Conduction in Non-crystalline Materials
III. Localized States in a Pseudogap and Near Extremities of Conduction and Valence Bands

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Abstract

If the distance between atoms in a crystalline lattice is increased, an energy gap appears, which in a divalent material will separate occupied from unoccupied states of an electron. In a non-crystalline substance, a minimum is expected in the density of states (a 'pseudogap'). An approximate theoretical estimate is given of the depth of the minimum at which the one-electron states become localized so that $\langle \sigma_{\mathrm{E}}(0) \rangle$ vanishes; this turns out to be such that $N(E_{\mathrm{F}})/N(E_{\mathrm{F}})_{\mathrm{free}}$ is about $\frac{1}{3}$. The result depends rather sensitively on the parameters used; the value deduced from the experiments of Hensel and Franck (1966, 1968) on the resistivity of mercury at high temperatures gives for this ratio a value of $\frac{1}{5}$. It is shown also that the localized states at the extremities of a valence or conduction band are of negligible importance if the wave functions are s-like on the atoms or ions, but may be of importance if they are not. A discussion is given of the electrical behaviour of chalcogenide glasses, amorphous germanium and of some liquid semiconductors based on these ideas.

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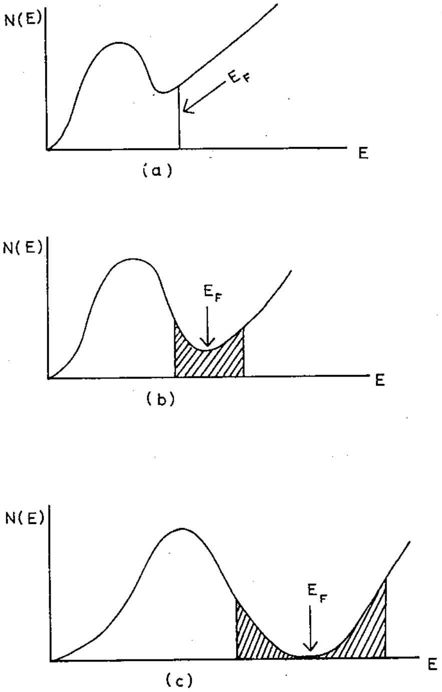
§ 1. Introduction

If the distance a between atoms in a crystalline array is increased, the overlap between the first and second energy bands for an electron decreases and eventually a gap appears between them. An array of divalent atoms, normally metallic, then behaves as a semiconductor or insulator, the two bands being the 'valence' and 'conduction' bands. This is a result of the Bloch–Wilson model of non-interacting electrons and is not a direct consequence of the correlation energy e^2/r_{12}. This paper discusses what happens to the band gap when the arrangement of the atoms is non-crystalline. Except where otherwise stated, the discussion is in terms of the Hartree–Fock model of non-interacting electrons. A comparison is made with the results of Franck and Hensel (1966) and Hensel and Franck (1966, 1968) on liquid mercury at high temperatures, and a discussion is given of conduction in chalcogenide glasses, amorphous germanium and some liquid semiconductors.

The present author (1966, 1967) has suggested that the density of states s likely to behave in the following way for large values of a:

(*a*) For disordered structures the gap will be replaced by a 'pseudogap' or minimum in the density of states $N(E)$ as illustrated in fig. 1. A gap may be retained if a limitation is set on the fluctuations of the interatomic

Fig. 1



Density of states for liquid divalent metals at low densities, showing the 'pseudogap' under the following conditions: (*a*) Conduction is metallic. (*b*) Conduction is by hopping. (*c*) Conduction involves excitation of electrons from the valence to the conduction band; excited electrons and holes may move by hopping.

distance: but in a liquid—or indeed in a crystalline solid—thermal fluctuations of density are bound to lead to a few states within the gap for an electron interacting with the ions in their instantaneous positions. *A fortiori* there can be no true gap when centres are distributed at random.

(*b*) States with energies E in the pseudogap may be localized in the sense of paper I of this series (Mott 1968 a); by this is meant that $\langle \sigma_E(0) \rangle = 0$ at $T = 0$, where the notation is that of paper I. In the author's earlier papers (1966, 1967) the factor $g = N(E_F)/N_{\text{free}}(E_F)$ was defined, and it was conjectured that for $g < \frac{1}{2}$ the mean free path would become comparable with the electron wavelength and that for smaller values of g localization must occur. In this expression $N(E)_{\text{free}}$ denotes the free-electron density of states $(2m/\hbar^2)^{3/2}\sqrt{E}/4\pi^2$, where m is the effective mass at the bottom of the band.

The first aim of this paper is to find a value for g at which 'localization' sets in, starting from a criterion proposed by Anderson (1958). Using a number of assumptions, a similar value is obtained, namely $1/g \sim 3$. The approximations made in our calculation are however crude and the experiments of Franck, to be discussed in § 3, suggest that $1/g \sim 5$ is the correct value. This would mean that for a divalent amorphous or liquid metal the lowest possible conductivity that is not thermally activated, since the mean free path L cannot be less than the interatomic distance a, is:

$$Se^2ag^2/12\pi^3, \quad g^2 \sim 0{\cdot}04, \qquad \ldots \ldots \ldots \quad (1)$$

where S is the free-electron Fermi surace area which is equal to $4\pi k^2$, where $k = 2\pi(3N/4\pi)^{1/3}$, and N is the number of atoms per unit volume. For mercury† this is $2600\,g^2 \sim 100\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$, and varies little from metal to metal. For lower values of σ, conductivity is either by thermally activated hopping from one localized state to another (a process similar to impurity conduction), or by excitation across an energy gap (or a pseudogap in which the density of states is too low for tunnelling from one localized state to another to occur). In either case an activation energy is required and σ should tend to zero as $T \to 0$ (assuming the position of the atoms remains unchanged).

Other results of this paper are:

(*a*) In a band at the bottom of which the wave function is s-like on all atoms (e.g. the conduction bands of liquid argon or of NaCl), localized states only occur as a consequence of large fluctuations of density and are probably of negligible importance in liquids. This is why electrons injected into the conduction band of liquid argon do not show a thermally activated mobility (for references see Lekner 1967). For an impurity band, on the other hand, where unlike a liquid the distances between centres are distributed at random, localized states can be important, *both* due to large fluctuations in the interatomic distance *and* (as in Anderson's model) to random fields.

(*b*) When however the wave functions are p- or d-like at an extremity of a band, localization at the top of a valence band or bottom of a conduction band can occur without large fluctuations of density but as a consequence only of the absence of long-range order as suggested by Banyai (1964). This kind of localization occurs *in* the band, and is additional to any strongly localized states in a tail of the $N(E)$ curve due to big fluctuation in the coordination number, density or composition.

In the light of these results, a discussion is given of conduction in chalcogenide glasses and amorphous germanium.

§ 2. LOCALIZATION FOR A DISORDERED ARRAY OF ATOMS IN s STATES

In principle localization ($\langle\sigma_E(0)\rangle = 0$) can occur for a given energy E for the following reasons:

(*a*) A random potential at each atom (Anderson 1958).

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† The conductivity of liquid mercury at the melting point is $11\,000\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$.

(*b*) Fluctuations in the density or mean interatomic distance.

(*c*) Absence of long-range order.

This section will deal with disorder due to (*b*) for bands, such as the conduction band of liquid argon, liquid metals or highly doped semiconductors in which at the bottom of the band the symmetry of the wave function on each atom is s-like. The present author (1967) has suggested that in the tail to the band due to large thermal fluctuations of density discussed by Zittartz and Langer (1966) the states are localized; for s states, fluctuations of density or interatomic distance are (in the absence of (*a*)) the essential cause of localization. In this section we shall estimate the condition for localization throughout the band due to (*b*). We shall use the method of Lifshitz (1964), who divides the atoms into pairs which are sufficiently close together to be treated as molecules. This is discussed in § 4.3 of his paper. Here we suppose that there are N atoms per unit volume and the mean distance between an atom and its nearest neighbour is:

$$R = \int_0^\infty r \exp(-4\pi N r^3/3)\, 4\pi N r^2\, dr$$

$$\simeq (4\pi N/3)^{-1/3}.$$

The energy of an electron resonating between an atom and its nearest neighbour will be spread over a range of energies J which we shall write:

$$J \sim W \exp(-\alpha R),$$

where α is defined as the rate at which the atomic wave function falls off with distance $[\Psi \sim \exp(-\alpha r)]$. We suppose that the pairs form a random lattice, that the average number of nearest neighbours is z (say six as in a simple cubic) and that the mean distance between a pair and one of its z nearest neighbours is:

$$R' = (\tfrac{1}{2}N)^{-1/3} \sim 2R.$$

The corresponding band width will be:

$$J' = zW \exp(-\alpha R').$$

Following Anderson's criterion, then, we conjecture that localization should occur throughout the band when

$$J > 5J',$$

and thus, if $z = 6$, when

$$\alpha(R' - R) > \ln 30.$$

Putting in numerical values we see that this gives:

$$N^{1/3}\alpha \simeq 0{\cdot}17.$$

Thus the one-electron states for an electron in sodium vapour may be localized if $N^{-1/3}$ is of the order of six times the atomic radius $1/\alpha$. The metal–insulator transition due to the term e^2/r_{12} will occur for rather smaller values of R': the condition found valid for semiconductors is:

$$N^{1/3} a_{\mathrm{H}} \sim 0{\cdot}25,$$

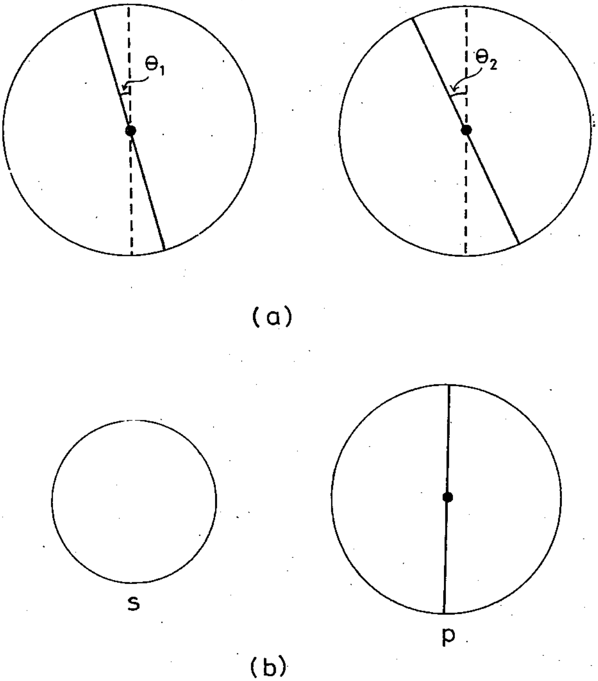
with $a_{\mathrm{H}} = 1/\alpha$. So in our view localization due to e^2/r_{12} will *always* take place before localization due to disorder, as the interatomic distance is increased. In the presence of compensation, of course, localization due to e^2/r_{12} (the Mott transition) does not occur: but compensation will always introduce random fields (as in (*a*) above), which increase the tendency to localization.

§ 3. LOCALIZATION IN A p-BAND OR PSEUDOGAP

This section puts forward the view that if the wave functions on the atoms are p- (or d-) like, localization can occur due to the absence of long-distance order without larger fluctuations in the interatomic distance than are usual in a liquid. For the energies in a pseudogap the present author (1967) has pointed out that the mean free paths are of order a when $g = \frac{1}{2}$: they cannot get any shorter and so it is likely that localized states occur when $g \ll \frac{1}{2}$. To obtain a rather better estimate of the value of g for which localization occurs, we seek to divide the atoms into strongly interacting pairs as in Lifshitz's work. We think in terms of a tight-binding approximation. We take a given eigenstate of the system, and *assume* that, for energies near to that at which localization occurs, the orientation of the p-wave functions varies in a random way from atom to atom. Thus, *for a given eigenstate*, we can divide the atoms into pairs such that interaction between the two atoms of a pair is as strong as the choice of neighbours allows. In fig. 2 (*a*), where the nodes of p functions on adjacent atoms are illustrated, the interaction will be strongest when $\theta_1 = \theta_2 = 0$, so that pairs must be chosen such that θ_1, θ_2 are as small as possible. If in a pseudogap the wave function is s-like on some atoms, p-like on others, the interaction will be a maximum in the case illustrated in fig. 2 (*b*). Thus near the bottom of a p-band, we argue that, for the eigenstate under consideration, $E = \int \psi^* H \psi d^3x$ will be negative for all pairs except a small proportion of pairs for which θ is particularly small, so that ψ will vary exponentially with distance except near these pairs. The wave-function, therefore, will have peaks at these pairs as in figs. 6 and 7 of Mott (1968 a). The Anderson criterion should determine whether or not each characteristic solution of the Schrödinger dies away exponentially from one of these peaks, giving localization.

We denote by J the overlap integral between two p-wave-functions oriented as in fig. 2 (*a*) with θ_1, θ_2 zero, and assume for the orientation with $\theta_1 = \theta_2 = \frac{1}{2}\pi$ that the integral is negligible. For a simple cubic crystal the p bandwidth would thus be $2J$ and the same will be assumed for the non-crystalline state. The density of states per atom will thus have the average

Fig. 2



Nodes in wave-functions on two atoms in a non-crystalline material.

value $1/2J$. As a rough approximation we take this formula for $N(E_{\mathrm{F}})_{\mathrm{free}}$ in the neighbourhood of the pseudogap. The factor g we take equal to the proportion of pairs on which the integral E is positive, so that a localized state or a peak in the wave-function can form there.

Now if we took these g/a^3 'molecules' and gave them all the same energy and arranged them on a lattice, they would form a band of width $2J'$ which we shall have to calculate. But actually they do not have the same energy: the fluctuation between their energies is the same as it would be if they were spread over an energy range $2J/g$. Thus the Anderson criterion says that localization should occur if

$$J/g > \sim 5J'.$$

We have next to estimate J'. Suppose the wave-function of an electron on one of these pairs falls off as $\exp(-\gamma r)$. Then the half band width, which is J when $g \sim 1$, should be when g is small:

$$J' = J \exp(-\gamma a/g^{1/3})/\exp(-\gamma a),$$

where a is the interatomic distance. Thus localization occurs when

$$\exp(-\gamma a/g^{1/3})/\exp(-\gamma a) = \tfrac{1}{5}g.$$

The next problem is to find a rough estimate for γ. In a crystal the wave-function falls off as $\exp(-\gamma x)$ as an electron penetrates from outside into a forbidden energy gap. According to Sommerfeld and Bethe (1933, see Mott 1966, p. 995):

$$\gamma = \tfrac{1}{2}\langle k_x \mid V \mid k_x\rangle/(\hbar^2 k_x/2m),$$

where V is the potential. We are interested in the situation where the electron gas is *nearly* a non-metal, and suppose that γ will be about the same as in the solid when this is so. To obtain a rough estimate, put the band gap $2\langle k \mid V \mid k\rangle$ equal to the energy at the zone boundary $(\hbar^2 k_x{}^2/2m)$: then

$$\gamma = \tfrac{1}{4} k_x.$$

But for a simple cubic lattice:

$$k_x = \pi/a,$$

so that $\gamma a = \tfrac{1}{4}\pi$. We thus obtain:

$$\exp\{-\tfrac{1}{4}\pi(g^{-1/3}-1)\} = \tfrac{1}{5}g,$$

which gives approximately:

$$1/g \simeq 3{\cdot}5.$$

Evidently this is a very rough approximation: but it leads to the conclusion that the author's (Mott 1967) former estimate $g = \frac{1}{2}$ was rather too large. Although any error in the estimate of γ makes little difference to g, little reliance can be put on our numerical value. The experiments described in the next section suggest that $1/g \sim 5$ is the value at which localization starts.

§ 4. APPLICATION TO MERCURY

In the work of Franck and Hensel (1966) and Hensel and Franck (1966, 1968) (fig. 3) the conductivity of mercury is observed to drop continuously by a factor 10^2 from about 10^4 to $10^2\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$ as the density falls to half its normal value. As the density decreases still further the drop in conductivity becomes much more rapid. The drop to $10^2\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$ can be accounted for by

(*a*) a drop in the mean free path L from 7 Å for normal liquid mercury to some quantity near the interatomic distance, 2 Å;

(*b*) a drop of g^2 from unity† for normal liquid mercury to the value for localization. The experiments suggest therefore that $g^2 = 1/30$, $g = 1/5{\cdot}5$ at the density at which localization starts.

For smaller densities g will have lower values and states at the Fermi energy must be localized and conduction will be by thermally activated hopping. Probably a comparatively small further expansion will produce a situation where the mobility for electrons having the Fermi energy is low

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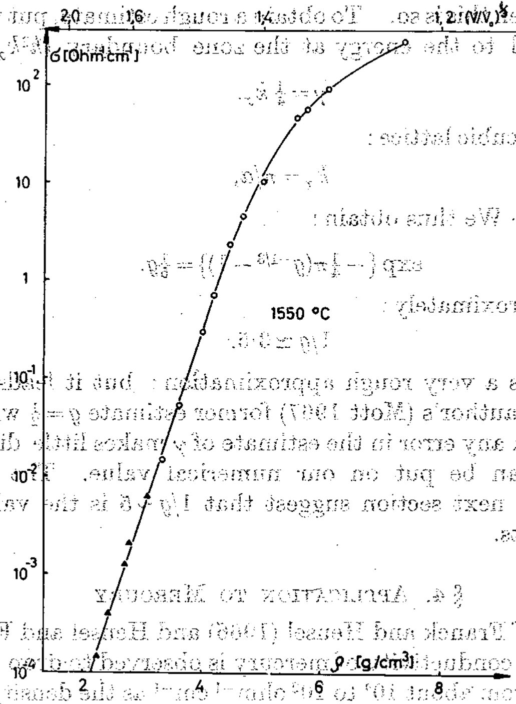
† The present evidence suggests that g differs little from unity for liquid mercury at normal pressures.

(fig. 1 *c*), and the main current is carried by excited electrons and holes, as in a conventional intrinsic semiconductor. As Hensel and Franck (1968) point our, the activation energy must tend to $I-E$, as for a vapour, as a increases indefinitely: they were able to measure activation energies from 1 to 5 ev by measuring $(d\sigma/dT)_V$. Their results are shown in fig. 3 of this paper.

Fig. 3



Conductivity of mercury as a function of volume at 1500°c (Hensel and Franck 1968).

§ 5. APPLICATION TO STATES NEAR THE EXTREMITIES OF THE CONDUCTION AND VALENCE BANDS

Banyai (1964) and Gubanov (1963) were the first to suggest that states at the extremities of a conduction or valence band in an amorphous material could be localized. In the light of the above considerations, I believe the following to be the position.

(*a*) If the wave-functions are s-like at the bottom of the band, as in the conduction band of liquid argon (Miller, Howe and Spear 1968, Lekner 1967), localized states will occur only through large fluctuations of density (Zittartz and Langer 1966). In the sense of the Franck–Condon principle thermal fluctuations will always produce such fluctuations in a liquid and indeed in a crystalline solid. Apart from these, any 'frozen-in' fluctuations in density would not necessarily produce any localized states.

(*b*) If the wave-functions are p- or d-like, the argument of § 3 leads us to suppose that localization can occur in a disordered system for energies near the extremities of the band. We shall not attempt an estimate of the energy at which localization occurs. We shall however use the model of the last section to obtain the density of states at the extremity of a band. Figure 2 shows the nodes of two p functions on a given pair of atoms. The energy will be a minimum when the nodes are as in fig. 2 (*a*) with $\theta_1 = \theta_2 = 0$. The energy of the pair when θ_1, θ_2 do not vanish is of the form

$$-A(\theta_1{}^2 + \theta_2{}^2).$$

The number of such states with θ_1 in the range θ_1 to $\theta_1 + d\theta_1$ and with θ_2 in the range $d\theta_2$ is proportional to

$$\sin\theta_1 \sin\theta_2 \, d\theta_1 \, d\theta_2.$$

From these equations it follows that $N(E)$ varies linearly with E at the extremity of a band, and the model gives no tail to $N(E)$.

§ 6. MOBILITY IN VARIOUS RANGES OF ENERGY

We next summarize the behaviour of the mobility μ to be expected in various ranges of energy in any situation near an energy E_c which separates localized and non-localized states.

(*a*) Suppose a pseudogap exists in which σ is negligible so that the carriers in the range of energy where current flows are non-degenerate, and the conductivity can be written, denoting the Fermi distribution function by $f(E)$:

$$\sigma = e \int N(E) \mu(E) f(E) \, dE. \tag{1}$$

If the states are localized, one could write:

$$\mu(E) = (e\nu_{\mathrm{ph}} a^2 \phi / kT) \exp(-W/kT), \tag{2}$$

where W is the hopping energy and ν_{ph} a phonon frequency ($\sim 10^{13}\,\mathrm{sec}^{-1}$). The factor $e\nu a^2/kT \sim 0{\cdot}5\,\mathrm{cm}^2/\mathrm{v\,sec}$. Note that the approximation $\nu \sim 10^{13}\,\mathrm{sec}^{-1}$ is valid only if $W > k\Theta_{\mathrm{Debye}}$ and is not valid for impurity conduction at low temperatures (cf. Miller and Abrahams 1960). ϕ is a number depending on the overlap between wave-functions and contains the factor $\exp(-2\alpha R)$ if the overlap between states is small. If however the overlap is considerable this factor will be of order unity. Moreover, as $E \rightarrow E_c$ each localized state will overlap a large number of others, so ϕ becomes much larger than unity.

Suppose now that $E > E_c$ and the states are non-localized. We start with the Kubo–Greenwood formula (cf. Mott 1968 a):

$$\sigma = \int \langle \sigma_{\mathrm{E}}(0) \rangle \frac{\partial f}{\partial E} \, dE.$$

Near E_c the phase of ψ will change in a random way from atom to atom, so that

$$\left|\int \psi_E^* \frac{\partial}{\partial x}\psi_E \; d^3x\right|^2$$

integrated over a volume Ω for which the wave-functions are normalized becomes, apart from a numerical factor:

$$|(\Omega/a^3)^{1/2}(a^3/\Omega)a^{-1}|^2 = a/\Omega.$$

The first two terms come from adding the contributions from each atom each with random sign, the last from $\partial/\partial x$. Thus:

$$\langle\sigma_E\rangle \sim \frac{2\pi e^2\hbar^3}{m^2}\frac{a}{\Omega}\{N(E)\}^2 . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we write $\partial f/\partial E = (1/kT)f$ (in the non-degenerate range), we see that

$$\mu = \frac{2\pi e\hbar^3}{m^2}\frac{a}{\Omega}\frac{N(E)}{kT}.$$

If $N(E)$ is written $1/E_0a^2$, where E_0 is a spread of energy levels and Ω is unit volume:

$$\mu = e\hbar^3/m^2E_0a^3\,kT.$$

Writing $\hbar^2/ma^2 \sim E$, and $\nu_{el} = E/\hbar$ this comes into the form:

$$\mu \sim ea^2\nu_{el}/kT. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

A similar formula has been obtained by M. L. Cohen using a Green function method, and was presented at the Gordon Conference (August 1968). The mobility is (say) 100 times greater than for thermally activated hopping, because $\nu_{el}/\nu_{ph} \sim 100$, and is of order 100 cm²/v sec. This surprisingly high mobility can be compared with the conventional formula for long mean free path L:

$$\mu = eL/\sqrt{(3mkT)},$$

and becomes identical with it when

$$L \sim \hbar/mv,$$

v being the thermal velocity. Unless the density of states is low, we do not expect values of μ lower than this in the non-hopping range.

(*b*) We consider now the low-temperature case when there is no energy gap and the conductivity depends on the behaviour of electrons with energies near E_F. In the case of non-localization, the above formulae give:

$$\sigma = \left[\frac{2\pi e^2\hbar^3 a}{m^2}\{N(E)\}^2\right]_{E=E_F}$$

This can be transformed to the form corresponding to (1) by writing as before:

$$N(E)=g/E_0a^3=gm/\hbar^2a,$$

so that

$$\sigma=g^2e^2/\hbar a.$$

If $1/a^3$ corresponds to the number of electrons per unit volume, the mobility is (for $g\sim 1$):

$$ea^2/\hbar \text{ cm}^2/\text{v cm}, \qquad (5)$$

which is considerably less ($\sim 0{\cdot}5 \text{ cm}^2/\text{v cm}$) than for non-degenerate electrons.

In the case of thermally activated hopping we estimate the conductivity as follows. Following Miller and Abrahams (1960) we note that only electrons with energies $\sim kT$ below E_F have a significant probability of hopping. The conductivity is thus of the form:

$$\sigma=N(E_F)\,kT\phi\,(e^2a^2\nu_{ph}/kT)\exp(-W/kT). \qquad (6)$$

The factor kT goes out and, apart from the factor ϕ already discussed, there is a drop of ~ 100 in the factor outside the exponential in σ as E decreases through the value E_c. However, near E_c, ϕ may be large and we do not think any discontinuity in σ is to be expected for a non-zero value of T.

In the author's earlier works it has been pointed out (Mott 1968 a) that W must tend to zero at low temperatures and (Mott 1968 b) that for σ a behaviour like $\exp(-\text{const}/T^{1/4})$ should occur. This argument will now be developed in greater detail. The assumption will be made that the Fermi energy lies in the hopping region, that kT is small compared with the band-width and with E_F and that the states are strongly localized ($\alpha R\gg 1$).

We need to consider electrons with energies a few multiples of kT from the Fermi energy only, of which there are per unit volume say $N(E_F)kT$: those with lower energy will on the average require a larger activation energy for each hop. If the electron jumps a distance less than R, then the number of states in the range dE is:

$$(4\pi R^3/3)\,N(E)\,dE,$$

so that the average spacing between energies is:

$$W=3/4\pi R^3N(E).$$

This will be the hopping energy. The jump frequency is thus:

$$\nu_{ph}\exp\{-2\alpha R-W/kT\}.$$

This will be a maximum for a value of R such that

$$2\alpha=(9/4\pi)/R^4\,N(E)\,kT.$$

If this gives a value of R *less* than the average distance R_D between centres, then the activation energy is:

$$\Delta E=3/\{4\pi R_D{}^3\,N(E)\}$$

and is independent of T. This is similar to the result obtained by Miller and Abrahams for impurity conduction: but for low T, if $R > R_D$, we see that the jump frequency and hence the conductivity behaves like:

$$\ln \sigma = A - B/T^{1/4}.$$

We shall show later that the conductivity of amorphous germanium is observed to behave in this way.

§ 7. HALL COEFFICIENTS

7.1. *Non-degenerate Gas*

In amorphous and liquid materials there are three ranges of energy to be considered.

(*a*) Energies so high that $L > \hbar/mv$, in which the usual band theory is applicable. v is here the thermal velocity of an electron.

(*b*) A range in which $L < \hbar/mv$, in which case a mean free path cannot be defined but the mobility is expected to be of order 10–100 cm²/v cm.

(*c*) The region of thermally activated hopping. Here Holstein and Friedman (1968) predict that, if $\mu_{\mathrm{Drift}} = \mu_0 \exp(-W/kT)$, the Hall mobility is $\mu_0(\exp(-\frac{1}{3}W/kT))$, and $\mu_0 \sim 0{\cdot}5$ cm²/v cm. However, Emin and Holstein (1969) suggest that in the adiabatic approximation of polaron theory, the activation energy is much less. This may be so for the kind of hopping considered here.

In case (*b*), as far as I know, no theoretical estimates of the Hall coefficient exist nor in particular of its sign for p-type conductors in cases (*b*) and (*c*). Since, if the electron states are written as superpositions of Bloch states, the superpositions contain essentially all the k vectors in a band, a negative value is not ruled out†. There is much evidence that these materials give a negative value of the Hall coefficient. We also remark that the usual derivation of a positive sign, which depends on a negative value of d^2E/dk^2 near the top of a band, cannot apply in these cases.

7.2. *Degenerate Gas*

Here in case (*b*) the mobility (5) is much smaller ($\sim 0{\cdot}5$ cm/sec). Again no theoretical treatment exists for the Hall effect.

§ 8. APPLICATION TO GLASSES AND AMORPHOUS GERMANIUM

The discussion in the previous sections suggests the following model. In materials which are intrinsic semiconductors like the chalcogenide glasses, valence and conduction bands will exist with a range of weakly localized states at the bottom, shown shaded in fig. 4, together with a tail of

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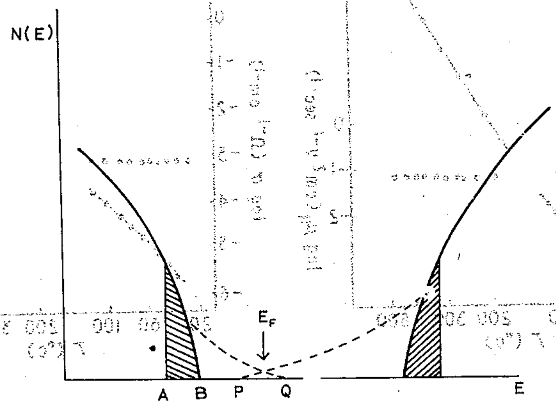
† Holstein, private communication.

strongly localized states due to structural defects which may give rise to d.c. or a.c. impurity conduction. This tail may be absent in liquids. It is generally supposed that there are more states in the tail below the conduction band than above the valence band, so that the Fermi energy E_F lies nearer the valence than the conduction band and these materials are consequently p-type.

Fig. 4



Suggested density of states in chalcogenide glass. Localized states are shaded. The states in the tails are also localized. States between P and Q are charged. E_F is the Fermi energy.

As emphasized by Stuke (1966, 1969), chalcogenide glasses and other amorphous materials show values of the conductivity of the form†:

$$\sigma = \sigma_0 \exp(-E/kT),$$

where (*a*) E is constant over a wide range of T, (*b*) σ_0 is approximately the same as for the crystal ($\sim 10^5$ ohm^{-1} cm^{-1}). Both these are shown particularly by Male's (1967) results (fig. 5). This suggests that the holes carrying the current are at energies near A in fig. 5 (non-localized), where the high predicted mobility (~ 50 cm^2/v sec) and the finite density of states may well give a value of σ_0 similar to that for the crystal.

On the other hand, Male's (1967) values of the Hall coefficient are negative, independent of T and the Hall mobility is 2–3 orders of magnitude lower (fig 5). As already stated, negative Hall coefficients are usual in p-type

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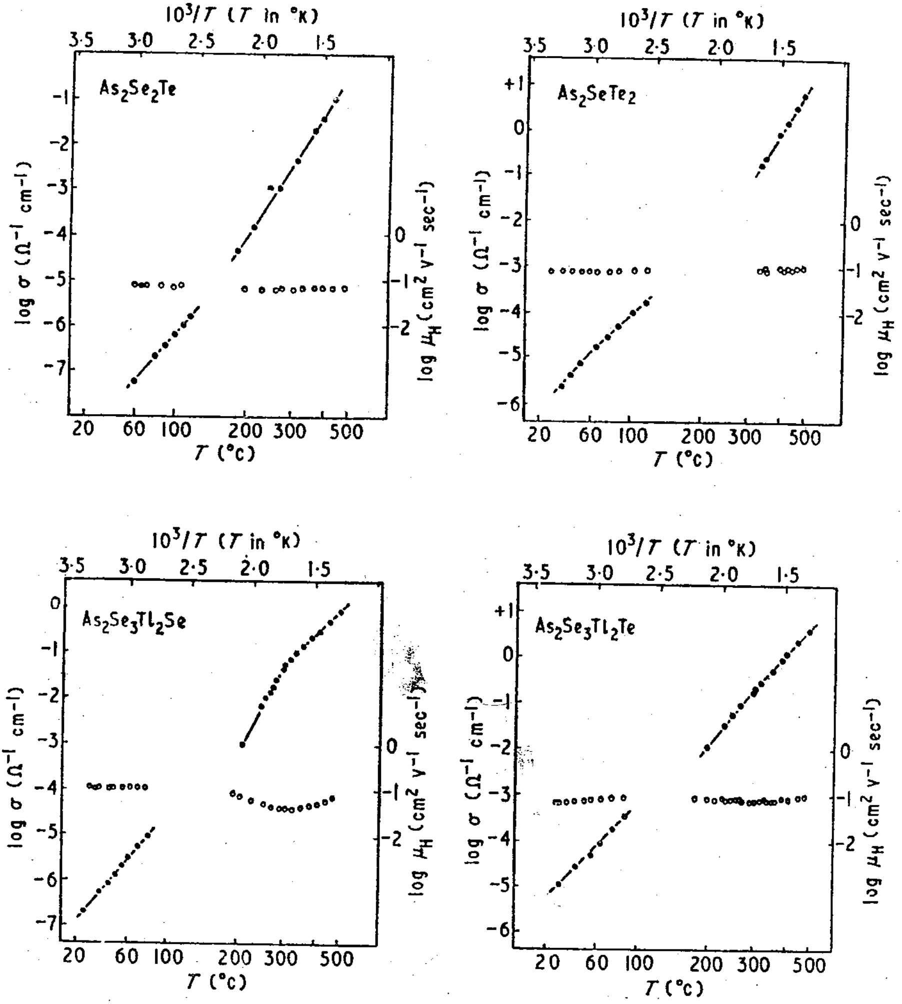
† In a crystalline semiconductor the mobility μ is proportional to $T^{-3/2}$ and the number of conduction electrons to $T^{3/2} \exp(-E/kT)$, so T cancels out from the term σ_0 outside the exponential. In the amorphous state for E just above E_c, μ is proportional to $1/T$ according to (2), and the number of electrons with E above E_c is proportional to T; so T still cancels out from σ_0.

non-crystalline materials and we believe that a correct theory would predict this. The small values of the Hall mobility are unexplained.

Fig. 5

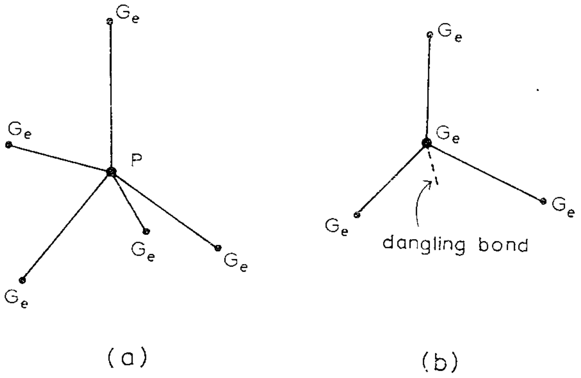


Hall mobility and conductivity of chalcogenide glasses (Male 1967).

We turn now to amorphous germanium. We first emphasize that the low conductivity of amorphous germanium and the fact that doping does not appear to be possible are probably because all the electrons in (say) phosphorous are likely to be taken up by bonds. We envisage a phosphorous atom as normally surrounded by five electrons as in fig. 6. Centres which can act as acceptors or donors are likely to be structural and normally to involve the host atom (fig. 7 *b*).

Grigorovici, Croitoru, Dévényi and Teleman (1964) have distinguished three temperature ranges in the conductivity of amorphous germanium and this is strongly confirmed by the measurements of the piezoresistance by Grigorovici and Dévényi (1968) (fig. 7). We follow Grigorovici in supposing that fairly well-defined acceptors exist, perhaps 'dangling bonds' as in fig. 6 (*b*), and that in the lowest range of temperature, conductivity is by 'impurity conduction', the electron moving by thermally activated hopping between centres with a concentration of say 10^{19} cm^{-3} and $\sim 0{\cdot}2$ ev above the valence band (fig. 8). Some compensation would fill a few of these acceptors, giving negative thermopower at low temperatures (compare Mott 1967). If this is a correct explanation, we should expect a plot of $\ln \sigma$ against $1/T^{1/4}$ at low temperatures to give a straight line. Figure 9 shows the results of Walley and Jonscher (1968) plotted in this way†.

Fig. 6



(*a*) Conjectural position of phosphorous atom in amorphous germanium. (*b*) Structural defect in Ge.

In the 'extrinsic' range we suppose that holes are excited into the range between E_c and $E_c{}'$, where localization is weak or non-existent, the mobility quite high, but the Hall effect *negative* as observed by Clark (1967).

We may speculate on the nature of the acceptors. In fig. 7 (*b*) a single electron is unpaired. The states of such an electron are split by spin–orbit coupling and it is possible that the infra-red absorption observed by Tauc, Grigorovici and Vancu (1966) is due to these centres.

Germanium seems to differ from the chalcogenide glasses in having an acceptor of fairly well-defined energy, so that the Fermi level is nowhere

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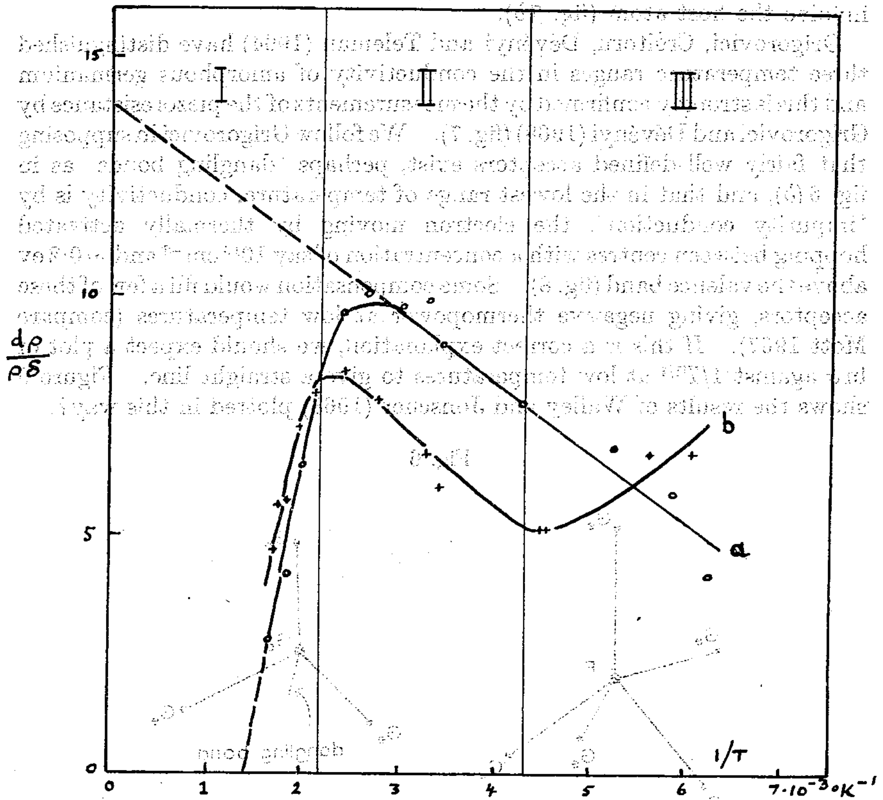
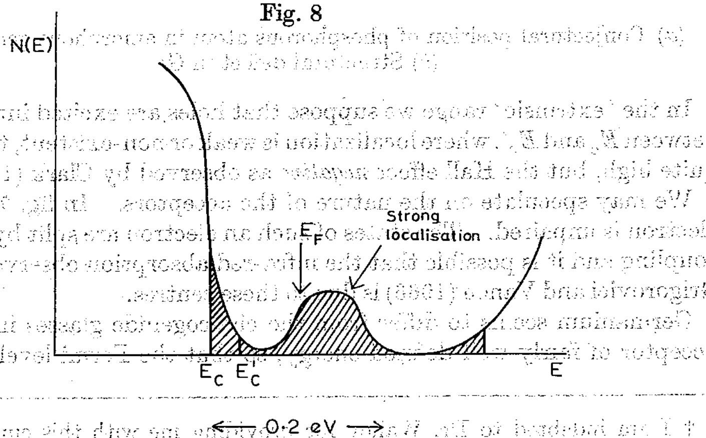
† I am indebted to Dr. Walley for providing me with this curve. Clark's (1967) results can be plotted in a similar way (Mott 1969).

Fig. 7



Piezoresistance of amorphous Ge (Grigorovici and Dévényi 1968). (*a*) Longitudinal and (*b*) transverse relative change in resistivity.

Fig. 8

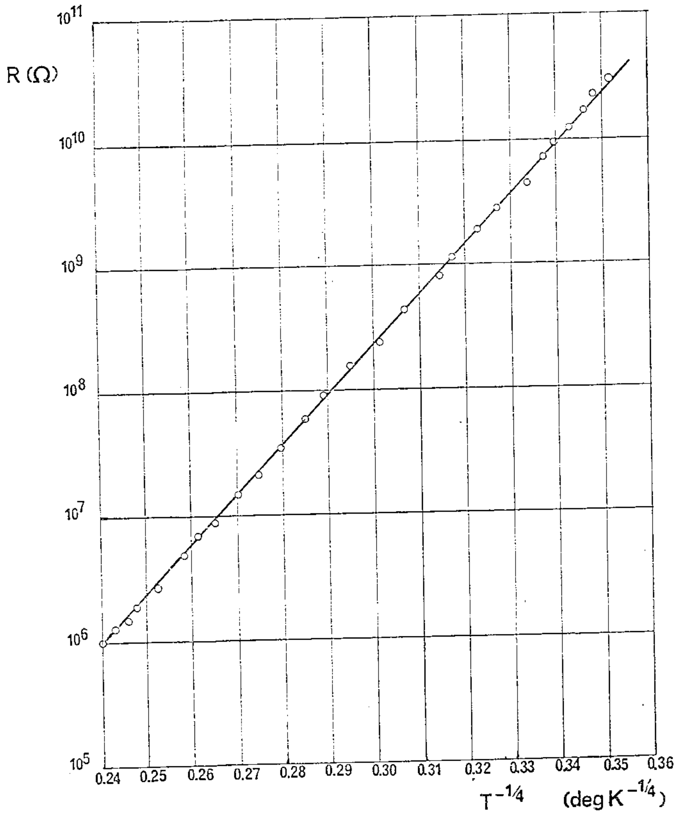


Suggested density of states in amorphous Ge. Localized states are shaded.

near the centre of the band. Perhaps this is because in the chalcogenide glasses the fluctuations of composition set up random fields which broaden the levels due to any structural defect.

The thermoelectric power of amorphous germanium is negative at low temperatures, then positive and negative again at high temperatures (see Mott 1967, fig. 16). This gives additional evidence for the existence of three conduction processes. We note that for germanium, unlike the chalcogenide glasses, the material has negative thermopower in the intrinsic range, suggesting that the mobility is higher in the conduction band.

Fig. 9



Resistance of amorphous germanium film plotted as ln R versus $1/T^{1/4}$. The plot is from curve A of fig. 6 of Walley and Jonscher (1968).

§ 9. LIQUID AND AMORPHOUS SEMI-METALS

For such materials we suppose that a pseudogap exists and that states may be weakly localized near the centre of the gap (fig. 1 (*b*)) and that the properties of electrons with energies E such that $E \simeq E_F$ determine the conductivity. We take as an example the case of liquid Te–Tl alloys investigated by Cutler and Mallon (1966), Enderby and Walsh (1966) and Donally and Cutler (1969). For liquid tellurium $\sigma \sim 500\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$ and for so high a value our analysis suggests that the Fermi level is not in the range of energies in which states are localized, and $g^2 \sim 0{\cdot}2$. At compositions near TeTl_2, σ drops to $\sim 100\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$, and $d\sigma/dT$ (which is positive) increases: at this composition the material is on the borderline of the hopping range. The Hall mobilities of order 0·3–0·5 cm^2/v sec. (Donally and Cutler 1969) are about what we expect for the drift mobility in the range (*b*) of § 7.2. We note that the Hall effect is *negative* for this p-type material: Allgaier has pointed out to the author that in many liquid semiconductors p-type thermopower is associated with negative Hall effect, and the experimental evidence suggests that either a very short mean free path or thermally activated hopping leads in general to a negative Hall coefficient, even for the motion of holes.

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