the ^5S state from the $3p^2 \rightarrow 3s3d$ excitation. The intensity ratio ^7S:^5S should be the MHT value, 1.4, which also agrees with experiment (1.4 ± 0.1).

We have been able to obtain a striking and detailed agreement between CMHT and experiment for the various hole states observed for Mn^{2+} ions in solids. Clearly, correlation effects will be preferentially important when the hole is created in the shell having the same principal quantum number as the open valence shell. Thus, we may use CMHT to explain the observations in the rare-earth compounds[11] which show that while the $5s$ splittings agree with simple FO-MHT calculations,[15] the observed $4s$ splittings are reduced by about a factor of 2 with respect to the MHT predictions.

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Thickness Dependence of Hopping Transport in Amorphous-Ge Films[*]

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The conductivity of gas-free thin films of amorphous germanium was measured as a function of temperature and film thickness. Existing theories of hopping conduction have been modified to apply to very thin films. The results are consistent with experiment, indicating that hopping conduction near the Fermi energy is the mechanism responsible for the conductivity below room temperature. The radius a of the localized wave functions and the density of states N_F at the Fermi energy found are $a = 10$ Å and $N_F = 1.5 \times 10^{18}$ eV^{-1} cm^{-3}.

Various attempts have been made to explain the transport properties of amorphous germanium in terms of hopping conduction. In particular, the transport below room temperature seems to obey the ubiquitous $T^{-1/4}$ law derived by Mott.[1] Extensive criticism[2-6] has been voiced of the hopping interpretation of the observed $T^{-1/4}$ law for the amorphous group-IV films. The evidence here is that the hopping interpretation is correct.

We present here an extension of the theory to two dimensions[7] and experimental data for a-Ge films of varying thickness,[8] which show that hopping theory accounts very well for the features seen. In addition, the size and density of the localized states is obtained from a comparison of our experiments with theory.

All measurements reported here were taken in an ultrahigh vacuum (*in situ*) in a system with a base pressure of 5×10^{-11} Torr. The a-Ge samples were evaporated from a water-cooled nickel-plated copper e-gun onto sapphire substrates which had an interdigital array of 75 chrome electrodes, 0.5 cm in length separated by 50 μm, deposited on them. The electrodes were predeposited in a different vacuum system than the measuring system. The electrodes were heat cleaned in vacuum at 200°C for several hours before the evaporations. Pressure during deposition was in the $(2-5)\times10^{-8}$-Torr range, and the data were taken immediately after deposition at pressures on the order of 1×10^{-10} Torr.

In treating hopping in three dimensions (3D) for a system such as was postulated for a-Ge, one gets the result[1,3,9,10]

$$\ln\rho \propto A_3 - S_3/T^{1/4}, \tag{1}$$

where

$$S_3 = c_3\left(\frac{\alpha^3}{kN_{\rm F}}\right)^{1/4} \tag{2}$$

where $\alpha = 1/a$, $N_{\rm F}$ is the density of states at $E_{\rm F}$, and k is Boltzmann's constant. Various authors give slightly varying values for c_3, but they all are within 15% of each other [Mott, $c_3 = 2.05$; Pollak, $c_3 = 1.84$; Ambegaokar, Halperin, and Langer (AHL), $c_3 = 2$; Jones and Schaich, $c_3 = 1.78$].

If we use considerations similar to those used for the 3D treatment and extend the calculation to sample thicknesses d such that the hopping distance is greater than the thickness (termed 2D here), one finds the result

$$\ln\rho \propto A_2 - S_2/T^{1/3}, \tag{3}$$

where

$$S_2 = c_2\left(\frac{\alpha^2}{kdN_{\rm F}}\right)^{1/3}, \tag{4}$$

where Mott's method gives $c_2 = 2.05$; Pollak's $c_2 = 1.74$; AHL's, $c_2 = 2.00$. Thus if one performs an experiment in the range of thicknesses mentioned, one should get linear $\ln\rho$-versus-$T^{-1/3}$ plots with a slope $S_2\alpha d^{-1/3}$. As the thickness increases we expect a transition from $T^{-1/3}$ to $T^{-1/4}$ behavior. The slope on a $T^{-1/4}$ plot, S_3, should then be invariant with thickness. We have done such an experiment in the following way. Under conditions described above we deposited a thin layer of a-Ge at substrate temperature $T_s = 50$°C. The sample was cycled down in temperature (until $R = 10^{13}$ Ω in this case), and then returned to 50°C when another layer of a-Ge was deposited over the first. The current was monitored as a function of temperature at constant voltage both on cooling and heating. The data were stable, and repeatable for all data shown. This process was repeated several times to give the data shown in Fig. 1.

Curves 1–5 were made on one run, and 6–8 were done on a subsequent run on a different pump-down under conditions as identical as our controls allow. One might worry whether we are observing the same transport mechanism on a 22-Å film as on a 500- or 1000-Å film. The inset of Fig. 1 shows a plot of log intercept versus

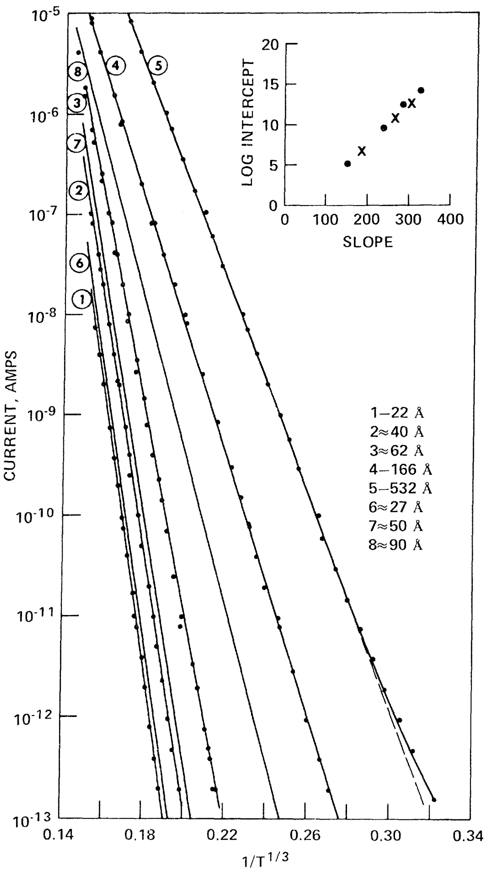

FIG. 1. Log of the current versus $T^{-1/3}$ with film thickness as a parameter for a-Ge grown on 50°C substrate. Inset, log of the $T=\infty$ intercept versus slope on a $T^{-1/3}$ plot for films 1–4 and 6–8. Film No. 5 shows $T^{-1/4}$ rather than $T^{-1/3}$ behavior over most of the curve. (The $T^{-1/3}$ dependence is indicated by the dashed line.)

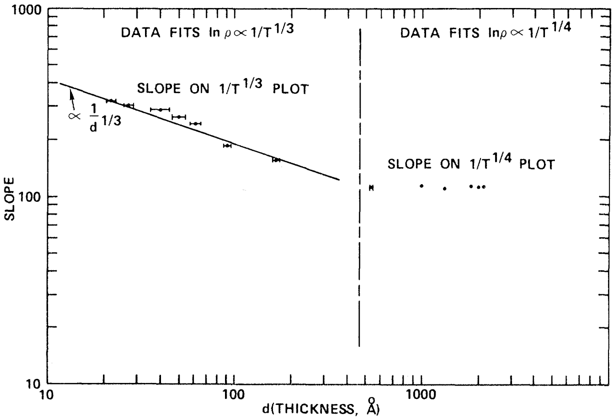

FIG. 2. Slope on a plot of best fit versus thickness for the film shown in Fig. 1 as well as additional thicker films grown under identical conditions. Solid line, behavior predicted by Eq. (4). This clearly shows a transition from 2D to 3D behavior.

slope for all of the curves shown. As is seen, there is a smooth relationship from film to film, and this leads us to believe that the transport mechanism is invariant from thickness to thickness. In addition, electron micrographs show continuous films for $d \gtrsim 20$ Å in thickness. The inset shows a fit with

$$\ln\rho = B - 0.115 S_2 + S_2/T^{1/3}. \tag{5}$$

We use this only as an internal consistency check at this time.

Figure 2 shows a plot of the slope on a $\ln\rho$-versus-$T^{-1/3}$ plot versus thickness for the thin films as well as the $T^{-1/4}$ slope for thicker films. The solid line is the form expected from Eq. (4) for the thin films. Considering our uncertainties in the thickness d, we regard this as good agreement. The data fit a $\ln\rho$-versus-$T^{-1/3}$ straight-line plot for the thickness up to 166 Å. For all samples studied with thicknesses greater than 500 Å, the slope on a $T^{-1/4}$ plot was invariant with thickness for identically prepared films and is $S_3 \approx 110°\mathrm{K}^{1/4}$. Some details of the fit of the thicker films to $T^{-1/4}$ are given in the following Letter.[11] We analyze these data in the following way: From Eqs. (2) and (4) we find

$$\alpha d = (S_3^4/S_2^3)c_2^3/c_3^4 \tag{6}$$

or

$$a = d(c_3^4/c_2^3)S_2^3/S_3^4 \tag{7}$$

[Mott, $a = 2.05 d S_2^3/S_3^4$; Pollak, $a = 2.0 d S_2^3/S_3^4$; AHL, $a = 2.0 d S_2^3/S_3^4$]. Thus the predictions for a are essentially the same for all three forms.

TABLE I. Orbital size and density of states at the Fermi level.

d	S_2	a	N_F
22	320	10.1	1.35×10^{18}
27	305	10.7	1.14×10^{18}
41	290	14.0	5.1×10^{17}
50	265	13.0	6.4×10^{17}
65	235	11.8	8.5×10^{17}
90	185	8.0	2.7×10^{18}
166	155	8.65	2.16×10^{18}

From Eq. (2)

$$N_F = (S_3/c_3)^{-4}\alpha^3/k, \tag{8}$$

$S_3 = 110°\mathrm{K}^{1/4}$ for these films.

Table I is a composite of the results of a and N_F for each thickness. The results for the line on Fig. 2 are $a = 9.4$ Å, $N_F = 1.5\times 10^{18}$ eV^{-1} cm^{-3}. Notice also that these values are in good agreement with the values of $N_F a^3$ obtained from the thick films and the three-dimensional hopping theory.[11] The total concentration of localized states in the vicinity of E_F is $N \approx (2-5)\times 10^{17}$ cm^{-3}.[12]

It is interesting to note that given $a = 10$ Å, the saturation of the slope at $d = 300-400$ Å is very consistent with what one would expect. The characteristic hopping distance for a 3D film is $\approx 12a$ at $\simeq 200°$K. This is ≈ 120 Å, and we expect a transition to three-dimensional behavior at d equal to about 3 to 4 times that value. Further details of this work as well as the data and interpretation in Ref. 11 will be given in a more comprehensive paper.[13]

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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[1-5] that the $T^{-1/4}$ dependence of the dc conductivity cannot be accounted for by Mott's variable-range hopping model.[6] 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[7,8] 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[2,6,9] 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,[2,9]

$$E_m = kT\xi_m, \tag{1}$$

where ξ_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