

similar results, are given by E. M. Hamilton, *Phil. Mag.* **26**, 1043 (1967), and by W. Brenig, G. H. Döhler, and H. Heyszenan, *Phys. Lett.* **39**, 175 (1972).

<sup>8</sup>C. J. Adkins and E. M. Hamilton [in *Proceedings of the International Conference on Conduction in Low Mobility Materials* (Taylor and Francis, London, 1971), p. 229] report on the thickness dependence of conductivity in amorphous carbon films. The authors also interpret their results in terms of percolation, but cannot analyze their data in any detail because the temperature dependence was not measured.

<sup>9</sup>M. Pollak, *J. Non-Cryst. Solids* **11**, 1 (1972).

<sup>10</sup>R. Jones and W. Schaich, *J. Phys. C: Proc. Phys. Soc., London* **5**, 43 (1972).

<sup>11</sup>M. Pollak, M. L. Knotek, H. Kurtzman, and H. Glick, following Letter [*Phys. Rev. Lett.* **30**, 856 (1973)].

<sup>12</sup>We use here a bandwidth of  $\sim 0.3$  eV reported in Ref. 11. Notice that our results for  $N$  are consistent with optical experiments as reported by T. M. Donovan, W. E. Spicer, and J. Bennett, *Phys. Rev. Lett.* **22**, 1058 (1966).

<sup>13</sup>M. L. Knotek, to be published.

## dc Conductivity of Amorphous Germanium and the Structure of the Pseudogap\*

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This work centers on the now disputed interpretation of the observed  $T^{-1/4}$  dependence of the conductivity in amorphous group-IV semiconductors by hopping near the Fermi energy. We find the arguments against this interpretation inapplicable. We present experimental results of the temperature dependence of the resistivity  $\rho(T)$  of gas-free and void-free amorphous germanium, as well as theoretical results of  $\rho(T)$  for a hopping model with a band of localized states near the Fermi energy. The agreement is good and leads to the estimate of the bandwidth of 0.3 eV.

It is the main purpose of this note to relate the dc conductivity of amorphous germanium to the structure of the pseudogap. We first must present arguments and evidence against the often-stated opinion<sup>1-5</sup> that the  $T^{-1/4}$  dependence of the dc conductivity cannot be accounted for by Mott's variable-range hopping model.<sup>6</sup> One of the main arguments brought against such an explanation was that in the temperature range in which the  $T^{-1/4}$  has been reported, Mott's and other  $T^{-1/4}$  theories do not apply. We show in the following that this argument is erroneous; the variable-range hopping theories are applicable to much higher temperatures than has been realized. The other strong argument against the hopping mechanism has been the incompatibility between the high concentration of states implied by the hopping model and various optical experiments, which set an upper limit on such a concentration much below that concentration. We show in this and two other notes<sup>7,8</sup> that this discrepancy is not nearly as large as has been believed. The two types of measurements agree, in fact, quite well. We find here and in Refs. 7 and 8 that the observed transport behavior is so consistent with hopping conduction through localized states in the pseudogap that little doubt can be left about

the correctness of such an interpretation.

The arguments that the variable-range hopping mechanism cannot account for the  $T^{-1/4}$  behavior reported for amorphous silicon and germanium between room temperature and liquid nitrogen is, in essence, as follows. From various theories of hopping conduction<sup>2,6,9</sup> it is clear that the conduction occurs only through localized states whose energy is within a certain distance  $E_m$  from the Fermi energy. States further removed from the Fermi level than by  $E_m$  are entirely unimportant. In terms of the percolation theories,<sup>2,9</sup>

$$E_m = kT\xi_m, \quad (1)$$

where  $\xi_m$  is the exponent of the critical percolation impedance of a random-impedance network. It can be obtained from the slope of a  $\ln\rho$ -versus- $T^{-1/4}$  plot, and turns out to be about 20 for amorphous germanium and silicon. The argument against the hopping explanation of the  $T^{-1/4}$  now is that at room temperature  $E_m = kT\xi_m \approx 0.5$  eV is an unreasonably high energy since it is greater than the distance of the mobility edge from the Fermi level. Conduction clearly cannot be by hopping under such conditions.

We show in the following why the above argument is not entirely accurate. While it is true

that percolation occurs up to a distance  $E_m$  from the Fermi energy, it is also true that there exists an enormous weighting factor in favor of sites which are much closer to the Fermi energy than  $E_m$ . Qualitatively the reason for this is as follows. In order that conduction can go through some site, it is necessary (but not sufficient) that two impedances, one incoming and one outgoing, both with values less than  $Z_m = Z_0 \exp(\xi_m)$  be connected to such a site. From Eq. (17) of Ref. 9 the value of  $\xi$  is given by

$$\xi = E/kT + 2r/a. \tag{2}$$

As explained above Eq. (14) of Ref. 9, the smallest possible value of  $E$  in Eq. (2) for an impedance connected to some site is the energy distance of that site from the Fermi level. This means that for the current to go through the site, the value of  $r$  must be less than  $a(E_m - E)/2kT$  for at least two impedances connected to it; i.e., there must be at least two sites within such a distance from the site considered, and within  $E$  from the Fermi energy. The probability that a site is within a certain distance is proportional to this distance cubed; so the probability that two sites are within the maximum permissible distance is proportional to  $(E_m - E)^6$ . This shows qualitatively how unlikely it is to have sites with large  $E$  on the percolation path.

To demonstrate this effect quantitatively, we apply a recent theory of dc hopping conduction<sup>9</sup>

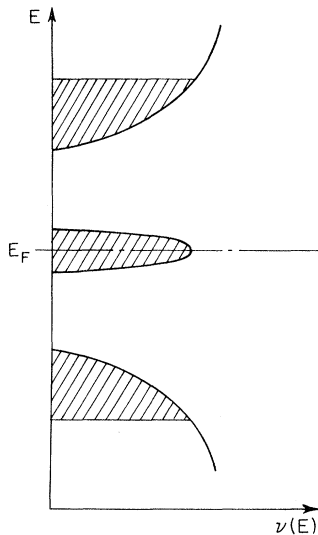


FIG. 1. Mott and Davis's model for the density of states in amorphous germanium and silicon. The hatched regions are localized states, the unhatched regions are delocalized states.

to the postulated model<sup>10</sup> of the pseudogap in amorphous germanium and silicon. The model is reproduced in Fig. 1. Equations (24), (25), and (28) of Ref. 9 permit the calculation of the temperature dependence of  $\ln\rho$  when the density-of-states function is known. To represent the model of Fig. 1 we use the density-of-states function

$$\begin{aligned} \nu(E) &= \nu(0)[1 - (E/E_0)^2] \text{ for } |E| < E_0, \\ &= 0 \text{ for } |E| > E_0, \end{aligned} \tag{3}$$

where  $\nu(0)$  is the density of states at the Fermi energy,  $E_0$  is half the width of the band of localized states, and the energy  $E$  is referred to the Fermi energy, i.e.,  $E_F = 0$ . The derivation was done analytically as well as by computer. The analytical formula is very cumbersome, so we present here only a plot of the result. This is shown in Fig. 2.

Clearly demonstrated in Fig. 2 is the correctness of the above qualitative argument that, although percolation paths can go up to  $E_m$  from the Fermi energy, there is an enormous weighting factor in favor of much smaller energies. Even when  $E_m$  becomes  $E_0$ , where the density of states vanishes, the deviation from a  $T^{-1/4}$  behavior is imperceptible. In fact, the deviation

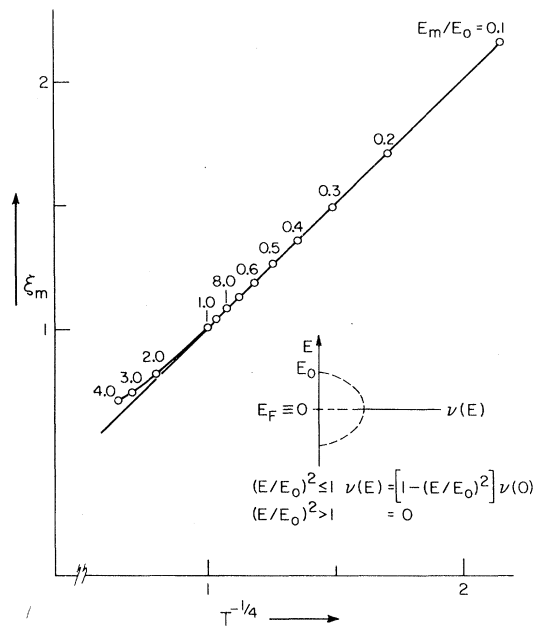


FIG. 2. Calculated dependence of  $\xi_m = \ln\rho + k$  versus  $T^{-1/4}$ , from the theory of Ref. 9, for a band of localized states such as is indicated in the inset. The temperature is in units of  $0.47a\nu(0)^{1/3}E_0^{4/3}/k$ , and  $\xi_m$  is in units of  $2.14/\nu(0)^{1/3}aE_0^{1/3}$ .

from a  $T^{-1/4}$  behavior is barely noticeable even if  $E_m$  is 3 times larger than  $E_0$ , i.e., when no states exist over two thirds of what seemingly is the important energy range.<sup>11</sup>

For an experimental verification we present new measurements of the resistivity on high-density amorphous germanium films. The films were grown in a uhv system and measured *in situ*. A more detailed description of the samples and the measurement will be presented elsewhere. The results for a typical sample are presented in Fig. 3. Notice that the behavior is continuous from the low temperatures, where hopping is believed to be applicable, to room temperature, where it has been believed not to be applicable. Above room temperature the conductivity is activated with an activation energy of 0.25 eV; this is presumably activation above the mobility edge. Just below room temperature the resistivity is observed to be above the  $T^{-1/4}$  line, just as in the theoretical curve for  $T$  above  $E_m/E_0 \cong 1$ . This behavior is quite consistent for all our samples. While it may seem far fetched at this point to identify such a detailed feature with a theoretical prediction, we do so to see whether reasonable results are obtained. The analysis of the data gives the following results.

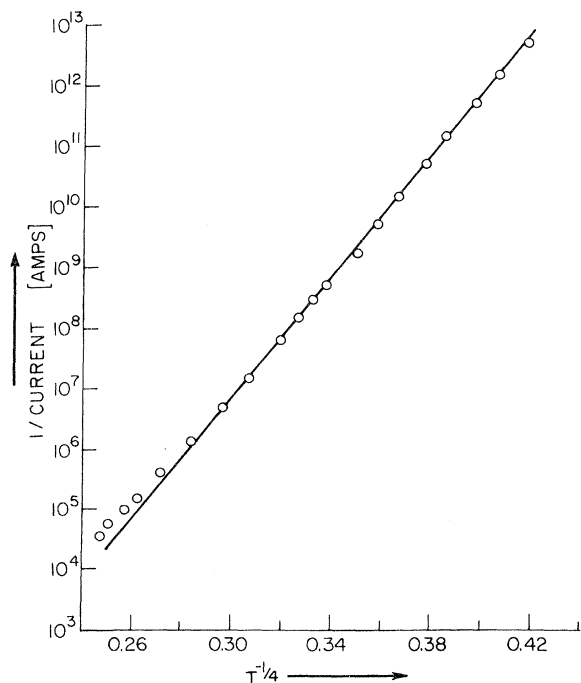


FIG. 3. Experimental dependence of  $\log \rho$  versus  $T^{-1/4}$  of a high-density film of amorphous germanium deposited and measured at  $10^{-11}$  Torr.

Matching the breakoff from the  $T^{-1/4}$  lines in Figs. 2 and 3 we can calibrate the abscissa in Fig. 2 in terms of real temperature. From the slopes of the  $T^{-1/4}$  line in Fig. 3, and using Eq. (41) of Ref. 9, we can calculate

$$\nu(0)a^3 = (1.84/s)^4 k^{-1},$$

so that finally we can evaluate  $E_0$  by comparing the calibrated abscissa of Fig. 2 with the scale in the caption of that figure. The result is  $E_0 = 0.18$  eV, which of course should now be identified with the value of the half-width of the band of localized states in the model in Fig. 1. If we use the result  $a = 10 \text{ \AA}$  from Ref. 7, we can calculate the peak density of states  $\nu(0)$ , as well as the total concentration of localized states,

$$N = \int_{-E_0}^{E_0} \nu(E) dE.$$

The results are  $\nu(0) = 10^{18} \text{ eV}^{-1} \text{ cm}^{-3}$ ,  $N = 2.2 \times 10^{17} \text{ cm}^{-3}$ . We believe that these results are reasonable, and in view of the uncertainties concerning the optical transition matrix elements, not irreconcilable with the optical data.<sup>12</sup>

In conclusion, a few comments are in order. It must be realized that the temperature dependence of the pre-exponential of the conductivity [see Eq. (43) of Ref. 9] has been neglected here. We do not believe that this is of any importance. The temperature dependence of the logarithm is certainly quite slow. At the most it may have some effect on the slope, but certainly cannot cause a sudden change in the slope, such as discussed above.

The theory on which the calculations are based assumes  $a$  to be a constant, rather than a random variable which it may possibly be in practice, and neglects also any spatial autocorrelation of the internal potential. The latter was, however, found in a preliminary study to be most probably unimportant.

We do not wish to determine, at the present, the detailed features of the localized band and the exact location of the Fermi level from the data now available. However, some band of localized states about 0.3 eV wide is strongly suggested. For some indication of the effect of the shape of the band and of the Fermi energy we mention that a rough comparison of the experimental data with a theory for a parabolic band, but with  $E_F$  displaced by  $\frac{1}{2}E_0$  from the peak, gives a half-bandwidth of approximately 0.1 eV, a peak density of  $1.5 \times 10^{18} \text{ eV}^{-1} \text{ cm}^{-3}$ , and  $N = 2 \times 10^{17} \text{ cm}^{-3}$ ; and a comparison with a theory for a square

band gives a half-bandwidth of approximately 0.07 eV,  $\nu \approx 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$ , and  $N = 1.4 \times 10^{17} \text{ cm}^{-3}$ .

We believe that a much more detailed analysis of the band near the Fermi level will be possible with more extensive measurements of the temperature dependence of the dc conductivity.

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<sup>1</sup>N. F. Mott, *J. Non-Cryst. Solids* **8-10**, 1 (1972).

<sup>2</sup>V. Ambegoakar, B. I. Halperin, and J. S. Langer, *J. Non-Cryst. Solids* **8-10**, 492 (1972).

<sup>3</sup>M. H. Brodsky, *J. Non-Cryst. Solids* **8-10**, 739 (1972).

<sup>4</sup>H. Fritzsche, in *Amorphous and Liquid Semiconductors*, edited by J. Tauc (Plenum, New York, to be published).

<sup>5</sup>W. Paul, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, 1972*, edited by the Polish Academy of Sciences (PWN—Polish Scientific Publishers, Warsaw, 1972).

<sup>6</sup>N. F. Mott, *J. Non-Cryst. Solids* **1**, 1 (1968).

<sup>7</sup>M. L. Knotek, M. Pollak, T. M. Donovan, and H. Kurtzman, preceding Letter [*Phys. Rev. Lett.* **30**, 853 (1973)].

<sup>8</sup>M. L. Knotek and T. Donovan, *Phys. Rev. Lett.* **30**, 652 (1973).

<sup>9</sup>M. Pollak, *J. Non-Cryst. Solids* **11**, 1 (1972).

<sup>10</sup>N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Oxford Univ. Press, Oxford, England, 1971).

<sup>11</sup>We find it worthwhile to point out here that the “apparent” slope (such as one would plot from experimental data in the region of slight curvature in Fig. 2) would deviate slightly from the true  $T^{-1/4}$  slope. This would have some effect on the density of states calculated from such an experiment. More importantly, the deviation of the “apparent” slope from the correct slope depends on the width of the localized band. A change in this width from sample to sample could easily cause the crossing of curves reported, for example, in Ref. 3. There are, however, more important reasons why such a crossing may occur. These will be discussed in a separate paper (M. Knotek and T. Donovan, to be published).

<sup>12</sup>T. M. Donovan, W. E. Spicer, and J. Bennett, *Phys. Rev. Lett.* **22**, 1058 (1966); T. M. Donovan, thesis, University of Stanford, 1970 (unpublished).

## Anisotropic Exchange Effects in the Exciton Spectrum of $\text{GdCl}_3$ and $\text{Gd}(\text{OH})_3$

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The first detailed application of a general anisotropic exchange operator to energy-transfer problems in magnetic insulators is described for exciton dispersion in  $\text{GdCl}_3$  and  $\text{Gd}(\text{OH})_3$ . Relationships, which are independent of the two parameters in the theory and are consistent with experiment, are found between transfer-of-energy matrix elements for different excited states, providing strong evidence that anisotropic exchange is the dominant mechanism of energy transfer.

The electronic exchange interaction in insulators is responsible for a variety of phenomena, some of which have not been widely exploited as probes of the *form* of the interaction. In addition to contributing to the magnetic ordering and to the splitting of excited states, it also contributes to energy transfer between ions, to the energy dispersion of excited electronic states, to exciton-magnon interactions, and to multiple-excitation transition mechanisms. The purpose of this paper is to show the importance of the *anisotropic part of the exchange interaction* as a mechanism of energy transfer and dispersion and to illustrate how this can be determined and taken

into account in a real system for which there is experimental information.

Anisotropy in the exchange interaction arises from the dependence of the exchange integral on the orbital states of the electrons. Past experiments have shown that this orbital dependence must be taken into account, as the isotropic Heisenberg exchange alone cannot generally explain the phenomena described above.<sup>1-5</sup> Since there are a large number of two-electron exchange integrals (1225 for *f* electrons and 325 for *d* electrons<sup>6</sup>), one must carefully choose a system which can be treated with the desired generality regarding the interactions and yet remain amen-