2013 Hawaii University International Conferences
Education & Technology
Math & Engineering Technology
June 10th to June 12th
Ala Moana Hotel, Honolulu, Hawaii

Wannier functions and 3d electron localization of Magnetite

A. Carpentier

C. Boekema

San José State University

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A. Carpentier, C. Boekema, Dept of Physics and Astronomy, San José State University

Abstract

Magnetite (Fe_3O_4) is a ferrimagnetic oxide. A remarkable property of Fe_3O_4 is a metal-to-insulator transition at the Verwey temperature (~123 K) due to the properties of the "extra 3d" (3d*) conduction electrons. Magnetic anomalies, observed between Verwey temperature (T_v) and Wigner Temperature (T_w) show that Fe_3O_4 can be considered a Wigner electron glass. Wannier states for these 3d* conduction electrons can be characterized by a covalency parameter. The Wannier states in Fe_3O_4 indicate a mixture of localized and delocalized electron states. Further research on the Wannier states of these "hopping" 3d* conduction electrons may provide more insight as to whether these spin-polarized electrons are localized or not, on the origin of the Verwey phase transition, and perhaps on its spintronics properties.

I. Introduction

Magnetite (Fe_3O_4) a naturally occurring mineral, is a ferrimagnetic oxide. A remarkable property of Fe_3O_4 is its transition from semimetallic behavior to an insulator behavior at the Verwey temperature (T_v ~ 123 K) due to the properties of the 3d*conduction electrons (Fig 1). This transition called Verwey Transition is a first order phase transition with an energy gap of about 50–70 meV[3,4,5]. Above T_v Fe ions are disordered (semimetallic behavior) and below T_v Fe ions are ordered (insulator behavior).

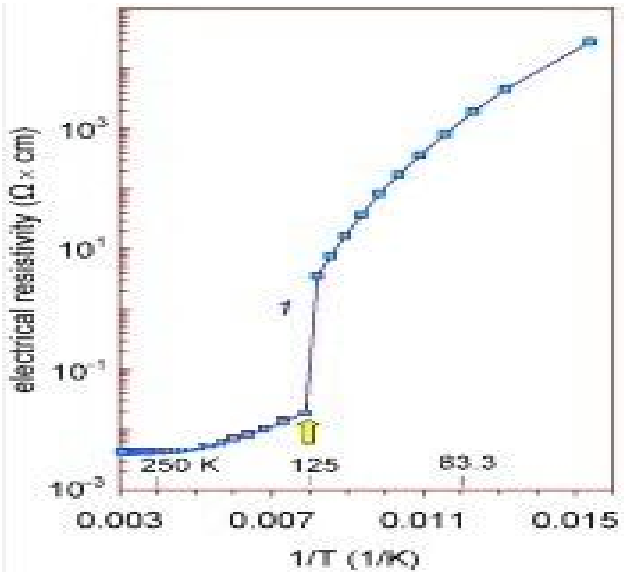

Fig 1: Temperature (T) dependency of electrical resistivity (ρ) for as-grown single-crystalline Fe_3O_4 magnetite, across the Verwey transition near 120–125K (marked by the arrow)[6]. A minimum in resistance is present at about 250 K, near T_w (see text).

Magnetic anomalies, observed between Verwey temperature (T_v) and Wigner temperature (T_w), show that Fe_3O_4 can be considered a Wigner electron glass. The resistivity is lowest at T_w, around twice T_v (~ 247 K). There is a factor of 100 in resistivity between T_v and T_w.

Currently, two models are under consideration in regards to the semi-metallic behavior above T_v:

1. Broad energy band (W=1eV) conduction mechanism
2. Phonon-assisted electron hopping.

In case 2, the narrow energy bands are fully spin polarized. In spintronics, fully spin-polarized bands play a most important role in applied magnetism studies. We wish to study this Verwey transition and the mechanism involved as this transition is still a problem today in material science.

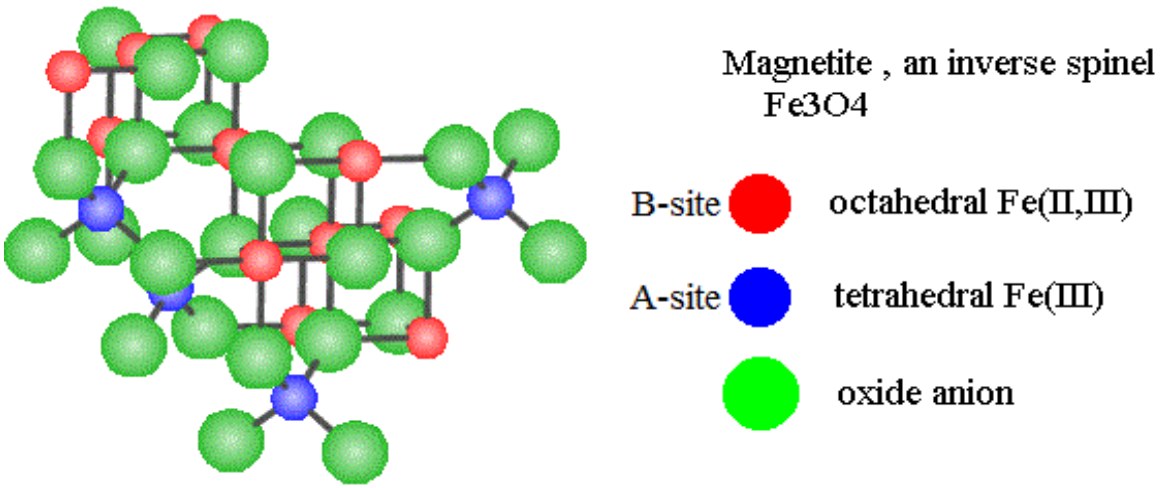

Fig 2: Spinel structure of Fe_3O_4

II. Energy Bandstructure of Magnetite

The chemical-physical equation of magnetite is: $(Fe^{3+})_A$ $[Fe_2^{3+}$ $e^{-1}]_B$ O_4^{2-}. The Fe ions crystallize in two different configurations (Fig 2): 1) Tetrahedral iron site (A) is surrounded by four oxygens O^{2-} 2) Octahedral iron site (B) is surrounded by six oxygens O^{2-}. The Fe^{2+} ions are in the octahedral sites (B) and the Fe^{3+} ions are in both the octahedral (B) and the tetrahedral (A) sites[7,8,9].

Electron configuration of $(Fe^{3+})_A$ is $3d^5$ and spins are all in the same direction to lower the energy. Moreover, these iron spins on the A sublattice are antiparallel (↓) to those on the B sublattice (↑). On the B sublattice, we also have an "extra 3d" (3d*) conduction electron with a spin down orientation. This extra fully spin-polarized conduction electron is the most energetic conduction electron. The top energy band in the energy band structure is so half filled by this 3d* conduction electron, which is spin polarized antiparallel to spins of the other electrons on the B sublattice. This 3d* electronic configuration is spin down (Fig 3). We write the magnetite formula more precisely as: $\mathbf{(^{\downarrow}Fe^{3+})_A\ [^{\uparrow}Fe_2^{3+}\ ^{\downarrow}e^{-1}]_B\ O_4^{2-}}$. Thus we have an average of spin up configuration with energy of -4 μB (+5 μB for the A sublattice and -9 μB for the B sublattice).

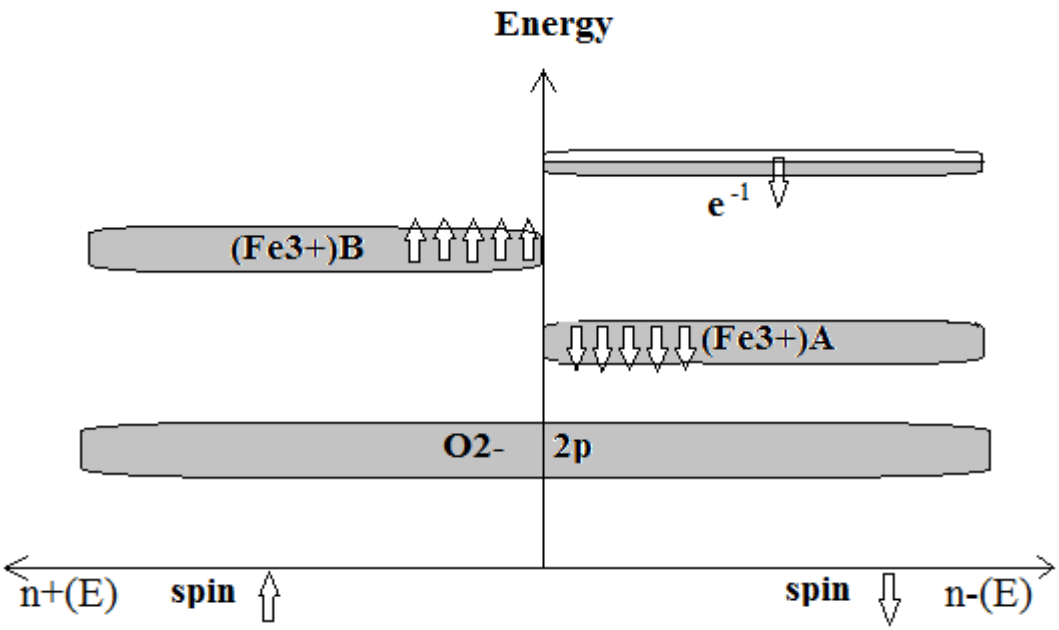

Fig 3: Energy bandstructure of magnetite (Energy vs Spin density)

III. Wannier functions and electron localization

Wannier function $W(\vec{r}-\vec{R})$ is the Fourier transform of the Bloch function $\psi(\vec{k})$ is written as: $W(\vec{r}-\vec{R}) = \frac{1}{v_0}\int_{-\infty}^{+\infty}\psi(\vec{k})e^{-i\vec{R}\vec{k}}d\vec{k}$ [1]. Wannier functions at different sites are orthogonal and inform us about the electron localization. In general, the energy range of Wannier function decreases as the band gap increases[10]. Wannier states for these 3d* conduction electrons can be characterized by calculating covalency parameters $\gamma(\vec{k})$. When $\gamma(\vec{k})$ is negative or zero, then an antibonding state and/or localization of electron are indicated, and when $\gamma(\vec{k})$positive, more covalency and delocalization is are present in the Wannier states[2]. For each subband a covalency parameter Γ can be determined.

IV. Results and Conclusive remarks

Present results reveal that the Wannier states in magnetite are a mixture of localized and delocalized electron states[2] (Table 1). Due to the B-site sublattice of Fe_3O_4, the "extra 3d" (3d*) conduction electron must be in a four-fold state. The upper singlet and doublet (narrow) 3d* bands are primarily responsible for the conduction process. At sufficiently high temperatures of about T_v a localized behavior of the 3d* states is predicted. The strong localization indicates the necessity to take account Hubbard-like terms to describe the Coulombic 3d* interactions.

3*d** **bands**	**Γ parameter**	***W*W* state**	**Occupancy 0 K**	**Broadening**
Doublet	-1.4	very localized	0	0
Upper singlet	-0.0	localized	1	< |2*H*|
Lower singlet	+2.9	delocalized	1	< |2*H*|

Table 1: State and localization of the 3d* electron depending of the covalency parameter Γ. H is about -0.05eV.[2]

We analyze the energy bandstructure of magnetite as well as electron localization and Wannier functions of the extra 3d* electrons to investigate this remarkable behavior of magnetite around T_v. Above T_v, our Wannier picture supports the idea of phonon-assisted electron hopping. The Wannier states in magnetite appear to be a mixture of localized and delocalized electron states. Further work on the Wannier states of the "hopping" 3d* electrons are in progress and more research is needed to have a better understanding of the Verwey transition, and to assist in spintronics studies.

References

1. J. R. Cullen and E. R. Callen, Phys. Rev. B7 (1973) 397
2. T. Her and C. Boekema, J. Appl. Phys. 76 (1995) 6703
3. A. Chainani et al, J. Electron Spectrosc. Relat. Phenom. 78 (1996) 99
4. J.H. Park et al, Phys. Rev. B55 (1997) 12813
5. A. Moewes et al, .J. Phys.: Condens. Matter, 15 (2003) 2017
6. V. V. Shchennikov, S. V. Ovsyannikov, A. E. Karkin, S. Todo, Y. Uwatoko, Solid State Communications Vol. 149, Issues 19-20, (2009) 759-762
7. M.E. Fleet, Acta Crystallogr. B37 (1981) 917
8. S. Sasaki, Acta Crystallogr. B53 (1997) 762
9. F.J. Berry et al, J. Phys.: Condens. Matter, 10 (1998) 215
10. N.W. Ashroft and N.D. Mermin Solid State Physics (1976) 188