Transport in Disordered Materials

N. F. Mott
Cavendish Laboratory, Cambridge, England
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A criticism is given of the concept put forward by Cohen and Jortner of an "inhomogeneous regime" in disordered semiconductors. It is suggested that this regime does not exist in general in disordered materials, though it may in fluids near a critical or convolution point.

The purpose of this note is to query a concept put forward by Cohen and Jortner.[1] They distinquish several regimes for the conductivity σ in disordered materials. These, for increasingly strong interaction between the electrons and the random field, are the following:

(I) The "propagation regime" where the mean free path L is greater than the interatomic distance a, as in Ziman's theory for liquid metals; in liquids $\sigma > 3000\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

(II) The diffusion regime where $L \sim a$ and σ lies in the range 3000–300 $\Omega^{-1}\ \mathrm{cm}^{-1}$.

(III) An "inhomogeneous" regime in which they say microscopic inhomogeneities exist, allowing the use of classical percolation theory to describe conduction along metallic channels between regions which are nonconducting at zero temperatures. In this regime σ at 0°K drops continuously from $\sim 300\ \Omega^{-1}\ \mathrm{cm}^{-1}$ to zero as the width of the channels decreases.

(IV, not specifically mentioned) The regime where all states at the Fermi energy are Anderson-localized, so that conduction at low temperatures is by variable-range hopping and $\ln\sigma$ is proportional to $-1/T^{1/4}$.

(V) The situation for a true semiconductor when the density of states at the Fermi energy is negligible and a band gap (or mobility gap) exists.

Cohen and Jortner, as in previous papers by Cohen and co-workers, state that regime (III) necessarily exists in any disordered system, and therefore that the authors' concept of a "minimum metallic conductivity" is only valid in regime (II). This we believe to be wrong. To show this we consider the simple model used by Anderson.[2] Suppose in the regime (III) of Cohen and Jortner their nonmetallic fluctuations extend over a distance R. The localized wave functions within this region have envelopes falling off as $\exp(-\alpha r)$, and, as several workers[3,4] have shown, $\alpha \to 0$ as one approaches the mobility edge. Any wave function penetrating from the metallic into the nonmetallic regions will also fall off as $\exp(-\alpha r)$, and if Cohen's model is correct it must be possible to choose R such that $\exp(-\alpha R) \ll 1$ over much of the volume. But it is easily shown[5] that if R is large, fluctuations in potential such that this is the case are improbable, and one cannot find a value of R such that opaque regions fill a significant part of the volume. Cohen and co-workers do not in fact give any arguments to show how large they think the quantity R should be or of the range of energies over which their regime (III) extends.

If long-range fluctuations do not have the effect that Cohen and co-workers suppose, the minimum metallic conductivity calculated by the author has the value [Eq. (11) of Mott[6]]

$$(e^2/10\hbar a)(B/V_0)^2, \tag{1}$$

where B is the bandwidth without disorder and V_0 the critical value of the random potential V for Anderson localization. This comes out to be 200–1000 $\Omega^{-1}\ \mathrm{cm}^{-1}$ if $a \simeq 3$–4 Å, and if V increases beyond the Anderson limit, σ at $T = 0$ drops discontinously to zero.

There is very strong experimental evidence against the suggestion of Cohen and Jortner. Many examples of an Anderson transition now have been observed; we quote $\mathrm{Si}_{1-x}\mathrm{P}_x$ for varying degrees of compensation, VO_x for varying x, $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{VO}_3$, $\mathrm{Ce}_{2+2x}\mathrm{S}_{3-3x}$. Discussions are given in Refs. 5 and 6 and by Mott and Davis.[7] In all these, as the concentration changes, an activation energy for hopping conduction, with σ proportional to either $\exp(-A/T)$ or $\exp(-A/T^{1/4})$, decreases uniformly and disappears at a critical value of x; the metallic conductivity is then, within the factor of uncertainty in our knowledge of the Anderson ratio V_0/B, given by (1). The experiments of Allen and Adkins[8] on heavily compensated n-type Ge down to 0.05 K were undertaken to see whether $T^{1/4}$ behavior is maintained or whether the curves flatten off and show metallic behavior at low T, as Cohen and Jortner's ideas must predict. No such behavior was observed.

Also, we do not know of any disordered metallic conductor in which the limiting conductivity as $T \to 0$ has any nonzero value less than Eq. (1). Of course, if there were fluctuations in composition or in the degree of disorder extending over large distances, then classical percolation theory could be applied and σ would tend continuously to zero as the disorder is increased. But as soon as tunneling is admitted, then there must exist a lowest energy at which states are nonlocalized; localized and nonlocalized states cannot coexist at the same energy, since the former would become virtual bound states. The conductivity when states are nonlocalized cannot be zero. There will thus always be a minimum metallic conductivity, occurring at energies near the percolation edge, though its value will be much less than (1) if fluctuations are long range.

Cohen and Jortner apply their ideas to liquid tellurium and also to mercury near its critical point. For these they assume a mixture of regions with different conductivities, to which percolation theory can be applied. Near critical points such regions must exist. This is of course quite different from assuming the existence of metallic regions surrounded by *insulating* regions, and the validity of this treatment is not necessarily compromised if Cohen's basic assumption turns out to be false. However, the main argument that they give for their model is the failure in their regime (III) of Friedman's[9,10] formula for the Hall coefficient, worked out for regime (II). We think that a somewhat better understanding of the Hall coefficient in liquid alloys is necessary before this evidence can be taken as conclusive; thus for liquid Hg-In alloys, certainly in regime (I) and for which the electrical conductivity can be explained by the Ziman theory with Evans's[11] pseudopotentials, the Hall coefficient does not obey the simple formula $R_H = 1/nec$. Faber[12] (see also Mott[13]) has accounted for its behavior by the use of macroscopic theory appropriate to a mixture of high- and low-resistivity regions, and it is not clear why this has to be done.

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EPR in Triplet States of the Self-Trapped Exciton

M. J. Marrone, F. W. Patten, and M. N. Kabler
Naval Research Laboratory, Washington, D. C. 20375

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A microwave-optical double-resonance technique has been used to investigate the self-trapped exciton in KBr and CsBr. Electron and hole orbitals for triplet states are characterized on the basis of observed zero-field splittings and hyperfine parameters.

In a variety of simple halide crystals, bound electron-hole pairs occur as self-trapped excitons (STE). Time-resolved spectroscopic observations of the recombination luminescence[1,2] and optical absorption[3] which they originate have provided much information about the nature of these states, but optical experiments alone have not revealed the quantitative detail which EPR can yield. Prior magneto-optic measurements[4] indicated the potential for producing microwave-optical double resonance in the lowest triplet states, an experiment which has now been accomplished.[5] This note outlines data obtained for KBr and CsBr and derives exchange parameters and hyperfine constants which relate directly to the electronic charge distributions. These data confirm the