

in GaAs, in material initially diffused at rather high temperatures ( $\sim 800^\circ\text{C}$ ). There is no clear evidence for such an effect for  $V_{\text{Ga}}-O_{\text{P}}$  in GaP from the present work. However, more detailed electrical and optical studies are required to clarify this point.

<sup>41</sup>C. S. Fuller and K. B. Wolfstirn [J. Appl. Phys. **34**, 1914 (1963)] have found evidence for a very large heat of association of  $V_{\text{Ga}}\text{Te}_{\text{As}}$  pairs in GaAs.

<sup>42</sup>R. Berman and A. S. Barker, Jr. (private communication).

<sup>43</sup>A. Onton and M. R. Lorenz, Appl. Phys. Letters **12**, 115 (1968).

<sup>44</sup>J. Wiley, J. Phys. Chem. Solids (to be published).

<sup>45</sup>This is so because binding characteristic of a double acceptor may greatly increase the Auger transition rate through the strong hole-hole overlap and ease of momentum

conservation for the ejected hole (see Ref. 17).

<sup>46</sup>M. Gershenson and R. M. Mikulyak, Appl. Phys. Letters **8**, 245 (1966).

<sup>47</sup>H. Reiss, C. S. Fuller, and F. J. Morin, Bell System Tech. J. **35**, 535 (1956).

<sup>48</sup>W. Rosenzweig, W. H. Hackett, Jr., and J. S. Jayson, J. Appl. Phys. **40**, 4477 (1969).

<sup>49</sup>We have seen that the low-temperature electron binding energy at Li-Li-O is 210 meV [ $= (E_{\text{bx}} + E_x - E_h)$ ], where  $E_x$  is the internal binding energy of the exciton and  $E_h$  is the binding energy of the hole to the electron on Li-Li-O]. The corresponding energy is  $\sim 300$  meV for the Zn-O trap (Ref. 35).

<sup>50</sup>L. L. Chang and G. L. Pearson, J. Appl. Phys. **35**, 374 (1964).

## Hopping Conductivity in Disordered Systems

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By considering a model in which charge is transported via phonon-induced tunneling of electrons between localized states which are randomly distributed in energy and position, Mott has obtained an electrical conductivity of the form  $\sigma \propto \exp[-(\lambda\alpha^3/\rho_0 kT)^{1/4}]$ . Here  $T$  is the temperature of the system,  $\rho_0$  is the density of states at the Fermi level,  $\lambda$  is a dimensionless constant, and  $\alpha^{-1}$  is the distance for exponential decay of the wave functions. We rederive these results, relating  $\lambda$  to the critical density of a certain dimensionless percolation problem, and we estimate  $\lambda$  to be approximately 16. The applicability of the model to experimental observations on amorphous Ge, Si, and C is discussed.

### I. INTRODUCTION

The dc conductivity of amorphous germanium, in the temperature range  $60^\circ\text{K} \leq T \leq 300^\circ\text{K}$ , has been found to be consistent with the law<sup>1-5</sup>

$$\sigma(T) \propto \exp[-(T_0/T)^{1/4}], \quad (1.1)$$

where  $T_0 \cong 7 \times 10^7$  K. Similar temperature dependences have been found in amorphous silicon and carbon,<sup>3, 6, 7</sup> and in vanadium oxide (VO).<sup>8</sup> A temperature dependence of this general form has been predicted by Mott.<sup>9, 10</sup> His ideas are based on a model in which charge is transported by the thermally assisted hopping of electrons between states localized near randomly distributed "traps"—potential fluctuations that can bind electrons. The

temperature  $T_0$  in (1.1) is given by Mott as

$$kT_0 = \lambda \alpha^3 / \rho_0, \quad (1.2)$$

where  $\alpha$  is the coefficient of exponential decay of the localized states,  $\rho_0$  is the density of states at the Fermi level, and  $\lambda$  is a dimensionless constant. Mott's derivation of Eq. (1.1) seems to us to be somewhat unsatisfactory from a statistical point of view. In this paper we present what we feel is a more systematic derivation of the  $T^{-1/4}$  law, starting from Mott's model. Our analysis is rather different from Mott's, however, and seems to us to uncover some important aspects of an extremely interesting problem in statistical physics. In addition, we express the constant  $\lambda$  in terms of the critical density for a certain dimensionless percola-

tion problem, and we estimate  $\lambda$  to be approximately 16.

It should be remarked at the outset that there is no way at present of directly measuring the parameters  $\alpha$  and  $\rho_0$  which enter the theory, and there may be reason for questioning the applicability of the specific model to amorphous Ge, Si, and C in the temperature range measured. Nonetheless we believe that consideration of this simple model will be helpful for the understanding of dc conductivity in a variety of disordered systems.

The main sections of this paper, Secs. II–IV, deal with localized electronic states, the one-quantum mechanism for hopping from one such state to another, and a method for estimating the conductivity of a system composed of a random array of such states. A critical discussion of the possible applicability of the simple model to real amorphous systems is given in Sec. V. Further comments on the significance of our percolation approach to the evaluation of the conductivity, and on the relation to other calculations, are given in Sec. VI.

Appendix A contains details of an approximate evaluation of the critical density of the percolation problem necessary for the calculation of the coefficient  $\lambda$  in Eq. (1.2).

An important step in our evaluation of the conductivity is the reduction of the hopping model to an equivalent random resistance network, in a manner similar to the work of Miller and Abrahams<sup>11</sup> on a hopping model for impurity states in a crystalline semiconductor. Our evaluation of the resistance of the network is very different from the estimate of these authors, however, as explained in Sec. VI.

The evaluation of the resistivity in our model is restricted to dc conduction and to the limit of weak fields.<sup>12</sup>

## II. LOCALIZED STATES

Following Mott, we consider a highly disordered semiconductor containing an appreciable density, say,  $10^{18}$ – $10^{20}$  cm<sup>-3</sup>, of localized electronic states within a mobility gap of width of order 1 eV. We assume that the positions of these states, i.e., the trapping sites, are randomly distributed, and that their energies are also random on a scale at least of the order of  $kT$ . That is, the density of states  $\rho(E)$  will be assumed to be a constant, roughly  $10^{18}$ – $10^{20}$  cm<sup>-3</sup> per eV, within the region of interest.

The terms “localized state” and “mobility gap” deserve further discussion because they are basic to all of our analysis. What we wish to consider is a situation in which the electronic wave functions for states near the Fermi level do not extend throughout the system but are each localized near some trapping site or some cluster of defects. It is well known that, given such localization, the dc con-

ductivity will vanish at zero temperature, as does the  $\sigma$  given in Eq.(1.1).<sup>9</sup> If the electronic states are not localized, the residual resistivity will be finite. In an amorphous semiconductor, the density of states may be finite at the energies where there are gaps in the spectrum of the ordered material; but, within the gaps, there may exist energy intervals containing only localized states. Such an interval is called a mobility gap. The idea that the localization of the wave functions may change abruptly at certain energies, i.e., at the edges of a mobility gap, is originally due to Anderson<sup>13</sup> and has been developed recently by Mott<sup>14</sup> and others.<sup>15–20</sup>

It is possible to formulate a simple criterion for localization in a way which will be useful in our later discussion of transport properties. Consider a pair of traps such that, when in isolation from one another, their two relevant electronic energy levels differ by  $\Delta E$ ; and let these traps be separated by a finite distance  $R$ . As long as  $\Delta E$  is large enough, there will be no appreciable coupling between the electronic states on each of the traps, and the wave functions will remain localized at each of the sites. If, however,  $\Delta E$  is smaller than the overlap energy (the off-diagonal matrix element of a  $2 \times 2$  Hamiltonian in a representation in which the wave functions are localized on the separate sites), then the energy eigenstates must be delocalized. For example, if  $\Delta E = 0$ , the two correct wave functions will be exactly symmetric and antisymmetric under exchange of the sites. The condition for delocalization can be written mathematically in the form

$$|\Delta E| < U e^{-\alpha R}, \quad (2.1)$$

where  $U$  is an energy of the order of the binding energy of a trap, say, 0.3 eV, and  $\alpha^{-1}$  is a length which describes the spatial extent of the wave function localized at a single site.

Consider now a large volume containing a finite density of such sites distributed randomly in position and energy, and imagine drawing a line—a bond—between any pair of sites which satisfies condition (2.1). If the electronic eigenstates for the whole system are localized, then these bonds will be rare, and will occur only in isolated clusters. On the other hand, if the bonds form a network which spans the whole system, the wave functions will be delocalized. More mathematically speaking, the eigenstates remain localized as long as the number of bonds per site is less than the critical percolation density. Note, however, that the percolation problem we pose here is not quite a standard one.<sup>21</sup>

It is easiest for our purposes to characterize the solution of this percolation problem by specifying a number  $\bar{\eta}$  which is the average number of bonds

per site at the critical percolation density. That is, the wave functions will remain localized if the average trapping site is "on speaking terms" [according to condition (2.1)] with fewer than  $\bar{\eta}$  neighboring sites. Presumably  $\bar{\eta}$  is a number of order 2 or 3. The important point is that  $\bar{\eta}$  is purely geometrical in origin, and does not depend upon the physical parameters  $\rho_0$ ,  $\alpha$ , or  $U$ . Thus, the condition for localization is

$$16\pi\rho_0 U/\alpha^3 < \bar{\eta}, \quad (2.2)$$

where the left-hand side of (2.2) is just  $\rho_0 \int d^3R \times \int d(\Delta E)$ , integrated over the region where  $|\Delta E| < U e^{-2\alpha R}$ . In this way we obtain a rough upper bound on the density of states,  $\rho_0$ , for which our hopping model might be applicable.

### III. HOPPING MECHANISM

In the following, we shall consider only systems in which the electronic states at the Fermi level are all localized, and conduction takes place via direct hopping of electrons from one trapping site to another.<sup>9,11</sup> Because the traps are randomly distributed in energy (a requirement for localization according to the argument of Sec. II), the conduction process requires the assistance of the thermal fluctuations of the lattice to ensure energy conservation. At finite temperatures there will also occur an indirect conduction mechanism involving thermal excitation of band electrons across the mobility gap. We shall assume that the temperature is sufficiently low, and that the tunneling rates and density of localized states are high enough that the direct hopping process is the dominant one.

Let us denote the intrinsic transition rate for an electron hopping from a site  $i$  to an empty site  $j$  by

$$\gamma_{ij} = \gamma(R_{ij}, E_i - E_j), \quad (3.1)$$

where  $R_{ij}$  is the distance between the sites and  $E_i$  and  $E_j$  are the respective electronic energy levels. The average transition rate from site  $i$  to site  $j$  is then

$$\Gamma_{ij} = \langle n_i(1 - n_j) \gamma_{ij} \rangle, \quad (3.2)$$

where the  $n_i$  are the occupation numbers and the angular brackets denote an average over time. Throughout this work we shall neglect electron-electron interactions except to say that not more than one electron can occupy a single site. Then  $\gamma_{ij}$  is independent of the occupation numbers and may be removed from the brackets. Furthermore, in thermal equilibrium, the occupation numbers for different sites are statistically independent, so that  $\langle n_i n_j \rangle = \langle n_i \rangle \langle n_j \rangle$ , and

$$\langle n_i \rangle = n_i^0 = \frac{1}{1 + \exp(E_i/kT)}, \quad (3.3)$$

where the energy  $E_i$  is measured from the Fermi level. [Equation (3.3) applies even in the case where the localized states on each site have a degeneracy  $g$  (as from a spin degeneracy), provided one includes an entropy term  $kT \ln g$  in the definition of the Fermi level.] Finally, from detailed balance,  $\Gamma_{ij}$  must be symmetric in  $i$  and  $j$ , and thus

$$\gamma_{ij} = \gamma_{ji} e^{(E_i - E_j)/kT}. \quad (3.4)$$

We next must predict a more detailed form for  $\gamma_{ij}$ . Because we are considering a tunneling process, we know that the dominant dependence of  $\gamma_{ij}$  on  $R_{ij}$  must be exponential<sup>9,11</sup>:

$$\gamma_{ij} \propto e^{-2\alpha R_{ij}}, \quad (3.5)$$

where  $\alpha^{-1}$  is the same length which was introduced in Eq. (2.1).

The energy dependence of  $\gamma_{ij}$  is less obvious than the  $R$  dependence; and, in fact, a number of different kinds of behavior seem possible. The simplest situation occurs when  $kT$  is small compared to  $|E_i - E_j|$ , and the energy difference  $|E_i - E_j|$  is of the order of the Debye energy or smaller. It is then a good approximation to write

$$\gamma_{ij} = \begin{cases} \gamma_0 e^{-2\alpha R_{ij} - (E_j - E_i)/kT} & \text{for } E_j > E_i \\ \gamma_0 e^{-2\alpha R_{ij}} & \text{for } E_j < E_i, \end{cases} \quad (3.6)$$

where  $\gamma_0$  is some constant which depends on the electron-phonon coupling strength, the phonon density of states, and other properties of the material, but which depends only weakly on the energies  $E_i$  and  $E_j$  or on  $R_{ij}$  relative to the exponential factors which we have shown explicitly. We shall refer to Eq. (3.6) as the "quantum-limit" hopping formula. The hopping rate (3.6) may also be valid for energy differences  $|E_i - E_j|$  large compared to the Debye energy provided that the matrix elements for multiphonon emission processes do not decrease too rapidly with increasing  $|E_i - E_j|$  relative to the detailed balance factor  $\exp[-(E_j - E_i)/kT]$  which makes the energy absorption process difficult.<sup>22</sup>

Combining Eqs. (3.2), (3.3), and (3.6), and assuming  $kT$  small compared to all the energies which appear, we find that the value of  $\Gamma_{ij}$  in thermal equilibrium can be written in the relatively simple form

$$\Gamma_{ij}^0 \cong \gamma_0 \exp[-2\alpha R_{ij} - (|E_i| + |E_j| + |E_i - E_j|)/2kT]. \quad (3.7)$$

### IV. CONDUCTIVITY

#### A. Formulation as a Resistance Network

In the presence of a weak external electric field  $\vec{\mathcal{E}}$ , the intrinsic transition rates  $\gamma_{ij}$  will be changed to

$$\gamma_{ij}(\vec{\mathcal{E}}) = \gamma(R_{ij}, E_i - E_j + e\vec{\mathcal{E}} \cdot \vec{R}_{ij}) \equiv \gamma_{ij} + \delta\gamma_{ij}. \quad (4.1)$$

Also, the occupation numbers will be changed by amounts  $\langle \delta n_i \rangle$ , which we may express as changes  $\delta\mu_i$  in the chemical potentials at the various sites. That is, we may write

$$\langle n_i \rangle = n_i^0 + \langle \delta n_i \rangle \equiv \frac{1}{1 + \exp[(E_i - \delta\mu_i)/kT]}. \quad (4.2)$$

We shall assume, even in the current carrying state, that there are no correlations between the occupation numbers at different sites; i. e., we approximate  $\langle n_i n_j \rangle = \langle n_i \rangle \langle n_j \rangle$ . We can then write the average net flow from site  $i$  to site  $j$  in the form

$$\begin{aligned} \Gamma_{ij}(\vec{\mathcal{E}}) - \Gamma_{ji}(\vec{\mathcal{E}}) &= \Gamma_{ij}^0 \left( \frac{\delta\gamma_{ij}}{\gamma_{ij}} - \frac{\delta\gamma_{ji}}{\gamma_{ji}} + \frac{\langle \delta n_i \rangle}{\langle n_i \rangle \langle (1 - n_i) \rangle} \right. \\ &\quad \left. - \frac{\langle \delta n_j \rangle}{\langle n_j \rangle \langle (1 - n_j) \rangle} \right) \\ &= \frac{1}{kT} \Gamma_{ij}^0 (e\vec{\mathcal{E}} \cdot \vec{R}_{ij} + \delta\mu_i - \delta\mu_j), \end{aligned} \quad (4.3)$$

where we have used Eq. (3.4) (detailed balance) to evaluate the terms involving  $\delta\gamma_{ij}$ . The factor in parentheses in the final version of (4.3) is the total potential difference between sites  $i$  and  $j$ . Thus, the quantity

$$G_{ij} = \frac{e^2}{kT} \Gamma_{ij}^0(R_{ij}, E_i, E_j) \quad (4.4)$$

may be interpreted as a conductance between the two sites. For a given field  $\vec{\mathcal{E}}$ , the quantities  $\delta\mu_i$  are, in principle, determined by the requirement of current conservation; i. e., the total current entering each site  $i$  must be zero. In the following analysis we shall not have to compute the  $\delta\mu_i$  explicitly.

It is useful to think of this model as a real network consisting of randomly distributed points (trapping sites) linked to one another by conductances  $G_{ij}$ . In general, any site on the network will be connected by an appreciably large conductance only to its close neighbors in the four-dimensional position-energy space. Moreover, the strongest connections will occur for pairs of sites whose energies are near the Fermi level. Sites which lie far from the Fermi level will be effectively disconnected from the network.

#### B. Reduction to a Percolation Problem

The over-all electrical conductivity of any connected resistance network can be written in the form

$$\sigma = \bar{G}/\bar{R}, \quad (4.5)$$

where  $\bar{G}$  is some characteristic value of the con-

ductances in the network, and  $\bar{R}$  is some characteristic length scale for the network. We assert that for a network such as the one we are considering, where the values of the individual resistances vary over many orders of magnitude, the correct choice for  $\bar{G}$  is the critical percolation conductance  $G_c$ , defined as the largest value of the conductance such that the subset of resistors with  $G_{ij} > G_c$  still contains a connected network which spans the entire system. Although we do not know how to calculate the remaining factor  $\bar{R}^{-1}$  with any great accuracy, this latter factor will be a relatively slowly varying function of the parameters of the network, and the dominant variation of  $\sigma$  will be contained in  $G_c$ . For the particular network under consideration here, we shall find that the critical conductance  $G_c$  has the exponential dependence given in Eq. (1.1), while the prefactor  $\bar{R}^{-1}$  probably varies as some power of  $T/T_0$ .

The reasoning behind our estimate of the conductivity is as follows. The resistance network can be considered as composed of three parts:

(i) A set of isolated "regions" of high conductivity, each region consisting of a group of sites linked together by conductances with  $G_{ij} \gg G_c$ .

(ii) A relatively small number of resistors with  $G_{ij}$  of order  $G_c$ , which connect together a subset of the high conductance clusters to form an infinite network which spans the system. In the following, we shall refer to the set of resistors in categories (i) and (ii) as forming the "critical subnetwork."

(iii) The remaining resistors with  $G_{ij} \ll G_c$ . It is clear that the conductances of order  $G_c$  determine the resistance of the network. The conductances in category (i) could all be set equal to infinity without greatly affecting the total conductivity—the conductivity would still be finite because the current has to pass through conductances of order  $G_c$  to get from one end of the system to the other. On the other hand, the resistances with  $G_{ij} \ll G_c$  make a negligible contribution to the conductivity because they are effectively shorted out by the critical subnetwork of resistors with  $G_{ij} \gtrsim G_c$ .

#### C. Estimate of the Critical Conductance

We now turn to the evaluation of the critical percolation conductance  $G_c$  for the network under consideration. Using Eqs. (4.4) and (3.7), we may write the condition  $G_{ij} > G_c$  as

$$2\alpha R_{ij} + (|E_i| + |E_j| + |E_i - E_j|)/2kT < \ln(\gamma_0/\Gamma_c), \quad (4.6)$$

where

$$\Gamma_c \equiv kTG_c/e^2. \quad (4.7)$$

Let us further rewrite (4.6) in the dimensionless form

$$\frac{R_{ij}}{R_{\max}} + \frac{|E_i| + |E_j| + |E_i - E_j|}{2E_{\max}} < 1, \quad (4.8)$$

where

$$R_{\max} = \frac{1}{2\alpha} \ln(\gamma_0/\Gamma_c), \quad (4.9)$$

$$E_{\max} = kT \ln(\gamma_0/\Gamma_c). \quad (4.10)$$

Any link with  $R_{ij} > R_{\max}$  will violate the inequality (4.6) or (4.8) regardless of the values of  $E_i$  and  $E_j$ . Similarly, any site with  $|E_i| > E_{\max}$  will violate the inequality for any choice of  $E_j$ , no matter how small the value of  $|\vec{r}_i - \vec{r}_j|$ , and thus will be disconnected from the critical subnetwork. The total number of sites per unit volume with  $|E_i| \leq E_{\max}$  is

$$n = 2\rho_0 E_{\max}. \quad (4.11)$$

These  $n$  sites are still randomly distributed in space, while the dimensionless variable  $E_i/E_{\max}$  is randomly distributed between  $-1$  and  $1$ .

In constructing the critical subnetwork, we consider there to be a bond between two sites  $i$  and  $j$  if and only if the inequality (4.8) is satisfied, and we must choose  $\Gamma_c$  so that the set of bonds included is just large enough to ensure that at least some part of the network spans the entire space. Clearly, this criterion will have the form

$$nR_{\max}^3 = \nu_c, \quad (4.12)$$

where  $\nu_c$  is a dimensionless constant of order unity. For example, if one estimates  $\nu_c$  by requiring that the expected number of bonds attached to a site  $i$  with energy  $E_i = 0$  be equal to some given number  $\eta$  of order unity, then we have

$$\frac{1}{3}\pi\nu_c = \eta. \quad (4.13)$$

The coefficient  $\frac{1}{3}\pi$  in Eq. (4.13) is simply the average volume of a sphere of radius  $(1 - |E_j|/E_{\max})$ , when  $|E_j|$  is uniformly distributed between  $0$  and  $E_{\max}$ . Thus Eq. (4.13) gives  $\nu_c = 2.86$ , if we guess  $\eta = 3$ . In the Appendix we present a more sophisticated analysis of the percolation problem which leads to the estimate

$$\nu_c \cong 4. \quad (4.14)$$

We also point out that, in principle, the number  $\nu_c$  can be calculated as accurately as desired by a Monte Carlo calculation similar to those that have been used by a number of authors to study percolation problems on various two- and three-dimensional lattices.<sup>23, 24</sup>

It is now a simple matter to relate  $\Gamma_c$  to  $\nu_c$ . Combining Eqs. (4.9)–(4.12), we see that

$$\ln(\gamma_0/\Gamma_c) = (4\nu_c \alpha^3/\rho_0 kT)^{1/4}. \quad (4.15)$$

From this we obtain the form  $\sigma \propto \exp[-(T_0/T)^{1/4}]$  for the conductivity with

$$kT_0 = 4\nu_c \alpha^3/\rho_0. \quad (4.16)$$

We believe this estimate of the conductivity of our resistance network to be asymptotically exact in the sense that

$$\frac{\ln(\sigma kT/e^2 \gamma_0 \alpha)}{-(T_0/T)^{1/4}} \rightarrow 1 \quad (4.17)$$

as  $(T/T_0) \rightarrow 0$ .

Note that, if  $\alpha$  is in the range  $10^7$ – $10^8$  cm<sup>-1</sup> and  $\rho_0$  is of order  $10^{19}$ , Eq. (4.16) gives a  $T_0$  of order  $10^6$  °K. Note also the similarity between this expression for  $T_0$  and the localization condition, Eq. (2.2). If we eliminate  $\alpha^3/k\rho_0$  from these relations, and approximate  $\nu_c \cong \bar{\eta}$ , we obtain a simple lower bound for  $T_0$  involving only the quantity  $U$ , an energy which should be independent of the distribution of the trapping sites. That is,

$$T_0 > 200U/k. \quad (4.18)$$

Equation (4.18) is a consistency requirement for the theory in the sense that, if the inequality were violated, the assumption of localized electronic states could not have been valid. In our case, if  $U \cong 1$  eV, the right-hand side of (4.18) is of order  $10^6$  °K, and the inequality is satisfied.

## V. APPLICABILITY TO REAL SYSTEMS

A number of the assumptions used in constructing the model of the previous sections must be questioned before the model can be applied to the experimental observations in amorphous materials. These assumptions are: the neglect of correlations between the energies of neighboring sites; the neglect of interaction between electrons on different sites; the neglect of the variation of the density of states with energy; and the assumption of the "quantum limit" for the hopping rate, Eq. (3.6). The last two of these seem to pose the most serious problems for the validity of the Mott hopping model. In particular, if the maximum distance from the Fermi energy,  $E_{\max}$ , is evaluated according to (4.10), we find  $E_{\max} = kT^{3/4} T_0^{1/4} \cong 0.17$  eV for Ge at  $60$  °K and  $E_{\max} \cong 0.57$  eV for Ge at  $300$  °K. Since the energy gap in crystalline Ge is equal to  $0.8$  eV, one would not expect the density of states to be constant over so large a range. There might also be an appreciable energy dependence of  $\alpha$ , the inverse length which occurs in the overlap integral.

If the second derivative of the density of states with respect to energy is positive, then  $\ln\sigma$  might have a positive curvature when plotted against  $T^{-1/4}$ . On the other hand, the values of  $E_{\max}$  are sufficiently large that the quantum hopping rate (3.6) is probably not valid. For example, if  $E_i - E_j$  is positive and of order  $0.2$  eV, the matrix element for the emission of a sufficient number of

phonons to remove the necessary energy may be quite small, perhaps small compared to  $\exp[-(E_i - E_j)/kT]$ . If so, the equilibrium transition rates  $\Gamma_{ij}^0$  will fall off more rapidly than  $\exp(-|E_i - E_j|/kT)$  as  $E_i$  and  $E_j$  move away from each other. This effect would tend to give  $\ln\sigma$  a negative curvature when plotted against  $T^{-1/4}$ .

It would, of course, seem very surprising for the above effects to cancel and give a conductivity such that  $\ln\sigma$  is perfectly linear in  $T^{-1/4}$ . It is not clear, however, to what extent the experimental data might be fitted by formulas other than Eq. (1.1).<sup>4</sup> It would also be interesting to follow the conductivity experimentally down to lower temperatures where the assumptions behind the Mott model would be more likely *a priori* to be valid.

Two further possibilities concerning the hopping mechanism deserve mention. First, we note that the difficulty in (3.6) arising from the large value of  $E_{\max}$  might be overcome if each trapping site consisted, not of a single electronic energy level, but of a number of such levels, still well localized at the site, but spread over a range of energies of order  $E_{\max}$ . Then the thermal fluctuations of the system might establish equilibrium at each trap separately; and our simple hopping formula (3.6) would be valid with  $E_i$  and  $E_j$  referring to, say, the ground-state energies at two sites.

A second, almost completely opposite, possibility involves a classical picture of the thermal fluctuations. At high enough temperatures, the vibrational modes might be highly excited, and multiple phonon processes could be important. In this picture, the energy of a trap should be visualized as fluctuating very slowly (on an electric time scale), with transitions occurring between one trap and another when these fluctuations happen to make the energies of the two traps coincide.<sup>22</sup> The frequency of such coincidences turns out to have the form  $\exp[-(E_i - E_j)^2/ckT]$ , where  $C$  is a constant; and the resulting conductivity is  $\ln\sigma \propto T^{-1/7}$ . We see no reason to believe, however, that this mechanism is operative in the materials under consideration here.

Let us now consider the effects of the Coulomb interaction between electrons, restricting ourselves initially to a discussion of these effects within a Hartree or Hartree-Fock approximation. In this approximation, the energy of each site  $i$  is modified by the potential due to the time-averaged occupation number  $\langle n_j \rangle$  of the other sites  $j$ . Let us assume that the potentials in thermal equilibrium have already been included in the definition of the site energies  $E_i$ , so that we need only consider the effects of the changes in site potentials when the electric field is applied. We are thus led to replace Eq. (4.3) for the net current between two sites by

$$\Gamma_{ij}(\vec{\mathcal{E}}) - \Gamma_{ji}(\vec{\mathcal{E}}) = \frac{1}{kT} \Gamma_{ij}^0 (e\vec{\mathcal{E}} \cdot \vec{R}_{ij} + \delta\tilde{\mu}_i - \delta\tilde{\mu}_j), \quad (5.1)$$

where

$$\delta\tilde{\mu}_i = \delta\mu_i + \sum_{j \neq i} \frac{e^2}{\epsilon R_{ij}} \langle \delta n_j \rangle, \quad (5.2)$$

$\epsilon$  is the background dielectric constant, and  $\delta\mu_i$  is defined by (4.2) as before. The values of the  $\delta\tilde{\mu}_i$  are determined by the equations of current conservation, which have exactly the same form as the equations which determined  $\delta\mu_i$  when the Coulomb potential was neglected. Thus the substitution of (5.1) for (4.3) makes no difference whatsoever in the current flow, and the only effect of the Coulomb interaction in the Hartree or Hartree-Fock approximation is to affect the statistical distribution and correlations of the energy levels  $E_i$  in the thermal equilibrium state.

It has been suggested by a number of authors<sup>25-30</sup> that the energy levels in amorphous materials are influenced by relatively large random electric fields, arising presumably from the Coulomb potentials due to charged impurities, broken bonds, etc.; or, in other words, from atoms in the material whose normal valence requirements are not locally satisfied. These random fields will then produce fluctuations in the potential with a characteristic wavelength related to the screening radius, which may be of the order of 50 Å or larger. This length scale may be large compared to the average distance between localized states and it would then be incorrect to neglect the correlation between the energies of adjacent sites. In the limit where the spatial scale of the fluctuations is large, the effects of the random potential may be described as a local variation of the Fermi level relative to the mobility edge of the material. There will then be regions of higher conductivity where the Fermi level is close to a mobility edge, surrounded by regions of lower conductivity, where the Fermi level is deep in the gap, and the local density of states is presumably small. If the regions of high conductivity are sufficiently far apart so that direct tunneling between these regions is not possible, then the conductivity of the system is determined by the distribution of the local conductivities. Once again, in the limit of widely varying conductivities, we have a percolation problem to solve. The conductivity of the system will just be given by the critical conductivity  $\sigma_c$ , defined as the largest conductivity such that the volume of space with local conductivity  $\sigma(\vec{r})$  greater than  $\sigma_c$  still includes a connected volume which spans the entire system. Roughly, the conductivity will be given by the requirement that the volume of space with  $\sigma(\vec{r})$  greater than  $\sigma_c$  be equal to one-quarter of the total volume<sup>31</sup> (see Appendix). If the

mechanism for conductivity in the critical regions where  $\sigma(\vec{r}) \approx \sigma_c$  is properly described by Mott's model of hopping between localized states, then the total conductivity of the system will still have the temperature dependence of Eq. (1.1). The quantity  $\rho_0$  entering Eq. (1.2) for  $T_0$  would not now be interpreted as the density of states at the Fermi energy for the system as a whole, but rather as the local density of trap sites per unit volume and energy at the Fermi level in the regions with  $\sigma = \sigma_c$ . If  $\rho(\vec{r})$  is the local density of states at point  $\vec{r}$ , then  $\rho_0$  would be roughly determined by the condition  $\rho(\vec{r}) > \rho_0$  for one-quarter of the volume of the sample.

Let us remark, also, that if states can be characterized as valencelike or conductionlike, with a very slow rate of interconversion between the two kinds of states,<sup>25</sup> then the total conductivity  $\sigma$  must be calculated separately for the two kinds of states, and the results added together at the end (usually one or the other would dominate). This would lead to a lower conductivity than one would estimate with both kinds of states included in  $\rho(\vec{r})$ .

One final effect of the electron-electron Coulomb interaction must be mentioned. This is the lowering of the energy of an occupied electronic level, relative to the unoccupied levels, due to the induced polarization of the remaining electrons by the electron on the occupied state. To the extent that the polarization cannot easily rearrange itself as the electron hops from an occupied site to an unoccupied site, the polarization self-energy  $\Delta$  will serve as a barrier to the conduction process. If we make the most severe possible assumption, that the electronic polarization cannot rearrange itself at all, then the electrical conductivity would be reduced by a factor  $e^{-\Delta/kT}$ . We may estimate the polarization self-energy of an occupied state as the Coulomb potential at the origin arising from the screening charge distribution induced by the electron, calculated in the Thomas-Fermi approximation. This leads to the result

$$\Delta = \frac{e^2}{\epsilon} \left( \frac{4\pi e^2 \rho_0}{\epsilon} \right)^{1/2}. \quad (5.3)$$

For Ge, with  $\epsilon \approx 16$ , this gives  $\Delta \approx 0.003$  eV for  $\rho_0 = 10^{16}$  eV<sup>-1</sup> cm<sup>-3</sup>, or  $\Delta \approx 0.03$  eV for  $\rho_0 = 10^{20}$ . The factors  $e^{-\Delta/kT}$  would be negligible compared with  $\exp[-(T_0/T)^{1/4}]$  for temperatures higher than 1 or 10 °K, respectively.

## VI. FURTHER REMARKS ON THE EVALUATION OF THE CONDUCTIVITY

A number of features of the calculation in Sec. IV deserve note.

In the first place, we point out that the form of the conductivity cannot be deduced by dimensional analysis alone. Dimensional analysis requires

that the conductivity of the resistance network described by Eqs. (3.7) and (4.4) have the general form

$$\sigma = \frac{e^2 \gamma_0 \alpha}{kT} F \left( \frac{\alpha^3}{\rho_0 kT} \right); \quad (6.1)$$

but dimensional arguments say nothing about the specific form of the dimensionless function  $F$ .

We also remark that the percolation analysis we have used to obtain the conductivity of the random resistance network is essential for correct understanding of the problem, and that incorrect results can be obtained for the conductivity if this feature is overlooked. An incorrect evaluation of the conductivity is obtained, for example, if one ignores the requirement of current conservation, and neglects the changes in the chemical potential  $\delta\mu_i$  in Eq. (4.3). In this approximation one would say that the current flowing from  $i$  to  $j$  is simply  $(e^2 \Gamma_{ij}^0/kT) \vec{\mathcal{E}} \cdot \vec{R}_{ij}$ . If one then computes the average current density in the network, one finds for the network conductivity the incorrect result

$$\sigma = \frac{e^2}{3kT} \left\langle \frac{1}{V} \sum_{ij} \Gamma_{ij}^0 R_{ij}^2 \right\rangle, \quad (6.2)$$

where  $V$  is the volume of the system. For the random network considered in Sec. IV, this would give

$$\sigma = \text{const} \times e^2 \rho_0^2 \alpha^{-5} kT, \quad (6.3)$$

a gross overestimate of the conductivity at low temperatures. This overestimate, of course, results from the exaggerated contribution of the resistors with atypically high conductance.

In their analysis of a hopping model similar in many respects to the model considered in the present paper, Miller and Abrahams<sup>11</sup> assumed that a random network is effectively equivalent to a set of independent conducting paths, each path carrying electrons from one end of the system to the other via transitions between near-neighbor trapping sites. In this picture, the conductances linking the sites are connected in series; and, thus, the conductivity of the system is determined by the mean resistance between a site and its first or second nearest neighbor. Because the Miller-Abrahams mean resistance calculation is dominated by very large resistors, that in fact are bypassed by the critical resistance subnetwork, this analysis leads to a much lower estimate of the conductivity of the system than the correct percolation analysis produces.

To make a direct comparison of the two approaches, let us first consider a model which is somewhat simpler than the one discussed in Sec. IV. We discuss a model in which there is a density  $n = (4\pi R_D^3/3)^{-1}$  of trapping sites, all of which have energies sufficiently close to the Fermi surface

so that the energy dependence of  $\Gamma_{ij}^0$  can be neglected. In this model, the percolation analysis equivalent to (4.9)–(4.12) gives simply

$$\ln \sigma \propto -\alpha R_D. \quad (6.4)$$

The Miller-Abrahams point of view requires a more complicated calculation. Let  $R_n$  be the distance between any given site and its  $n$ th nearest neighbor. The probability distribution for  $R_n$  is

$$P_n(R_n) = \frac{1}{(n-1)!} \left(\frac{R_n}{R_D}\right)^{3(n-1)} \frac{3R_n^2}{R_D^3} \exp\left[-\left(\frac{R_n}{R_D}\right)^3\right]. \quad (6.5)$$

If the conductance of the link of length  $R_n$  is  $G_0 \exp(-2\alpha R_n)$ , then the average resistance of such links is

$$\begin{aligned} \left(\frac{1}{G_n}\right)_{\text{av}} &= \frac{1}{G_0} \int_0^\infty e^{2\alpha R_n} P_n(R_n) dR_n \\ &= \frac{3}{(n-1)! G_0} \int_0^\infty u^{3n-1} \exp(2\alpha R_D u - u^3) du, \end{aligned} \quad (6.6)$$

where  $u = R/R_D$ . As usual, we consider only the case of a very dilute distribution of traps (we still insist on localized wave functions), so that  $\alpha R_D \gg 1$ . The integral in (6.6) is then sharply peaked at  $u^2 = \frac{2}{3}\alpha R_D$ . Thus this analysis would lead to the incorrect result

$$\sigma \approx \exp[-2(\frac{1}{3}2\alpha R_D)^{3/2}], \quad (6.7)$$

which is essentially Miller and Abrahams's Eq. (III-29).

In the actual model considered by Miller and Abrahams, the energy spread  $\Delta$  of the impurity states is large compared to  $kT$  but is small compared to  $kT\alpha R_D$ . This leads to a temperature dependence  $e^{-\Delta/kT}$  which will be present equally well in the Miller-Abrahams analysis and in the percolation analysis of that model. [Note that, under these conditions,  $e^{-\Delta/kT}$  is a more slowly varying function of temperature than  $\exp[-(\alpha^3/\rho_0 kT)^{1/4}]$ , if we set  $\rho_0 = n/\Delta$ .]

The application of the Miller-Abrahams analysis to the model of the present paper, in which the density of states is taken to be constant, and the energy dependence of the hopping is important, is somewhat ambiguous. If one estimates the resistivity of the network as the mean value of the first or second smallest resistance connected to a site at the Fermi energy, then one finds

$$\ln \sigma \propto -(\alpha^3/\rho_0 kT)^{1/3}.$$

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#### APPENDIX: APPROXIMATE SOLUTION OF THE PERCOLATION PROBLEM

In this Appendix, we shall attempt to make a more sophisticated estimate of the critical density  $\nu_c$  for the dimensionless percolation problem defined in Sec. IV.

Let  $\epsilon_i = E_i/E_{\text{max}}$ , and let  $\rho_{ij} = R_{ij}/R_{\text{max}}$ . If  $\epsilon_i$  and  $\epsilon_j$  have opposite signs, then the inequality (4.8) will be satisfied, and there will be a bond between sites  $i$  and  $j$ , if and only if

$$\rho_{ij} < 1 - |\epsilon_i| - |\epsilon_j|. \quad (A1)$$

If  $\epsilon_i$  and  $\epsilon_j$  have the same sign, there will definitely be a bond if (A1) is satisfied, but there may be a bond between  $i$  and  $j$  even if (A1) is not satisfied. There will certainly not be a bond, however, unless  $\rho_{ij}$  satisfies

$$\rho_{ij} < 1 - \frac{1}{2}|\epsilon_i| - \frac{1}{2}|\epsilon_j|. \quad (A2)$$

Let us associate with each site  $i$  a sphere of radius  $R_i$ , centered at  $\vec{r}_i$ , with

$$\begin{aligned} R_i &= R_{\text{max}}(\frac{1}{2} - |\epsilon_i|) \quad \text{if } |\epsilon_i| \leq \frac{1}{2} \\ &= 0 \quad \text{if } \frac{1}{2} \leq |\epsilon_i| \leq 1. \end{aligned} \quad (A3)$$

We shall assume there to be a bond between two sites  $i$  and  $j$  if and only if their associated spheres intersect. [This is correct for  $\epsilon_i \epsilon_j < 0$ , but somewhat underestimates the number of bonds for  $\epsilon_i \epsilon_j > 0$ . On the other hand, if we had chosen a sphere of radius

$$R_i = (\frac{1}{2} - \frac{1}{2}|\epsilon_i|) R_{\text{max}}, \quad (A4)$$

we would have overestimated the number of bonds regardless of the signs of  $\epsilon_i$  and  $\epsilon_j$ .] The average volume of the spheres in (A3) is

$$\bar{V} = \frac{4}{3}\pi R_{\text{max}}^3 \int_{-1/2}^{1/2} (\frac{1}{2} - |\epsilon|)^3 d\epsilon / \int_{-1}^1 d\epsilon = \frac{1}{48}\pi R_{\text{max}}^3. \quad (A5)$$

[If we had used (A4), the volume  $\bar{V}$  would have been twice as large.]

We now estimate the critical percolation density for this problem to be

$$n\bar{V} = \frac{1}{4}, \quad (A6)$$

which means that slightly less than one-quarter of the volume should be filled by the spheres. (Filled volume =  $1 - e^{-1/4} \approx 0.22$ .) We base this estimate on the calculated critical site-occupation probabilities for various three-dimensional lattices<sup>32</sup>:

$$p_c \approx 0.195 \quad \text{for fcc, hcp,}$$

$$p_c \approx 0.24 \quad \text{for bcc,}$$

$$p_c \approx 0.31 \quad \text{for sc,}$$



$p_c \cong 0.43$  for diamond structure.

We feel that the close-packed lattices should be more representative of a random array of spheres than the more open structures. Our estimate (A6) is slightly larger than the general estimate for the critical filled volume of 0.15 given by Scher and Zallen.<sup>33</sup> For a random distribution of spheres of equal volume  $\bar{V}$ , one can establish a rigorous lower bound to the critical density of

$$n\bar{V} > \frac{2}{11} = 0.1818. \quad (\text{A7})$$

For spheres of variable size, the corresponding

rigorous lower bound is somewhat weaker.

Combining (A6) with (4.12) and (A5) leads to the estimate  $\nu_c \cong 4$  quoted in (4.14). The estimated uncertainty in this result is of order 50%.

*Note added in proof.* The authors have received a preprint from M. Pollak,<sup>34</sup> in which a number of the ideas of the present paper have been independently derived. In particular, Pollak also deduces Mott's form for the conductivity from considerations in which the percolation aspects of the problem play a central role. Another rederivation of the  $T^{-1/4}$  law has been given by Brenig, Wölfe, and Döhler.<sup>35</sup> Their derivation seems to be quite different from the present one, however.

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