ANTIFERROMAGNETISM IN Ti_2O_3

David Adler
Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received 13 June 1966)

A Hartree-Fock theory of itinerant antiferromagnetism is presented and is applied to explain the observed electric and magnetic properties of Ti_2O_3.

In a recent series of Letters,[1] deGraaf and Luzzi have attempted to explain the antiferromagnetic properties of Ti_2O_3[2] by a spin-density-wave calculation. However, the theory they presented assumes that the spin-density-wave energy gap is much greater than the band width, an assumption which always gives a sublattice magnetization very close to saturation. But Abrahams found that the actual sublattice magnetization for Ti_2O_3 is very small, only $0.2\mu_B$.[2] Thus this particular model cannot apply to Ti_2O_3.

Matsubara and Yokota[3] developed a zero-temperature band theory of antiferromagnetism which showed how a small moment could be obtained by using an itinerant model, but the extension to finite temperatures did not give good results. In this Letter, we shall present a zero-temperature theory equivalent to that of Matsubara and Yokota, and then extend it self-consistently to finite temperatures. We shall then apply the results to the electric and magnetic properties of Ti_2O_3.

Consider a one-dimensional antiferromagnetic crystal, with N magnetic ions spaced $a/2$ apart. Let the one-electron Hamiltonian of the system be written

$$H(x,\sigma)=T(x)+V(x)+V_{\text{ex}}(x,\sigma), \qquad (1)$$

where $T(x)$ is the kinetic energy of the electron and its interactions with the fixed ions, $V(x)$ represents that part of the electronic Coulomb and exchange interactions which does not depend on spin, and $V_{\text{ex}}(x,\sigma)$ is the spin-dependent part of the exchange interactions. In the Hartree-Fock approximation, the last two terms are self-consistent ones which depend on the state of the system. We write the Bloch wave functions as

$$\psi_i(k,x)=(N/2)^{-\frac{1}{2}}C_{1i}(k)\sum_n e^{ikna}\varphi(x-na)+(N/2)^{-\frac{1}{2}}\times C_{2i}(k)\sum_n e^{ik(n+\frac{1}{2})a}\varphi[x-(n+\tfrac{1}{2})a], \qquad (2)$$

where $\varphi(x-x_n)$ are the Wannier functions associated with x_n. Solving the resulting secular equation in the approximation of nearest-neighbor interactions yields

$$E(k)=E_0\pm[(E_g/2)^2+4\beta^2\cos^2(ka/2)]^{1/2}, \qquad (3)$$

where

$$E_0\equiv(\alpha+\alpha')/2,\quad E_g\equiv\alpha-\alpha',$$
$$\alpha\equiv\int dx\varphi^*(x)H(x)\varphi(x),$$
$$\alpha'\equiv\int dx\varphi^*(x-a/2)H(x)\varphi(x-a/2),$$
$$\beta\equiv\int dx\varphi^*(x)H(x)\varphi(x-a/2).$$

Thus, if $\alpha\neq\alpha'$, there is a splitting of bands into two, with an energy gap equal to $\alpha-\alpha'$ introduced at the edges of the new reduced first Brillouin zone. If there is one electron per ion outside of the closed shells, the paramagnetic solution ($\alpha=\alpha'$), always a possible self-consistent state, results in a half-filled band, and the material will be metallic. However, if a self-consistent solution is possible with $\alpha\neq\alpha'$, the lower half of the band is depressed in energy, and the electrons present fill this band exactly, resulting in an insulating state. Calculation of the spin density in this case shows that the state is antiferromagnetic with a moment of

$$M(0)=\sum_k[\tfrac{1}{2}\cos\theta(k)]N\mu_B, \qquad (4)$$

where μ_B is a Bohr magneton, and

$$\tan\theta(k)\equiv4\beta\cos(\tfrac{1}{2}ka)/E_g.$$

Since 4β is the paramagnetic band width, the sublattice magnetization is a function of the ratio of band width to band gap. If this ratio is large, $\theta(k)$ is near $\pi/2$ everywhere except very close to the band edges, $\cos\theta(k)$ is thus very small almost everywhere, and the antiferromagnetic state produced has a very small moment. In order to obtain the moment $0.2\mu_B$ appropriate to Ti_2O_3, the width of the valence band must be 6 times the band gap. Since Ti_2O_3 has a band gap of 0.06 eV,[4] this would imply a valence band 0.4 eV wide.

The above is a zero-temperature theory only, and cannot be extended to finite temperature simply by treating the material as a normal semiconductor, even though such a theory would show a typical decrease of magnetization with thermal population of the upper band. However, this procedure is incorrect for a number of reasons which emerge when a careful self-consistent theory is developed.

The first point to consider is that we are dealing with a fully interacting system. In fact, it was crucial to include the exchange-energy term in the Hamiltonian (1) in order to obtain any magnetic solutions at all, and this term represents a pure interaction term. Thus, if we were to write down the total energy of the ground state of the antiferromagnetic system by filling up the lower band in (3) with electrons and adding up the one-particle energies of the band, we would obtain an incorrect result since we would have counted the electronic interactions twice. In order to find the correct total energy, we must subtract off half the sum of the interactions. The important term, insofar as the magnetic properties of the system are concerned, is the spin-dependent term $V_{\text{ex}}(x,\sigma)$ in (1). It is the fact that matrix elements of this term can differ for spin-up and spin-down states which leads to a nonzero $\alpha-\alpha'$ in (3), and thus a nonzero sublattice magnetization in (4). If we turn off the exchange interactions given by this term, we always obtain the paramagnetic bands represented by (3) with $E_g=0$. Thus we can easily subtract the sum of these exchange interactions from the sum of the one-particle energies and obtain a better value for the total ground-state energy of the system. A simple way of calculating this quantity is to evaluate

$$E(0)=\tfrac{1}{2}\sum\nolimits_k[E(k)+E_{E_g=0}(k)],\tag{5}$$

where the sum is over the states in the lower band and the second term on the right represents the energies in (3) with $\alpha=\alpha'$.

We still have said nothing about the excited states. One might now think that the energies of the excited states can be obtained in a manner completely analogous to (5) by filling up states in the upper band of (3), leaving holes in the lower band, and remembering to subtract off half the sum of the interactions from the sum of the one-particle energies. However, even this would not be correct. The reason in this case is that the one-electron spectrum given by (3) is true only for the ground state, and is wrong for the excited states.

The simplest way of seeing this is to excite a sufficient number of electrons from the lower to the upper band of (3) such that the magnetization given by (4) vanishes. In the procedure described above, this point would be identified as the Néel point of the system. The state is not antiferromagnetic, and thus the matrix elements of the exchange potential must be spin independent. Consequently, it is inconsistent to use the spectrum (3) with an energy gap, E_g, which can arise only from a spin dependence of V_{ex}.

The proper result emerges directly from the Hartree-Fock approximation. The term V_{ex} in (1) is a self-consistent one, and contains in it a sum over occupied states. Thus changing the occupations not only changes the total energy of the state, but it also changes the Hamiltonian itself, and thus the entire one-particle spectrum. It is clear, in general, that the spectrum of (3) is properly modified by taking E_g to be a power series in odd powers of sublattice magnetization. In particular, for cases such as Ti_2O_3, for which the initial moment is small, the gap can be taken proportional to the magnetization:

$$E_g(x)=E_g(0)M(x)/M(0),\tag{6}$$

where x is a parameter which describes the excited states of the system. In the model under consideration, a two-band semiconductor, x can be taken to be the fraction of carriers excited from the lower to the upper band: $x\equiv n/N$. Using (6) and again remembering to subtract off half the sum of the interactions from the sum of the one-particle energies, we obtain the total energy of the excited states:

$$E(x)=\tfrac{1}{2}\sum\nolimits_{\text{occ }k}[E_{E_g(x)}(k)+E_{E_g=0}(k)],\tag{7}$$

where the sum is over the occupied states in each band. For the excited states, we must use the generalization of (4):

$$M(x)=\sum\nolimits_{\text{occ }k}(\mp)[\tfrac{1}{2}\cos\theta(k)]N\mu_{\text{B}},\tag{8}$$

where the upper sign is taken for an electron in the upper band and the lower sign is taken for an electron in the lower band. Equation (8) can be expressed in terms of incomplete elliptic integrals of the first kind, which can be

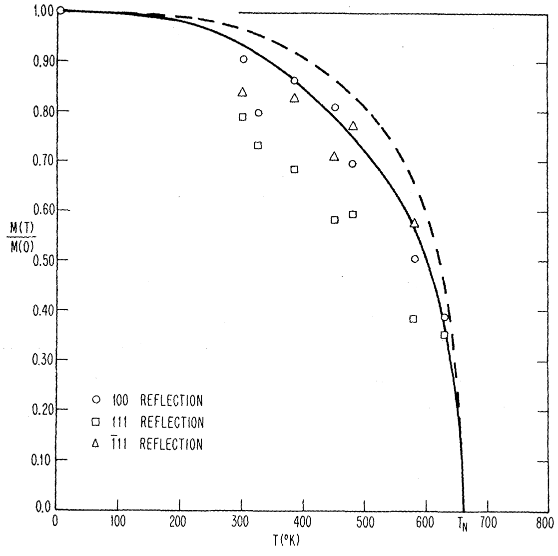

FIG. 1. Magnetization as a function of temperature for Ti_2O_3. The solid line represents the theoretical results for the model presented here. The dotted line is that Brillouin function normalized to the same initial magnetization and same Néel temperature. The experimental points are the neutron-diffraction results of Ref. 2.

evaluated from tables. Furthermore, substitution of (3), (6), and (8) in (7) leads to an expression for $E(x)$ which consists of incomplete elliptic integrals of the second kind.

Having evaluated $E(x)$, we have all the energy levels of the system; $E(0)$ represents the ground state and $E(\frac{1}{2})$ represents the paramagnetic, metallic state. Thus we can write down the partition function:

$$Z=\sum_{x=0}^{1/2} e^{-E(x)/kT},$$

and the free energy

$$F=-kT\ln Z.$$

At a given temperature the system will be in the state which minimizes the free energy. Thus minimization of F with respect to x gives an expression for x as a function of T. Since resistivity can be expressed

$$\rho=[Ne\mu x]^{-1},$$

where μ is the mobility, assumption of a constant mobility gives us $\rho(T)$. Furthermore,

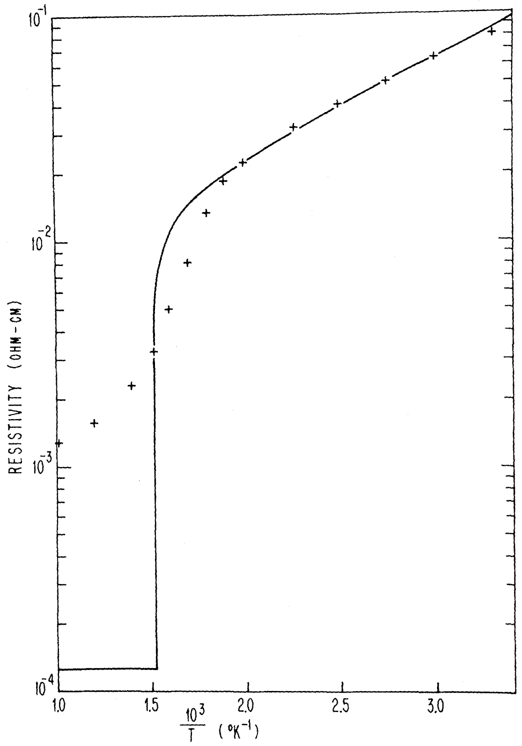

FIG. 2. Resistivity as a function of temperature for Ti_2O_3. The experimental points are taken from Ref. 2.

substitution of $x(T)$ into (8) enables us to evaluate sublattice magnetization as a function of temperature, $M(T)$.

There are two parameters in the present model. However, for the case of Ti_2O_3, we know from the work of Abrahams[2] that $M(0)=0.2N\mu_B$ and $E_g(0)=0.06$ eV. Thus we can evaluate resistivity and magnetization as functions of temperature. The results are given in Figs. 1 and 2 and compared with Abraham's experimental results. The resistivity was calculated assuming a temperature-independent mobility of 2 cm^2/V-sec.

---

*Work supported by the Advanced Research Projects Agency.

[1] A. M. DeGraaf and R. Luzzi, Phys. Letters 18, 235 (1965); 19, 92 (1965).

[2] S. C. Abrahams, Phys. Rev. 130, 2230 (1963).

[3] T. Matsubara and Y. Yokota, in Proceedings of the International Conference on Theoretical Physics, Kyoto and Tokyo, September, 1953 (Science Council of Japan, Tokyo, 1954), p. 693.

[4] J. Yahia and H. P. R. Frederikse, Phys. Rev. 123, 1257 (1961).