WANNIER FUNCTIONS AND 3D ELECTRON LOCALIZATION OF MAGNETITE

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Abstract

Magnetite (Fe₃O₄) is a ferrimagnetic oxide. A remarkable property of Fe₃O₄ 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 (Tᵥ) and Wigner Temperature (Tₜₜ) show that Fe₃O₄ 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 Fe₃O₄ 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 (Fe₃O₄) a naturally occurring mineral, is a ferrimagnetic oxide. A remarkable property of Fe₃O₄ is its transition from semimetallic behavior to an insulator behavior at the Verwey temperature (Tᵥ ~ 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 Tᵥ Fe ions are disordered (semimetallic behavior) and below Tᵥ Fe ions are ordered (insulator behavior).
Fig 1: Temperature ($T$) dependency of electrical resistivity ($\rho$) for as-grown single-crystalline Fe$_3$O$_4$ 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$_3$O$_4$ can be considered a Wigner electron glass. The resistivity is lowest at $T_w$, around twice $T_v$ ($\sim 247$ 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 ($W=1$eV) 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$_3$O$_4$
II. Energy Bandstructure of Magnetite

The chemical-physical equation of magnetite is: \((\text{Fe}^{3+})_A [\text{Fe}^{2+} \text{e}^{-}]_B \text{O}_4^{2-}\). The Fe ions crystallize in two different configurations (Fig 2): 1) Tetrahedral iron site (A) is surrounded by four oxygens \(\text{O}^{2-}\) 2) Octahedral iron site (B) is surrounded by six oxygens \(\text{O}^{2-}\). The \(\text{Fe}^{2+}\) ions are in the octahedral sites (B) and the \(\text{Fe}^{3+}\) ions are in both the octahedral (B) and the tetrahedral (A) sites\(^{[7,8,9]}\).

Electron configuration of \((\text{Fe}^{3+})_A\) 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 (\(\downarrow\)) to those on the B sublattice (\(\uparrow\)). 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: \((\downarrow \text{Fe}^{3+})_A [\uparrow \text{Fe}^{2+} \downarrow \text{e}^{-}]_B \text{O}_4^{2-}\). Thus we have an average of spin up configuration with energy of -4 \(\mu\)B (+5 \(\mu\)B for the A sublattice and -9 \(\mu\)B for the B sublattice).

![Energy bandstructure of magnetite](image)

Fig 3: Energy bandstructure of magnetite (Energy vs Spin density)
III. Wannier functions and electron localization

Wannier function $W(\mathbf{r} - \mathbf{R})$ is the Fourier transform of the Bloch function $\psi(\mathbf{r})$, and is written as:

$$W(\mathbf{r} - \mathbf{R}) = \frac{1}{\sqrt{V}} \sum_{k} \psi_k(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{R}} \quad [1].$$

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 $\Gamma(\mathbf{k})$. When $\Gamma(\mathbf{k})$ is negative or zero, then an antibonding state and/or localization of electron are indicated, and when $\Gamma(\mathbf{k})$ positive, more covalency and delocalization is are present in the Wannier states$^{[2]}$. For each subband a covalency parameter $\Gamma$ 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 $\text{Fe}_3\text{O}_4$, 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.

<table>
<thead>
<tr>
<th>3d* bands</th>
<th>$\Gamma$ parameter</th>
<th>$W*W$ state</th>
<th>Occupancy 0 K</th>
<th>Broadening</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doublet</td>
<td>-1.4</td>
<td>very localized</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Upper singlet</td>
<td>-0.0</td>
<td>localized</td>
<td>1</td>
<td>$&lt;</td>
</tr>
<tr>
<td>Lower singlet</td>
<td>+2.9</td>
<td>delocalized</td>
<td>1</td>
<td>$&lt;</td>
</tr>
</tbody>
</table>

Table 1: State and localization of the 3d* electron depending of the covalency parameter $\Gamma$. $H$ 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