THEORY OF LOCALISATION IN DISORDERED SYSTEMS

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TRIESTE, JULY 1971.

1. Introduction.

Some ten years ago an eminent Cambridge physicist said that there were no outstanding problems left in solid state physics which were sufficiently challenging to be given to the best students when they started on their post-graduate careers. I think the theory of localisation in disordered systems is one (perhaps not the only one) example that this statement is perhaps an exageration. Even now there is no formal theory of disordered systems which we can use to calc late standard properties such as conductivity, optical absorption, and Hall effect. However, the foundations of such a theory are in the process of being laid, and perhaps this branch of solid state physics will become what Ziman calls "normal science" within the next five years.

The pattern of the present lectures is that I want first (section 2) to review some experimental facts about disordered systems which given knowledge of the existence and character of the electronic states, i.e. whether they are present or not, and whether they are localised or not. This review will present certain chosen aspects and is not intended to be exhaustive.

Section 2 is a brief review of experimental evidence for the metal insulator transition in disordered systems. Section 3 deals with the failure of "traditional" G.F. approaches to the problem. Section 4 deals with a simple approach to the impurity band problem which is essential to the approach we shall use to the M.I. transitions. Section 5 introduces and discusses the Anderson model The remaining sections deal with a new approach to the M.I. transition in the three types of systems with which we are concerned.

2. We shall follow Mott in defining a state to be localised if it does not contribute to the static electrical conductivity. Let us review briefly some experimental facts about crystalline systems and their theoretical explanation.

The conductivity of a normal metal at the absolute zero of temperature is found to be infinite. For other crystalline systems the conductivity is found to be zero. These differences were explained on the Wilson-Sommerfeld model in terms of the one electron branch structure which arises from the solution of the Schrödinger equation. According to this, the wave functions in allowed regions have the form

$$\psi(\underset{\sim}{r}) = e^{i \underset{\sim}{k}.\underset{\sim}{r}} u_{n\underset{\sim}{k}}(\underset{\sim}{r}) \qquad 2.1$$

in "allowed" regions which are separated from each other by forbidden regions where no bounded solutions exist. The difference between metals and insulators is then explained by the position of the Fermi level: in metals it lies in an allowed region, in insulators it lies in a gap. It can easily be shown that if the Fermi level lies in an allowed region the conductivity is infinite. This result follows either from linear response theory or from arguments which show that $\underset{\sim}{k}$ increases indefinitely on application of a field. In the insulator the Fermi level is in a gap, and the Valence band is full and the conduction band empty. It is therefore a sufficient condition for the conductivity to be zero for the density of states to be zero at the Fermi level. It is essential to understand that this is a sufficient and not a necessary condition.

Insulators exist whose existence is not explained in the one-electron theory (e.g. NiO). At least in some cases this can be explained on the basis of a many body argument due to Mott and Hubbard. Essentially the argument is that in a band Coulomb interactions can split the band so that a Fermi level which would lie in a band on one-electron theory in fact lies in a gap. The correct electron spectrum having been found, the distinction between metals and insulators follows as before.

If the gap between valence and conduction bank is sufficiently small thermal excitation can create an appreciable number of electrons in the conduction bank and holes in the valence band. In this case simple theory shows that the conductivity has the form:

$$\sigma = \sigma_0 \exp - E_g/2kT \qquad 2.2$$

This relation is experimentally confirmed and provides a method for determining E_g. A plot of $\log \sigma$ vs T^{-1} has the form show in Fig. 1.

Conversely an experimental result of this form is interpreted as implying the existence of an activation energy, i.e. of an energy gap.

Optical absorption also measures the energy necessary to excite an electron from the valence band to the conduction band. For parabolic bands and direct transitions the absorption coefficient has the approximate form:

$$\alpha(\omega) = C(\omega-\omega_0)^{1/2} \qquad 2.3$$

where

$$k\omega_0 = E_g \qquad 2.4$$

Experimental results of the form of Fig. 2 again are interpreted as implying the existence of a gap in the spectrum of electron states.

We now turn to experimental results on disordered systems. Here I wish to consider three types: 1) systems which give rise to impurity bands; 2) highly doped semiconductors; 3) amorphous semiconductors.

Some impurities, when put into a semiconductor in low concentration, produce additional states in the gap (e.g. Sb in Ge). These states can be seen, e.g. in optical absorption, as sharp lines. It is also possible to see transitions between two impurities as shown in luminescence.

As the density of donors is increased the luminescent line shape changes from a line to a Gaussian type curve (Fig. 3). On a simple argument this shape is proportional to the density of states and such results are therefore interpreted as showing that impurity - impurity interactions broaden the line into a continuous curve. As the density of impurities increases, the the experiments suggest that the density of states merges with the conduction band. With very high doping the absorption curve eventually looks like Fig. 4.

Comparison with Fig. 2 suggests that there is now a continuous distribution of states below the conduction band. Normally the experimental results are fitted by a curve of the form:

$$\alpha(\omega) = A \exp -\left(\frac{E}{E_0}\right)^{\alpha} \qquad 2.5$$

The absorption curve of most amorphous materials also has the same form, $\alpha - 1$ being the most common value. The density of states is now continuous with the conduction band and has a similar form shown in Fig. 5.

All the evidence suggests that when a semiconductor has a low density of impurities, the Fermi level is in the impurity band It is therefore surprising that where the density of impurities falls below a certain value, the conductivity falls by several orders of magnitude to a value which is experimentally indistinguishable from zero. The concentration when this happens is of the order of 3-4 effective Bohr radii. Since the conductivity is found to be zero in the impurity band, although luminescence measurements show that there are states at the Fermi level, we are found to conclude that there are certain states which can contribute to optical properties but which give zero conductivity. We call these localised states. Fig. 6 gives the experimental results for the conductivity as a function of T^{-1}. which also illustrate this transition. As the concentration increases the activation energy is seen to increase and eventually to go to zero. Fig. 7 gives further results for the conductivity for experiments in which acceptors are also present.

Experiments have also been carried out with much higher concentrations, e.g. for Na in Argon and Cs in Argon. The concentration at which the transition takes place is much higher, corresponding to about 15% and 40% respectively. The density of states is then presumably of the form shown in Fig. 5. There is no reason to believe that the Fermi level is in a region where the density of states is zero.

In the case of amorphous semiconductors, the conductivity has typically the temperature dependence shown in Fig. 8, showing the existence of a well defined activation energy. On the other hand, the absorption coefficient behaves as shown in Fig. 9. This again presents apparent contradictions: the presence of an activation energy shows that these are states which do not contribute to the conductivity, whereas the absorption coefficient data suggest a continuous distribution of states. The contradiction was resolved by the Mott-Cohen theory of a mobility gap which is illustrated in Fig. 10.

The experiments which we have described are typical of those which support the idea that there are electronic states present which do not contribute to the conductivity. In the next section we shall consider the "traditional" Green's function approach to such problems and why it fails.

3. The failure of "traditional" theories of disordered systems.

What we describe as the traditional theory of disordered systems is summarised in "Lectures on the Mathematical Theory of Disordered Systems", to which we shall refer.

In the traditional theory we study the behaviour of the average G.F., e.g. in $\underset{\sim}{k}$ representation, which may be written

$$\langle\langle G^{+}(\underset{\sim}{k}) \rangle\rangle = \frac{1}{E - k^2 - \Sigma(\underset{\sim}{k}, E)} \qquad 3.1$$

Now linear response theory enables us to write the conductivity as

$$\sigma \sim Tr\left[v \, (\eta_m G^{+}) \, v \, (\eta_m G^{+}) \right] \qquad 3.2$$

Here $\langle\langle \; \rangle\rangle$ denotes an average in a statistical sense over whatever cause of disorder is present, e.g. impurity positions (cf. L.M.T. 3.5).

Suppose that for the moment we assume $\langle\langle q \, v \, q \rangle\rangle = \langle\langle q \rangle\rangle \, v \, \langle\langle q \rangle\rangle$ where

$$q = \eta_m(G^{+}) \qquad 3.3$$

Then put $\Sigma(k,E) = A + iB$ 3.4

3.5

It can be shown on general grounds that $B \geq 0$. If $B \neq 0$ then 3.2 has the form

$$\sigma \sim \int \frac{k^2 B^2}{[(E - k^2 - A)^2 + B^2]^2} d^3k \qquad 3.6$$

which is clearly non zero if $B \neq 0$ and $\to \infty$ as $B \to \infty$
It is therefore difficult to see how, from such a theory, a result of the form

$$\sigma = 0 \qquad 3.7$$

$$N(E) = -\pi^{-1} Tr\, Im(G^+) \qquad 3.8$$

could emerge. It is not difficult to find more detailed contradictions. Thus, consider how we could try to describe an impurity band by approximation 4 of L.M.T.D.S. (p. 26). Essentially here $\Sigma(k,\omega) = \xi t(k,k)$. A look at the details in the one dimensional case shows that while an impurity band is formed Σ is purely real within the band, implying infinite life time and therefore conductivity. Again, all approximations for Σ in the one dimensional case lead to $Im\,\Sigma = 0$ at some finite E , for all concentrations, in contradiction to the exponential behaviour which would be expected from the absorption data for high densities.

These shortcomings are, I believe, essentially due to the fact that the k representation is not a good one for the problem. A localised state implied local asymmetry; the k representation implies translational invariance. This symmetry must be broken if localised states are to be obtained.

4. The density of states in an impurity band.

In order to obtain a feel for the problem, let us consider the impurity band case first; the understanding of this is essential to enable a correct theory to be formulated, as has been emphasized by Mott.

A defect of the mormal self energy expansions considered in L.T.D.S. is that it does not provide a form of self energy which reduces to the correct atomic limit in the low density case. In the atomic limit we can write the G.F.

$$G^{+}(\underline{r},\underline{r}',E) = \sum_{n} \frac{\psi_n(\underline{r})\,\psi_n(\underline{r}')}{E-E_n} \qquad 4.1$$

where the $\psi_n(\underline{r})$ are the atomic wave functions. For E_n near a particular E_{n_0}, say E_0, we can write

$$G^{+}(\underline{r},\underline{r}',E) \doteq \frac{\psi_0(\underline{r})\,\psi_0(\underline{r}')}{E-E_0+i\varepsilon} \qquad 4.2$$

which gives $$\mathrm{Im}\, G^{+}(\underline{r},\underline{r}') = -i\pi\,\psi_0(\underline{r})\psi_0(\underline{r}')\,\delta(E-E_0) \qquad 4.3$$

then we get $$-\pi^{-1}\,\mathrm{Tr}\left[\mathrm{Im}\, G^{+}(\underline{r},\underline{r},E)\right] = \delta(E-E_0) \qquad 4.4$$

which is intuitively correct.

Now consider the corrections due to this as a result of a low density of impurities, so that an electron can see several impurities. By analogy with the virial expansion we can consider interactions between pairs only in first approximation. Defining the propagator $K(t)$ by

$$\int_0^{\infty} e^{iEt}\, K(t)\,dt = i\,G^{+}(E) \qquad 4.5$$

we obtain using the approximation 4.2

$$K(\underline{r},\underline{r}',t) = \psi_0(\underline{r})\,\psi_0(\underline{r}')\,e^{-iE_0t} \qquad 4.6$$

and for an atom at site α $\quad K_0(\underline{r},\underline{r}',t) = \psi_0(\underline{r}-\underline{R}_\alpha)\,\psi_0(\underline{r}'-\underline{R}_\alpha)\,e^{-iE_0t}$ 4.7

we now write $$H = H_0 + H_I \qquad 4.8$$

where $$H_0 = p^2/2m + v(\underline{r} - \underline{k}_\alpha) \qquad 4.9$$

$$H_I = v(\underline{r} - \underline{R}_\beta) \qquad 4.10$$

$$K(\underline{r},\underline{r}',t) = \langle \underline{r}| e^{-i(H_0+H_I)t} |\underline{r}'\rangle \qquad 4.11$$

4.11 can be expanded in the usual way

$$K(\underline{r},\underline{r}',t) = K_0(\underline{r},\underline{r}',t) + \int_0^t K_0(\underline{r},\underline{r}'',\tau)\, H_I(\underline{r}'')\, K_0(\underline{r}'',\underline{r}',t-\tau)\, d\underline{r}''\, d\tau + \cdots \qquad 4.12$$

If we took just the first term this would correspond to the Born approximation which would not be adequate as we are interested in a perturbation which changes the poles of 4.2 and must therefore sum an infinite series of terms, in some sense or other. The simplest procedure is to be a cumulant approxiamation (Lukes, Somaratna, and Tharmalingam, 1970).

Essentially we write

$$K(\underline{r},\underline{r}',t) = K_0(\underline{r},\underline{r}',t)\, \exp \sum_{n=1}^{\infty} \frac{k_n}{n!} (-i)^n \qquad 4.13$$

where for example

$$k_1 = \int_0^t K_0(\underline{r},\underline{r}'',\tau)\, H_I(\underline{r}'')\, K_0(\underline{r}'',\underline{r}',t-\tau)\, d\tau\, d\underline{r}'' \Big/ K_0(\underline{r},\underline{r}',t-\tau) \qquad 4.14$$

Using 4.10 and 4.6 we obtain

$$k_1 = t \int \psi_0(\underline{r} - \underline{R}_\alpha)\, v(\underline{r} - \underline{R}_\beta)\, \psi_0(\underline{r} - \underline{R}_\alpha)\, d\underline{r} \qquad 4.15$$

If we take the $\psi_0(\underset{\sim}{r})$ to be an s state this can be written

$$k_1 = t F(|\underset{\sim}{R}_\alpha - \underset{\sim}{R}_\beta|) \qquad 4.16$$

We now use 4.5 to obtain

$$G(\underset{\sim}{r},\underset{\sim}{r}',E) = \frac{\psi_0(\underset{\sim}{r}-\underset{\sim}{t}_\alpha)\,\psi_0(\underset{\sim}{r}-\underset{\sim}{t}_\alpha)}{E-E_0-F(R)} \qquad 4.17$$

This expression must now be average over both $\underset{\sim}{R}_\alpha - \underset{\sim}{R}_\beta$ and over $\underset{\sim}{t}_\alpha$. i.e. we sum over all pairs of atoms.
For N impurities in a volume (see L.T.D.S.)

the average over the α is

$$\sum_\alpha \psi_0(\underset{\sim}{r}-\underset{\sim}{t}_\alpha)\,\psi_0(\underset{\sim}{r}-\underset{\sim}{R}_\alpha)\,\frac{d\underset{\sim}{t}_\alpha}{\Omega} = \sum_\alpha \frac{1}{\Omega} = \frac{N}{\Omega} = \rho \qquad 4.18$$

where ρ is the number density of impurities.

We now average over the distances $\underset{\sim}{R} = |\underset{\sim}{R}_\alpha - \underset{\sim}{R}_\beta|$. For a random distribution the distribution of nearest neighbours is a Hertz distribution:

$$p(R) = 4\pi R^2 \rho \exp -\frac{4}{3}\pi R^3 \rho \qquad 4.19$$

The average density of states can then be written

$$\begin{aligned} N(E) &= -\pi^{-1} T_r \ll \mathrm{Im}\, G^+(\underset{\sim}{r},\underset{\sim}{r},E) \gg \\ &= \int_\Omega d\underset{\sim}{r}\,\rho\,\delta[E-E_0-F(R)]\,p(R)\,dR \\ &= \Omega\rho \sum_i \frac{\exp -(\frac{4}{3}\pi R_i^3 \rho)\, 4\pi R_i^2 \rho}{\left|\frac{dF}{dR}\right|_{R=R_i}} \end{aligned} \qquad 4.20$$

where the sum is taken over all values of R which satisfy

$$E - E_0 + F(R) = 0 \qquad 4.21$$

For a known $\psi_0(r)$ the integral over 4.20 can be carried out of necessary numerically. This has been done taking for $\psi_0(r)$ hydrogenic ground state wavefunctions. Near $E-E_0$ the result can be expressed analytically:

$$n(\varepsilon) = \frac{4\pi\zeta}{C}\left[\frac{C}{E-E_0}\right]^4 \exp -\frac{4}{3}\pi\zeta\left(\frac{C}{E-E_0}\right)^3 \qquad 4.22$$

where $n(\varepsilon)$ is the density of states per atom. For $\zeta \to 0$ this reduces to $\delta(\varepsilon-\varepsilon_0)$ [equation 4.4] as it should. The result looks like Fig. 11 . Fig. 12 shows a typical result of a more complicated calculation carried out by the same sort of method where we have included the effect of both donors and acceptors and also, in a simple way, electron correlation [Lukes, Somaratna and Agrell, unpublished]. At least in this approximation the Coulomb interaction splits the band, but I shall not consider the effect of electron correlations in any detail in these lectures. These results could (and perhaps should) be extended to include higher order cumulants.

5. The Anderson model for the insulator metal transitions.

Having obtained a reasonable model for the density of states in an impurity band we now discuss the question of whether these states are localised or not. A great step forward in attacking such problems was taken by Anderson (1958). We shall refer to his discussion as the Anderson model (not to be confused with the Anderson Hamiltonian).

In the context of the results we have discussed, Anderson's argument may be expressed as follows. The result 4.16 shows that the energy levels ε are modified by a fluctuating term $F(R)$. Therefore instead of considering a distribution of distances in 4.16 we could write

$$F(R) = \varepsilon \qquad 5.1$$

$$p(R)\,dR = p(\varepsilon)\frac{dR}{d\varepsilon}\,d\varepsilon \qquad 5.2$$

We could now write 4.17

$$G^{+}(\underline{r},\underline{r}',E) = \frac{\psi_0(\underline{r}-\underline{R}_\alpha)\,\psi_0(\underline{r}'-\underline{R}_\alpha)}{E-E_0-\epsilon} \qquad 5.3$$

where the ϵ have a probability distribution.

The problem we have been considering is complicated by the fact that the $\underline{R}_\alpha$ have a random distribution. An essential part of Anderson's contribution was to recognise that this was really irrelevant to the problem. Anderson in fact put his atoms in a periodic lattice. This enables him to introduce Wannier functions which are labelled by the sites α,β; in fact his model is defined by the Hamiltonian

$$H_{\alpha\beta} = \epsilon_\alpha \delta_{\alpha\beta} \qquad \alpha = \beta \qquad 5.4$$

$$H_{\alpha\beta} = V \qquad \alpha,\beta \qquad \text{nearest neighbours.} \qquad 5.5$$

We shall only consider a simple cubic lattice here. Here V is taken to be a constant independent of α,β ; it can be taken to be analogous to $F(R)$ for a periodic lattice.

In terms of these

we can write down the equation for the G.F. as

$$G = G_0 + G_0 H_I G \qquad 5.6$$

where $$\langle\alpha|G_0|\beta\rangle = \frac{1}{E-\epsilon}\delta_{\alpha\beta} \qquad 5.7$$

Expanding 4.24 iteratively we get

$$\langle\alpha|G|\beta\rangle = \frac{1}{E-\epsilon_\alpha}\delta_{\alpha\beta} + \frac{1}{E-\epsilon_\alpha} V_{\alpha\gamma} \frac{1}{E-\epsilon_\gamma} \qquad 5.8$$

where we have temporarily labelled the V'_n by the lattice sites which they connect but shall, in fact, take them all to be the same. The ϵ'_γ in 4.26 are now defined with respect to E_0 .

From the shape of the density of states we can guess that a rectangular density of states would not be a bad approximation. We keep the height of the distribution the same and fix the width W by the normalisation condition.

Using 4.22 we get for example

$$N(E_{max}) = \bar{R} \exp -\tfrac{4}{3} \pi^{-4/3} (0{\cdot}554)^{-1} \qquad 5.9$$

where $\bar{R}$ is the mean distance between the impurities which is related to the density by

$$\bar{R} = 0{\cdot}554\, \rho^{-1/3} \qquad 5.10$$

hence we define $$W = N(E_{max})^{-1} \qquad 5.11$$

For the moment, we can now forget about the random positions of the impurities and study the model Hamiltonian defined by 4.22 and 4.23, with the proviso that the ϵ_i's are independently distributed of one another with distribution

$$p(\epsilon) = W^{-1} \qquad -\tfrac{W}{2} < \epsilon < \tfrac{W}{2} \qquad 5.12$$

For a long time the relationship of the Anderson model to the random impurity problem was badly understood. It was Mott who, in a series of papers, recognised the major importance of Anderson's work and that it could form the basis of a new approach to the metal-insulator transition in a number of apparently different cases.

Anderson's argument was now essentially as follows. In a time dependent representation the proper factor corresponding to 5.7 is

$$\langle \alpha | u(t) | \beta \rangle = e^{-i\epsilon_\alpha t} \delta_{\alpha\beta} \qquad 5.13$$

and corresponds to an electron localised at site α. If the electron is to diffuse away from the site, this localised state must decay. Now, using the standard G.F. methods we can sum 5.6

into an expression by means of the self energy. If we do so we would expect 5.13 to have a factor

$$e^{-i(\epsilon-\Sigma)t} = e^{-i[\epsilon-A-iB]t}$$

Hence we must have $B>0$ for the state to decay.
Hence the condition for the electron to diffuse away is for the imaginary part of the self energy to be non zero. Now if one writes down an expression for the self energy, curiously enough the first few terms are real. A simple example of this occurs in our expression 4.16 in which $F(A)$ can be interpreted as a term in Σ . Thus it appears that the state never decays! Anderson's argument now was to examine the convergence of the series for Σ . This was found to be determined by the ratio V/W , and Anderson argued that the value of V/W at which the series diverged could be interpreted as that at which an electron begins to diffuse away from the state. Thus we have a model of an insulator-metal transition in the one-electron approximation. Mott has suggested that this model can in fact be used to explain metal insulator transitions in all the cases we have considered, using semi-quantitative arguments.

A review of Anderson's work has been given by Thouless (1970) and comments have been made by Ziman (1970). Nevertheless, Anderson's theory is not very suited to practical applications. The connection of his argument with the observed phenomenon, electrical conductivity, is very formal, nor can his work be directly applied to the three types of system we have in mind. In the following sections I want to describe a different approach which attempts to remedy these deficiencies.

6. The Conductivity in the Anderson Model.

In contrast to the usual situation in the theory of disordered systems, it is the unperturbed G.F. which is subject to a probability distribution and we define average G.F.

$$g_0 = \langle\langle G_0 \rangle\rangle \qquad 6.1$$

$$g = \langle\langle G \rangle\rangle \qquad 6.2$$

where the bracket $\langle\langle\ \rangle\rangle$ now denotes an average over the ϵ_i .

In the Wannier representation Dyson's equation becomes a matrix equation :

$$\underset{\sim}{G} = \underset{\sim}{G_0} + \underset{\sim}{G_0}\,\underset{\sim}{H_I}\,\underset{\sim}{G} = \underset{\sim}{G_0} + \underset{\sim}{G}\,\underset{\sim}{H_I}\,\underset{\sim}{G_0} \qquad 6.3$$

with solution $$\underset{\sim}{G} = \left[\underset{\sim}{G_0}^{-1} - \underset{\sim}{H_I}\right]^{-1} \qquad 6.4$$

From 6.3 we can define a self-energy Σ by

$$g = g_0 + g_0 \Sigma g \qquad 6.5$$

$$\Sigma = g_0^{-1} - g^{-1} \qquad 6.6$$

The equation for the static electrical conductivity can be written in the form (we use units such that $\hbar = 1$)

$$\sigma_{\mu\nu} = \lim_{\omega\to 0} e^2\omega^2\pi^2 \int \frac{df}{dE}\, dE\, \mathrm{Tr}\left\{ \delta(E_F - H)\, r_\mu\, \delta(E_F^{+\hbar\omega} - H)\, r_\nu \right\} \qquad 6.7$$

Hence f is the Fermi function.

Specialising to the case of zero temperature and putting

$$\delta(E-H) = -(2\pi i)^{-1}\left[G^+(E) - G^-(E)\right] \qquad 6.8$$

6.7 can be written

$$\sigma_{\mu\nu} = \lim_{\omega\to 0} \frac{\omega^2}{\pi}\, \mathrm{Real}\, \mathrm{Tr}\left[r_\mu \left\{ G^+(E)\, r_\nu\, G^+(E+\hbar\omega) - G^+(E)\, r_\nu\, G^-(E+\hbar\omega) \right.\right. \qquad 6.9$$

For the Anderson Model we need to write this in terms of Wannier functions. In order to do so, we use the result

$$\langle i|r|j\rangle = r_i \delta_{ij}$$

Here i, j label sites. Equation 6.9 can now be written

$$\sigma_{\mu\nu} = \lim_{\omega\to 0} \frac{\omega^2}{\pi}\, \mathrm{Real}\left[\sum_{ij} r_i^\mu\, G_{ij}^+(E_F)\, r_j^\nu\, G_{ji}(E_F+\hbar\omega) \right. \qquad 6.10$$

$$\left. - r_i^\mu\, G_{ij}^+\, r_j^\nu\, G_{ji}^-(E+\hbar\omega) \right]$$

We define

$$\Pi_\nu = \ll G^\alpha \gamma_\nu G^\beta \gg \qquad 6.11$$

It is seen that the contribution to the conductivity must be of order ω^{-2} in order that a finite conductivity is obtained. In the present case no such factor occurs. Thus the conductivity goes to zero as ω^2 . We can also use this argument to show, e.g. that for a single electron in an atomic state the conductivity is zero. We shall therefore agree that the condition for a finite value of conductivity is that the series for Π_ν will diverge. Since the separate terms of the series are finite $\omega \to 0$ we shall take this limit in the summand of 6.10 from now on.

7. The integral equation for Π_4 .

If $F(z)$ denotes the power series

$$F(z) = C_0 + C_1 z + C_2 z^2 + \cdots$$

Then the Cauchy-Hadamard method of determining the ratios of convergence depends on the series $|C_1|, |C_2|^{1/2} \ldots |C_n|^{1/n}$. If the greater limit of the sequence is by then $r = c^{-1}$.

$$\ll G \gg = \frac{1}{q^{-1} + C_0^{-1} - (H_E + q^{-1})} = \frac{1}{q^{-1} - A} \qquad 7.1$$

where $$A = H_E + q^{-1} - C_0^{-1} \qquad 7.2$$

Thus $$q = q + qAG \qquad 7.3$$

putting this into 6.11 and considering $\alpha = \beta = +$ for simplicity we obtain

$$\Pi_4 = \ll q + qAG \gg \gamma_4 (q + qAG) \gg$$

$$= q\gamma_4 q + \ll qAG\gamma_4 q \gg + \ll q\gamma_4 GAq \gg$$

$$+ \ll qAG\gamma_4 GAq \gg \qquad 7.4$$

This equation is, so far, exact. We now consider the second term

$$\begin{aligned} \ll q A G \tau_1 q \gg &= q \ll A G \gg \tau_1 q \\ &= q \ll [\, G_0^{-1} - G^{-1} + q^{-1} - G_0^{-1} \,] G \tau_1 q \gg \\ &= 0 \end{aligned} \qquad 7.5$$

The third term is similarly found to be zero.
The last term is

$$\ll q [\, H_E + q^{-1} - G_0^{-1} \,] G \tau_1 G [\, H_E + q^{-1} - G_0^{-1} \,] q$$
$$\sim q (H_E - \Sigma_1) \Pi_1 (H_E - \Sigma_1)$$

We now obtain

$$\Pi_1 = q \tau_1 q + q (H_E - \Sigma_1) \Pi_1 (H_E - \Sigma_1) \qquad 7.6$$

an equation of the Bethe-Salpeter type for Π_1 . This leads to the iterative expansion

$$\begin{aligned} \Pi_1 = {} & q \tau_1 q + q (H_E - \Sigma_1) q \tau_1 q (H_E - \Sigma_1) q \\ & + q (H_E - \Sigma_1) q (H_E - \Sigma_1) \tau_1 q (H_E - \Sigma_1) q (H_E - \Sigma_1) q \\ & + \cdots \end{aligned}$$

8. Divergence of the Bethe-Salpeter Eq^{n}.

In order to study the divergence of the series for Π_1 we meat an exact expression for q which is difficult to obtain.

However, we can obtain an upper bound to the value of V/W by replacing q by q_0 in 7.7 , i.e. we put

$$\langle \alpha | q | \beta \rangle \sim q_0 = \ll \frac{1}{E - \varepsilon} \gg \delta_{\alpha\beta} \qquad 8.1$$

Using the distribution 5.12 we get

$$q_0 = W^{-1} \ln \left[\frac{E + i\varepsilon + W/2}{E + i\varepsilon - W/2} \right] \qquad 8.2$$

To estimate Σ_1 we consider the approximation of a self-avoiding walk. Asymptotically the number of terms is K^n for both the diagonal and off diagonal terms, where K is the connectivity constant of the lattice.

Hence we obtain for the n^{th} term $g_0 V^{N-1} K^N$ and for the sum

$$g_{\lambda\rho} = \frac{1}{g_0^{-1} - VK} \qquad 8.3$$

Hence in this approximation the diagonal and off diagonal elements of the G.F. are the same and given by

$$\Sigma = VK \qquad 8.4$$

Putting 7.11 and 7.9 into 7.7, we again consider a self avoiding walk approximation. In this case the series 7.7 is geometric and the condition for the series to diverge is

$$g_0^2 |(V - \Sigma)|^2 K^2 \geq 1 \qquad 8.5$$

We now consider the centre of the band and put $E = 0$ in 8.2 This leads to a critical value of $W/V = 54$ which is in fact an upper bound to this value.

Using methods which I do not have time to discuss, we can also estimate the lower bound to be about 25.4. The upper bound is, in fact, fairly close to the estimate obtained by Anderson.

9. The impurity band problem.

We now consider the impurity band problem which forms an important part of the evidence for the Anderson transition.

In order to apply the method of the previous sections, we need to consider the G.F. for this model, which can be obtained from the Dyson expansion

$$G(\underline{r}, \underline{r}', E) = \sum_{\lambda} \frac{\psi_0(\underline{r} - \underline{R}_\lambda)\, \psi_0(\underline{r}' - \underline{R}_\lambda)}{E - E_0} + \sum_{\lambda} \frac{\psi_0(\underline{r} - \underline{R}_\lambda)\, \psi_0(\underline{r}'' - \underline{R}_\lambda)}{E - E_0} \sum_{\rho} v(\underline{r}'' - \underline{R}_\rho) \sum_{\gamma} \frac{\psi_0(\underline{r}'' - \underline{R}_\gamma)\, \psi_0(\underline{r}' - \underline{R}_\gamma)}{E - E_0} \qquad 9.1$$

where it is understood that the diagonal element $\lambda = \rho = \gamma \ldots$ is omitted since it gives rise to the atomic G.F. The remaining terms now consist of overlap integrals which may be classified into two types, namely those of the first type

and those of the second type

$$v_2(\underline{R}_\alpha - \underline{R}_\beta) = \int \psi_0(\underline{r}'' - \underline{R}_\alpha)\, v(\underline{r}'' - \underline{R}_\beta)\, \psi_0(\underline{r}'' - \underline{R}_\alpha)\, d\underline{r}'' \qquad 9.3$$

We now redefine the zero order G.F., by including in it all terms of the first type. This may be done by the cumulant procedure described in section 4. The result is that the G.F. redefined in this way is now

$$G(\underline{r}, \underline{r}', E) = \ll \frac{\psi_0(\underline{r} - \underline{R}_\alpha)\, \psi_0(\underline{r}' - \underline{R}_\alpha)}{E - E_0 - F(R)} \qquad 9.4$$

where $R = |\underline{R}_\alpha - \underline{R}_\beta|$ and the brackets denote an average over both the intersite distances and over the sites α themselves. The advantage of carrying out such a partial summation is that we can now put the theory into a similar form to that previously considered for the Anderson problem. The distribution of can be replaced by a distribution of energies with a parameter defined by 5.11.

Again we obtain the Bethe-Salpeter equation as previously

$$\Pi_4 = q\, v_4\, q + q\,(H_\Sigma - \Sigma)\,\Pi_4\,(H_\Sigma - \Sigma) \qquad 9.5$$

where the only difference between these equations and those of the Anderson model is that the averages are now carried out over the random positions of the atoms and only implicitly over the energy levels.

The terms of 9.5 now involve factors of the form

$$\ll \frac{\psi_0(\underline{r} - \underline{R}_\alpha)\, \psi_0(\underline{r}'' - \underline{R}_\alpha)}{E - \epsilon_1} \gg \Big[\sum_\alpha v(\underline{r}'' - \underline{R}_\alpha) - 3\, v(R_{max}) \Big] \ll \frac{\psi_0(\underline{r}'' - \underline{R}_\beta)\, \psi_0(\underline{r}'' - \underline{R}_\beta)}{E - \epsilon_2} \gg \qquad 9.6$$

where we have evaluated the averages over intersite distances at the maximum of the Hertz distribution which, to our order of accuracy is indistinguishable from the mean. The value of Σ is easily found to be

$$\Sigma_1 = 3\, v(R_{max}) \qquad 9.7$$

Hence we obtain for the condition 8.5

$$\left(\frac{R}{W}\right)^2 |\eta-1|^2 v(R_{max})^2 \gtrsim 1 \qquad 9.8$$

Substituting a value of $\eta \sim 10$ and 5.11, 5.9 into 9.8, we obtain for the upper limit of concentration

$$\bar{R} = 3.9\ K a \qquad 9.9$$

Where K is the dielectric constant and a the Bohr radius. We have used hydrogenic S state wave functions

$$v(R_{max}) = -2E_0\left[1+\frac{R_{max}}{a}\right] \exp - R_{max}/a \qquad 9.10$$

Using methods which I do not have time to discuss, we can show that a lower limit of the concentration is given by approximately

$$\bar{R} = 5.3\ K a \qquad 9.11$$

10. <u>A more general form of the localisation condition</u>.

For the case of an impurity band, a more general and perhaps more useful form of the upper bound for V/W can be obtained. Making use of the Dirac relation

$$\frac{1}{E-\epsilon+i\epsilon} = \frac{P}{E-\epsilon} - i\pi\delta(E-\epsilon) \qquad 10.1$$

$$\eta_m\left[E-\epsilon-i\epsilon'\right] = -\pi N(E) \qquad 10.2$$

where $N(E)$ is the density of states per atom. The real part of 10.1 is given by the dispersion relation

$$\ll \frac{P}{E-\epsilon} \gg = \int \frac{N(E')\,dE'}{E-E'} \qquad 10.3$$

The form of this for a typical band has been discussed (Izyumov, 1965). It is antisymmetric about the maximum and zero there. Thus for energies near the maximum we can write

$$\ll \frac{1}{E-\varepsilon+i\zeta} \gg \sim -\pi N(E) \qquad 10.4$$

and hence the condition 9.8 can be written

$$\pi(\gamma-1) N(E) r(R_{max}) \gtrsim 1 \qquad 10.5$$

This relation shows that a low density of states is favourable for localisation and exhibits clearly the existence, in general, of mobility edges in impurity bands.

11. Localisation in highly doped and amorphous semiconductors.

Experimental evidence suggests that in both highly doped and amorphous semiconductors the density of states is a montonically decreasing function of energy as we move away from the band edge of the pure material. Therefore the theory of the preceding sections cannot be directly applied to these materials. We shall, however, suggest that it can be applied in a modified form.

It is characteristic of both highly doped and amorphous materials that the random potentials are much more densely distributed than in systems which give rise to impurity bands. For such systems it is reasonable to assume that the potential at a point has a multivariate Gaussian distribution

$$p[V(r)] = A \exp -\frac{1}{2}\int dr\, dr' V(r) K(r,r') V(r') \qquad 11.1\ (a)$$

where the kernel $K(r,r')$ can be defined in terms of the correlation function $w(r,r')$ of the potential by the equations

$$w(r,r') = \langle V(r) V(r') \rangle \qquad 11.1\ (b)$$

$$\int dr'\, K(r-r'') w(r'',r') dr'' = \delta(r-r') \qquad 11.1\ (c)$$

In systems containing a low density of impurities, natural centres of localisation exist in the impurity atoms themselves. In a highly doped material, however, the density of electrons is sufficiently great to screen out atomic bound states and the same is presumably true of amorphous semiconductors. In any case, the density of atoms is so high that it is meaningless to associate an electron with a particular atom.

A theory of localisation which applies generally to a random collection of atoms of high density has been given by Zittartz and Langer (1966) (Z.L.) and by Halperin and Lax (1966) (H.L.) Although the existence of localised states is demonstrated, no discussion is given of how the transition to non-localised states takes place. It is this particular point with which we are here concerned.

The Z - L and H - L theories put forward the idea of a non-zero average local field which is sufficiently strong to localise an electron. The effective potential acting on one electron in weak binding theories can be identified with the self energy. Because it is averaged over the free particle Green function, such an effective potential is spatially homogenous and cannot bind an electron. By assuming the existence of localised states it can be shown that an average potential can be derived which depends on the Green's function. It is given by

$$V_{eff}(\underline{r}) = -\int d\underline{r}'' \, w(\underline{r},\underline{r}'') \frac{G(\underline{r},\underline{r}'')G(\underline{r}'',\underline{r}')}{G(\underline{r},\underline{r}')} \qquad 11.2$$

Under certain simplifying assumptions this reduces to

$$V_{eff}(\underline{r}) = -\int d\underline{r}' \, w(\underline{r}-\underline{r}') \, \psi^2(\underline{r}') d\underline{r}' \qquad 11.3$$

where the wavefunction $\psi_0(\underline{r})$ is given by a Hartree type non-linear differential equation

$$-\tfrac{1}{2}\nabla^2\psi_0(\underline{r}) - \frac{1}{E_0 - E}\int d\underline{r}' \, w(\underline{r},\underline{r}')\,\psi^2(\underline{r}')\,\psi_0(\underline{r}) = E_0\psi_0(\underline{r}) \qquad 11.4$$

Although these equations assume that the distribution of potential can be described by the second moments alone, the theory could, in principle, be extended by including higher order correlations.

The assumption of localised states can be regarded as a symmetry condition which produces a non-zero mean field, given by 11.2, which can localise the electron.

Deep in the tail the potential given by 11.2 can be taken to be randomly distributed throughout the material with little overlap. Each potential then gives rise to a delta function in the density of states. The density of states nevertheless remains a continuous function of energy because the potentials themselves depend on energy through 11.2. As the density of states increases, the number of solutions of 1.4 in a given energy range per unit volume increases proportionately and therefore there will be increasing overlap of wavefunctions.

We can now discuss the localisation in similar terms to those which have been used to discuss impurity bands. It is convenient to refer to the centres of localisation with which we associate the potentials 11.2 as quasi atoms; with each quasi atom, we associate a quasi atom wavefunction given by 11.4. We can now define an overlap integral of quasi potentials between quasi atom wavefunctions similar to the $\psi_0(z)$ discussed in §4. By considering the conductivity deep in the tail, we obtain a value of zero, because the Green functions used in evaluating 6.7 are of the form 4.2 where the $\psi_0(z)$ are now given by 11.4. Again, we look for a divergence in the series for the conductivity. By applying precisely the same reasoning as before we can recapture all the results of §10. Assuming that the width W association with each energy is sufficiently small, both the bounds given previously are now close together and are given by

$$(\beta-1)\, e v(k_{max})\, N(E) \geq 1 \qquad 11.5\ (a)$$

$$(\beta-1)\, \pi r^2 (k_{max})\, N(E) \geq 1 \qquad 11.5\ (b)$$

where $N(E)$ is now the average number of nearest neighbour quasi atom solutions and $N(E)$ is the density of states per quasi atom This equation again predicts the existence of mobility edges in

References. Anderson, P.W., (1958), Phys. Rev. 109, 1492.
The classical paper on the subject of localisation.
Other discussions of this are:

Brouers, F., (1970), J. Non Cryst. Solids 4, 428.
Lloyd, P., (1969), J. Phys. C., 2, 1717.
Ziman, J.M., (1969), J. Phys. C., 2, 1230. See also papers I and III by Ziman in the same series.
Thouless, D., (1970), J. Phys. C., 3, 1559.

Halperin, B.I., and Lax, M., (1966), Phys. Rev. 148, 722.

Izyumov, I., (1965), Advances in Physics 14, 569.

Mott, N.F., (1970), Phil. Mag. 22, 1. This paper contains references to the earlier papers by Mott on the subject of disordered systems. This body of work during the last ten years is a remarkable attempt to provide a unified theory of disordered systems based on the Anderson model.

Zittartz, J. and Langer, J.S., (1966), Phys. Rev. 148, 741.

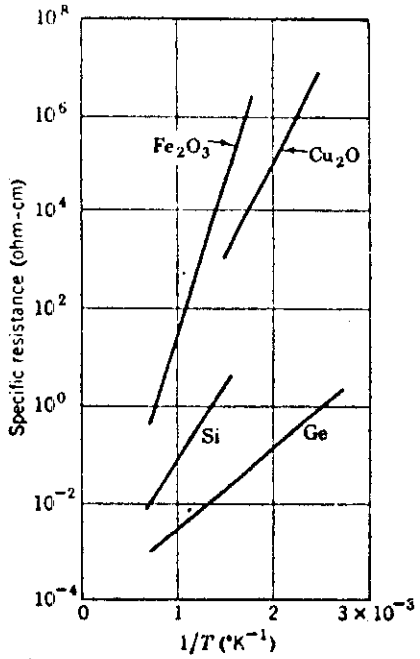

Fig. 13.3. Plot of log ρ vs. $1/T$ for several semiconductors in the intrinsic range. (After J. A. Becker.)

Fig. 1 Typical plot of log conductivity in the intrinsic region for several semiconductors in the intrinsic range [after Becker].

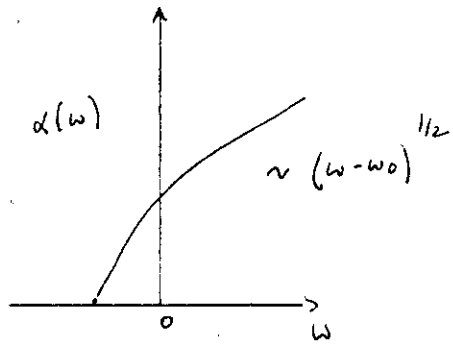

Fig. 2 Typical shape of absorption coefficient at the fundamental edge for direct transitions.

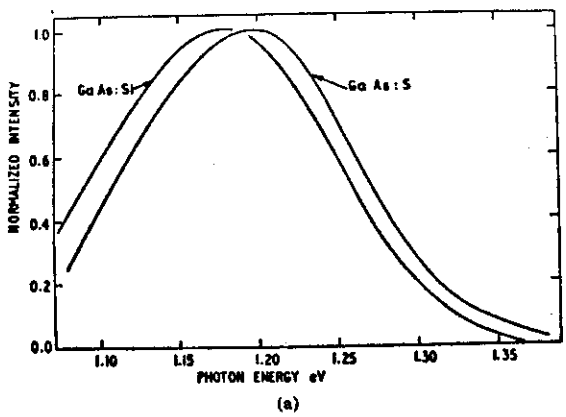

Fig. 3 Typical lineshapes observed in luminescence.

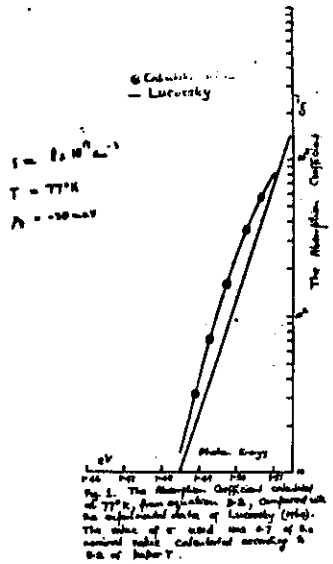

Fig. 4 Typical experimental absorption curve of a highly doped semiconductor (.). The continuous curve is that calculated by Lukes and Somaratna [1970, J. Phys. C., 3, 2044].

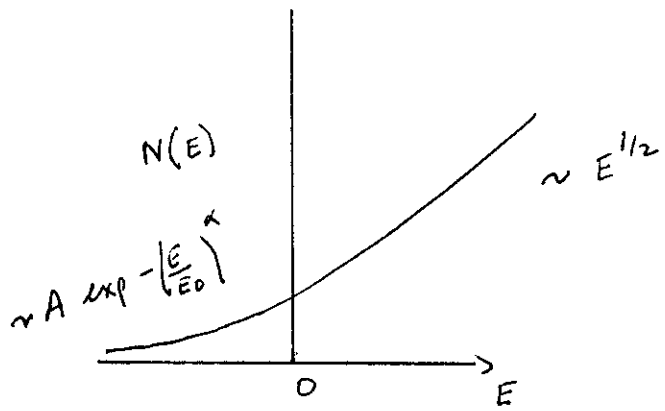

Fig. 5 Conjectured density of states curve in a highly doped semiconductor.

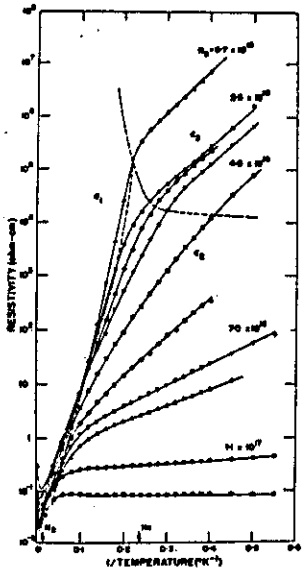

Fig. 6 Resistivity $\sim T^{-1}$ for impurity band conduction in Sb doped Ge. Note the way in which, as the concentration is increased, the curves level off [after Davis, E.A.,

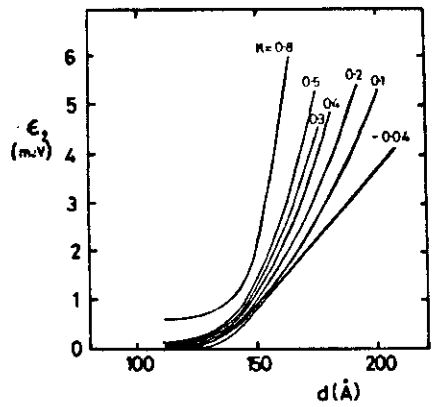

Fig. 7 Variation of activation energy, as a function of impurity separation and compensation /after Mott & Davis, 1968, Phil. Mag., 17, 1269/.

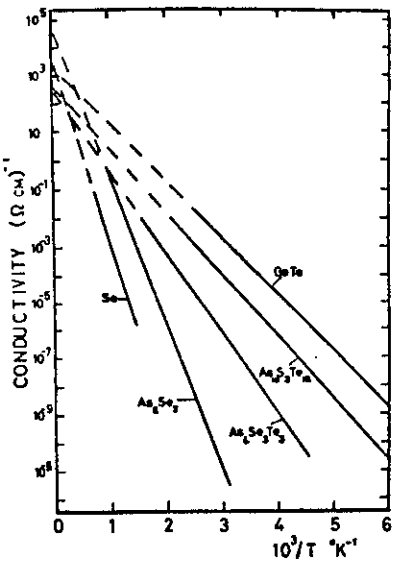

Fig. 8 Typical temperature dependence curves of conductivity in some amorphous semiconductors /after Davis, unpublished/.

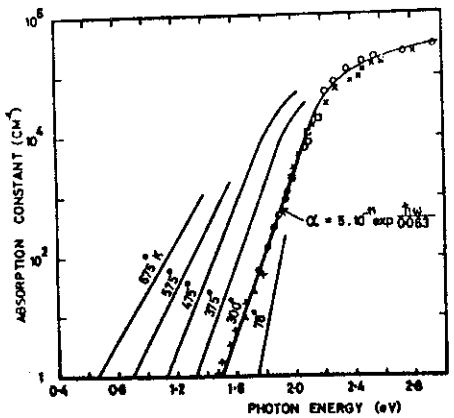

Fig. 9 Absorption coefficient of at different temperatures showing existence of a tail /after Davis, unpublished/.

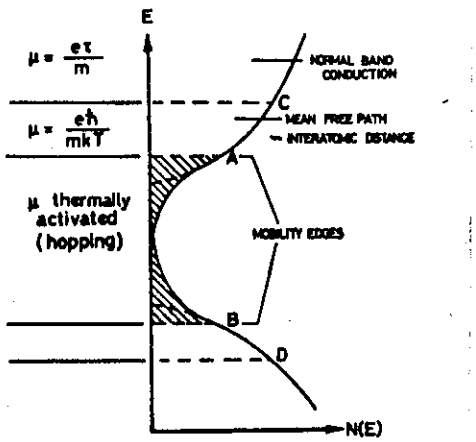

Fig. 10 Mott–Cohen theory of mobility gap.

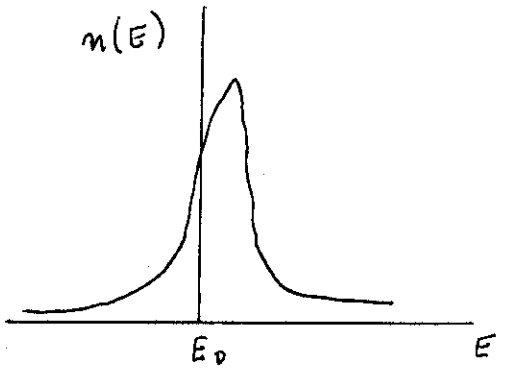

Fig. 11 Density of states due to donor–donor interaction /after Lukes, Somaratna and Tharmalingam, 1970, J. Phys. C., 12, 1631/.

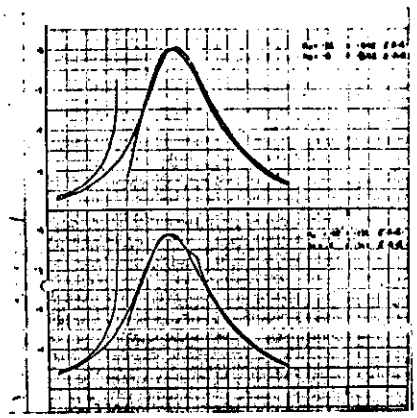

Fig. 12 Density of states in an impurity band in the presence of compensation and electron correlation /Lukes, Somaratna and Agrell, unpublished/.

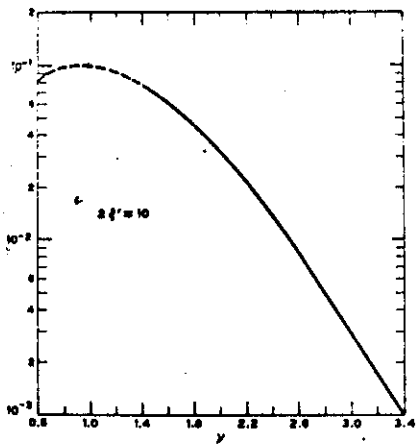

Fig. 13 Typical result for density states against energy in the theory of Halperin and Lax.