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ON INSULATOR-METAL TRANSITION IN Fe₃O₄

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Résumé. — On analyse la transition isolant-métal dans Fe₃O₄ à partir de la corrélation électron-électron sur les sites proches voisins. On utilise une technique de fonction de Green de Zubarev, deux fois retardée (1). On montre, à l'aide de considérations sur l’énergie libre, que l’état localisé des électrons est plus stable à basse température que l’état de bande et qu’une transition état localisé-état de bande doit avoir lieu à 120 °K.

Abstract. — Insulator-Metal transition in Fe₃O₄ is analysed on the basis of nearest neighbor electron-electron correlation. A double time Zubarev Green function (1) technique is used. Free energy considerations show the localised state to be thermodynamically more stable than band state. System makes a localised state band state transition at 120 °K.

On the basis of the observed abrupt conductivity change at the insulator-metal transition temperature 120 °K, Verwey [2] proposed that below this temperature the Fe²⁺ and Fe³⁺ cations on the octahedral sites are completely ordered. The so-called Verwey transition corresponds to a classical electronic order-disorder change. Experimental results on this system have been summarised by Adler [3]. The ferrimagnetic property, neutron diffraction and Mossbauer effect have subsequently substantiated partly the Verwey picture, although Anderson [4], as early as 1958, cast some doubt on this completely localised electron model, on the basis of abnormally low observed critical temperature. In this article, we develop a band picture (*) of the electrons, compare the internal energies of the band and the localised model and derive certain conclusions.

The basis of our concept is the next nearest neighbor electron-electron repulsion in the octahedral sites. We imagine the sixth extra 3-d electron to be exchange split (crystal field is smaller) from the other five, and hence forming a band by site to site hopping (there is always an empty place available on a neighboring octahedric site). On the other hand the repulsion of this electron from another one of its kind tends to create an ordered cation). On the other hand the repulsion of this electron
to create an ordered cation). On the other hand the repulsion of this electron and Fe³⁺ ions amongst the octahedral sites.

The interaction terms are Hartree-Fock linearised by use of expansions of the type (to avoid 2-particle Green functions decoupling)

\( v_{AB} n_i^a n_j^b = v_{AB} < n_i^a > n_j^b + v_{AB} < n_j^b > n_i^a \), etc...

(1a)

where \(< >\) signifies average quantity.

We want the one-particle Green functions

\[
G^{AA} = < C_i^a C_i^a > \\
G^{BA} = < C_i^a C_i^b > 
\]

(2)

From the equation of motion of the Green’s function

\( \omega < A, B > \geq \frac{1}{2\pi} < [A, B] > + < [A, H] > B > ... \)

(3)

where \( A, B \) are the \( C_i \) operator set sin équation (2), we obtain

\[
(\omega - \mu + < n^b > \nu) G^{AA} - T(k) G^{BA} = -\frac{1}{2\pi} \]

(3a)

\[
(\omega - \mu + < n^b > \nu) G^{BA} - T(k) G^{AA} = 0 \]

Here \(< n^b > < n^a > \) are the average expectation values of finding an electron on \( B \) & planes are normalised by

\[
< n^a > + < n^b > = 1 \\
< n^a > - < n^b > = S
\]

(4)

where \( S \) is the Verwey order-parameter.

In (3a) \( T(k) \) \( T_0 \cos \alpha_0 k, \) \( T_0 \) being the band-width.

\( v = Z_{AB} - Z_0 v_0 \), being an effective inter-particle repulsive interaction, \( Z \) being the number of nearest neighbors on AB planes, \( Z_0 \) \( v_0 \) that on AA or BB pairs.

From (3a) and the poles of the Green function, one obtains the excitation energy

\( (*) \) Cullen in this Conference also presents a band model of Fe₃O₄, although his conclusions, as well as approach, are different from ours.
Thus electron-electron repulsive correlation gives a band-gap.

$$E_g = vs (5a),$$

which brings about the insulating state at \( T = 0 \).

The order-parameter is determined exactly the same way as the superconducting gap, with the self-consistency equation

$$\sum \frac{v}{N E(k)} [f(-E_k) - f(E_k)] = 1 \quad (6)$$

where \( f's \) are the Fermi functions.

The critical order-disorder temperature is also similar to superconductors and is given by

$$T_d = \frac{T_0 \exp - T_0}{4 k_B T} \quad (7)$$

For experimentally observed \( v \sim 0.5 - 1 \) eV (from \( E_g \) value measured from conductivity measurement), one can obtain a \( T_d \sim 120 \) K, if one assumes a band-width interaction. This however raises two serious difficulties:

a) For a \( (T_0/v) \sim 2 \), the value of \( S \) at \( T = 0 \), is never 1 but is \( \sim 0.5 \); as a matter for any non-zero value of \( T_0/v \), \( S \) from equation (6) at \( T = 0 \), is never \( (\text{saturated}) \) i.e. 1. This is contrary to neutron-diffraction results.

b) 120 K can hardly be identified with \( T_d \), as the experimentally measured conductivity monotonically rises after 120 K up to 300 K by a factor of 5.

In order to test whether the band-state is truly the lowest energy state (at \( (T_0/v) \sim 2 \)) compared to the localised classical Verwey state, we have compared their relevant enthalpies (that of band-state obtained directly for the Green's function correlation function & hamiltonian of equation (1) and that of localised state is just the Bragg-Williams value); these are (similar results have also been obtained by Penn [6], Johansson and Mattis)

$$<H>_{\text{band}} = \frac{v}{4} (1 - S^2) - \frac{1}{N} \sum T^2(k) \tanh \frac{E(k)}{2 k_B T} \quad (8a)$$

$$<H>_{\text{localised}} = \frac{v}{4} (1 - S^2) . \quad (8b)$$

Note the relevant \( S's \) are determined by different equations. We find that for \( (T_0/v) \sim 2 \), the localised « Verwey » state is indeed of lower energy than band state up to a critical temperature \( T_0 \sim 120 \) K (i.e. \( S \sim 0.5 \), at which a localised state to band state transition takes place. From \( T_0 \) onward the system behaves in accordance with equations (6) and (7), being completely disordered at a \( T_d \sim 300 \) K. If the system stayed in the localised state, it would have had a transition temperature \( \sim 10^8 \) K-10^9 K. The proposed disordering scheme is shown in figure 1.

A further support that below \( \sim 100 \) K, the system is not in a band state comes from a close examination of the conductivity Vs temperature curve of Calhoun [7]. Contrary to Adler's hypothesis, that the observed continually varying activation energy is due to some extrinsic impurity states, we have applied to the data, the Mott equation [8] for random localised state conduction (\( \log \sigma \sim A/T^{4/5} \)) which is shown in figure 2. We see that the Mott-equation is completely vindicated. An exact choice of \( T_0/v \) value to obtain the correct \( T_c \) and \( T_d \) is under calculation.

![Proposed disordering scheme in Fe_3O_4](image)

**Fig. 1.** — Proposed disordering scheme in Fe_3O_4.

**Fig. 2.** — Conductivity of Fe_3O_4 vs inverse temperature.
References


