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SIMPLE MODEL FOR SEMICONDUCTOR-METAL TRANSITIONS: SmB_6 AND TRANSITION-METAL OXIDES

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We propose a simple model for a semiconductor-metal transition, based on the existence of both localized (ionic) and band (Bloch) states. It differs from other theories in that we assume the one-electron states to be essentially unchanged by the transition. The electron-hole interaction is responsible for the anomalous temperature dependence of the number of conduction electrons. For interactions larger than a critical value, a first-order semiconductor-metal phase transition takes place.

Many substances, including SmB_6 [1] and a number of transition-metal oxides,[2] exhibit semiconductor-metal transitions.[3] The transitions are in many cases first-order phase transitions (e.g., in V_2O_3); however, they can also result from a gradual but anomalously large increase in conductivity over a range of temperatures (e.g., in SmB_6 and Ti_2O_3). In addition, measurements of large magnetic susceptibilities with anomalous temperature dependences suggest that in many of these materials localized magnetic moments exist and that they are intimately connected with the transition. As an example, it has been hypothesized[1] that in SmB_6 the conduction electrons and the localized moments are produced simultaneously by the promotion of a single localized electron from the spherically symmetric Sm^{++} ion ($J=0$) into a conduction band. The Sm^{+++} ion left behind ($J=\frac{7}{2}$) acts as a localized moment.

We present here a simple theory of the semiconductor-metal transition based on a model having both localized and itinerant interacting quasiparticle states. The relevant single-electron states consist of (a) bands of extended Bloch functions and (b) a set of localized states centered at the sites of the metallic ions in the crystal. As $T\rightarrow 0$ the localized states are lower in energy than the band states and are fully occupied by electrons. Therefore the quasiparticle excitations are either localized holes or itinerant electrons. In the language of second quantization and in the spirit of the Landau theory of Fermi liquids, we write the one-particle terms as

$$H_0=\sum_{\nu\vec{k}\sigma}\epsilon_\nu(\vec{k})a_{\nu\vec{k}\sigma}{}^\dagger a_{\nu\vec{k}\sigma}+\sum_{i\sigma}Eb_{i\sigma}{}^\dagger b_{i\sigma}, \tag{1}$$

where $a_{\nu\vec{k}\sigma}{}^\dagger$ creates an electron in state $\vec{k}$, band ν, with spin σ, and $b_{i\sigma}{}^\dagger$ creates a hole with spin σ at site i. The energies $\epsilon_\nu(\vec{k})$ and E are positive definite and such that

$$\Delta\equiv\min[E+\epsilon_\nu(\vec{k})]>0 \tag{2}$$

is the energy gap for the formation of an electron-hole pair. We further assume that the quasiparticle interaction is screened, and its range short enough so that only intra-atomic terms need be considered. In this case the interaction

Hamiltonian consists of terms of six basically different kinds, characterized by six different interaction constants G:

$$G_1 b_{i\sigma}{}^\dagger b_{i\bar{\sigma}}{}^\dagger b_{i\bar{\sigma}} b_{i\sigma}, \tag{3}$$

$$G_2 b_{i\sigma}{}^\dagger b_{i\bar{\sigma}}{}^\dagger c_{\nu i\bar{\sigma}}{}^\dagger b_{i\sigma}, \tag{4}$$

$$G_3 b_{i\sigma}{}^\dagger b_{i\bar{\sigma}}{}^\dagger c_{\nu i\bar{\sigma}}{}^\dagger c_{\nu' i\sigma}{}^\dagger, \tag{5}$$

$$G_4 b_{i\sigma}{}^\dagger c_{\nu i\sigma'}{}^\dagger c_{\nu' i\sigma'} b_{i\sigma}, \tag{6}$$

$$G_5 c_{\nu i\sigma}{}^\dagger c_{\nu' i\sigma'} b_{i\sigma'} c_{\nu'' i\sigma}, \tag{7}$$

$$G_6 c_{\nu i\sigma}{}^\dagger c_{\nu' i\sigma'}{}^\dagger c_{\nu'' i\sigma'} c_{\nu''' i\sigma}, \tag{8}$$

where the operators $c_{\nu i\sigma}{}^\dagger$ ($c_{\nu i\sigma}$) create (destroy) the Wannier states corresponding to the Bloch bnads ($\nu\sigma$). The hole-hole repulsion term (3) is the largest interaction term; if $G_1 \gg \Delta$ it becomes the dominant term in the Hamiltonian. In this case electronic configurations with two holes per ion do not contribute to any of the low-energy eigenstates, and they can be projected out. In the manifold of states with not more than one hole per ion, terms of the form (3), (4), and (5) give identically zero contribution. In this fashion, as $G_1 \to \infty$, those terms are exactly taken into account by this projection technique. The most important remaining terms are of form (6) and represent an attraction between electrons and holes: These are the terms responsible for the formation of excitons. Interactions (7) and (8) are much smaller, since they involve three or four extended wave functions instead of only two; we ignore them. The electron-hole attractive terms (6) can now be treated in a self-consistent-field approximation, or equivalently, to second order in Fermi-liquid theory.

To simplify our presentation we take the energy bands to be narrow so that $\epsilon_\nu(\vec{k})$ can be replaced by a constant value ϵ in the thermodynamic calculations.[4] With these assumptions the Hamiltonian can be written

$$H = N[\epsilon\hat{n}_a + E\hat{n}_b - G\hat{n}_a\hat{n}_b], \tag{9}$$

where N is the number of metal ions,

$$\hat{n}_b = N^{-1}\sum_{i\sigma} b_{i\sigma}{}^\dagger b_{i\sigma}, \tag{10}$$

and similarly for $\hat{n}_a$. In the self-consistent-field approximation (with no bound excitonic states) the free energy of the system can be written

$$F = N[\Delta n - Gn^2 + k_B T\{2n\ln n + (1-n)\ln(1-n) + (2m-n)\ln(2m-n) - 2m\ln(2m) - n\ln(2J+1) + n\ln(2J'+1)\}], \tag{11}$$

where

$$n = \langle\hat{n}_a\rangle = \langle\hat{n}_b\rangle \tag{12}$$

is the number of conduction electrons as well as the number of holes, m is the number of relevant conduction bands of each spin, and $(2J+1)$ and $(2J'+1)$ are the multiplicities of the metallic ions with and without a hole, respectively. Minimization of (11) with respect to n yields an equation which determines the number of electrons in the conduction band as a function of temperature and of the parameters Δ and G. This equation describes, at low termperatures, a semiconductor with a shrinking gap

$$\Delta_{\text{eff}} = \Delta - 2Gn. \tag{13}$$

If the conductivity[5] is taken to be proportional to n, a nonvanishing G leads to an anomalous increase in conductivity with temperature. This is illustrated in Fig. 1. If $G \ll \Delta$, as illustrated in curve(a), the typical semiconducting behavior is observed at all temperatures. For $G \lesssim G_c$, a

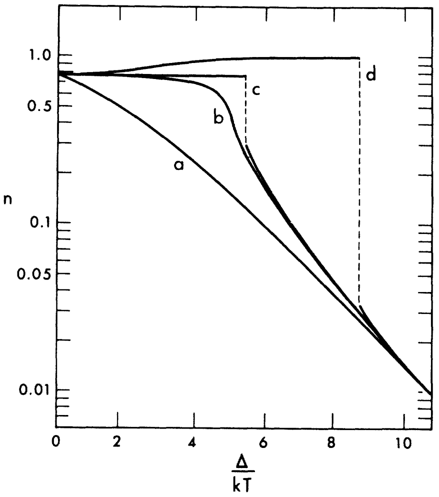

FIG. 1. The relative occupation of the conduction band in a simple model as a function of T^{-1}. The parameters are $m = 1$, $q = 2$, and $G_c = 0.633\Delta$ for all curves. Curve a, $G = 0$; curve b, $G = 0.625\Delta$; curve c, $G = 0.641\Delta$; and curve d, $G = 0.770\Delta$.

critical value which depends on Δ, m, and $q \equiv (2J+1)/(2J'+1)$, no first-order transition takes place, but the temperature dependence of the conductivity shows the gradual transition illustrated in curve (b) of Fig. 1 $[m=1, q=2]$; this behavior strikingly resembles the conductivity curves[1,2] for SmB_6 and Ti_2O_3. For $G \gtrsim G_C$, a first-order phase transition takes place at $T=T_C$ to a value of n which remains essentially constant at all temperatures higher than T_C [see curve (c)]. For $G_C < G \lesssim \Delta$ there is a first-order transition from a state of small n to a state of $n \sim 1$ at a temperature T_C, while n decreases for $T > T_C$ [curve (d)]; such behavior is found in V_2O_3. For $G > \Delta$, the state $n=1$ becomes stable at $T=0$ and the system is metallic at all temperatures.

For $k_BT_C \ll \Delta$, our simple model yields for the transition temperature

$$k_BT_c = (\Delta - G)[2m \ln(2m) - (2m-1)\ln(2m-1) + \ln q]^{-1}. \tag{14}$$

In this case n varies exponentially with T^{-1} for $T < T_C$ and extrapolates to $[2mq]^{1/2}$ for $T^{-1} = 0$. At T_C, n jumps to a value very close to 1 and decreases smoothly to another limiting value which is an algebraic function only of m and q as $T^{-1} \to 0$. This behavior is quite similar to those of V_2O_3 and VO. If we take $m=1$ and $q=2$ we obtain

$$\Delta = 0.365 \text{ eV}, \quad G = 0.336 \text{ eV for } V_2O_3;$$

$$\Delta = 0.248 \text{ eV}, \quad G = 0.226 \text{ eV for VO}.$$

Other substances, such as Fe_3O_4 and VO_2 which also exhibit first-order transitions, yield poorer agreement with this simple two-level model; improved agreement is found when a finite width of the conduction band is considered.

For gradual transition cases, similar agreement is found. In our simple model, with $m=1$, $J=\frac{7}{2}$, and $J'=0$, we obtain for SmB_6

$$\Delta = 0.0044 \text{ eV}; \quad G \cong 0.0018 \text{ eV},$$

while a critical value $G_C = 0.0022$ eV would be required for a first-order transition. Conductivity data on Ti_2O_3 show too large an anomalous increase, which our simple model cannot produce without a first-order transition.

In conclusion we would like to point out that our model for a semiconductor-metal transition is basically different from a Mott transition[3] or an excitonic-insulator transition.[6] It is based on a change in the occupation numbers of electronic states which remain themselves basically unchanged in their character.

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†Hertz Foundation Predoctoral Fellow.

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DENSITY OF "AMORPHOUS" Ge

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The density of vapor-deposited "amorphous" Ge was determined from x-ray-diffraction absorption measurements and found to be the same as the density of crystalline Ge within ±5 %.

Recently Herman and Van Dyke[1] estimated the electronic density of states of amorphous Ge by assuming a dilated Ge crystal having the same density as "amorphous" Ge. The density value used was that (3.9 g/cm^3) determined by Clark[2] using film scraps shattered from the substrates These scraps were weighed in air and in Dow-Corning No. 704 silicone oil. It is possible that the shattered scraps had many microcracks that would not have been penetrated by the oil thus