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THE METAL-NON-METAL TRANSITION

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Abstract. — The metal-non-metal transition discussed in this paper is that which takes place as a consequence of the correlation energy \( e^2/r_{12} \), when the distance \( r \) between atoms is changed. The clearest example is heavily doped germanium. In a crystalline cubic or disordered lattice of one-electron atoms, as \( r \) increases, two transitions are to be expected:

(a) The appearance of itinerant antiferromagnetism. This will split the band, as first suggested by Slater (1951).

(b) The disappearance of metallic conduction (the MNM transition). It is suggested that this occurs when the two (Hubbard) sub-bands overlap, that antiferromagnetism will normally persist in the metallic state, and that the density of states \( N(E_F) \) drops near the transition. Evidence that this is so for heavily doped semiconductors and metal-ammonia is presented. According to Landau’s criterion the formation of moments should be second order, but it is suggested that for two slightly overlapping bands it may be first order and that this is what is happening in \( \text{V}_2\text{O}_3 \). Finally, a discussion is given of NiS in terms of spin polarons.

I would like to start by discussing nickel oxide, the material which in 1937 first made us realise that the Bloch-Wilson theory of metals and insulators was not always adequate (de Boer and Verwey [1]). There is no mystery about this; for these antiferromagnetic materials, if one uses a spin-dependent potential, one can treat such materials at zero temperature by normal band theory (Slater [2, 3], Wilson [4]). However, I think it is simpler to start with a many-body approach, which shows at once why the non-metallic property does not disappear at the Néel temperature. One knows that \( \text{NiO} \) becomes a semiconductor through the introduction of \( \text{Li}_2\text{O} \); the \( \text{Ni}^{2+} \) ion thus introduced can move through the lattice with a wave-vector \( \mathbf{k} \) and a band of possible energy values [5]. The process is illustrated in Figure 1. Let \( \Psi_n \) be the many-electron wave function (Slater determinant) for the crystal in which the electron is missing from the atom at site \( n \). Then the function

\[
\sum_n \exp(\mathbf{i} \mathbf{k} \cdot \mathbf{r}_n) \Psi_n
\]

represents the « hole » moving through the lattice with wave vector \( \mathbf{k} \) (Fig. 1). The energy \( W \) of a hole moving in this way will have the familiar form for tight binding theory, namely (in one dimension)

\[
W = J(1 - \cos k a)
\]

In the same way one can describe the crystal in a situation when an extra electron is introduced onto atom \( n \), and set up the many-electron wave function \( \Psi'_n \); I shall denote by \( 2J' \) the band width corresponding to the movement of this electron.

If the overlap between atomic orbitals is small, so that \( J \) and \( J' \) are small, the energy to form a pair of carriers is \( I - E \), where \( I \) is the ionisation energy and \( E \) the electron affinity of each ion, in the environment of the oxide crystal. As \( a \), the distance between centres, decreases, the energy \( \varepsilon \) necessary to form a pair of carriers, given by

\[
\varepsilon = I - E - J - J'
\]

will decrease. It will eventually become zero, which is the point at which the MNM transition takes place. This simple model was first put forward by Nishimura [6] in a paper on impurity conduction.

With this model, we see that:

(a) Antiferromagnetic order is supposed to continue on the metallic side of the transition [7], so that the two Hubbard bands can overlap (Fig. 2).

(b) The density of states just on the metallic side is zero, as in Hubbard’s [8] model.

(c) On the metallic side, the material should behave as a semimetal as regards its thermopower, Hall effect.
FIG. 2. — Two overlapping Hubbard bands, on the assumption that the disappearance of the moments is second order. \( s_2 \) is the energy required to produce a pair of carriers. AF ordering disappears at M. The density of states is also shown for a value of \( a \) such that bands overlap but moments have not yet disappeared. In this case in disordered structures there may be a range of localised states (shown shaded) and the MNM transition will occur when this disappears.

Coefficient, etc. In particular, the resistivity at low temperatures should behave like \( T^2 \) (Baber [9] scattering).

(d) The magnetic moments should give rise to a negative magnetoresistance.

Very near the transition, as pointed out in my earlier papers [10], a small concentration of electrons and holes is not possible, as they will combine to form pairs (like excitons). This consideration led me to predict the formula

\[
n^{1/3} a_{1/2} \sim 0.25
\]

for the concentration \( n \) of electrons at the transition, a formula which is in good agreement with experiment for doped semiconductors. The recent work [11] on the "excitonic insulator" has developed this theme in detail. Such effects have not with certainty been observed.

The description I have given here of the MNM transition makes the setting up of magnetic moments the cause of the transition. One has next to ask whether, starting from the metal when the interatomic distance is increased, the setting up of moments is a first or second order transition. The considerations of Landau (1937) suggest that it should be second order. The argument is a simple one. At \( T = 0 \) one would always expect the energy \( E \) of the system to be a quadratic function of \( M \) (the moment on each atom), so that

\[
E = AM^2 + BM^4 + \ldots
\]

The transition occurs, as the lattice parameter \( a \) or some other parameter changes, when \( A \) vanishes; beyond this point \( M = \sqrt{(-A/2)} \), giving a variation of \( M \) with \( a \) as in figure 3. The anticipated plots of \( E \) against % for the transition are shown in figure 4a. There is however nothing in Landau’s argument to prevent the plot of \( E \) against \( M \) from looking as in figure 4b; if so there will be a first order transition. Moreover, the decision between (a) and (b) is likely to depend on the density of states. One can produce small moments (as in chromium not necessarily coherent with the lattice) by using wave functions with energies near the Fermi energy, so that the expenditure of kinetic energy is small; to make large moments one must use the whole band. I will therefore hazard a conjecture, and suggest that when the density of states has a maximum near the Fermi energy the curve is of type 3 a and the transition is of second order; starting from the metal, magnetic ordering then appears before the MNM transition; when on the other hand the density of states has a minimum there, then case (3 b) obtains and the transition is first order. The latter is likely to be the case when, in the non-magnetic state, there are two separate or slightly overlapping bands, the lower one containing one electron per atom. A transition of this kind from a magnetic to a non-magnetic can occur in a non-metal as pointed out by Zinamon [13], and I believe it should be first order.

You will hear later in this conference about the impressive experimental work on V\(_2\)O\(_3\) carried out at the Bell Telephone and Oak Ridge Laboratories [14, 15] and this is what I think is happening in this material. The metallic phase, which is not antiferromagnetic, following the work of Nebenzahl and Weger [16] is a semimetal with slightly overlapping bands, the carriers having mass considerably enhanced by polaron formation [17]. The MNM transition is essentially due to the formation of moments and these lead to a band splitting as in NiO. In the metallic phase, states with moments are easily excited by temperature, as the magnetic properties show.

I now turn to my hypothesis that moments can form by a second order transition, in which case the MNM must involve a sequence of transitions as Kohn [18] envisaged in 1967. If this is so one might hope to find some simple antiferromagnetic metals. A possibility is the compound Li(NH\(_2\))\(_4\) which is metallic and has

FIG. 3. — Showing the AF moment according to Landau as a function of lattice parameter or some other parameter.

FIG. 4. — Suggested plots of \( M \) against \( a \)
(a) Normal metal \( (a_1 < a_2 < a_3) \).
(b) Semimetal \((N(E_F) \) small).
some of the electrical properties of a two band metal [19]; NMR or neutron diffraction experiments to determine whether the lithium atoms have moments would be of real interest.

But on the whole one must rely on heavily doped semiconductors, metal-ammonia and other disordered systems to study the MNM transition under conditions when I would expect a second order transition. One has to ask for such systems:

(a) Do moments persist some way into metallic concentrations?

(b) Does the density of states drop near the transition, as it should according to the model of figure 2 with two overlapping Hubbard bands? This is particularly important because according to the recent treatment of Brinkman and Rice [20] a highly correlated electron gas near the transition but with no AF ordering should show a high density of states.

First of all, the disorder presents no problem. Following the recent work on Anderson localisation [21], the two bands of figure 2 (the $e_2$ and $e_3$ bands in semiconductor notation) should have localised states in their tails, and the MNM transition appears as an Anderson transition which occurs when the states at $E_F$ are first non-localised. Considerations given by Mott [21] suggest that $e_2$ should behave like $(a - a_0)^{3/2}$ at such a transition where $a$ is the distance between centres and this seems to agree with experiment (see the plot of $e_2$ in ref. 22). As regards the question of moments, if random fixed moments (Anderson [23]) exist on the centres they would greatly increase the disordered potential seen by the electrons, and I believe that one may in this way be able to explain qualitatively the negative magnetoresistance shown by these materials [24]. Toyazawa [25] was the first to assume the existence of moments to explain the negative magnetoresistance; his moments were due to density fluctuations, mine to proximity to the MNM transition.

What evidence have we that the density of states drops? In liquid metals and semimetals the Knight shift is a powerful tool for investigating the density of states; in liquid tellurium and more particularly such liquid alloys as Ga$_2$Te$_3$ it seems that at low temperatures one has more or less separate valence and conduction bands but that, as the temperature is raised, the co-ordination number changes and the energy gap fills up. The Knight shift, therefore, measures $N(E_F)$ in the middle of a pseudogap and rises markedly with temperature (Warren [24]). The same should happen for the pseudogap occurring when the two Hubbard bands of figure 2 overlap. But these bands can only exist if the atoms carry fixed moments, and in a solid the moments will broaden the NMR line. In a liquid, however, the changing configuration of the atoms will average out the magnetic field due to the moments so that the Knight shift can be measured. Acrivos and Mott [26] have analysed various measurements of the Knight shift in metallic Na-NH$_3$ near the transition; the Knight shifts falls with conductivity as the concentration of metal decreases and values of the density of states deduced from the two quantities correspond well.

Finally, I would like to say something about the spin polaron. The work particularly of the IBM group [27] shows that in semiconductors such as EuS heavily doped with GdS the electrons in the 6 $s$ conduction band have the following effects:

(a) They line up the 4 $f$ spins parallel to themselves, forming spin polarons.

(b) The spin polarons interact ferromagnetically, so that the Curie temperature is greatly enhanced.

In materials on the metallic side of the MNM transition, if moments persist, there should be some such effect. I would like to draw your attention to NiS, which shows (Sparks and Komoto [28]) a MNM transition at 270 $\text{K}$; the material is antiferromagnetic in the semiconducting phase with a moment of 2 $\mu_B$, but with no long range order above the transition. Now it seems to me most unlikely that the moments on the Ni$^{2+}$ ions just disappear, the Ni going into a zero spin state. It is much more plausible that the 3 $d^8$ states nearly overlap the conduction (4 $s$) band; at the transition a small number of conduction ($4s$) electrons and 3 $d^7$ ions are formed, the entropy of which provides the driving force, but the ferromagnetic interaction between the $4s$ electrons and the spins on the 3 $d^8$ and 3 $d^7$ ions is sufficient greatly to lower the Néel temperature, or even to produce a low Curie temperature, so that the material is above its magnetic transition temperature. The small change ($\sim 10\%$) in the susceptibility suggests that the moments do not disappear.

Sparks and Komoto find that more than 3 $\%$ excess sulphur greatly depresses the transition temperature, and extrapolation suggests that the metallic phase would be stable at $T = 0$ for more than 4 $\%$. Studies of the magnetic properties of these alloys at low temperatures would be of great interest; ferromagnetism or antiferromagnetism with a low Néel temperature is predicted.

Another material to which this model might perhaps be applied is CrO$_2$, which is ferromagnetic and metallic [29].

References

[26] Acivos (J.), Mott (N. F.), Phil. Mag., 1971, to be published.