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## Band Theory of Multiple Ordering and the Metal-Semiconductor Transition in Magnetite

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A tight-binding calculation of the band structure of magnetite with Verwey ordering alone does not, for any strength of interatomic Coulomb energy, yield insulating behavior; for this, additional orderings in transverse directions are required. Below the Verwey temperature  $T_V$ , iron  $B$ -site charge densities are fractional (nonionic), continuous functions of  $T$ , and the gap is probably indirect with  $T$ -dependent band extrema ( $T \lesssim T_V$ ). There is semimetallic behavior above  $T_V$ . Multiple orderings allow a natural description of the extra Mössbauer spectra and neutron- and electron-diffraction patterns recently observed.

Originally, the low-temperature (119°K) metal-insulator transition in magnetite ( $\text{Fe}_3\text{O}_4$ ) was described as an ionic order-disorder transition,<sup>1</sup> the low-temperature phase consisting of alternate layers of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$   $B$ -site ions. Because of this ordering, electrons could hop only at the cost of a large intra-atomic Coulomb repulsion. Above 119°K ( $T_V$ ), because of the disorder, electrons were no longer inhibited from hopping, and the observed conductivity is in fact 100 times larger above  $T_V$  than below. Although many refinements<sup>2</sup> of this picture were subsequently introduced, the two essentials of the model, namely, its ionic nature and the type of ordering (alternate planes of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , Verwey order), remained unchanged.

It is now clear that the above picture is inadequate. Mössbauer<sup>3</sup> measurements are separable into five sets of spectra below  $T_V$ , one for the  $A$ -site  $\text{Fe}^{3+}$  ion and four for the  $B$ -site ions. Neutron<sup>4</sup> and electron-diffraction<sup>5</sup> studies show many more peaks, again below  $T_V$ , than those

describable as due to Verwey ordering.

We have recently<sup>6</sup> introduced a collective-electron description of magnetite which allowed us to break the first constraint mentioned above, namely, the description solely in terms of 2+ and 3+ ions. By oversimplifying to a one-dimensional model, we were able to calculate self-consistently the temperature dependence of an "order parameter" (the charge difference between two ions in the unit cell). The order parameter was proportional to the energy gap between valence and conduction bands, and vanished at the transition temperature, leaving a half-filled band at higher temperatures. There is strong experimental support and theoretical precedent for a band picture.<sup>7</sup> Although the charge around any site was no longer an integer, the symmetry was the same as that of Verwey, i.e., there was one-dimensional order.

We now find qualitatively different features in three dimensions, and the concept of a multiple order parameter arises *perforce*. In the magne-

tite structure Verwey ordering alone can never produce an insulator, but ordering along the transverse axes is also required. The calculation is based on the following Hamiltonian:

$$H = \sum_{i,j,\alpha\beta} \epsilon_{i\alpha j\beta} c_{i\alpha}^\dagger c_{j\beta} + \sum_{i\alpha,j\beta} u_{i\alpha j\beta} n_{i\alpha} n_{j\beta}. \quad (1)$$

The  $i$  and  $j$  sums are over the fcc lattice of  $B$ -site ions.  $\alpha$  and  $\beta$  refer to the four ions within the unit cell.  $c_{i\alpha}^\dagger$  creates an electron in the Wannier state  $i, \alpha$ , and  $n_{i\alpha} = c_{i\alpha}^\dagger c_{i\alpha}$ .

There are no spin indices; the very large Hund's-rule energies rule out spin-flip transitions. Thus, we regard the spin-down  $d$  bands as completely full and inert for our purposes. Crystal fields further split the five spin-up  $d$  bands into two doublets, and a singlet lying lowest.<sup>8</sup> It is these singlet states which are described by the Hamiltonian (1). Since magnetite has two spin-up electrons in the unit cell, the Brillouin zone is half full.

We now make the Hartree-Fock approximation,

$$n_{i\alpha} n_{j\beta} \rightarrow \langle n_\alpha \rangle n_{j\beta} + \langle n_\beta \rangle n_{i\alpha}, \quad (2)$$

where angular brackets indicate both temperature and quantum averages. We consider the "disordered" phase first. Using (2) with  $n_\alpha = n_\beta = \frac{1}{2}$  in (1), and making a Fourier transform of the operators appearing in (1), we find

$$H_{\text{HF}} = \sum_{\vec{k}} \sum_{\alpha\beta} \epsilon_{\alpha\beta}(\vec{k}) a_\alpha(\vec{k}) a_\beta(\vec{k}),$$

where, in tight binding,

$$\epsilon_{\alpha\beta}(\vec{k}) = \hbar [1 + \exp(2i\vec{k} \cdot \vec{\tau}_{\alpha\beta})], \quad \epsilon_{\alpha\alpha} = \epsilon. \quad (3)$$

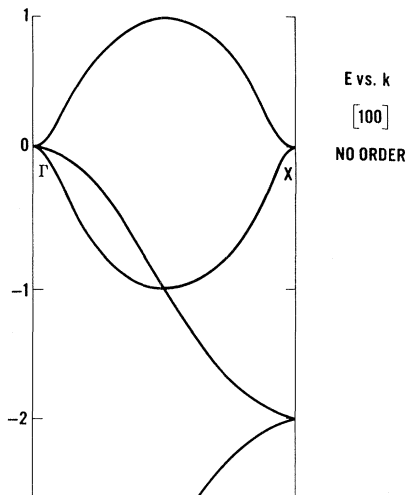


FIG. 1.  $E$  vs  $k$  along [001] in the metallic phase. Note the two overlapping bands. (There are two electrons per unit cell.)

$\hbar$  is proportional to overlap and potential integrals, and is independent of  $\vec{k}$ ;  $\vec{\tau}_{\alpha\beta}$  is the vector connecting sites  $\alpha$  and  $\beta$  in the unit cell; and  $\epsilon$  is the energy of the singlet level. The term proportional to  $u\langle n \rangle$  has been dropped, since it only shifts the energy by a constant. (This term should be considered to have already contributed to the crystal-field splitting mentioned above.) Results of a diagonalization of (3) are given in Fig. 1, where the eigenvalues  $E(k)$  of (3) are plotted for  $\vec{k} \parallel [001]$ . We see that the high-temperature phase is semimetallic, two bands overlapping at the Fermi level, determined by requiring the four-band zone to be half full.

Next, suppose we attempt to describe the  $T < T_V$  phase by Verwey ordering, i.e.,

$$\begin{aligned} \langle n_\alpha \rangle &= n_1, & \alpha &= 1, 3, \\ \langle n_\alpha \rangle &= n_2, & \alpha &= 2, 4. \end{aligned} \quad (4)$$

$H_{\text{HF}}$  is again of the form (3), but with

$$\epsilon_{\alpha\alpha} = \epsilon + (-1)^\alpha u m_1, \quad (5)$$

where

$$m_1 = n_1 - n_2. \quad (6)$$

This ordering causes the threefold degenerate level at  $k=0$  to split in three, but does not break the twofold degeneracy at  $\vec{k} = [100]$  and  $[010]$ . This is illustrated in Fig. 2 for  $u m_1 = 0.4$ . Because of this degeneracy and the fact that the ordering of the  $k=0$  levels is fixed, no gap appears in  $E(k)$ , no matter how large we choose  $u m_1$ . Thus within the band scheme, Verwey order

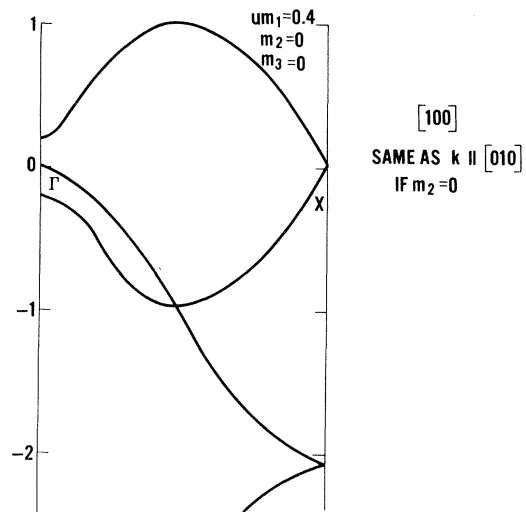


FIG. 2.  $E$  vs  $k$  along [100] for Verwey order alone ( $m_1 \neq 0$ ). The bandwidth is 1. Two bands still overlap no matter how large  $u m_1$ .

alone cannot yield insulating behavior. This is in striking contrast to the one-dimensional models, where infinitesimally small interactions make the metallic state unstable.

We next lower the symmetry by making  $n_1 \neq n_3$ ,  $n_2 \neq n_4$  (ordering along the  $a$  and  $b$  axes), and finally  $n_2 - n_4 \neq n_1 - n_3$  ( $a$ -axis ordering different from  $b$ -axis ordering). We then have two more order parameters

$$2m_2 = (n_1 - n_3 + n_2 - n_4), \quad (7)$$

$$2m_3 = n_1 - n_3 - (n_2 - n_4). \quad (8)$$

We have diagonalized  $H_{\text{HF}}$  with these three order parameters (for charge neutrality the average number of electrons per cell was fixed at two) for different values of  $um_1/h$ ,  $um_2/h$ , and  $um_3/h$ . We find that semiconduction can be achieved provided  $m_1, m_2 \neq 0$ , at the expense of large  $u/h$ . However, the  $u/h$  value required to split the bands completely can be considerably lowered by making  $m_3 \neq 0$ , as well as  $m_1, m_2 \neq 0$ . Figure 3 shows the band structure along [001] for  $um_1 = 2$ ,  $um_2 = 1$ , and  $um_3 = 1$ . The valence-band maximum for this case is actually near an  $L$  point. We believe that a self-consistent calculation will require all three  $m$ 's to be nonzero in the  $T < T_V$  phase. This of course means four different charge densities in the unit cell, accounting for the four distinct  $B$ -site Mössbauer spectra seen below  $T_V$ , and for many of the observed neutron- and electron-diffraction peaks.

The orderings so far described have not affected the crystal symmetry, i.e., we restricted ourselves to breaking site equivalence within the cubic unit cell. Lowering the crystal symmetry by doubling the unit cell, for example, introduces at least one more order parameter. This extra broken symmetry would account for the  $(h, k, l \pm \frac{1}{2})$  lines seen in both neutron and electron diffraction.

As a final point, we note that the valence- and conduction-band edges are at different points in the Brillouin zone. Both the size of the indirect

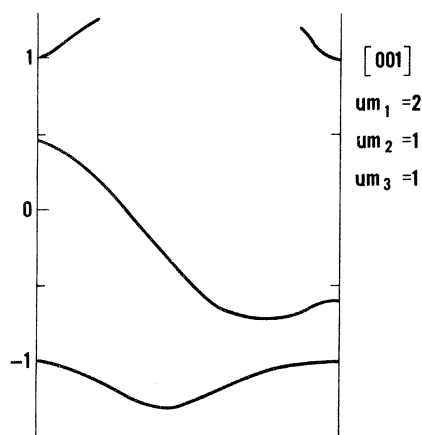


FIG. 3.  $E$  vs  $k$  along [001].  $m_1, m_2, m_3 \neq 0$ . There are gaps in all directions. The valence-band maximum is at an  $L$  point for the  $m_i$  chosen. The conduction-band minimum is near [001]. For these  $m_1$  and  $m_2$ , the indirect gap disappears for  $um_3 \leq 0.85$ .

gap and the positions of the extrema should be temperature dependent.

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