INSULATOR-METAL TRANSITION

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ABSTRACT

A theory of the insulator-metal transition in transition-metal compounds is developed in terms of the collapse of the effective energy gap which is a function of the thermally excited electron-hole pairs. This dependence is shown to arise from the hole-lattice interaction. The reaction of the lattice is found to be equivalent to generating an internal positive pressure (strain). Estimates show that the observed typical behaviour of the conductivity jump and the change of volume at the transition temperature can be explained by the present theory.

1. INTRODUCTION

THE experimental behaviour of several transition-metal oxides and chalcogenides such as VO, $(V_{1-x}\ Cr_x)_2\ O_3$, VO_2, Fe_3O_4, NiS, Ti_2O_3, etc., has received considerable theoretical attention in the recent past (Ramirez, Falicov and Kimball, 1970). These compounds exhibit insulator to metal transition as a function of increasing temperature and pressure (Mott, 1969; Adler and Brooks, 1967; Falicov and Kimball, 1969). For these systems the conventional Bloch-Wilson band picture would predict a metal-like behaviour at the absolute zero of temperature in that the metal ions contain partially filled $3d$ shells which should be broadened into sub-bands by the overlap effects. However, some of these are known to exist in a low-temperature insulating phase. The latter phase shows antiferromagnetic ordering of the metal ions (V_2O_3, NiS). The magnetic ordering is, however, not necessarily correlated with resistive properties. Further, the insulator-metal (IM) transition with increasing temperature and pressure can either be a smooth transition involving a large resistivity change (Ti_2O_3) or an abrupt transition involving conductivity jump of several orders of magnitude, *e.g.*, VO, V_2O_3, VO_2, NiS. The latter is essentially a first-order transition. It may be accompanied by a change in volume, crystal symmetry and long-range magnetic order. The most striking example of such systems is V_2O_3, pure and doped (Feinleib and Paul, 1967; McWhan and Rice, 1969). Thus the samples

having the composition $(V_{1-x}Cr_x)_2O_3$ with $x \geqslant 0{\cdot}009$ exhibit a first-order transition from the low temperature insulating antiferromagnetic phase to a high temperature metallic (non-magnetic) phase at 150° K with a 3·5 per cent reduction in volume. This transition for the doped system (unlike pure V_2O_3) does not show any change in crystal symmetry (Dernier, 1970). It has been claimed by some authors that $(V_{1-x}Cr_x)_2O_3$ is the system which exhibits true Mott type IM transition (McWhan and Rice, 1970). Several mechanisms of the Mott transition have been put forward and they differ as to the nature of the thermodynamic "driving force" causing the transition (Doniach, 1969). Before discussing the various mechanisms of transition, a few words about the nature of the insulating phase are in order. In the insulating (semi-conducting) phase these materials are assumed to have intrinsic band gaps arising from the following. First there may be the usual one-electron Hartree-Fock band structure wherein a filled band is separated from an unfilled band by an energy gap owing to the occurrence of extra periodicity (and consequent halving of the Brillouin zone) introduced by antiferromagnetic ordering or lowering of crystal symmetry (Slater, 1951; Adler and Brooks, 1967). Secondly, the gap may be related with electron-electron correlation when two electrons sit on the same atom in the same orbital (Hubbard, 1964). This is the so-called Mott-Hubbard gap. As a result of this, a single otherwise half-filled band gets split up into a filled band and an unfilled band separated by a gap of the order of correlation energy. For the occurrence of the insulator-metal transition the energy gap must diminish as a function of increasing temperature and pressure. To this end various mechanisms have been invoked. While no single mechanism seems to account for the behaviour of all these substances, a notion common to several of these appears to be that of an excitation-dependent gap. The important feature of this excitation-dependent gap is that it allows a first-order phase transition. This can arise from the following effects:

(i) Adler-Brooks model (1967) wherein this gap arises from the free carrier concentration-dependent crystal distortion or magnetization.

(ii) Falicov-Kimball model (1969) wherein the attractive electron-hole interaction gives an effective gap decreasing linearly with carrier concentration.

(iii) The Fronlich (1966)-Hyland (1968) model where the carrier concentration-dependent screening of the long-range repulsive Coulomb interaction reduces the effective gap. This presumably is a weak effect and will show up only at a very high carrier concentration.

Finally, it should be noted that the spin and orbital entropy difference between the insulating phase and the metallic phase may further enhance the thermodynamic driving force.

In all these treatments a certain kind of the reaction of the lattice (*i.e.*, change of volume but no change of symmetry) to an electronic excitation from localised to delocalised states has not been taken into account. In what follows, we shall take explicit cognizance of such a lattice reaction to the creation of a hole when an electron is excited to a delocalised state. It will be shown that the hole-lattice interaction gives rise to two distinc effects. First the well-known lowering of lattice energy and secondly an excitation-dependent hole energy shift. The latter is an intensive effect and is a consequence of the fact that the localised hole energy is a parametric function of the lattice configuration co-ordinates of the surrounding and increases when the lattice closes in towards the hole site. In effect, the creation of a hole amounts to generating a positive pressure (strain) in the vicinity of the hole. This will be found to be the essential point of our mechanism.

2. Formulation of Model Hamiltonian

In the present model we consider a situation described by localised atomic states at the respective metal-ion sites. These atomic states are singly occupied at the absolute zero of temperature. The electronic configurations involving double occupancy of such states are projected out in that the Hubbard correlation gap is much too large. There is, however, an empty band of delocalised states (Bloch states) separated from the above valence states by an energy gap. These empty sub-bands may arise due to crystal field splitting effects (Austin and Mott, 1970). Alternatively, the 4*s* band may lie between the localised 3*d*-like states and Hubbard's upper band. This seems to be the case for the ideal Mott-Hubbard insulator NiO (Adler, 1970). We shall address ourselves to systems such as $(V_{1-x}\ Cr_x)_2\ O_3$ where the present picture is easily applicable. The physics of the present model may be described as follows. At a finite temperature some electrons from the localised valence states may get promoted to the extended band states leaving localised holes at the original sites. Now, we envisage a strong hole-lattice interaction in view of the polar nature of the system. This will result in a displacement of the lattice around the hole. For simplicity we shall consider here the interaction of the hole with the totally symmetric phonon mode (breathing mode) only to be of importance. In addition to a shift in the lattice reference energy, the 'closing in' of the surrounding atoms will lead to a decrease in the hole energy rendering the electron-hole excitation more favourable. This

implies an effective reduction of the excitation gap. Also, a further reduction effect will come from electron-hole interaction as considered by Falicov and co-workers (1969, 1970). We assume that the interaction between the lattice and band electrons is relatively weaker and will not be considered.

The above situation is adequately described by the model Hamiltonian in the second quantization representation as

$$H = H_0 + H_L,$$

where

$$H_0 = \sum_k \epsilon_k C_k^\dagger C_k + \sum_i E(\langle Q_i \rangle)\, b_i^\dagger b_i - \frac{1}{N} G \sum_{i,k,k'} e^{i(k-k').R_i} C_{k'}^\dagger C_k b_i^\dagger b_i \quad (1)$$

and

$$H_L = \sum_q \hbar \omega_q (\beta_q^\dagger \beta_q + \tfrac{1}{2}) + \sum_{q,i} (i)\, \Gamma_q\, \epsilon^{iq.R_i} (\beta_q^\dagger - \beta_{-q})(b_i^\dagger b_i), \quad (2)$$

where $C_k^\dagger$, C_k are fermion creation, annihilation operators of electrons in the conduction band in the Bloch state $|k\rangle$ with quasi particle energy ϵ_k, k being the wave vector; $(b_i^\dagger, b_i)$ are the hole creation, annihilation operators at the site R_i, $E(\langle Q_i \rangle)$ is the hole energy which depends parametrically on the mean configuration co-ordinates Q_i of the neighbouring atoms. The sign in front of the hole-lattice interaction term has been chosen to correspond to attraction. The third term of Eq. (1) gives the electron-hole Coulomb interaction of strength $G (> 0)$; $\beta_q^\dagger$, β_q are the phonon creation, annihilation operators; ω_q is the mode-branch frequency, q is the wave vector. In the above expressions, the spin indices have been suppressed as no spin flip terms are involved. The last term of Eq. (2) is the dynamical hole-phonon interaction with Γ_q representing the interaction matrix element. The fundamental energy gap between the localised states and the minimum of the conduction band is given by

$$\Delta = (\epsilon_k + E(\langle Q_i \rangle))_{min} > 0.$$

We eliminate the dynamical hole-lattice interaction [last term of Eq. (2)] exactly by a well-known canonical transformation given by

$$H_T = e^{iS} H e^{-iS}, \quad (3)$$

where S is chosen to be

$$S = \sum_q (\xi_q \beta_q + \beta_q^\dagger \xi_q^*) \tag{4}$$

with

$$\xi_q = \sum_i \frac{\Gamma_{-q}}{\hbar\omega_q} e^{-iq.R_i} (b_i^\dagger b_i). \tag{5}$$

Thus the transformed lattice Hamiltonian H_{LT} becomes

$$H_{LT} = e^{iS} H_L e^{-iS}$$

$$= \sum_q \hbar\omega_q \left(\beta_q^\dagger \beta_q + \frac{1}{2}\right) - \sum_{i,q} \frac{|\Gamma_q|^2}{\hbar\omega_q} (b_i^\dagger b_i). \tag{6}$$

As regards the various terms in H_0 they are affected as follows. $\sum_k \epsilon_k C_k^\dagger C_k$ remains unaltered and so does the electron-hole interaction term.

For the term involving single particle hole energy, we have

$$e^{iS} \left(\sum_i E(\langle Q_i\rangle) b_i^\dagger b_i\right) e^{-iS}$$

$$= \sum_i E(\langle e^{iS} Q_i e^{-iS}\rangle) b_i^\dagger b_i$$

$$\equiv \sum_i E(\langle Q_{iT}\rangle) b_i^\dagger b_i. \tag{7}$$

The above form is obtained because $E(\langle Q_i\rangle)$ depends parametrically on the mean configurational co-ordinates of the neighbouring atoms. To derive an explicit form for the above dependence, we choose, for simplicity, a simple cubic lattice and consider only the totally symmetric mode (Q_i^S) constituted from the longitudinal acoustic (LA) mode for the hole-lattice interaction. (For more realistic situations, *e.g.*, two atoms per unit cell, longitudinal optical modes will be more effective.) Thus we get

$$\langle Q_{iT}^S\rangle = \langle Q_{i0}^S\rangle$$

$$+ 2 \sum_{q,j} \left(\frac{\hbar}{2MN\omega_q}\right)^{\frac{1}{2}} \frac{1}{\hbar\omega_q} \Gamma_q^* F(qa) \langle b_j^\dagger b_j\rangle e^{iq\cdot(R_i - R_j)}, \tag{8}$$

where $\langle Q_{i0}{}^S \rangle$ is the equilibrium configuration co-ordinate in the absence of electron-hole excitation, *i.e.*, $\langle b_i{}^\dagger b_i \rangle = 0$. On carrying out the summation over j and taking $\langle b_j{}^\dagger b_j \rangle (= n_0 \leq 1)$ constant over the crystal we get

$$\langle Q_{iT}{}^S \rangle = \langle Q_{i0}{}^S \rangle + 2 \sum_q \left(\frac{\hbar}{2MN\omega_q} \right)^{\frac{1}{2}} \frac{\Gamma_q}{\hbar \omega_q} F(qa) \delta_{q,0} N n_0. \tag{9}$$

The fractional value of n_0 is to be understood in the time average sense. Here

$$F(qa) = (\alpha \sin \alpha qa + \beta \sin \beta qa + \gamma \sin \gamma qa) \tag{10}$$

is a group theoretical form factor associated with the totally symmetric mode considered here; α, β, γ are the direction cosines of the phonon wave vector q, 'a' is the lattice constant, M is the atomic mass and N the number of unit cells in the crystal. For the longitudinal acoustic mode, we have (Ziman, 1960)

$$\Gamma_q = C \left(\frac{\hbar}{2MN\omega_q} \right)^{\frac{1}{2}} | q |, \tag{11}$$

where C is the usual electron-phonon coupling constant. Also for the LA mode, we use $\omega_q = v_s q$ where v_s is the velocity of sound. Thus Eq. (9) reduces to

$$\langle Q_{iT}{}^S \rangle = \langle Q_{i0}{}^S \rangle + \frac{Can_0}{Mv_s{}^2} \tag{12}$$

Finally, we get

$$E(\langle Q_{iT}{}^S \rangle) \approx E(\langle Q_{i0}{}^S \rangle) + \frac{\partial E}{\partial Q_{i0}{}^S} \left\{ \frac{Can_0}{Mv_s{}^2} \right\} + \ldots, \tag{13}$$

where $\partial E / \partial Q_{i0}{}^S$ is the force which corresponds to the reciprocal of the radial compressibility of the localised hole state. For a particle in the ground state in a spherical enclosure of radius 'a' it can be shown that

$$\frac{\partial E}{\partial Q_{i0}{}^S} = \frac{\partial}{\partial a} \left(\frac{\hbar^2}{2ma^2} \pi^2 \right) = - \frac{\hbar^2}{ma^3} \pi^2; \tag{14}$$

m is the mass of the particle.

We assume that the above will be a fair estimate for the present situation with m replaced by the effective mass m^* of the particle. Thus

$$E(\langle Q_{iT}{}^S \rangle) \approx E(\langle Q_{i0}{}^S \rangle) - \frac{\hbar^2 \pi^2}{m^* a^2} \frac{Cn_0}{Mv_s{}^2}. \tag{15}$$

Accordingly, the total transformed Hamiltonian can be rewritten as

$$H_T = \sum_k \epsilon_k C_k^\dagger C_k + \sum_i \left\{ E(\langle Q_{i0}^s \rangle) - \frac{C^2}{2Mv_s^2} - g\langle b_i^\dagger b_i \rangle \right\} b_i^\dagger b_i$$

$$- \frac{G}{N} \sum_{k,\, k',\, i} e^{i(k-k')\cdot R_i} C_{k'}^\dagger C_k b_i^\dagger b_i + \sum_q \hbar\omega_q (\beta_q^\dagger \beta_q + \tfrac{1}{2}), \tag{16}$$

where g is given by

$$g = \left(\frac{\pi^2 \hbar^2 C}{m^* a^2 M v_s^2} \right). \tag{17}$$

3. Thermodynamics of Insulator-Metal Transition

In a mean-field approximation (Falicov and Kimball, 1969) the above reduced Hamiltonian [*cf.* Eq. (16)] gives an excitation-dependent gap

$$\triangle_{\text{eff.}}(n_0) = \triangle_0 - 2(g + G)\, n_0, \tag{18}$$

where $\triangle_0$ is the gap in the absence of excitation and includes the constant shift

$$\left(- \frac{C^2}{2Mv_s^2} \right).$$

The above follows from the fact that the electron-hole interaction term [*i.e.*, the third term of Eq. (16)] lowers the conduction band minimum whereas the hole-lattice interaction reduces the hole energy. The Fermi level of the system having the above excitation-dependent gap is given by

$$N\langle b_i^\dagger b_i \rangle = N n_0 = \sum_k C_k^\dagger C_k$$

or

$$N\left(1 - \frac{1}{e^{-\beta e_F} + 1}\right) = N \int_0^W \frac{\rho_{at}(\epsilon)\, d\epsilon}{e^{\beta[\epsilon + \triangle_0 - 2(g+G) n_0 - e_F]} + 1}, \tag{19}$$

$$\beta \equiv \frac{1}{k_B T},$$

where ϵ_F is the Fermi level, $\rho_{at}(\epsilon)$ the density of states per atom. For a small width of the intermediate conduction band we get

$$n_0 \approx [e^{\beta/2[W/2+\Delta_0-2(g+G)n_0]} + 1]^{-1}, \tag{20}$$

where W is the band-width (assumed to be non-degenerate). It is convenient to express this in terms of dimensionless parameters as

$$\zeta \equiv \frac{k_B T}{W} = \frac{1 + \eta - \gamma n_0}{4 ln\left(\frac{1 - n_0}{n_0}\right)}, \tag{21}$$

where

$$\eta = \frac{2\triangle_0}{W}, \quad \gamma = \frac{4(g + G)}{W}.$$

4. Estimates and Discussion

Although we have included, for the sake of completeness, the electron-hole interaction (G) as considered by Falicov and Kimball, for our discussion we shall concentrate on the present mechanism, *i.e.*, on the hole-lattice interaction (g). Accordingly, we put $G = 0$. With the following choice of parameters involved, namely,

$C \approx 1$ eV

$M \approx 50 \times 10^{-24}$ gm.

$m^* \approx$ electronic mass $\approx 10^{-27}$ gm.

$a \approx 2{\cdot}5 \times 10^{-8}$

$v_s \approx 4 \times 10^5$ cm/sec,

we get $g \approx 2$ eV. Further, we choose $\triangle_0 \approx 0{\cdot}1$ eV and $W \approx 1$ eV.

With the above choice of parameters, we have plotted in Fig. 1, the carrier concentration per atom n_0 as a function of temperature. We see that at $T = 0$, $n_0 = 0$. With increasing T, n_0 gradually increases. There is, however, a discontinuous increase in n_0 at a certain critical temperature T_c which is akin to a first-order phase transition. This corresponds to a conductivity jump. (It may be noted that for some other choice of parameters, the jump in the carrier concentration may become negligibly small implying a conti-

nuous transition). The corresponding reduction in volume at T_c is estimated from

$$\frac{\triangle V}{V} = \left(\frac{C}{M v_s^2} \triangle n_0\right),$$

where $\triangle n_0$ is the discontinuous change in n_0. This turns out to be of the order of 10 per cent. This is of the same order as observed in a few systems. The effect of pressure can be incorporated in W and $\triangle_0$. In fact, as expected, W will increase with increasing pressure (P), while $\triangle_0$ will decrease. This will lead to a reduction of T_c in accordance with the phase diagram in T-P plane.

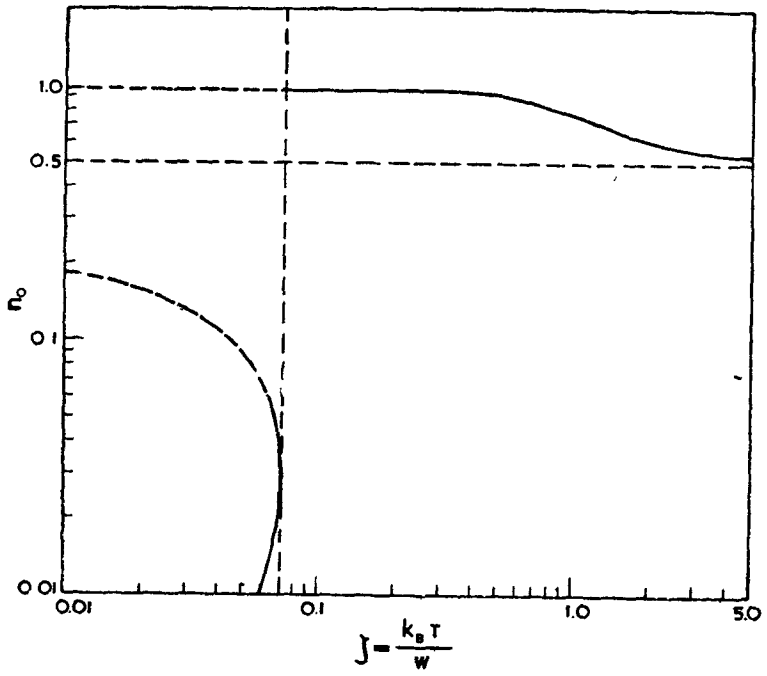

FIG. 1. The figure shows a log-log plot of the number of delocalised carriers per atom (n_0) against $\zeta (\equiv k_B T/W)$ for $W \approx 1\,eV$, $g \approx 2\,eV$ and $\triangle_0 \approx 0{\cdot}1\,eV$. The solid curve corresponds to a thermodynamically stable situation. The dashed portion corresponds to an unstable region.

The above results clearly show that the insulator-metal transition is driven by hole-lattice interaction. The physical process consists of the 'closing in' of the surrounding (displaced lattice modes) with increasing hole occupancy on a site. This 'closing in' of the surrounding atomic cluster results in an extra kinetic energy of localization for an electron at the given site rendering

the occupation of the localised state by an electron energetically less probable. In effect, the above amounts to a reduction in the electron-hole pair excitation energy. This in turn favours the creation of more electron-hole pairs. Thus we get a feed-back mechanism essential for a phase transition.

At this stage we must briefly discuss the present theory in relation to those given by others. The present mechanism of excitation-dependent gap differs fundamentally from the one considered by Adler and Brooks (1967). In their model the gap arises from crystal structure distortion (lowering of symmetry) caused by the energy gain due to chemical binding. The dependence of the gap on electronic excitation comes from the fact that the excited electron no longer contributes to the chemical binding. Their model is, in essence, a band generalisation of the Jahn-Teller effect. For systems such as $(V_{1-x}Cr_x)_2\ O_3$, where there is no change in crystal symmetry at T_c, their explanation seems to fail.

The model considered by Falicov and co-workers relies heavily on the attractive electron-hole Coulomb interaction. A strong Coulomb interaction of this kind can lead to the formation of excitons which are non-conducting. In point of fact, to exclude the probability of exciton formation they have made somewhat unrealistic choice of the parameters involved (Ramirez *et al.*, 1970). Furthermore, none of the models developed so far explicitly account for the change of volume at T_c.

In conclusion, it may be remarked that in the origional Mott-Hubbard suggestion also it is envisaged that when the lattice is squeezed by applying external pressure, the cost in kinetic energy in confining electrons to atomic sites increases. This should lead to lowering of the effective energy gap. In the present model the positive pressure (strain) is being generated internally by the hole-lattice interaction.

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