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IMPURITY BANDS AND THE METAL-INSULATOR TRANSITION

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Review Lecture

Metal-insulator transitions

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A survey is given of a variety of solids that show a metal-insulator transition. In crystals most transitions are expected to be of first order as the composition or temperature is changed; in disordered systems this is not necessarily the case. The transition in an impurity band with change of donor concentration is described, and also with change of stress, magnetic field or gate voltage. The concept of a minimum metallic conductivity is discussed, with special reference to materials of mixed valence.

1. Band-crossing transitions

Since the discovery of the electron in 1900 it has been recognized that metals contain electrons that are free to move under the influence of an electric field, while most non-metals do not. The Hall effect gave a measure of the number of free electrons, often of the order of one per atom and little dependent on temperature; a reasonable assumption was that, in monovalent metals at any rate, each atom lost its outer electron. On the other hand until the advent of quantum mechanisms no clear understanding was possible of why in non-metals the electrons were 'stuck', perhaps in chemical bonds as in SiO_2, or in closed shells as in NaCl. The explanation given by Wilson (1931 *a, b*), based on quantum mechanics, showed however that the electrons must not be thought of as stuck and in fact cannot be stuck in a perfect lattice. All solutions of the Schrödinger equation for an electron subject to a periodic field of potential $V(x, y, z)$, namely

$$\nabla^2\Psi + (2m/\hbar^2)(E - V)\Psi = 0, \tag{1}$$

are of the form

$$\Psi = \exp(i\boldsymbol{kr})\,u(x, y, z), \tag{2}$$

u being periodic with the period of the potential, and so represent an electron moving with wavenumber $\boldsymbol{k}$ and with no scattering. The solutions of (1) lead to a spectrum of energy states divided into bands as in figure 1; according to the Pauli principle, states with a given value of k can be occupied by only two electrons, so that, for cubic structures, two electrons per atom will completely fill the first band. If the first band is full and the second empty (figure 1*a*), the material cannot conduct, not because the electrons are trapped or stuck, but because exactly as many electrons are moving from left to right as from right to left. This is clear experimentally, as well as from the theory, because in crystalline non-metals, if electrons are removed from the full valence band, the resulting 'positive hole' is mobile.

The model makes clear why a sharp distinction exists in nature between metallic and non-metallic behaviour. In metals, in certain compounds (e.g. CrO_2) and in heavily doped semiconductors, the resistivity tends to a finite value (or zero in superconductors) as the temperature tends to zero; in insulators (among which we include lightly doped semiconductors) it tends to infinity. The term 'metal-insulator transition' in this paper denotes phenomena in which the conductivity of a material makes a sudden change from one form of behaviour to the other, when some parameter is changed. This parameter could be pressure, stress, magnetic field, composition or in some two-dimensional systems, gate voltage. Thus CrO_2 and heavily doped semiconductors are included under the heading of 'metals'.

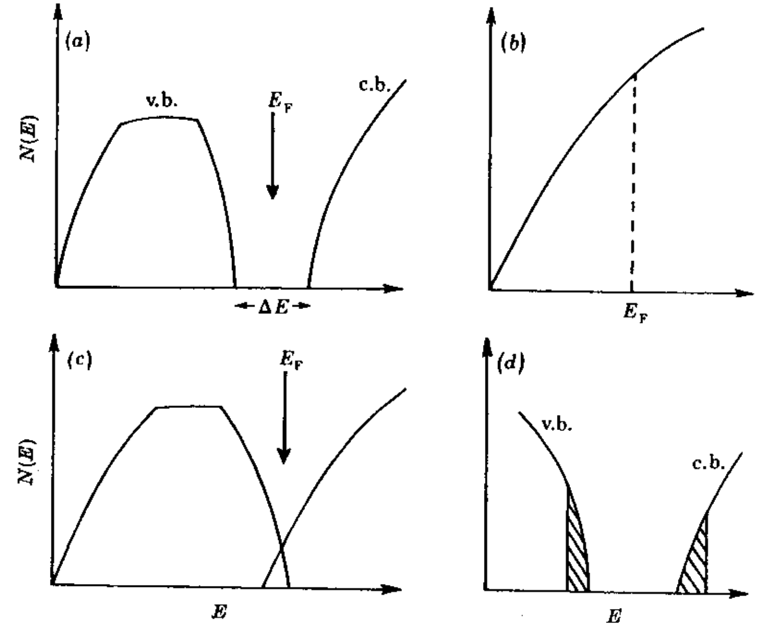

Figure 1. Density of states in a crystalline material: (*a*) for an insulator with a gap ΔE; (*b*) for a typical monovalent metal; (*c*) for a metal such as Sr, Yb or Bi in which occupied and valence bands overlap; (*d*) for an electron-hole gas in an insulator. Occupied states are shaded. The Fermi energy E_F is shown in (*a*), (*b*), (*c*). C.b. denotes the conduction band, v.b. the valence band.

Wilson's model seemed at first sight to predict that divalent materials such as calcium should be insulators. However, it was early realized that the first and second zones could overlap, as in figure 1*c*, and of course more recent experimental and theoretical determinations of the Fermi surface show that this is so. It follows therefore that if the bands could be separated, for instance by expanding the lattice, a metal–insulator transition should occur. The fact that no obvious means existed for expanding the lattice perhaps lessened interest in this possibility in the pre-World War II period. However, band theory calculations have shown that, for metallic Sr and Yb, pressure would initially separate the bands, and the phenomenon of a metal–insulator transition under pressure has been observed for some of these materials†.

A discussion of the difference between metals and non-metals earlier than that of Wilson was given by Goldhammer (1911) and Herzfeld (1927) in terms of the polarization catastrophe resulting from the Clausius–Mossotti relation; as systems such as Si:P (Castner *et al.* 1975), or metal–ammonia solutions (Mahaffey & Jerde 1968) approach the metal–insulator transition, the dielectric constant greatly increases. Whether this should be regarded as cause or effect has been a matter of controversy (see Castner 1980*a*, *b*; Leroux-Hugon & Ghazli 1976*a*, *b*; Mott & Davies 1980; Gunn & Ortuno 1980; Ortuno 1980; Edwards & Sienko 1981).

The post-War interest in metal–insulator transitions, however, arose from the realization that, when electron–electron interaction is taken into account, the transition in crystalline systems must always be discontinuous. Our present understanding of this phenomenon is based on extensive experimental and theoretical investigations of electron–hole droplets in silicon and germanium (for reviews see Rice 1977; Hensel *et al.* 1977). If an electron and hole are created, for instance by absorption of a quantum of radiation, in their lowest state they are bound together to form an exciton, but at low temperatures a gas of excitons condenses to form droplets of a *metallic* electron–hole gas; the gas may indeed fill the whole specimen. If we write the kinetic energy of the electron–hole gas as

$$2 \times \tfrac{3}{5}\hbar^2 n^{\frac{2}{3}}/m,$$

and its potential energy resulting from the electron–hole attraction as $-Ae^2n^{\frac{1}{3}}/\kappa$, where κ is $4\pi\epsilon\epsilon_0$ and ϵ is the dielectric constant, then the total energy has a minimum value

$$E_{\min} = -\tfrac{5}{24}A^2me^4/\hbar^2\kappa^2 \tag{3}$$

when

$$n^{\frac{1}{3}} = \tfrac{5}{12}Ame^2/\hbar^2\kappa. \tag{4}$$

The estimation of A for any given band form, together with a correction resulting from correlation, is not a simple matter; moreover it is by no means obvious that $E_{\min}$ is numerically greater than the energy gained in forming an exciton. If it were not, an exciton gas should condense into a Bose gas of excitons, the so-called excitonic insulator (Kohn 1967; Keldysh & Kupaev 1965; Halperin & Rice 1968). However, with the possible exception of CuO, there is no firm evidence that this occurs.

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† For Yb see McWhan *et al.* (1969) and Jullien & Jerome (1971); for Sr see Drickhamer *et al.* (1966).

Though the present author (Mott 1949) and Knox (1963) first pointed out the discontinuous nature of the transition, its relation to electron–hole droplets was first described by Brinkman & Rice (1973). These authors argued that if in figure 1 the gap ΔE is continuously decreased, when ΔE reaches the energy $E_{\min}$ of equation (3) there should be a sudden formation of an electron–hole liquid with density given by (4). If so, and if the free energy is plotted against the parameter of the change that 'drives' the transition (e.g. volume or composition), curves such as those of figure 2 will be obtained. If x is the volume, there will be a discontinuous change of volume, or, if x is the composition, a two-phase region and a critical temperature. In the former case it will be impossible to observe the volume at which a sudden disappearance of the band-gap occurs. In the latter, it can in principle be observed with quenched alloys. But a quenched alloy cannot be a perfect lattice: there is an element of disorder, and the effect of disorder will be described in § 3. A D X

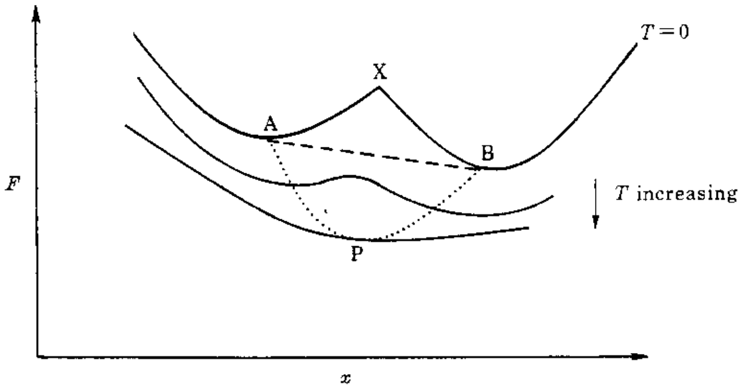

FIGURE 2. Free energy F of an electron gas in a material showing a metal–insulator transition, as a function of the parameter x that leads to the transition. If x is the composition in an alloy, the critical point is represented by P; T is the temperature.

2. THE MOTT TRANSITION

This kind of transition, first described by the present author in 1949, can now be seen as similar to the band-crossing transition but as occurring when the two bands are not the result of crystal structure but of antiferromagnetic order. In its simplest form we consider a lattice in which each atom (of one kind) contains a single electron (for example $TiCl_3$). If it were not for the exchange interaction, such materials would be metals, since a titanium d-band would be only partly filled. Exchange interaction leads to an antiferromagnetic lattice, which will split the band into two halves, occupied and unoccupied (Slater 1957). This cannot be the whole story, however, because such materials do not normally become metallic conductors 1 above the Néel temperature, a point which has been extensively discussed (see for example Brandow 1977). Intuitively, this is to be expected because the energy required to put an electron (e.g. from the Ti 3d^1 state) onto another Ti ion, so as to produce the state 3d^2, is in general large compared with the transfer integral. This quantity is called the 'Hubbard U'.

The band of levels given by the motion of an extra electron from one occupied state to another, that is the motion of the state d^2, is often called the 'upper Hubbard band': that which represents the motion of the hole (e.g. the d^0 state) is the 'lower Hubbard band'. If one considers a cubic array of one-electron centres with lattice constant a, then in the limit of large a the gap between the two bands is U, but as a decreases, the bands will broaden. If their breadths are respectively B_1, B_2, the gap will disappear when

$$\tfrac{1}{2}(B_1 + B_2) = U. \tag{5}$$

As first shown by Cyrot (1972), the use of this equation together with a number of approximations leads to the equation†

$$n^{\frac{1}{3}} a_{\mathrm{H}} \approx 0.26, \tag{6}$$

first deduced by Mott (1949) from different assumptions, where a_{H} is the hydrogen radius, and in agreement with experiment for a wide range of doped semiconductors (Edwards & Sienko 1978, 1981). The constant in (6) depends little on the assumptions made, because B_1 can be written $2zI$ where z is the coordination number and I the transfer integral, which in the tight binding approximation must contain the factor $\exp(-R/a_{\mathrm{H}})$, where R is the distance between centres ($R = n^{-\frac{1}{3}}$). Thus $\underline{n}a_{\mathrm{H}}$ $n^{\frac{1}{3}}$ is the reciprocal of the logarithm of a large number, and not very sensitive to (for instance) z or the many-valley form of a conduction band (Mott & Davies 1980). Thus, if R/a_{H} is about 4, doubling of the argument of the logarithm will change R/a_{H} by $\ln 2 = 0.6$ and thus by 15%, and thus the concentration by $(1.15)^3 \approx 1.60$. Fritzsche (1962: see also Cuevas & Fritzsche 1965*a, b*) was the first to show that a uniaxial [111] stress, which removes the degeneracy of the four Si conduction band valleys, increases the critical concentration n_c by 2.2 in Ge:Sb, though n_c is less in Ge:As. So rather drastic changes do affect n_c by the predicted amount; for a theoretical discussion see Bhatt & Rice (1981).

For Hubbard bands, as for bands determined by structure, in crystalline systems a discontinuous transition will be expected, and for the same reason. However, this should make little difference to the value of n_c.

We now discuss a property of Hubbard bands that does not occur for bands resulting from crystal structure. An electron in the upper band is expected to interact with the surrounding spins and form what is called a 'spin polaron', that is a mobile region around it in which the spins are orientated either parallel or antiparallel to its own spin (cf. Mott 1974*a*). If this occurs the current-carriers are 'quasi-particles',

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† A recent self-consistent band theory treatment for a crystalline system is given by Sander *et al.* (1981), and yields equation (6).

with moments considerably larger (perhaps about six times) than the moment μ_{B} of a single electron. The present author (Mott 1974$\underline{l}$) has suggested that the metallic / b phase near the transition must be considered in this way. If the metallic phase remains antiferromagnetic (an example is mentioned below), then if there are N carriers per unit volume of each sign it is suggested that there should be $1/Na^3$ spins in each polaron, so that the susceptibility should be

$$N(\mu_{\mathrm{B}}/Na^3)^2/\Delta E. \tag{7}$$

where ΔE is the Fermi energy and μ_{B} the Bohr magnetron. It may be, however, that the antiferromagnetic order is broken down by the spin polarons, so that the metal–insulator transition is from an antiferromagnetic insulating state to a normal metal:

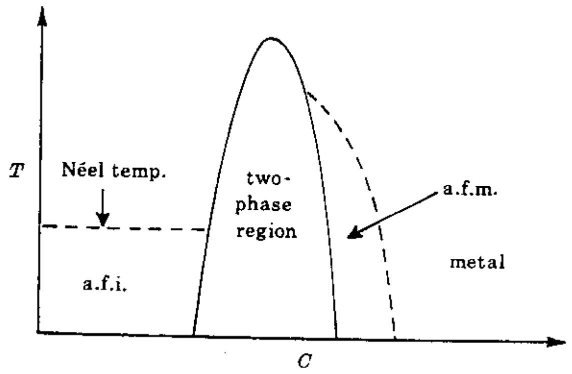

FIGURE 3. Typical phase diagram for a crystalline alloy system showing a metal–insulator transition. A.f.m. and a.f.i. denote antiferromagnetic metal and insulator respectively.

this is the case in some other systems. The present author (Mott 1974*a*) suggested that even in this case a degenerate gas of spin polarons is an appropriate description, the Pauli susceptibility and electronic specific heat being enhanced by about z, where z is the coordination number. The characteristic property here is that only a fraction *ca.* $1/z$ of the sites are doubly occupied. The analysis of Brinkman & Rice (1970) first approached this problem, giving values for the enhancement both of the Pauli magnetism and of the specific heat.

Examples of metal–insulator transitions in crystalline systems are provided by many transition-metal compounds. At low temperatures V_2O_3 is an antiferromagnetic insulator, which makes a transition to metallic behaviour under pressure, on alloying with Ti_2O_3 or with increasing temperature. Typical phase diagrams are as in figure 3. In alloys of V_2O_3 no antiferromagnetic metallic phase (a.f.m.) is observed; the opposite is the case in the system $Ni(S_{1-x}Se_x)_2$. Also high values of the electronic specific heat and Pauli paramagnetism have been observed in many of these materials.

It must be said that, though we think it likely that for $\underline{V}_2O_3$ a description as a mm

'Mott transition' is plausible, a structural change at the transition is observed and other descriptions have been given (Goodenough 1971, p. 291). Moreover it is clear that no one description is appropriate for the transition in all materials, for instance, in V_2O_3, VO_2, NiS and NiS_2; some references are given by Mott (1974) and more recent ones are: for VO_2, Zylberzstein & Mott (1975); for NiS recent experimental work is due to Brussetti *et al.* (1980) and theoretical discussions are given by White & Mott (1971) and Mott (1979); Ti_2O_3 is discussed by Mott (1980).

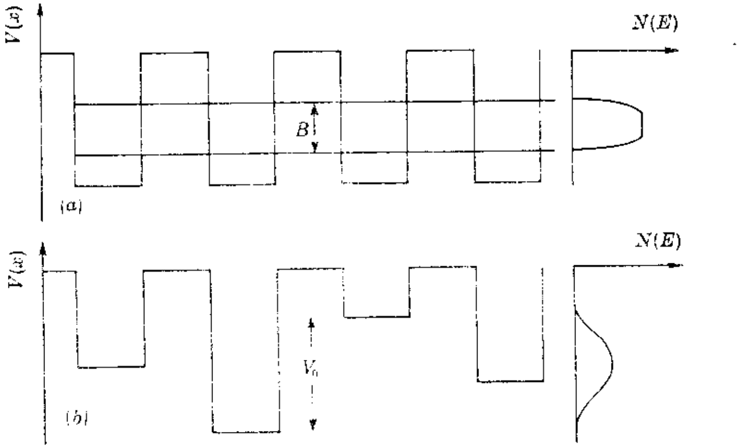

FIGURE 4. Potential energy function used by Anderson (1958): B is the band-width in the absence of disorder, V_0 the disorder parameter: (a) $V_0 = 0$; (b) strong disorder ($V_0 > B$). The density of states is also shown.

3. DISORDERED SYSTEMS

Much of our present interest in metal–insulator transitions is derived from their occurrence in non-periodic fields; examples that we shall discuss here are:

(i) the transition in doped semiconductors, compensated or otherwise;

(ii) certain fluid systems, such as metal–ammonia, and mercury and caesium vapours near their critical points;

(iii) inversion layers at the Si/SiO_2 interface, where charges in the oxide produce a random field.

To understand non-crystalline systems, we go back to the Schrödinger equation (equation (1)) and suppose that $V(x, y, z)$ is *not* a periodic function of position. The problem was first attacked by Anderson (1958) in his paper entitled 'Absence of diffusion in certain random lattices'. Anderson considered the potential energy function shown in figure 4. In the absence of disorder, solutions would be of the type (2), in the tight-binding approximation

$$\Psi = \sum \exp(\mathrm{i}\boldsymbol{k}\boldsymbol{a}_n)\,\psi_n(x, y, z). \tag{8}$$

where $\boldsymbol{a}_n$ denotes the lattice sites and ψ_n are functions for the individual wells. The band-width B is given by

$$B = 2zI, \tag{9}$$

where z is the coordination number and I the transfer integral

$$I = \int \psi_n H \psi_{n-1}\,\mathrm{d}^3x. \tag{10}$$

Introduction of the random term V_0 gives rise to a mean free path l given by

$$a/l \approx 0.7(V_0/B)^2. \tag{11}$$

When $V_0 \approx B$, l becomes of the order a, and according to a principle enunciated by Friedel (1978) and by Ioffe & Regel (1960), it cannot be smaller. The function (8) is thus of the form

$$\Psi_0 = c_n \exp(\mathrm{i}\phi_n)\,\psi_n, \tag{12}$$

where the phases ϕ_n are random. (The coefficient c_n will be discussed below.) Making use of the usual expression for the conductivity of a metal with a spherical Fermi surface of area S_F, namely s

$$\sigma = S_F e^2 l / 12\pi^3 \hbar (4\pi\epsilon_0). \tag{13}$$

and putting $l \approx a$, leads to a value

$$\sigma = \tfrac{1}{3}e^2/4\pi\epsilon_0 \hbar a \tag{14}$$

which is in the range $3 \times 10^5 - 5 \times 10^5\,\Omega^{-1}\,m^{-1}$, if a is a few Ångströms†. It is found that, in materials like liquid transition-metals and intermediate valence compounds, the resistivity as the temperature rises does not increase much above the reciprocal of this value; typical behaviour is shown in figure 5. Values of σ up to 2 higher or about more can be accounted for a larger area of a non-spherical Fermi surface.

Anderson showed that, if V_0/B is increased still further, at a value shown by more recent calculations (Edwards & Thouless 1972) to be

$$(V_0/B)_{\mathrm{crit}} \approx 2, \tag{15}$$

all states in the band become localized; that is, they have the form

$$\Psi = e^{-\alpha r}\Psi_0, \tag{16}$$

where Ψ_0 is given by (12). The quantity α tends to zero as V_0/B tends to the critical value. When states are localized, a degenerate gas of electrons with limiting Fermi energy E_F cannot conduct without thermal excitation. Thus if the parameter V_0/B is varied through the critical value, a metal–insulator transition is possible, in the explanation of which electron–electron interaction does *not* play an essential part. In a rather simple sense, the transition is one from a state in which electrons at the Fermi energy are trapped by the disorder to one in which they are not. The electrons

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† Ångström (Å) = 10^{-10} m = 10^{-1} nm.

are 'stuck'; a 'hole' would not be mobile, in marked contrast to the Wilson model for crystals. As the disorder increases, σ is given by

$$\sigma = S_F e^2 a g^2 / 12\pi^3\hbar$$

where g is the amount by which the density of states is decreased by disorder.

The present author (Mott 1966, 1967) first pointed out that, if the Anderson condition is not satisfied, so that

$$V_0/B < (V_0/B)_{\mathrm{crit}}, \tag{17}$$

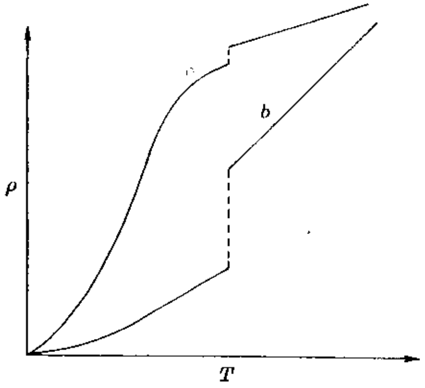

FIGURE 5. a, The resistivity of a transition metal below and above the melting point (schematic). b, The resistivity of an alkali metal.

states in the tail of the band will still be localized, and the localized and non-localized states are separated as in figure 6 by a critical energy E_c, called (Cohen *et al.* 1969) the 'mobility edge'. As E tends to E_c, α in equation (16) is believed to behave like

$$\alpha \sim (E - E_c)^s, \tag{18}$$

where s is $\frac{2}{3}$ according to some authorities, and 0.6 according to others (for references see Mott 1981). Thus for a degenerate electron gas, a metal–insulator transition (the 'Anderson transition') will occur if the Fermi energy E_F moves across E_c. If $E_F - E_c > 0$, conduction will be 'metallic', but depend little on temperature. If $E_F - E_c < 0$, two forms of conduction are expected: at high temperatures by excitation to a mobility edge, so that

$$\sigma = \sigma_0 \exp\{-(E_c - E_F)/kT\}, \tag{19}$$

/F

where the value of σ_0 will be discussed below; at low temperatures by variable-range hopping from one localized state to another. If electron–electron interaction is neglected, this leads to a conductivity of the form, in the limit of low T,

$$\sigma = A \exp(-B/T^{\frac{1}{4}}), \tag{20}$$

where $B = \text{const.} \times \{\alpha^3 N(E_F) k\}^{\frac{1}{4}}$. This form of conduction has been extensively observed, in non-crystalline semiconductors and impurity bands, but an exact correspondence with equation (20) in neither found nor expected, in view of the considerable deviations from (20) predicted as a result of electron–electron interactions (Pollak 1980, 1981; Mott 1979; Mott & Davies 1980; Efros & Shklovskii 1975; Davies *et al.* 1982). (The work of Efros and Shklovskii was criticized by the present author (Mott 1975), but we now believe it to be correct (cf. Davies *et al.* 1982).)

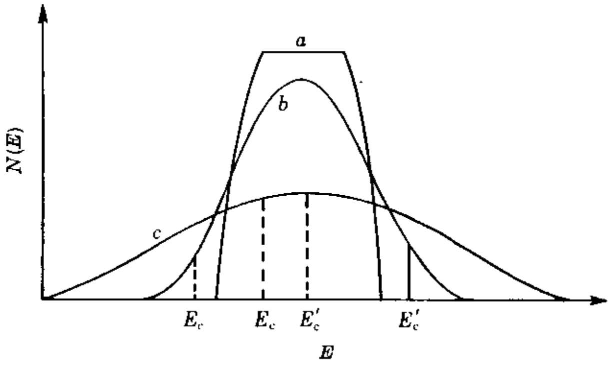

FIGURE 6. The density of states in a narrow band: a, for a crystal; b, when $l \approx a$ (the Ioffe–Regel condition); c, for disorder near the critical value. The mobility edges E_c, E_c' are shown.

If then E_F can be made to move through E_c, a metal–insulator transition is expected with resistivity as a function of temperature as in figure 7. The quantity σ_0 has been called by the present author the 'minimum metallic conductivity' ($\sigma_{\min}$) and is calculated, with the use of functions of the form (12) and a density of states as in figure 6 to be

$$\sigma_{\min} = Ce^2/4\pi\epsilon_0\hbar a, \tag{21}$$

with C in the range 0.025 to 0.05. Its existence is controversial. The present author believes that it is correct to write $\sigma_0 = \sigma_{\min}$ in equation (19) but whether the conductivity in the limit of low temperatures changes discontinuously, or only fairly rapidly as E passes through E_c, is at present uncertain. Mott (1981) has related it to the index s in equation (18). If $s < \frac{2}{3}$ (for instance 0.6) there should be a very narrow range of $E - E_c$ in which σ tends to a limit less than $\sigma_{\min}$ as $T \to 0$, and in which it should be highly T-dependent. (See the dotted line in figure 7.) Unfortunately the only experiments relating to this problem are for *uncompensated* Si:P (see § 5) for which electron–electron interaction plays a major role (Rosenbaum *et al.* 1980; Mott 1981; Kaveh & Mott 1982) which will be discussed below.

The position of the mobility edge must, in certain cases, approach the classical percolation limit (Kirkpatrick 1971), if the chance of tunnelling to a distant site drops rapidly with distance (Mott & Davis 1979, p. 40). A quantitative description of how this occurs has not been given. Various authors have used percolation theory to describe a metal–insulator transition, for instance Holcomb (198~~1~~), in materials 2 such as the tungsten bronzes, and Abeles *et al.* (1975) in dispersed metal particles in insulators. In the author's view these are, in fact, both Anderson transitions and show the phenomenon of a minimum metallic conductivity (Mott & Davis 1979, p. 158).

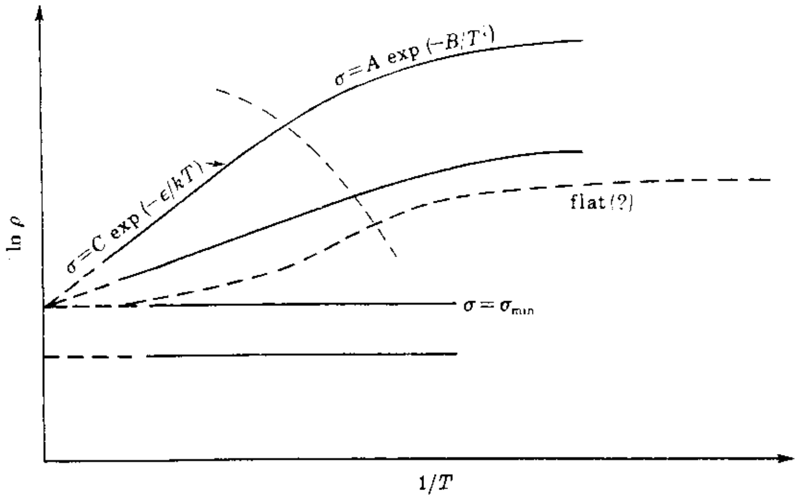

FIGURE 7. Resistivity as a function of temperature for a material undergoing an Anderson transition in three dimensions, it being supposed that α remains constant and the transition is driven by shrinking the orbits, for instance by a magnetic field. The dotted line shows the behaviour if $\sigma_{\min}$ does not exist.

4. IMPURITY CONDUCTION IN COMPENSATED SEMICONDUCTORS

Undoubtedly the most direct way of testing these ideas is by the study of conduction in impurity bands in doped and compensated semiconductors. Here the electronic orbits are large compared with the interatomic distance so effects concerned with distortion of the surrounding lattice are likely to be small.

Impurity conduction in compensated silicon and germanium was discovered by Hung & Gliessman (1950): in SiC it was first observed by Busch & Labhart (1946), the idea being earlier proposed by Gudden & Schottky (1935). It is a form of conduction in which an electron hops from an occupied to an unoccupied donor (or acceptor). The conductivity varies as $\exp(-2R/a_H)$, R being the mean distance between the donors. In modern terminology the electrons are thought to be Anderson-localized on the donors, the random field being that of the charged acceptors. Except that the donors are distributed at random in space (introducing

a further tendency towards localization), the situation is exactly that of the Anderson model of figures 4 and ~~5~~. The $T^{\frac{1}{4}}$ law is expected, and found approximately /6 in certain cases at low temperatures, but in much work (e.g. Fritzsche & Cuevas 1960; Davis & Compton 1965) a constant activation energy (ϵ_3) is found. This is usually described as caused by hopping to nearest neighbours only, but Pollak (1980) gives arguments to show that it is a form of variable-range hopping affected by electron–electron interaction. The evidence is discussed in detail in an extensive investigation of hopping conduction in p-type germanium for large uniaxial stresses and high magnetic fields by Chroboczek *et al.* (1981).

When the orbitals begin to overlap strongly, a metal–insulator transition of purely Anderson type is expected, correlation for a less than half-filled band being probably unimportant†. Both the random field and the random positions of the centres combine to give Anderson localization, the latter being probably the most important. Anderson localization in mid-band, resulting from the random positions alone, is calculated by Debney (1977) to occur when‡

$$n^{\frac{1}{3}}a_H \approx 0.34. \tag{22}$$

Puri & Odagaki (1981) find for the constant 0.252. I should like to emphasize that (22), just like (16), results from equating $1/n^{\frac{1}{3}}a_H$ to the logarithm of a *large* number (cf. Mott & Davies 1980), and so should be little dependent on the form of the conduction band.

We consider that for compensated materials the metal–insulator transition, with increasing concentration, is of pure Anderson type. Fritzsche (1978) points out that $\sigma_{\min}$, the value of the conductivity for which the activation energy disappears, agrees well with (21). Figure 8 illustrates this. For doped semiconductors the data are taken from Fritzsche (1978); for InSb with higher concentration, the transition being induced by a magnetic field, from Isheda & Otsuka (1977*a*, *b*); for amorphous Fe–Ge, for which the transition occurs at 20% Fe, from Daver *et al.* (1974); for $La_{1-x}Sr_xVO_3$ from Dougier (1975) and for carbons, where the transition occurs on annealing, from Bücker (1973). Some specimens are compensated, others less so. It will be seen that C in equation (21) appears to vary between the two values stated. Further evidence comes from such systems as solid argon–lanthanum mixtures (Romer *et al.* 1981), for which unactivated conduction appears at

$$10^4 \leqslant \sigma \leqslant 3\times10^4\,\Omega^{-1}m^{-1},$$

and from Swenumson & Even (1981) on amorphous mixtures of Cs and Sb.

Some of the evidence for *n*-InSb comes from the work of Ferré *et al.* (1975), illustrated in figure 9. In this work the activation energy for conduction, interpreted as ϵ_3, is changed by the application of magnetic fields, as shown in the diagram. Since

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† I know of no formal proof of this.

‡ Economou & Antoniou (1977) found with a rather different model that no localization is possible in mid-band. We think the model of Debney is more realistic (cf. Mott 1978). Fertis *et al.* (1981) also investigate the role of correlation combined with disorder and predict that the transition should occur at $n^{\frac{1}{3}}a_H \approx 0.16$.

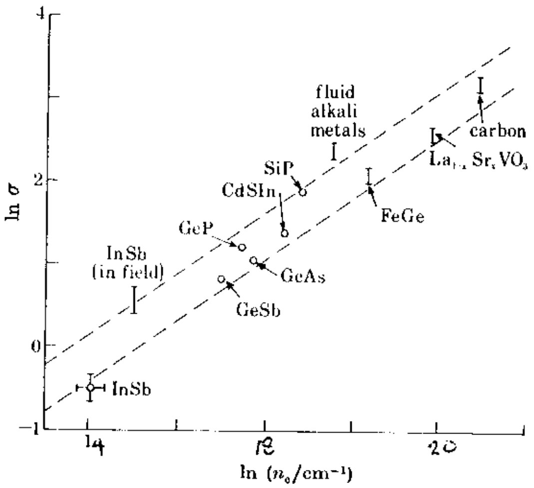

FIGURE 8. Comparison of experimental values of $\sigma_{\min}$ with theory. For doped semiconductors the data are from figure 2 of Fritzsche (1978), except for that in heavily doped InSb. Other data are from references given in text. The plot is a function of n_c, in electrons cm^{-3} at the transition. The lines are for $\sigma_{\min} = Ce^2/4\pi\epsilon_0\hbar a$ with $n_c = 1/a^3$ and $C = 0.05$ and 0.025.

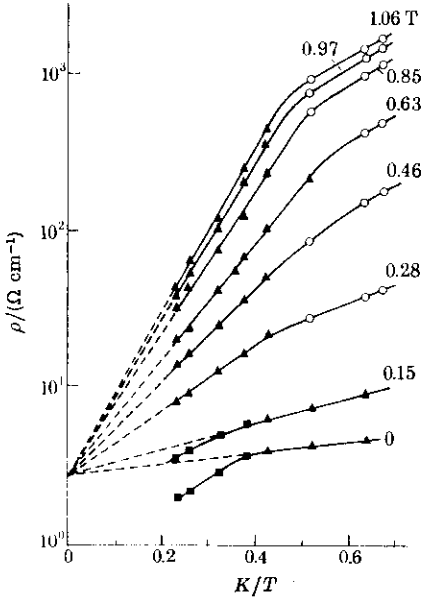

FIGURE 9. Variation of resistivity of samples of n-type InSb in various magnetic fields. The triangles represent ϵ_2 conduction, the circles hopping (ϵ_3) and the squares ϵ_1 (Ferré *et al.* 1975).

a is not varied, the curves are expected to extrapolate to the same point, as shown. The donor concentration is near 10^{20} m^{-3}; the observed point where the curves meet fits with a calculated value $\sigma_{\min} = 0.05e^2/4\pi\epsilon_0\hbar a$.

For discussion of the value of $\sigma_{\min}$, showing that the observed values scale correctly with a and fit the theoretical formula within a factor of about 2, see Pepper (1979).

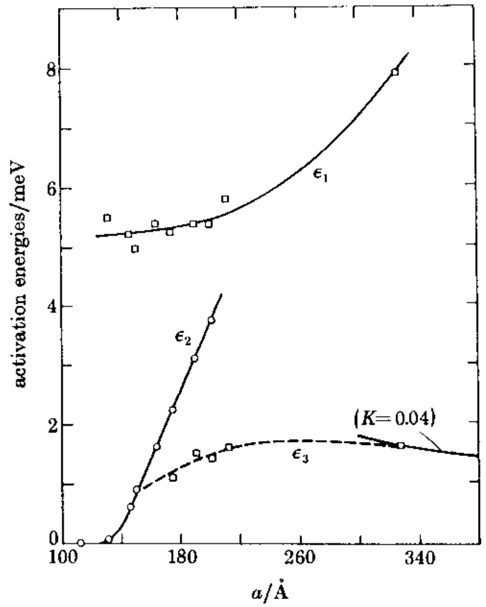

FIGURE 10. Plots of ϵ_1, ϵ_2 and ϵ_3 for doped Ge (Davis & Compton 1965).

Fritzsche (1958, see also 1978), and Davis & Compton (1965) introduced the concept of the D^- band, later referred to as the 'upper Hubbard band' and showed how to distinguish the energy ϵ_2 required to excite to the D^- band from that ϵ_1 required to excite to the conduction band. Figure 10 shows the results of the latter authors for the energies ϵ_1, ϵ_2 and ϵ_3 for germanium as a function of concentration of dopant. Fritzsche (1978) also shows the continuous decrease of ϵ_2 to zero. Mott & Davis (1968) interpret ϵ_2 as excitation to a mobility edge. Fritzsche (1978) pointed out that ϵ_2 is not observed in compensated germanium, though it appears to be in InSb (Mott & Davies 1980). Mott (1982) suggests that for compensated samples with $K \approx 0.5$ there should be no ϵ_2 conduction, because delocalization will first occur near the Fermi energy.

5. IMPURITY CONDUCTION: UNCOMPENSATED SAMPLES

In uncompensated samples both the Hubbard U and the disorder will play a role. The problem is similar to that of the transition in metal–ammonia solutions and in fluid caesium. The first question to answer is whether, as for crystals, a discontinuous transition is to be expected. The present author (Mott 1978*a*, *b*) has pointed out that, since a discontinuity depends on the Fermi energy behaving as $n^{\frac{2}{3}}$ (or n^t with $t > \frac{1}{3}$), if E_F lies in a band tail, no discontinuity is expected. The argument is as follows. Suppose that the density of states behaves like E^t (instead of $E^{\frac{1}{2}}$) in the tail. Then the kinetic energy will behave like

$$\int E^{t+1}\,dE = (t+1)^{-1}E_F^{t+2}.$$

The number of electrons is

$$n = \int E^t\,dE \sim t^{-1}E_F^{t+1},$$

so the kinetic energy per electron varies as

$$E_F^{t+2}/E_F^{t+1} \sim E_F \propto n^{1/(t+1)}.$$

For a minimum to occur, therefore, we must have $1/(t+1) > \frac{1}{3}$ and thus $t < 2$. In a tail one would expect a high value of t.

No discontinuity in the activation energy ϵ_2 has been observed for Si:P or any other doped semiconductor, though further investigation could be worth while. On the other hand, ~~both~~ for metal–ammonia solutions the solubility gap is well known, and just above the critical point $\sigma \approx 10^4\,\Omega^{-1}\,m^{-1}$, a reasonable value for σ_{min} with the appropriate value of a. Also in the fluid alkali metals, just above the critical point, σ is very near to the calculated value of σ_{min}, as the following table (taken from Freyland 1980) shows, with σ_1 in $\Omega^{-1}\,m^{-1}$ and $\sigma_1 = 0.05e^2/4\pi\epsilon_0\hbar a$):

	$10^{-5}\sigma$ (calc.)	$10^{-5}\sigma$ (obs.)	reference
Cs	1.6	2.5	Franz (1980)
Rb	1.8	2.5	Franz (1980)
K	1.9	3.0	Freyland & Hensel (1972)

We deduce that the Hubbard U 'wins' over disorder†.

Fluid mercury at high temperatures behaves differently; as the density decreases the 6s and 6p bands separate, giving rise to a pure Anderson transition. The present author (Mott 1974*a*) has given reasons for supposing that in band-crossing transitions the effect of correlation is likely to be small, so a discontinuity is unlikely. In fact, at the critical point in mercury, $\sigma \approx \underline{10^{-5}}\,\Omega^{-1}\,m^{-1}$, so the liquid–gas phase-diagram has the same origin as in, for instance, rare gases.

10^{-1}

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† Pitzer (1957) seems to have been the first to liken the liquid–liquid phase separation in metal–ammonia solutions to the critical concentrations of an alkali-metal vapour in the gas phase.

Turning now to the metal–insulator transition in doped semiconductors, since no discontinuity in ϵ_2 has been observed, until now it has been generally supposed that the transition must be due to the *gradual* overlapping of the two Hubbard bands. The bands will have localized tails, so the actual transition will be of Anderson type, occurring when states at E_F in the minimum of the density of states become delocalized. The material will have the electrical properties of an Anderson transition, as in figure 7, but the concentration at which the transition occurs will be given approximately by (6). As the surveys by Edwards & Sienko (1978, 1981) show, the concentration depends little on the nature of the conduction band. Figure 11 shows some of their results. Mott & Davies (1980) discuss the various terms that affect the energies of the two bands, particularly the large change in the polarizibility (that is, in κ) resulting from heavy doping (Castner 1980; Gunn & Ortuno 1980; Ortuno 1980). In our view all these make little difference, because the width of the lower band increases so rapidly with increasing concentration. The upper Hubbard band (described as a D^- band by Fritzsche (1962) prior to Hubbard's work) does not shift very much with energy according to Mott & Davies (1980); the radii of the orbitals are about four times larger than for the neutral donors. Also the band probably overlaps the conduction band. At the transition, then, the density of states should appear as in figure 11. It will be seen that a large difference between ϵ_2 and ϵ_1 seems hard to understand for uncompensated samples. However, it seems

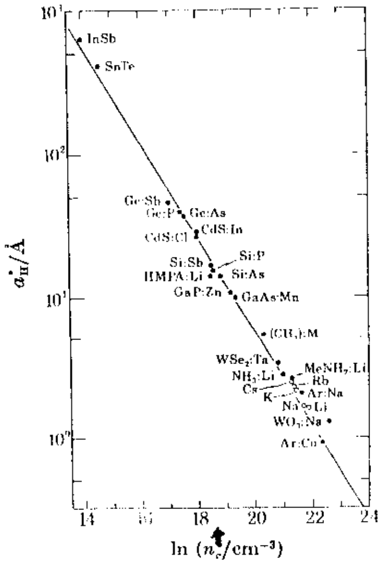

FIGURE 11. Comparison of the formula $n_c a_H = 0.26$ with experimental data (Edwards & Sienko 1981).

to be observed, and we may have to assume that the D⁻ band has a large tail (Mott 1982), probably due to the many-valley nature of the conduction band, not included in the calculations of Mott & Davies (1980). The considerations of Bhatt & Rice (1980, 1981) suggest that this is not unexpected.

I have already referred to the work of Rosenbaum *et al.* (1980) on the existence or otherwise of $\sigma_{\min}$. These authors measured the resistivity ρ of specimens of Si:P down to 2 mK; a specimen is counted as 'metallic' if ρ tends to a finite value, insulating if it tends to infinity. A plot of ρ, in the limit of low T, is given in figure 12.

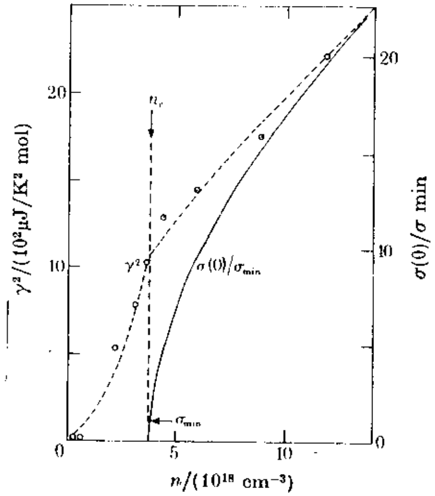

FIGURE 12. Conductivity of Si:P in the limit as $T \to 0$ as a function of phosphorus concentration (Rosenbaum *et al.* 1980); γ^2 is also shown, where γT is the electronic specific heat.

Below the calculated value of $\sigma_{\min}$ these authors find, within a range of concentration not greater than 1 %, specimens for which σ is as little as 0.01 $\sigma_{\min}$. It is not yet certain whether this is due to long-range fluctuations in composition, giving percolation channels, through the specimen. Rosenbaum *et al.* invoke the scaling theory of Abrahams *et al.* (1979) criticized by Mott & Kaveh (1981). The present author (Mott 1981) considers that the existence of $\sigma_{\min}$ depends on whether s in equation (18) is greater or less than $\frac{2}{3}$. Some authors have claimed that 0.6 is the correct value for s (for references see Mott 1981) and if so the present author (Mott 1981) has shown that results such as those of Rosenbaum *et al.* can be explained. On the other hand other authors find $s = \frac{2}{3}$, in which case homogeneous specimens should show a discontinuous drop from $\sigma_{\min}$ to zero as the concentration is changed. Neither of these values is universally agreed (C. Wegner private communication).

The present author (Mott 1981) considers that his derivation of $\sigma_{\min}$ remains valid in the formula

$$\sigma = \sigma_{\min} \exp(-\epsilon/kT),$$

for conduction at a mobility edge: it is only in the limit as $T \to 0$ that the concept is in doubt. Götze (1981) and Belitz & Götze (1981) point out that a theory developed by Götze in which $\sigma(E) \sim (E - E_c)^{\frac{1}{2}}$ is compatible with much of the data.

Above the metal–insulator transition Thomas *et al.* (1981) have measured the electronic specific heat, and find it follows the equation for free electrons in the conduction band, as was also found earlier by Sasaki (1980). On the other hand, the conductivity drops well below the Ioffe–Regel value (14). The present author in many papers has proposed that this is because the electrons move in a 'metallic' impurity band, in the Ioffe–Regel régime, so that (17) can be applied, the high value of the specific heat being due to electron–electron interaction†. But, in addition to the specific heat, there is much evidence (Senelius & Berggren 1979, 1981; Fritzsche 1980) that the electrons in the metallic range of concentration are in the conduction band (*not* in an impurity band), and that $l > a$. First Berggren (1982) and then in more detail Kaveh & Mott (1982) show that the conductivity does in fact drop as l approaches a, owing to a correction in the wavefunction fed into the Kubo–Greenwood formula. The latter authors find (as does Berggren, apart from the term in braces)

that

/r

$$\sigma = \sigma_{\mathrm{B}}\left[1 - \frac{3}{(k_{\mathrm{F}} l)^2}\left\{1 - \frac{l}{L_{\mathrm{i}}}\right\}\right], \tag{23}$$

where L_{i} is the inelastic diffusion length. The term in braces is expected to tend to zero rapidly with increasing temperature. All this applies only if l is due to elastic collisions, so the Ioffe–Regel formulae for, for instance, transition metals at high temperatures remains valid, because l is determined by collisions with phonons and these are inelastic.

If this is correct, it looks as if there must, after all, be a discontinuous transition in uncompensated Si:P; we have seen that the Fermi energy, when the transition is approached from below, remains in an impurity band. This conclusion is new and certainly controversial. Experimental work is needed to see if ϵ_2 really tends to zero as the transition is approached from below.

According to these considerations, σ *must* jump discontinuously to zero at the transition, and the lowest metallic values have nothing to do with $\sigma_{\min}$ (as observed for instance in compensated samples); it will be the value of σ at which the free energies of the states with bound and free electrons cross (as described by Senelius & Berggren 1980). Also, σ at finite temperatures should show a discontinuity as a function of concentration.

Recently much work has been carried out on the infrared absorption in impurity bands (see references in *Phil. Mag.* **42**, no. 6 (1980), the proceedings of conference held at Würzburg in 1979). Exciton-type lines, that is lines resulting from a transfer of electrons from one donor to another nearby already occupied, fill most of the gap.

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† For other investigations, see Kamimura (1980), Chao & da Silva (1979) and da Silva *et al.* (1981).

The randomness of the positions of donors has the result that the absorption caused by these transitions has a strong low energy tail. In fact Bhatt & Rice (1980, 1981) show that in many-valley semiconductors there will *always* be some D^- and D states, so that, when electron–electron interaction is taken into account, there is no Hubbard gap.

6. MATERIALS WITH INTERMEDIATE VALENCIES

The existence or otherwise of the minimum metallic conductivity is proving a controversial matter. Another case in which it may be in doubt is provided by SmB_6, a material in which the Sm ions exist in two valency states. The current interpretation is that in these materials there is a very narrow 4f band, hybridized with a conduction band, as shown in figure 13. The result is that this material is not truly metallic. Though it behaves like a metal at room temperature, there is a small gap separating a full valence band from an empty conduction band, as shown in figure 13. A typical plot of resistivity against temperature for this kind of material is shown in figure 14. As regards a minimum metallic conductivity, the question is whether the flattening off at low temperatures is due to impurity conduction resulting from non-stoichiometry. If so, and the theory of impurity conduction presented here is correct, there should be some correspondence between the observed low temperature conductivity and the density of donors, according to equation (21). Measurements of the conductivity are due to Nickerson *et al.* (1971), Kasuya *et al.* (1979) and Allen *et al.* (1979). The conductivity below 5 K is very dependent on the specimens, and tends to fall with increasing perfection. Kasuya *et al.* find

if

$$\sigma = A + 2940\exp(-32/T^{\frac{1}{4}})$$

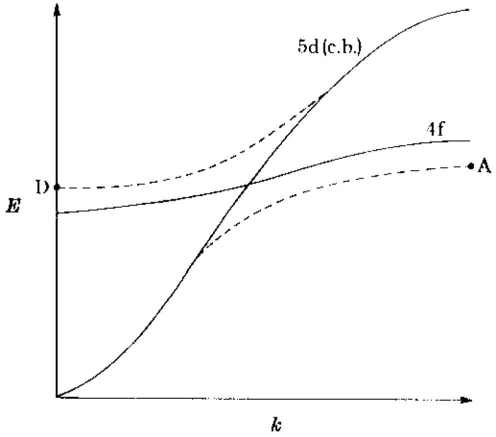

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FIGURE 13. Energies of 4f and 5d bands in SmB_6, showing how hybridization could lead to a gap ~~(c.b., conduction band)~~.

k is the wave number

between A and D.

with the constant A varying between 10 and $100\,\Omega^{-1}\,m^{-1}$. Allen *et al.* find a conductivity $30\,\Omega^{-1}\,m^{-1}$ for a specimen for which the Hall effect at low temperatures gives 5×10^{23} carriers m^{-3}. With this number of carriers equation (21) gives σ_{min} in the range $150–300\,\Omega^{-1}\,m^{-1}$, five to ten times that observed.

If SmB_6 is to be regarded as an uncompensated semiconductor, then we remark that, as a consequence of the ideas put forward here, equation (24) is empirical rather than theory-based, and long-range fluctuations in concentration are likely to cut down the conductivity near the transition. Kasuya's empirical equation does indeed suggest that metallic and non-metallic regions are in series. Further measurements of this system would be of interest. References for the hybridization theory are Coqblin & Blandin (1968), Mott (1974*a*, *b*, 1979) and, for the conductivity at low T, Martin & Allen (1979), Allen & Martin (1980).

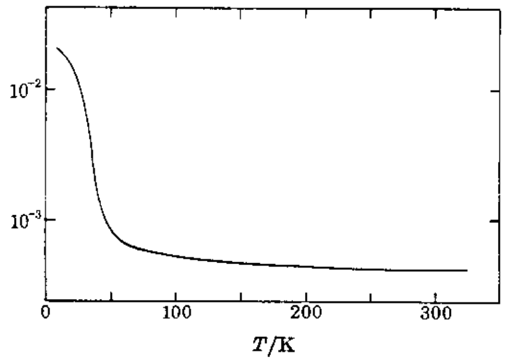

FIGURE 14. Resistivity in Ω cm ~~and Hall coefficient in cm³/Ω~~ as a function of temperature for SmB_6 (Nickerson *et al.* 1971).

7. VERWEY TRANSITIONS

Another form of metal–insulator transition is the 'Verwey' transition, of which Fe_3O_4 and Ti_4O_7 are the best known examples. In such materials two ions, Fe^{2+} and Fe^{3+}, or Ti^{3+} and Ti^{4+}, share equivalent sites in the lattice. At low temperatures they take up an ordered structure and the conductivity is activated; at the Verwey temperature the long-range order disappears and the conductivity increases by about two orders of magnitude to a value of about $10^4\,\Omega^{-1}\,m^{-1}$. Whether the mechanism of charge transport is then truly metallic is a matter of dispute.

An interesting feature of these materials is that a relatively small concentration of impurity (1–2 %) can destroy the sharp transition; at low temperatures the two charge states appear frozen at random sites.

Some references are: to Verwey's original work, Verwey (1935); to the experimental electrical properties of Fe_3O_4 and its alloys, Whall *et al.* (1977); to those of

Ti_4O_7. Lakkis *et al.* (1979) and Schlenker & Marezio (1980): to the author's theoretical discussion Mott (1979). Vol. 42, no. 3 of the *Philosophical Magazine* (1980) contains a fairly recent collection of papers on the subject, from a conference held in Cambridge in 1979.

8. TWO-DIMENSIONAL PROBLEMS

The m.o.s. (metal oxide semiconductor) transistor has made possible investigations in the inversion layer at the Si/SiO_2 interface. At low temperatures a degenerate two-dimensional gas is formed, in an environment where random charges in the oxide produce Anderson localization. E_F can be moved through E_c by a change in the gate voltage, so curves as shown in figure 7 can be obtained. This was proposed by the present author (Mott 1973) and by Stern (1974): a review of the early experiments was given by Mott *et al.* (1975). Briefly:

(*a*) The two-dimensional form of variable-range hopping ($\sigma \propto A \exp(-B/T^{\frac{1}{3}})$) is observed.

(*b*) The two-dimensional expression for $\sigma_{\min}(0.1\,e^2/\hbar)$ is also observed in many cases, though long-range fluctuations can lead to considerably larger values (Pepper 1977).

More recently, by the use of a scaling argument Abrahams *et al.* (1979) were able to show that in the 'metallic' régime the conductivity should be of the form

$$\sigma = e^2 k_F l/2\pi\hbar - (e^2/\pi^2\hbar)\ln(L/l). \tag{24}$$

The first term is the Boltzmann form in two dimensions, the second gives a logarithmic correction. Here l is the mean free path and L is the size of the specimen, *or* the distance L_i diffused before an inelastic collision with another electron, given by

$$L_i \sim (D\tau)^{\frac{1}{2}} \sim lE_F/kT. \tag{25}$$

The $\ln T$ correction has been extensively observed: it is normally not more than 10% of the first term. Other theoretical derivations have been given (Gorkov *et al.* 1979, Kaveh & Mott 1981*a*). It should be emphasized that the theory is not specifically for amorphous materials, but claims validity whenever there is a mean free path. It is concluded that a two-dimensional material is never truly metallic, but that a weak power-law localization is present. In the limit of low T, Mott & Kaveh (1981) find that

$$\sigma = \text{const.} \times (L/l)^{\gamma}, \quad \gamma = 1/\pi^2 k_F l. \tag{26}$$

tending to zero with T (if $L_i < L$) as a very low power of T.

All this theory is for non-interacting electrons. When electron–electron interaction is taken into account, another term of very similar form is predicted (Altshuler *et al.*; Kaveh & Mott 1981*b*). The two terms behave differently in a magnetic field, and some experimental work is devoted to separating them (Uren *et al.* 1980; Davies *et al.* 1981). This work is developing rapidly and will not be described in detail here.

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