagnet with an anomalously high Curie temperature of ~ 850 K which arises from the inverse spinel type crystal structure. This is formally written as AB_2O_4 where A and B are two crystallographically distinct tetrahedrally and octahedrally coordinated Fe sites. Both have different oxidation states due to the large difference of the corresponding average Fe–O distances, 1.876 and 2.066 Å (at 300 K), respectively. Thus the former (the A site) is occupied by Fe^{3+} ion, whereas octahedral B sites are occupied by an equal number of randomly distributed 2+ and 3+ Fe ions, which results in an average valence value of 2.5+ per Fe_B ion. The B sublattice is highly frustrated and can be viewed as a pyrochlore lattice of corner-sharing Fe_B tetrahedra. Therefore, mixed-valent magnetite is considered to be a charge frustrated system with a highly degenerate ground state.

Fe_3O_4 is a poor metal with an electrical resistivity of 4 mΩ cm (at 300 K) which is remarkably higher than the resistivity of simple metals, e.g. 0.96, 1.59 or 1.7 μΩ cm for Hg, Ag or Cu, respectively. Upon cooling below $T_V \sim 120$ K magnetite undergoes a sharp first-order metal–insulator transition (the so-called Verwey transition) at which the conductivity abruptly decreases by two orders of magnitude and the symmetry of the structure lowers from the cubic one [2]. To explain this anomaly Verwey proposed a theoretical model according to which the transition is caused by the ordering of Fe^{2+} ions on the B sublattice with formation of charged (001) planes alternately occupied by 2+ and 3+ Fe_B ions. This was the first report on a charge ordering as well as an orthorhombic (Verwey) superstructure model. The Verwey charge ordering (CO) model obeys the so-called Anderson criterion for minimal electrostatic repulsion which requires the occupation of each Fe_B tetrahedron by an equal number of 2+ and 3+ ions, thus leading to a short-range CO pattern [3].

At first confirmed by x-ray and neutron diffraction studies [4], the Verwey CO model was disproved by further experiments. The half-integer satellite reflections $(h, k, l + \frac{1}{2})$ clearly observed below T_V indicate a doubling of the cubic unit cell along the c axis and show the symmetry to be monoclinic Cc [5]. On the other hand, observation of the magnetoelectric effect revealed even lower $P1$ symmetry in the low temperature phase [6]. Nevertheless, no conclusive structural model or charge ordered arrangement was identified because of the complexity of the low temperature structure and the difficulties caused by microtwinning at the

Verwey transition. Even in a diffraction study of almost de-twinned single crystal by Iizumi *et al* [7], which resolved large atomic displacements of Fe and O atoms in a $\frac{a}{\sqrt{2}} \times \frac{a}{\sqrt{2}} \times 2a$ subcell of the Cc unit cell (with imposed orthorhombic $Pmca/Pmc2_1$ symmetry constraints), no charge ordered arrangement was found.

Most convincing structural evidence for charge ordering has been provided by a recent crystallographic refinement performed at 90 K by Wright *et al* [8]. The low temperature structure was shown to have a $\sqrt{2}a \times \sqrt{2}a \times 2a$ supercell with space group Cc from combined x-ray and neutron diffraction. However, the refinement was performed for a monoclinic $P2/c$ $\frac{a}{\sqrt{2}} \times \frac{a}{\sqrt{2}} \times 2a$ subcell of a Cc unit cell with $Pmca$ orthorhombic symmetry constraints. The latter is equivalent to averaging the true superstructure over the additional $Pmca$ symmetry operations, i.e. each B site in the $P2/c$ unit cell is averaged over four non-equivalent subsites in the large $\sqrt{2}a \times \sqrt{2}a \times 2a$ Cc supercell.

The four independent B sites in this model are split into two groups with different values of average Fe–O distances with bond lengths for the B2 and B3 sites being significantly smaller than for the B1 and B4 ones. A bond valence sum (BVS) analysis revealed a small charge disproportionation ($0.2 \bar{e}$) between ‘large’ (B1 and B4) 2.4+ and ‘small’ (B2 and B3) 2.6+ sites (which was referred to as a class-I CO model [8]). Based on subsequent resonant diffraction experiments it was shown that there are eight more possible charge arrangements (class II CO) in the Cc supercell compatible with the orthorhombic symmetry constraints [9]. Remarkably, the Anderson criterion is not satisfied by any of the above mentioned charge ordering models. However, later it was argued that the difference between the average Fe–O distances in compressed and expanded FeO_6 octahedra is of the same order as the total sensitivity of the BVS method, and the existence of charge disproportionation was questioned [10].

The contradiction has been resolved in the recent band structure calculations which employed the above mentioned $P2/c$ structural model [11, 12]. The calculations result in a charge- and orbitally-ordered insulator with a small 3d charge disproportionation between Fe^{2+} and Fe^{3+} ions ($0.23 \bar{e}$) which agrees well with the result of the BVS analysis (0.2). The charge order is well pronounced with an order parameter defined as a difference of t_{2g} occupancies of 2+ and 3+ Fe_B ions reaching the value of 0.7. It was shown that rearrangement of other Fe_B electrons, first of all $Fe_{B_e_g}$ states, results in the effective screening of the disproportionation of the total Fe_B charges [11]. The competition between *elastic* and *electrostatic* contributions to the total energy was proposed to be responsible for the charge order, which is realized in the experimentally observed low temperature structure [11]. The obtained charge arrangement, as compared to the Verwey CO model, may significantly decrease the lattice stress and reduce the contribution of the *elastic* energy to the total energy. This scenario naturally explains why the Verwey charge ordering model, which possesses the lowest electrostatic repulsion energy among all possible CO models provided structural distortions are neglected, is not realized below T_V .

However, it should be pointed out that the calculations were performed for the averaged $P2/c$ structural model [8]. Therefore, in view of the absence of a conclusive structural model of the low temperature phase the electronic structure calculations with lattice relaxation recently published by Pinto and Elliott are of great importance [13]. The authors present detailed total energy investigation of various symmetry-broken CO patterns in the cubic supercell. In addition, an optimization of the $Pmca$ internal coordinates of the structural model proposed by Wright *et al* [8] and a $C2/c$ supercell have been successfully performed. Optimization of the cell with $Pmca$ symmetry was found to give the lowest total energy⁴ with the CO pattern

⁴ Remarkably that similar result was obtained by relaxation of the $P2/c$ structural model using an *ab initio* pseudopotential method [14].

being in agreement with the previous calculations based on the experimental $P2/c$ structural model [11, 12]. While stressing the importance of the electron–electron repulsion they conclude that pure electrostatics is not the main factor determining the stability of CO.

The electron–lattice coupling seems to play an important role not only in magnetite but in many other CO systems. Further studies of the lattice relaxation effects in complex CO structures are desirable and may lead to a discovery of new electronic phenomena.

References

- [1] Mattis D C 1988 *The Theory of Magnetism I* (Berlin: Springer)
- [2] Verwey E J W 1939 *Nature* **144** 327
Verwey E J W, Haayman P W and Romeijan F C 1947 *J. Chem. Phys.* **15** 181
- [3] Anderson P W 1956 *Phys. Rev.* **102** 1008
- [4] Hamilton W C 1958 *Phys. Rev.* **110** 1050
- [5] Yamada T, Suzuki K and Chikazumi S 1968 *Appl. Phys. Lett.* **13** 172
Samuelsen E J, Bleeker E J, Dobrzynski L and Riste T 1968 *J. Appl. Phys.* **39** 1114
Chiba K, Suzuki K and Chikazumi S 1975 *J. Phys. Soc. Japan Lett.* **39** 839
- [6] Miyamoto Y and Shindo M 1993 *J. Phys. Soc. Japan* **62** 1423
- [7] Iizumi M, Koetzle T F, Shirane G, Chikazumi S, Matsui M and Todo S 1982 *Acta Crystallogr. B* **38** 2121
- [8] Wright J P, Attfield J P and Radaelli P G 2001 *Phys. Rev. Lett.* **87** 266401
Wright J P, Attfield J P and Radaelli P G 2002 *Phys. Rev. B* **66** 214422
- [9] Goff R J, Wright J P, Attfield J P and Radaelli P G 2005 *J. Phys.: Condens. Matter* **17** 7633
- [10] García J, Subías G, Blasco J and Proietti M G 2002 *Preprint cond-mat/0211407*
Subías G, García J, Blasco J, Proietti M G, Renevier H and Sánchez M C 2004 *Phys. Rev. Lett.* **93** 156408
- [11] Leonov I, Yaresko A N, Antonov V N, Korotin M A and Anisimov V I 2004 *Phys. Rev. Lett.* **93** 146404
Leonov I, Yaresko A N, Antonov V N and Anisimov V I 2006 *Phys. Rev. B* **74** 165117
- [12] Jeng H-T, Guo G Y and Huang D J 2004 *Phys. Rev. Lett.* **93** 156403
- [13] Pinto H P and Elliott S D 2006 *J. Phys.: Condens. Matter* **18** 10427
- [14] Binggeli N 2006 private communication