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To cite this version:
D. Thouless. TRANSPORT IN DISORDERED SYSTEMS. Journal de Physique Colloques, 1978, 39 (C6), pp.C6-1535-C6-1539. <10.1051/jphyscol:19786596>. <jpa-00218089>

HAL Id: jpa-00218089
https://hal.archives-ouvertes.fr/jpa-00218089
Submitted on 1 Jan 1978

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TRANSPORT IN DISORDERED SYSTEMS

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Résumé.- On résume les mécanismes principaux de conductivité dc dans les systèmes désordonnés et la dépendance en température de la conductivité. Si la longueur de localisation est grande, le comportement métallique doit être observé aux températures hautes, aux températures plus basses la résistance doit croître comme une puissance de $T^{-1}$, et aux températures très basses, quand les sauts de portée aléatoire se présentent, la résistance doit croître. Les conditions nécessaires pour l'observation de ces effets dans les fils minces métalliques sont discutées.

Abstract.- A survey is given of the main mechanisms of dc electrical conductivity in disordered systems and of how the conductivity depends on temperature. If the localization length is large, metallic behaviour will be observed at high temperatures, at lower temperature the resistance will increase with a power of $T^{-1}$, and at very low temperatures, when variable range hopping occurs, the resistance will increase exponentially. The conditions necessary to observe these effects in thin metallic wires are discussed.

During the past ten or twelve years there has been a lot of discussion of the manner in which localized electron states produced by the strong disorder in an amorphous material would affect the transport properties. This discussion has been important for two reasons. It has shown that there is a sharp qualitative distinction between extended and localized states, and that they are not just two extremes of a continuous transition. It has also led to new and powerful ways of displaying and interpreting data on transport properties. The difference between extended and localized states is shown up most sharply by the temperature dependence of the dc electrical conductivity, particularly at low temperatures. Because of the wide variety of systems involved "low" temperatures may mean room temperature for one material and millidegrees for another. Essential information does however come from other transport measurements such as the frequency dependence of the ac conductivity, the thermopower, the Hall effect, the photoelectric effect, and so on. Very interesting experiments have been done on the behaviour of injected carriers, and these give information which cannot readily be obtained by working close to equilibrium conditions. In this paper particular attention is paid to the differences between localized and extended states, and to the nature of the transition between them. It is important to understand very low temperatures to be able to distinguish between extended states and large localized states. It has been suggested that localized states should exist in ordinary metallic wires if they are long enough and thin enough, and a number of experimental groups are looking for evidence of localization. If it is not found it will indicate that something important is probably missing from our analysis of disordered systems.

Anderson argued that in a sufficiently disordered system electrons would be localized in a region of suitable potential energy, and that the wave function would fall off exponentially from the centre of localization at a rate which can be calculated by use of perturbation theory /1/. Even in a weakly disordered system states near the band edge should be localized, as the long wavelength states are sensitive to potential fluctuations. As the disorder is decreased or the energy is increased the localization length increases until eventually it becomes infinite and the states become extended. Mott has argued strongly that at this mobility edge the extended states have a minimum metallic conductivity /2/. If it is accepted that the electron wavelength, the distance over which the phase of the wave function changes by $2\pi$, cannot be much greater than the mean free path $\lambda$, the distance over which it loses phase coherence, and this condition $\lambda k_F > 1$ is used in the standard formulas of kinetic theory for the free electron model, the result

$$\sigma_{3D} = n e^2/\hbar = e^2 k_F^2/3\pi^2 \hbar > e^2 k_F^2/3\pi^2 \hbar$$

(1)

is obtained for the minimum metallic conductivity.
This formula involves a wavelength which has to be estimated, but in two dimensions the same argument gives

\[ \sigma_{2D} = e^2 k_f \lambda / 2 \pi h > e^2 / 2 \pi h \]

and there is no unknown length scale in this formula /3/. It has been argued that the two-dimensional minimum metallic conductivity should have a universal value corresponding to a resistance per square of about 30,000 Ohm /4/.

If the Fermi energy lies in a region of extended states then the dominant conduction mechanism is metallic which means, since we are considering highly disordered materials for which phonon scattering is relatively unimportant, that the conductivity is independent of temperature at low temperatures, and has a value at least as high as the minimum metallic conductivity. If the Fermi energy lies in a region of localized states the conductivity at zero temperature is zero, since electrons cannot move in response to a weak applied electric field without energy to enable them to make a transition from one localized state to a neighbouring one of different energy. At nonzero temperatures there are two important modes of conduction, excitation to the mobility edge and variable range hopping. The localized electron levels can act as donors, pinning the Fermi energy, and those electrons which are thermally excited to the mobility edge or above can carry the current. Since the number of carriers decreases exponentially with energy the conductivity is dominated by its value at the mobility edge, and this mechanism gives a conductivity of the form

\[ \sigma(T) = \sigma_{\text{min}} \exp \left[ (E_F - E_c) / kT \right] \]

so that a plot of \( \ln \sigma \) against \( T^{-1} \) should give a straight line whose slope gives the distance of the Fermi energy \( E_F \) below the mobility edge \( E_c \) and whose intercept measures \( \ln \sigma_{\text{min}} \). Figure 1 shows a series of such plots obtained by Sayer et al. /5/ for \( \text{La}_{1-x} \text{Sr}_x \text{VO}_3 \) of varying composition which indicate metallic behaviour for \( x \) somewhat greater than 0.2 and a minimum metallic conductivity of about 100 Ohm\(^{-1}\)cm\(^{-1}\).

At lower temperatures few electrons are excited to the mobility edge and electrons must hop between localized states. The rate at which electrons can hop between a pair of states a distance \( R \) apart is controlled by two exponential factors. Firstly there is a factor \( \exp (-W'/kT) \) for the number of carriers in the higher states, where \( W' \) is its distance from the Fermi energy, and secondly there is a factor of order \( \exp(-2 \alpha R) \) for the square of the matrix element between the states, where \( \alpha \) is the rate of exponential fall-off of the localized wave function. From a given site we can expect the lowest value of \( W' \) within a given distance to be proportional to \( R^{-3} \), since it should be inversely proportional to the number of states within that distance /6/. The product of the exponentials is maximal for

\[ \frac{1}{kT} \frac{9}{4 \pi R^2} \frac{dn}{dE} = 2 \alpha = 0 \]

and the maximum exponent is proportional to \( T^{-\gamma} \).

For dc conductivity we are not just concerned with the resistance of the link between two particular sites, but there must be a continuous path of such links right across the system /7/. This consideration only changes the numerical factor in the exponent which Mott /6/ deduced from equation (4), and the conductivity is of the form

\[ \sigma(T) \propto \exp \left[ -\theta / (T_0 T)^{\gamma} \right] \]

where \( T_0 \) is proportional to \( \alpha^2 \) times the density of states. Figure 2 shows the same data as figure 1, but with \( \ln \sigma \) plotted as a function of \( T^{-\gamma} \). From the slope of these lines the product \( \alpha^2 \frac{dn}{dE} \) can be deduced, with some theoretical uncertainty about the correct value of the constant factor. Similarly in two dimensions this argument leads to a \( T^{-\tilde{\gamma}} \) dependence of \( \ln \sigma \), and this has also been observed in a variety of systems. This behaviour
of the conductivity at low temperatures is often the most direct evidence that the Fermi energy lies in a region of localized states. There is one unsatisfactory feature of most treatments of this problem /7/ that I believe leads to unnecessary difficulties. The effective resistance between two states whose energies relative to the Fermi energy are $E_\alpha$ and $E_\beta$ with $E_\alpha > E_\beta$ is calculated from the transition rate between the states

$$W_{\beta\alpha} f_\alpha (1-f_\alpha) W_{\alpha\beta} f_\beta = W_{\beta\alpha} (1-f_\beta) f_\alpha - (1-f_\alpha) e^{-(E_\alpha - E_\beta)/kT} f_\beta$$

where $W_{\beta\alpha}$ is the transition rate from $\alpha$ to $\beta$ and $f_\alpha, f_\beta$ are the occupation probabilities of the states. This expression of course vanishes in the absence of a perturbation, but if potentials $V_\alpha, V_\beta$ are applied to the localized states it gives a net current

$$e^2 (V - V_\beta) W_{\beta\alpha} f_\alpha (1-f_\alpha) \approx e^2 (V - V_\beta) W_{\beta\alpha} \exp \left( \frac{|E_\alpha - E_\beta|}{2kT} \right)$$

For a given value of $(E_\alpha - E_\beta)$ this expression is greatest when $E_\alpha$ and $E_\beta$ have opposite signs, so that hopping across the Fermi energy seems to be favoured; just such a hop is shown in figure 2.1b of Mott and Davis /8/. I believe this is a spurious effect due to the use of equilibrium values of $f_\alpha, f_\beta$ in equations (6) and (7). If a hop occurs from a state below the Fermi energy to a state above it thermal equilibrium can only be restored by further hops - there is no other mechanism available to fill the hole or remove the electron which were involved in the first hop. In fact since the hole state is certainly empty and the electron state is certainly full, the most probable process is for the electron to return to its hole, and in that case the hop across the Fermi energy gives no net current. For that reason it would be better to ignore such processes, and consider only electrons hopping in states above the Fermi energy and holes hopping in states below it. In the temperature range in which variable range hopping is important the states involved have an energy which is somewhat greater than $kT$, and so either $f_\alpha$ or $1-f_\alpha$ is small. If hopping across the Fermi energy is not important one should not expect the Coulomb attraction between particles and holes to affect the hopping conductivity strongly /9/.

For thin metallic films and other granular materials it is expected that the Coulomb energy should be important for the hopping conductivity, since charge transport involves necessarily a departure from electrical neutrality of the grains. This suggests an activation energy proportional to $e^2/R$ for hops of length $R$, and the equation analogous to (4) for this problem leads to /10/

$$\sigma(T) = A \left[ \exp \left( \frac{E_0}{2kT} \right) \right]$$

for such systems. This is indeed observed together with a transition to metallic behaviour when the film is thick enough that the minimum metallic conductivity is reached. Figure 3 shows some recent results of Dynes, Ganno and Rowell /11/ for thin metallic films.

As the mobility edge is approached the localization length gets longer, and in some energy range close to the mobility edge there must be many localized states overlapping the same region of space. In this case the Boltzmann equation for hopping between such localized states may give misleading results. In the limit of very long localized states it is clearly absurd to expect an electron to travel the entire length of the state in the time between two successive hops, since this time does not depend strongly on the localization length. One must at least require that the time between hops should be greater than $R$ divided by the spacing between overlapping levels. If this condition is not satisfied there will be important phase coherence effects between the states. In fact under these conditions the motion of an electron wave packet made up of these large extended states should be initially indistinguishable from
the motion of a wave packet made up from extended states. The wavelength and mean free path of the waves should have the same significance in the two cases, and are expected to be continuous across the mobility edge, even though for the localized states there is a slowly varying exponential envelope multiplying the oscillatory wave function. Only if the electron has time to diffuse to the extent of its localization length without undergoing a hopping transition to another set of localized states should the localization be apparent. If the temperature is low enough that the electron can diffuse to its localization length without an inelastic collision but not so low that \( kT \) is as small as the spacing between energy levels, each inelastic collision then allows the electron to diffuse a distance of the order of the localization length. Since the rate at which phonons whose wavelength is much longer than the electronic mean free path scatter electrons is proportional to \( T^3 \), and the rate at which electron-electron collisions occur is proportional to \( T \), the resistance will be proportional to \( T^{-3} \) or \( T^{-2} \) according to which mechanism is more important. At temperatures such that \( kT \) is less than the spacing between overlapping levels variable range hopping will take over again /12/.

These considerations are particularly important for one-dimensional systems. Mott and Twose /13/ showed that a true one-dimensional system would have all electron states localized even if the disorder was slight. It can be argued that this should be true also for long thin wire, and the localization length should be of the order of the length of wire which gives a 10000 Ohm resistance at low temperatures. For a wire of diameter 50 \( \text{nm} \), sufficiently dirty that the electronic mean free path is 0.5 \( \text{nm} \), the localization length is about 10 \( \mu \text{m} \). An estimate of the transition times involved gives metallic behaviour of the wire down to about 1 K, and then a resistance increasing as \( T^{-2} \) down to about 50 \( \mu \text{K} \), below which variable range hopping, which in one dimension gives \( R \propto T^{-1} \), should be observed /12/.

Various remarks should be made about this system. If the hyperfine splittings of nuclear magnetic levels are comparable with or larger than the spacings between overlapping localized states it will be hard to see the localization because transitions between the localized states can then be induced by hyperfine interactions /14/. It is important that the wire should be reasonably uniform as small regions in which the wire is much thicker than usual, which would not affect the resistance much under normal conditions, may be regions where a high level density makes transitions between localized states much easier. For the same reason contact points, even if they are not actually connected to a voltmeter, can affect the conduction process. Finally it is not necessary to have the voltage so small that the energy difference between two ends of a localized state is small compared with the spacing. Even in the presence of a fairly strong field the states should be localized, although these localized states will be complicated superpositions of the states in the absence of a field. All that is necessary is that the potential difference between the ends of a localized state should be small compared with \( kT \), so that thermoelectric effects are not important. The localization should be destroyed by coupling between strands of a quasi-one-dimensional conductor consisting of conducting strands embedded in a poorly conducting medium. This problem has been considered by Abrikosov and Ryzhkin /15/.

Fig. 3: Resistance against \( T^{-1/2} \) for very thin films of copper and gold. High-temperature extrapolations for the high-resistance curves all tend to converge to about 30 000 Ohm. This figure is taken from Dynes, Garno and Rowell /11/.
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