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Maximally Localized Wannier Functions of Fe3O4; an Ab Initio study

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Abstract

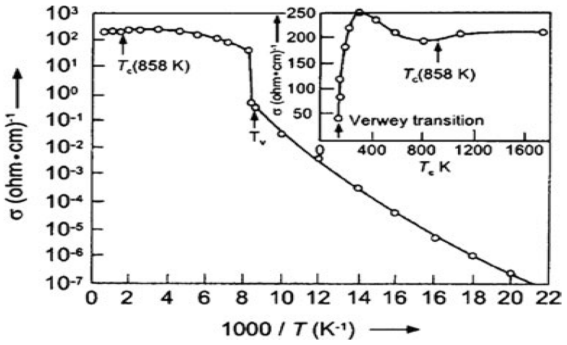
Magnetite has many remarkable physics properties are not well understood. Among these are the metal-insulator transition at the Verwey Temperature (123K) and a spin-glass-like transition at 247K. To better understand these properties, we calculate a set of maximally localized Wannier functions. We start from a first principles DFT+U band structure calculation and then perform a transformation of the Bloch orbitals to obtain maximally localized Wannier functions. We then perform a disentanglement procedure for the t_{2g} orbitals located on the B sublattice which contain the "extra" spin-polarized 3d electrons that are mainly responsible for the conducting state of magnetite above T_V.

1 Introduction

Magnetite is a naturally occurring mineral (Fe_3O_4) that crystalizes in the inverse spinel structure. Magnetite is magnetized ferrimagnetically with a Nèel temperature $T_N = 860K$. Due to this magnetization, magnetite may be used in spintronic applications. However, there are still physical properties of magnetite that have not been fully explained yet. Two remarkable properties are the metal-to-insulator transition at the Verwey Temperature (123K) and a spin-glass-like transition at 247K.

A metal-to-insulator transition is a first order phase transition where the material's resistivity changes from metallic behavior to insulating behavior below a certain critical temperature. In magnetite, this metal-to-insulator transition is named the Verwey Transition (VT). The VT occurs near 123K depending on the purity of the sample (see Fig 1).

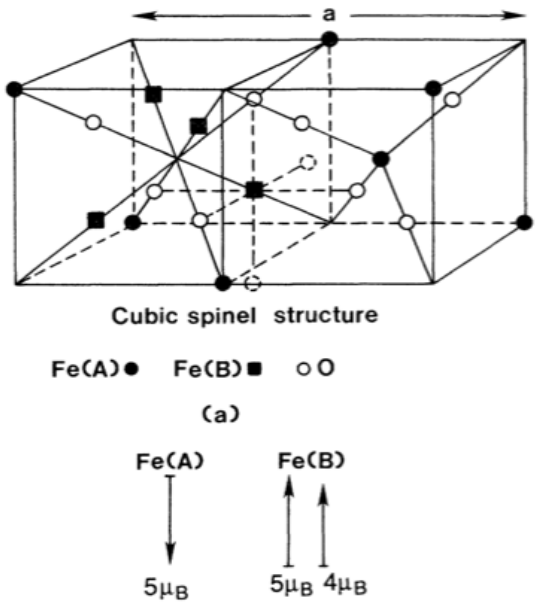
Figure 1: The Verywey Transition [6]



Another unusual property of Fe_3O_4 occurs at about twice T_V ($T_W = 247K$) where a minimum of the resistance is observed. At T_W magnetite undergoes a spin-glass-like transition where the spin of the electrons are no longer well ordered. Study of this transition is of great interest for understanding the theory of spin dynamics and spintronics.

The magnetite crystal has an inverse spinel structure. Spinel structures can be thought of as alternating stacking of two different cubes as shown in Figure 2. The O^{2-} ions form a face-centered-cubic structure where the Fe ions sit in the interstitial positions where they are tetrahedrally surrounded in the A sub-lattice and octahedrally surrounded in the B sub-lattice.

Figure 2: Fe_3O_4 crystal structure [5]



2 Wannier Functions

There has not yet been a conclusive theoretical model for the conduction mechanism above T_V and the physical mechanism of the Verwey transition. This is where Wannier functions can be most useful.

Wannier functions (WF) are a tool for studying electronic properties of the material. They can be thought of as solid-state physics versions of localized molecular orbitals used in chemistry. If we define WF centers (WFC) of electrons then we can track changes in the WFC which has a direct classical correspondence to tracking electrons as particles. Thus we can describe conduction of electrons as changes in their WFC.

Bloch Orbitals are defined as [2]:

$$|n\mathbf{k}\rangle = e^{i\phi_n(k)} u_{nk}(\mathbf{r}) e^{ik\cdot r}$$

Note, the second quantum number is in momentum space.

We can obtain WF via a Fourier transformation of the Bloch orbitals over the Brillouin Zone [2]:

$$|\mathbf{R}n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} \sum_{m=1}^{N} U_{mn}^{k} \, |m\mathbf{k}\rangle \, e^{-ik\cdot R} d\mathbf{k}$$

Note the WF for $\mathbf{R}$ is defined in real space and provides information about electron localization. A drawback of the WF is that they are not unique. They

are gauge invariant because we can multiply WF by any unitary matrix U^k_{mn}. That is why we will use the algorithm of [1] to obtain Maximally Localized Wannier Functions (MLWF).

The MLWF algorithm determines the unitary matrix U^k_{mn} such that the spread of the orbitals is minimized thus making the MLWF unique. The spread of the orbital is based on the functional Ω [2]:

$$\Omega = \sum_n [\langle 0n \mid r^2 \mid 0n \rangle - \langle 0n \mid r \mid 0n \rangle^2]$$

3 Band Structure Calculation

To compute the MLWF of magnetite we need the Bloch orbitals. Bloch orbitals are obtained from band structure calculations. We perform an ab initio calculation of the band structure using DFT+U. The functional for the DFT calculation will be the LSDA correlation functional. This functional is used because it takes into account the spin polarization of the bands is important for magnetite, a ferrimagnetic oxide (see above).

We also include a Hubbard term U for the band structure calculation. The justification of using the U is the anti-symmetric spin polarization of the A and B sublattice as shown in Fig 2. The mechanism of the anti-symmetric spin polarization of the A and B sublattice is the superexchange interaction mitigated by the ligands through a p-d hybridization of the orbitals. This shows strong

correlation between the short range electrons thus requiring a U term.

4 Disentanglment

Wannier functions have been used to study insulating systems, however we would also like to describe the conducting state of magnetite. This is where the use of MLWF is more advantageous over other methods of obtaining WF. We can use the algorithm of Souza, Marzari and Vanderbilt (SMV procedure) [1] to disentangle overlapping energy bands thus being able to use MLWF to study metallic behavior as well as insulating behavior.

We will use the SMV procedure to disentangle the overlapping bands of the t_{2g} orbitals of the B sublattice. The t_{2g} orbitals of the B sublattice contain the "extra" 3d electrons that are mainly responsible for the conduction properties of magnetite above T_V. This suggests that the extra 3d electrons are more delocalized than the rest of the electrons in the t_{2g} bands thus requiring disentanglement.

5 Conclusive Remarks

Magnetite is a technologically important material. There are still properties of magnetite that we do not understand and can be of future technological importance. To understand these properties we compute a set of Maximally Localized Wannier Functions which may shed light on the Verwey Transition

and the spin-glass-like transition. To obtain the MLWF we use an ab initio DFT+U calculation and transform the resulting Bloch orbitals. We need the Hubbard U term to account for the strong electron correlation that leads to the superexchange interaction that is the mechanism that keeps the spin polarization of the A and B sublattices anti-symmetric. A disentanglement procedure is then performed to account for the conducting state of magnetite above T_V.

References

1. I. Souza, N. Marzari, and D. Vanderbilt. "Maximally localized Wannier functions for entangled energy bands." Phys Rev B65 (2001) 0351909.

2. N. Marzari, and D. Vanderbilt. "Maximally localized generalized Wannier functions for composite energy bands." Phys Rev B56 (1997) 12847.

3. V. Anisimovy, F. Aryasetiawanz and A.I. Lichtenstein. "First-principles calculations of the electronic structure and spectra of strongly correlated systems: the LDA+U method". J. Phys. Condens. Matter 9 (1997) 767808.

4. D. Sholl and J. Steckel. "Density Functional Theory: A Practical Introduction". Wiley-Interscience (2009)

5. Z. Zhang and S. Satpathy. Electron states, magnetism, and the Verwey transition in magnetite. Phys Rev B44 (1991) 13319

6. D. L. Camphausen, J. M. D. Coey, and B. K. Chakraverty." One-electron energy levels in Fe3O4," Phys Rev Lett 29 (1972) 657

7. T. Her and C. Boekema. "Wannier states in magnetite", J. of Applied Physics 76 (1994) 6703