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Use of hydrogenation in the study of the transport properties of amorphous germanium*

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Amorphous germanium films were prepared by rf sputtering in the presence of hydrogen or deuterium gas, resulting in samples containing up to 8 at.% of these elements. Their dc conductivity and thermoelectric power were measured over a large temperature range (25–525 K). At low temperatures, increasing hydrogenation decreases the conductivity by five orders of magnitude while leaving its temperature dependence virtually unaltered. The thermoelectric power is negative (of order $-100\ \mu V/K$), has little temperature dependence, and only a weak dependence on hydrogen content. These results are interpreted with a model in which conduction takes place between nearest-neighbor sites of a narrow band. The model allows an estimate of 4 Å to be deduced for the localization length, an estimate which does not require assumed values for free parameters. The films were remeasured after annealing to 250°C. In the temperature range of about 280 to 500 K, the thermoelectric power is characterized by only one activation energy, typically 0.17 eV, whereas the conductivity displays two distinct activation energies, one for $T < 420$ K of about 0.35 eV, and one for $T > 420$ K of about 0.27 eV. It is suggested that this conduction occurs by small polaron hopping.

I. INTRODUCTION

The physical properties of amorphous germanium (a-Ge) and amorphous silicon (a-Si) may be divided into two categories: those that do not depend significantly on either thermal history or preparation conditions and those that do. A review of some properties in the former category has been given by Connell.[1] The latter category, which includes most properties attributed to states in the pseudogap, e.g., low-temperature dc transport, low-level optical absorption, and paramagnetic spin density, will be of concern in this paper. These properties appear to be correlated since changes in one are usually accompanied by changes in the others.[2–6]

Films of a-Ge and a-Si produced by evaporation or sputtering onto room-temperature substrates contain structural defects which have been established by small-angle scattering[7–10] to consist of regions of missing atoms, called voids.[11] In particular, for films of a-Ge prepared by sputtering onto room-temperature substrates at 2 Å/sec, the voids are estimated to be typically 7 Å in diameter and separated by about this same distance.[9] The existence of internal surfaces and of a thickness-independent paramagnetic spin density[12] can be interpreted to mean that there is a bulk distribution of electrons in states similar to those at surfaces.[7] However, Connell and Pawlik[13] have recently established that the paramagnetic resonance is due to only about 1% of these surface electrons. The rest are paired up. In any event, the observed correlation of the properties associated with states in the pseudogap leads to the suspicion that all of these properties can be attributed mainly to the electrons on void surfaces. Since these electrons are not involved in tetrahedral bonding, they should be susceptible to bonding with, for example, hydrogen. In a series of measurements on hydrogenated a-Ge, Lewis *et al.*[14] presented data on the optical-absorption coefficient, infrared index of refraction, paramagnetic spin density, dc conductivity, and thermoelectric power which firmly established that the states derived from the electrons on the void surfaces are primarily responsible for the pseudogap properties.

Previous attempts to remove the states in the pseudogap have usually consisted of raising the substrate temperature T_s during deposition or of heating samples grown at low T_s to an annealing temperature T_a just under the crystallization temperature of the material. This procedure probably minimizes them but has not been proven to reduce them to the extent that the properties which are sensitive to changes in T_a or T_s can be attributed solely to the properties of the fully coordinated, defect-free network. The philosophy of this paper is to pursue the hydrogen-bonding technique in the study of dc transport. Samples of a-Ge were grown by rf sputtering at a fixed T_s (~25 °C) in partial pressures of hydrogen or deuterium gas. All other growth conditions were kept as identical as possible. The effect of varying the amount of hydrogen incorporation is now isolated from other effects, most notably, the changes in network structure and void volume which occur with changes in[7] T_a or[9] T_s. This will turn out to be important for the modeling of the low-temperature transport data.

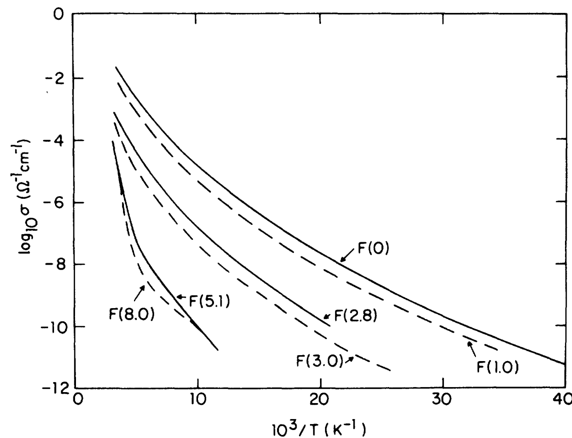

FIG. 1. Logarithm of the conductivity vs reciprocal temperature for a series of as-deposited hydrogenated a-Ge films.

In a companion paper, Connell and Pawlik[13] (CP) deduce the hydrogen content of these a-Ge samples from infrared-absorption measurements. They describe the changes that occur in the optical-absorption coefficient, infrared index of refraction, mass density, and paramagnetic spin density as a function of hydrogen incorporation. They also conclude that the total volume of voids on which the dangling bonds occur is not changed by hydrogen incorporation. In this paper, thermoelectric power (S) and conductivity (σ) data are presented for the same series of hydrogenated a-Ge films.

The low-temperature transport in these films takes place near the Fermi level but the data do not appear to be interpretable within the framework of the variable-range-hopping theories. In an earlier paper[15] this conclusion was reached after an analysis of the thermopower data of films of a-Ge and a-Si. In this paper, conductivity data will be given which support this conclusion.

Since hydrogen incorporation reduces the low-temperature conductivity by orders of magnitude, the high-temperature bandlike activated conductivity could be studied over a relatively large temperature range. A difference of 0.2 eV is found between the activation energy of the conductivity E_σ and the activation energy of the thermopower E_s. A similar difference has been seen in other amorphous materials and is interpreted as an activation energy for the mobility E_μ in one of two ways. E_μ is either the activation energy for hopping conduction between localized states in a band tail[16,17] or the activation energy for hopping conduction of excess carriers self-trapped by lattice relaxation, i.e., the activation energy for polaron hopping.[18] Of these two interpretations, the data presented in this paper favor the polaron interpretation for a-Ge.

Detailed descriptions of the sample preparation and measurement techniques have already been given.[13,15] The notation $F(N)$ where N (at.%) is the hydrogen incorporation estimated by CP, is used to identify the films.

II. RESULTS

The conductivity data for as-deposited films ($T_s \sim 25$ °C) of hydrogenated a-Ge are shown in Fig. 1. The deuterated sample is $F(3.0)$. For $T \lesssim 110$ K, σ decreases with increasing N in such a way that the slope, $d\ln\sigma/dT^{-1}$ is nearly constant at any temperature, but the value of the conductivity decreases by a total of about five orders of magnitude. Near room temperature, the conductivity in the two most hydrogenated films is activated with an energy $E_\sigma \sim 0.44$ eV. This activation correlates with the large change in S with N near room temperature (Fig. 2) as is expected when a bandlike conduction mechanism starts to dominate the conductivity.

The conductivity and thermopower of the deuterated sample $F(3.0)$ are clearly in line with the trends established by the films made with hydrogen. Thus, these measurements do not allow a distinction to be made between the electronic properties of films in which the surface electrons

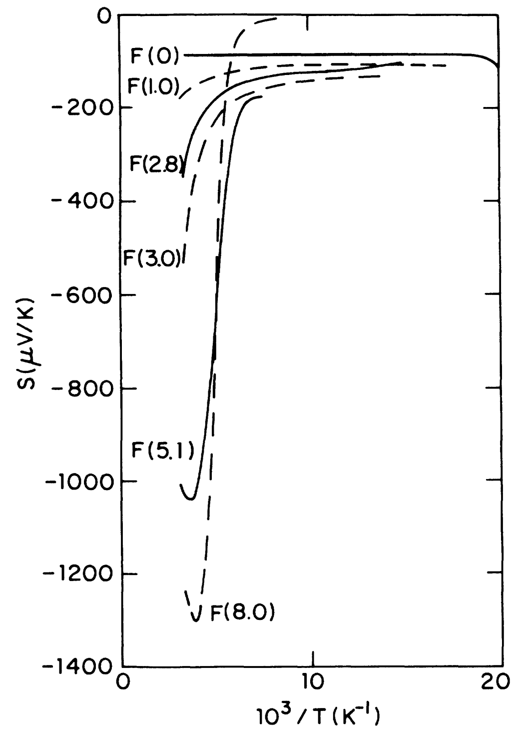

FIG. 2. Thermoelectric power vs reciprocal temperature for the same films and conditions as in Fig. 1.

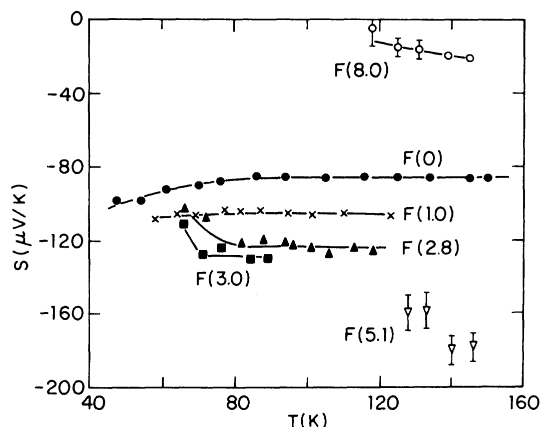

FIG. 3. Thermoelectric power vs temperature from the low-temperature range of Fig. 2 where S is nearly temperature independent.

have been bonded to hydrogen or to deuterium. This same conclusion is reached by CP for the electronic properties they measured. For purposes of this paper, no distinction between hydrogenated and deuterated samples need be made, and the deuterated sample will hereafter be referred to as hydrogenated sample $F(3.0)$.

It is interesting to note that the conductivity near 100 K has nearly the same value for the films $F(5.1)$ and $F(8.0)$. To understand this, it should be emphasized that the quoted values of N are made up of two contributions of Ge–H bonds,[13]

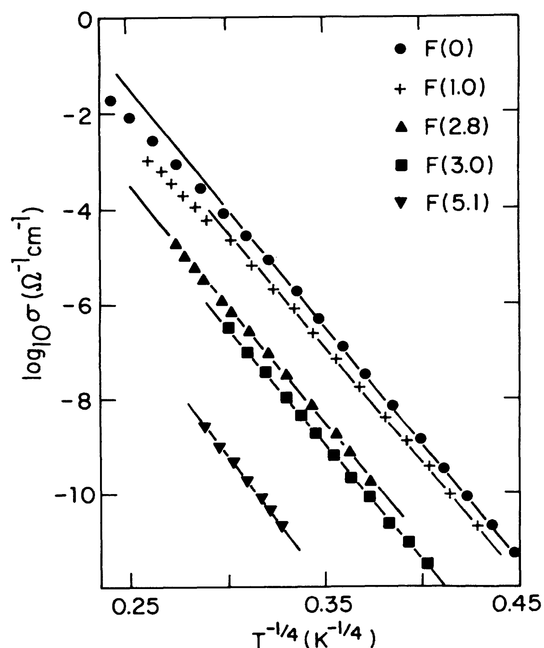

FIG. 4. Replot of the data of Fig. 1, vs $T^{-1/4}$, over the temperature range where the thermoelectric power is nearly constant.

TABLE I. Intercept and slope of the conductivity in the $T^{-1/4}$ regime for as-deposited hydrogenated a-Ge films.

Film	σ_0 (Ω^{-1} cm^{-1})	T_0 (K)
$F(0)$	1×10^{11}	1.8×10^{8}
$F(1.0)$	2×10^{10}	1.7×10^{8}
$F(2.8)$	1×10^{9}	1.8×10^{8}
$F(3.0)$	2×10^{8}	1.7×10^{8}
$F(5.1)$	2×10^{7}	2.6×10^{8}

N_s and N_b. N_s is a measure of the hydrogen bonded to electrons on the void surfaces and is limited to ~3.5 at.%, which is a measure of the total number of surface electrons. The other contribution N_b is for hydrogen incorporation into the bulk, i.e., into regions which would be fully coordinated in the absence of hydrogen. These contributions are distinguishable by the fact that their vibrational spectra occur at different energies. The important point for this work is that the measured values of N_s in the films $F(5.1)$ and $F(8.0)$ are little different because the internal void surfaces have been nearly saturated in both films. The extra 2.9 at.% of hydrogen has been bonded in the bulk. But it is unlikely that this conductivity is now a property of the fully coordinated, defect-free network since it is decreased in the film $F(5.1)$ by two orders of magnitude after annealing (Fig. 5), and because this film has[13] ~10^{18} spins/cm^3.

Returning to consideration of the thermopower, there is a temperature range where S is nearly constant (Fig. 3). S becomes more negative for increasing N except for the film $F(8.0)$ where S becomes small. At the lowest temperatures measured, the data for films with $N<4$ have a "tail," i.e., in the film $F(0)$, S becomes more negative as T is lowered, but for the film $F(3.0)$ it becomes more positive. Unfortunately, the resistances of samples $F(5.1)$ and $F(8.0)$ are so high that S cannot be measured for $T \lesssim 120$ K.

The overall σ, S data indicate that at least two mechanisms contribute to the dc transport. There is an activated bandlike mechanism which accounts for S becoming rapidly more negative with N near 300 K, and there is a low-temperature process for which S is either constant or has the tail. In the latter temperature regime, the plot of $\log\sigma$ vs $T^{-1/4}$ has a straight-line region, as shown by Fig. 4. Plotted in this way, the change in slope with N in the $T^{-1/4}$ regime is negligible for $N<4$ and only 50% for $N=5.1$, but the intercept at $T=\infty$ decreases by about four orders of magnitude (Table I). This combination is not expected if conduction is by variable range hopping. For

example, Mott[19] derived the relation

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}] \quad (1)$$

for conduction by variable range hopping at the Fermi energy in a constant density of states. Here,

$$T_0 = 18\alpha^3/kg(E_F)\,, \quad (2)$$

where k is the Boltzmann constant, $g(E_F)$ is the density of states at the Fermi energy, and α is the falloff rate of the localized state wave function which is assumed to be of the form $\psi \sim e^{-\alpha r}$ when $\alpha r \gg 1$. Estimates of the dependence of σ_0 on $g(E_F)$ have been made by Mott,[20] Pollak,[21] and Allen and Adkins[22] and summarized by Paul.[23] Writing $\sigma_0 \propto g(E_F)^p$, the various estimates fall within the range $|p| \leq 1$.

Now, CP present x-ray scattering data which show that any changes which may occur with N in the bond length and bond angle distribution of the bulk network are too small to be measured (e.g., measurable changes which occur with changes in[9] T_s or[7] T_a do not occur with changes in N). Hydrogenation does not appear to alter the atomic structure of the environment into which the localized wave function penetrates. Thus, under the assumption that a small amount of hydrogen incorporation does not significantly alter the charge distribution within a sphere of radius α^{-1} surrounding the remaining localized electrons, then α will be nearly constant and independent of N for small N. If so, then the four orders of magnitude decrease in σ_0 but near constancy of T_0 with N are obviously difficult to interpret with the variable-range-hopping theory. For example, T_0 can be compared in the films $F(0)$ and $F(5.1)$. The suggestion, according to Eq. (2), is that $g(E_F, N=5.1) = 0.7g(E_F, N=0)$. Then, in order to account for the change in σ_0, with $\sigma_0 \propto g(E_F)^p$, requires $p \sim 24$!

Problems of a similar nature have been raised before,[24,25] but in these other works the data did not extend below liquid nitrogen temperature, where the theory should be applicable with fewer assumptions. Also, these works report changes in the conductivity with annealing and so variation of α with anneal is a possibility, which has indeed been invoked in order to explain the results.[26]

Using Pollak's percolation theory, Overhof and Thomas[27] have shown that there are specific, nonconstant densities of states for which the plot of $\log\sigma$ vs $T^{-1/4}$ will be linear. They have also demonstrated parallel shifts over about eight orders of magnitude in such a plot by making appropriate choices of both the shape and magnitude of $g(E)$. Their calculation illustrates the principle that for arbitrary $g(E)$, T_0 is not directly related to $g(E_F)$. However, it seems at present unlikely that their model densities of states are realistic ones for a-Ge since they are symmetric about E_F and therefore do not explain a temperature independent thermopower of about $-100\ \mu V/K$. In addition, $g(E)$ would have to vary in the specified manner with both annealing and hydrogenation in order to explain the insensitivity of T_0 to both kinds of treatment. In the next section a model of fixed range hopping will be proposed.

A bandlike mechanism dominates the transport at $T > 250$ K in $N > 5$ films. In order to examine this mechanism over a large temperature range, measurements were carried out above room temperature. The as-deposited films were first annealed in the measurement apparatus for about 1 h at 250 °C, and subsequent measurements were done at lower temperatures. The data presented below for annealed films were usually taken while the sample was cooling down after heat treatment. However, some films were remeasured on reheating to just under 250 °C and the data were found to be within a few percent of the data taken on cooling. Also, two hydrogenated films were grown at $T_s \sim 250$ °C and measured for comparison. They are denoted $F'(1.0)$ and $F'(4.3)$, the prime to indicate the high T_s. The conductivity and thermopower for most of the films are displayed in Figs. 5 and 6.

The thermopower data show that activated, bandlike conduction sets in at temperatures as low as 160 K [film $F(5.1)$]. Roughly, the minimum in S occurs at lower temperatures as N increases, consistent with the trend for as-deposited films. It should be noted that the thermopower and conductivity of the film $F(8.0)$ are the least sensitive to annealing. Also, inspection of Figs. 5 and 6 show that it is only the film $F(8.0)$ which has prop-

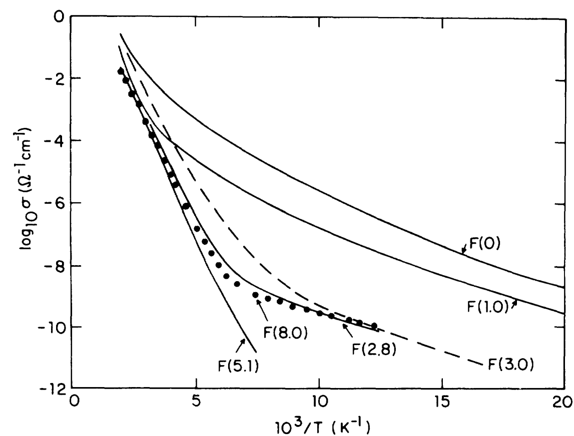

FIG. 5. Logarithm of the conductivity vs reciprocal temperature for annealed (250 °C, 1 h) hydrogenated a-Ge films.

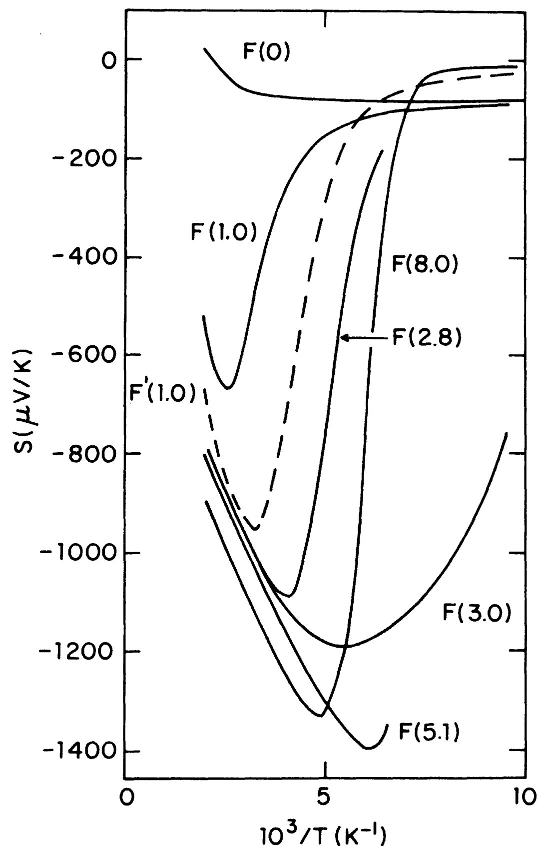

FIG. 6. Thermoelectric power vs reciprocal temperature for the same films and conditions as in Fig. 5. In addition, data are shown for a film [$F'(1.0)$] grown at $T_s \sim 250\,°C$.

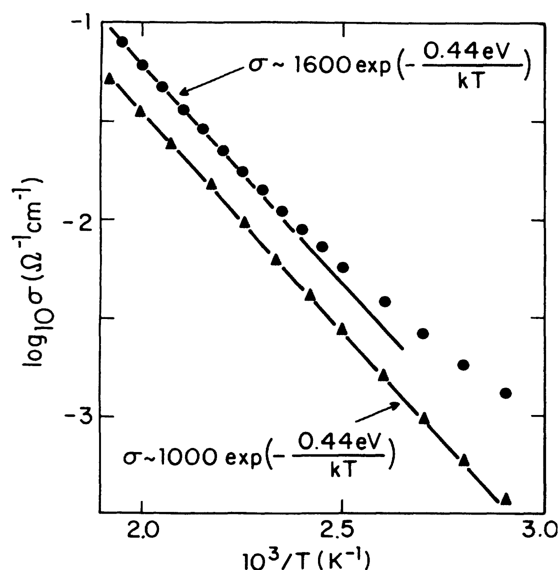

FIG. 7. Logarithm of the conductivity vs reciprocal temperature for the hydrogenated a-Ge films $F(1.0)$ (●) and $F'(1.0)$ (▲).

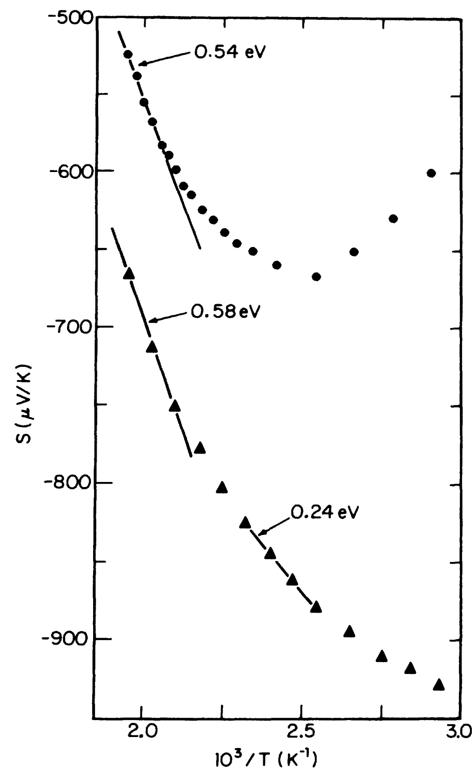

FIG. 8. Thermoelectric power vs reciprocal temperature for the same films and notation as in Fig. 7.

erties out of the sequence established by the other films, suggesting that the properties of this film should be judged with caution.

At the highest temperatures, the film $F(0)$ has a positive thermopower not characterized by $S \propto T^{-1}$. Presumably, there is still a large contribution of the low-temperature process to the conductivity. Nevertheless, it is still reasonable to infer that the positive sign of S means that the bandlike mechanism in the unhydrogenated film is dominated by holes, since this is found to be the case for a-Ge films prepared under conditions of good vacuum.[26,28,29] On the other hand, the negative thermopower for $N \neq 0$ films has the same sign as Beyer and Stuke's data taken on films prepared at slow evaporation rates in a moderate vacuum.[29] They speculated that oxygen incorporated during slow growth removes defect states from the pseudogap and causes E_F to move closer to the conduction band. The data presented here support their interpretation.

Figure 7 shows the details of the conductivity above room temperature for the two most lightly compensated films, $F(1.0)$ and $F'(1.0)$. The plot of $\log\sigma$ vs T^{-1} has a linear region at the highest temperatures with a slope $E_\sigma = 0.44$ eV. But the thermopower data (Fig. 8) do not display one acti-

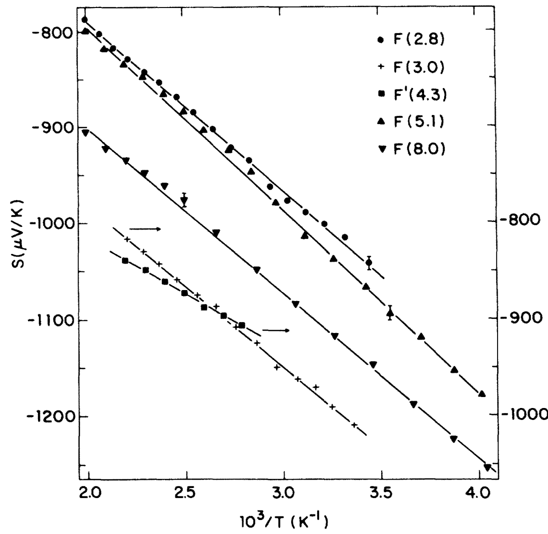

FIG. 9. Thermoelectric power vs reciprocal temperature for hydrogenated a-Ge films in the high-temperature range where the plot is linear. For clarity, the data for the films $F(3.0)$ and $F'(4.3)$ have been shifted vertically (right-hand scale). Typical error bars are shown on a few points.

vation energy. Rather, there is continuous curvature and S eventually displays an activation energy larger than E_σ. It is concluded that the activated conduction in $N=1$ films is bipolar, with the electron contribution dominating the hole contribution in the temperature range studied. In contrast, the thermopower data in more highly compensated films (Fig. 9) are linear in T^{-1} over a large temperature range, indicating unipolar conduction by electrons. The conductivity for these films, in the temperature range where $S \propto T^{-1}$, is shown in Fig. 10. One surprising feature of these data is the knee in the plot of $\log\sigma$ vs T^{-1}. It is observed in all samples for which S vs T^{-1} is linear and it occurs at one temperature, 420 K. A detailed plot in the high-temperature range of Fig. 10 is given in Fig. 11. The plot of $\log\sigma$ vs T^{-1} is again linear for $T \gtrsim 430$ K. The straight lines for $T \lesssim 420$ K are the same straight lines shown in Fig. 10, demonstrating that the change in slope occurs within an extremely small range of $10^3/T$. The linear dependence of S on T^{-1} over the whole of the temperature range suggests that the knee in the conductivity is caused by a decrease in the activation energy of the mobility. This will be discussed further in the interpretation section. For now, the emphasis is on characterizing the data.

In the film $F(5.1)$, the minimum in S occurs at 160 K. The σ and S data for $T > 160$ K can be decomposed into the sum of two bandlike mechanisms according to the usual formulas

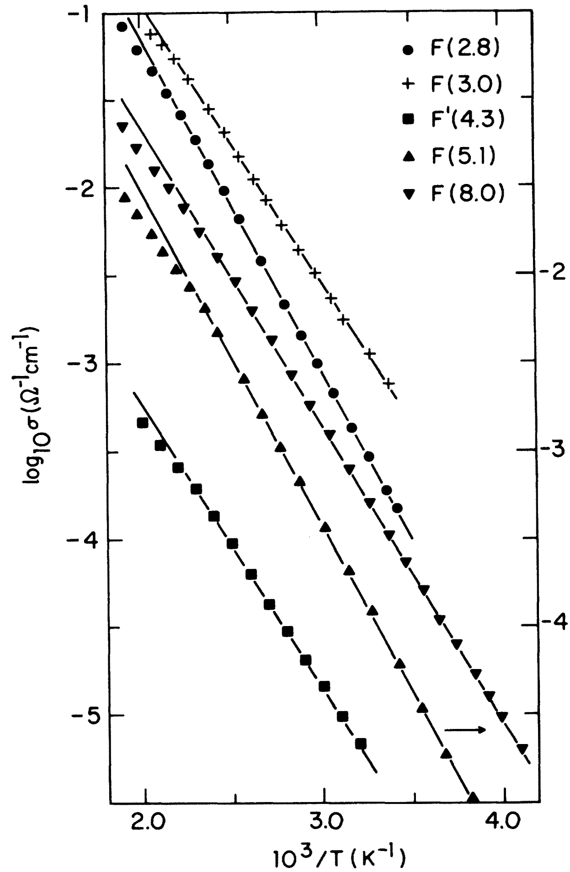

FIG. 10. Logarithm of the conductivity vs reciprocal temperature for the same films and temperature range as in Fig. 9. For clarity, the data for film $F'(4.3)$ have been shifted down by two orders of magnitude, and the data for the film $F(5.1)$ have been shifted by half an order of magnitude (right-hand scale).

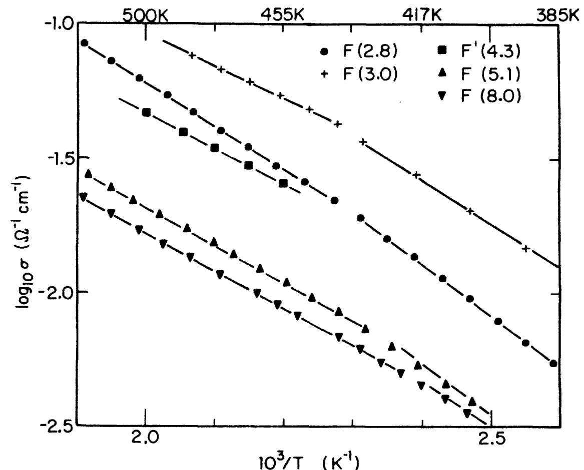

FIG. 11. Logarithm of the conductivity vs reciprocal temperature for the high-temperature range of Fig. 10. The straight lines at the lower temperatures ($T < 420$ K) are the same lines shown on Fig. 10.

TABLE II. Parameters of the transport data in the activated, high temperature regime for annealed hydrogenated a-Ge films. Two rows are given to the sample $F(5.1)$ since, below about 250 K, a mechanism with smaller activation energies is apparent.

Film	σ_0 (Ω^{-1} cm^{-1})	E_σ (eV)	E_s (eV)	A	$E_\sigma - E_s$ (eV)
$F(2.8)$	570	0.384	0.18	5.0	0.20
$F(3.0)$	180	0.318	0.16	5.3	0.16
$F'(4.3)$	133	0.330	0.12	6.7	0.21
$F(5.1)$	239	0.383	0.19	4.7	0.19
$F(5.1)$	0.43	0.29	0.08	9.6	0.21
$F(8.0)$	52	0.334	0.17	6.4	0.17

$$\sigma = \sigma_1 + \sigma_2 \tag{3}$$

and

$$S = (\sigma_1 S_1 + \sigma_2 S_2)/(\sigma_1 + \sigma_2) , \tag{4}$$

where σ_1, σ_2 have the form

$$\sigma = \sigma_0 \exp(-E_\sigma/kT) , \tag{5}$$

S_1, S_2 have the form

$$S = -(k/|e|)(E_s/kT + A) , \tag{6}$$

and where σ_0, E_σ, and A are temperature independent. Figure 12 shows the result of this fit for the parameters listed for the two rows given to the film $F(5.1)$ in Table II. Also given are the transport parameters for the other films which give the straight lines in Figs. 9 and 10. It must be emphasized that the conductivity parameters describe only the data for $T \lesssim 420$ K.

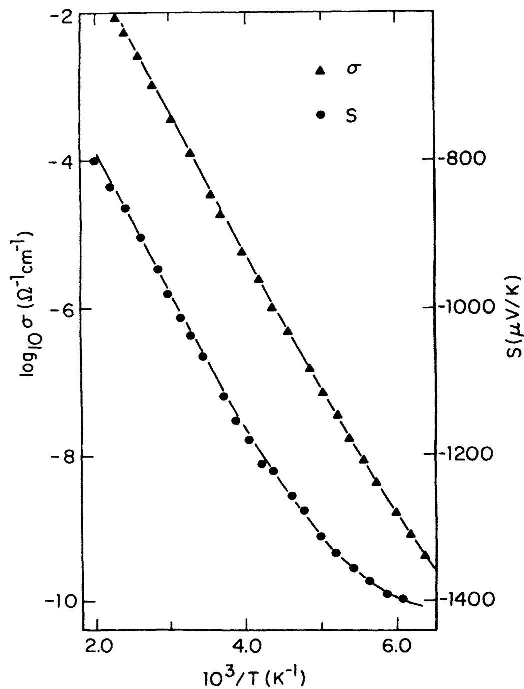

FIG. 12. Logarithm of the conductivity and thermoelectric power vs reciprocal temperature for the annealed hydrogenated a-Ge film $F(5.1)$. The solid lines are fits to Eqs. (3)–(6) of the text, using the parameters listed in Table II.

The σ_0 value for the film $F(8.0)$ is somewhat smaller than the σ_0 values of the other films, which can be characterized as within about a factor of two of 300 Ω^{-1} cm^{-1}. This amplifies the warning given earlier about this film.

The values in Table II are interesting for several reasons. First, the E_σ values for the films $F(5.1)$ and $F(8.0)$ have decreased after annealing, indicating that E_F has moved still closer to the conduction band. Second, the E_s values are considerably less than half the optical gap (~1 eV) measured on these films by CP. Third, the values of A are relatively large, but not unprecedented in the amorphous semiconductor literature.[18] Values of A in the range 5–7 could be consistent with hopping in a band tail of localized states[30] and with polaron hopping.[31] Finally, if $E_\sigma - E_s$ is taken to be the activation energy of the mobility, E_μ, then $E_\mu \sim 0.2$ eV for 420 K$< T <$160 K. These observations firmly establish that the charge carriers are electrons conducting above, but relatively close to, E_F with an activation energy of 0.2 eV for the mobility for $T < 420$ K. These transport data do not prove what mobility mechanism is operative, but, as discussed below, the weight of the evidence favors the small polaron interpretation over the model of hopping conduction in a band tail of localized states.

For completeness, the conductivity parameters for $T > 430$ K are given in Table III. E_μ is now of order 0.1 eV.

TABLE III. Conductivity parameters describing the data for T >430 K for the annealed hydrogenated a-Ge films.

Film	σ_0 (Ω^{-1} cm^{-1})	E_σ (eV)
$F(2.8)$	92	0.316
$F(3.0)$	18	0.228
$F'(4.3)$	14	0.246
$F(5.1)$	13	0.277
$F(8.0)$	10	0.277

III. DISCUSSION

A. Low-temperature regime

The low-temperature regime is defined to be the temperature range where S is nearly constant or has the low-temperature tail. In an earlier paper[15] it was shown that it is difficult to explain a temperature independent thermopower if conduction is by *variable range* hopping. In the previous section of this paper it was argued that the constancy of T_0 but large decrease in σ_0 with N also seem inconsistent with this model. Rather, the data suggest that σ_0 and T_0 do not depend on the same parameters. A density of states model in which this occurs was proposed earlier[15] on the basis that the thermopower in a-Ge and a-Si are consistent with conduction in a narrow band of width about 0.01 eV. The inference was drawn that the hopping conductivity for $T \gtrsim 70$ K should be dominated by hopping between spatially nearest localized states of the narrow band, and that the conducting electrons are unpaired electrons since a spin degeneracy factor of $\frac{1}{2}$ was suggested by the data. This model will now be applied to the low temperature transport data of the as-deposited hydrogenated a-Ge films.

The thermopower associated with conduction in a partially filled, thermally isolated band at $E=0$ and of width Δ was estimated in Ref. 15. Calling ρ the temperature independent fractional occupancy of the band, then, for $kT > \Delta$, the estimates are

$$E_F(T) = -kT\ln[(1-\rho)/\beta\rho] \tag{7}$$

and so

$$S = -(k/|e|)\ln[(1-\rho)/\beta\rho], \tag{8}$$

where β is the electron degeneracy factor. The kinetic energy term is ignored in writing Eq. (8) and, to this extent, the expression for S is independent of the details of the conduction mechanism.

The observation that the temperature independent part of the thermopower becomes more negative with increasing N (Fig. 3) is interpreted to mean that ρ is a decreasing function of N. Since ρ is the ratio of the number of electrons to the number of sites, the hydrogen must prefer to bond to the sites which are initially occupied with an electron. Since this electron is required in order to form the covalent bond, the decrease of ρ with increasing N is not unreasonable.

The low-temperature S data for the film $F(8.0)$ do not follow this trend established by the other films. This is actually to be expected if ρ is small enough, since, according to Eq. (7), $E_F/kT \to -\infty$ when $\rho \to 0$. The assumption that the narrow band is thermally isolated from the other states must break down and the transport properties will be increasingly influenced by states at other energies. Therefore, only data for films with $N<6$ will be analyzed below.

If $kT > \Delta$ and ρ is temperature independent, conduction proceeds by hopping between nearest-neighbor sites of the narrow band with a constant carrier concentration. The average hopping probability may be written

$$p = \rho(1-\rho)e^{-2\alpha R}f(T),$$

where R is the average hopping distance and $f(T)$ is dependent on the dynamics of the electron-phonon interaction. With the diffusion coefficient $D = \frac{1}{6}R^2 p$ and using Einstein's relation for the mobility $\mu = eD/kT$, the conductivity is given by

$$\sigma(T) = \nu R^2 \rho(1-\rho)e^{-2\alpha R}e^2 f(T)/6kT, \tag{9}$$

where ν is the carrier concentration. The rapid decrease in the magnitude of σ with N is attributed mainly to the $e^{-2\alpha R}$ term. Rewriting (9) as

$$\ln\left(\frac{6kT}{e^2 f(T)}\right) + \ln\left(\frac{\sigma(T)}{\nu R^2 \rho(1-\rho)}\right) = -2\alpha R \tag{10}$$

allows α to be estimated by plotting the left-hand side of Eq. (10) vs R. The result should be a straight line of slope -2α. Since the thermopower data suggest nearest site hopping between unpaired electron states,[15] ν is equated to the spin density measured in these films by CP. R, the intersite separation, is given by $(\rho/\nu)^{1/3}$ and ρ is deduced from the temperature independent part of S by using Eq. (8) with $\beta = \frac{1}{2}$ and the data of Fig. 3. For $\sigma(T)$, the measured values at $T = 100$ K are used. This temperature is high enough to satisfy $kT > \Delta$, but low enough that $\sigma(T)$ is not influenced by the bandlike mechanism. Also, the first term in Eq. (10) is assumed to be the same for all films with $N<6$ since the temperature dependence of $\sigma(T)$ is virtually independent of N. The values of ν, S, ρ, R, and $\sigma(100\text{ K})$ are listed in Table IV and plotted according to Eq. (10) in Fig. 13. The slope gives $\alpha^{-1} = 4$ Å, a reasonable value, and it agrees with the estimate 5 Å obtained by Bahl and Bluzer[32] from liquid helium temperature conductivity data on a-Ge.

If conduction occurs by fixed range hopping, there is no longer a theoretical basis for plotting $\log\sigma$ against $T^{-1/4}$. In fact, the data for the films $F(0)$, $F(1.0)$ and $F(2.8)$ are best represented by $\log\sigma \propto T^{-3/8}$, as shown in Fig. 14. (The data for the other two films, being more limited, could be fit to $T^{-1/4}$ or $T^{-3/8}$ about equally well.) This implies that $\log[f(T)/T]$ can be approximated by $T^{-3/8}$, but the exact form of $f(T)$ is probably a complicated expression resulting from a collection of hopping rates, as discussed in Ref. 15.

In summary, the interpretation of the low-tem-

TABLE IV. Listing of the spin density and transport properties of as-deposited, hydrogenated a-Ge samples.

Film	ν (cm^{-3})	S (μV/K)	ρ	R (Å)	σ (100 K) (Ω^{-1} cm^{-1})	$\ln\left(\frac{\sigma\ (100\ K)}{\nu R^2\rho(1-\rho)}\right)$
F(0)	1.64×10^{19}	−86	0.42	29.5	1.39×10^{-5}	−60.78
F(1.0)	1.23×10^{19}	−105	0.37	31.1	4.54×10^{-6}	−61.68
F(2.8)	5.83×10^{18}	−122	0.33	38.2	1.42×10^{-7}	−64.75
F(3.0)	5.00×10^{18}	−127	0.31	39.7	4.93×10^{-8}	−65.71
F(5.1)	1.80×10^{18}	−170	0.22	49.5	7.68×10^{-11}	−71.36

perature conductivity and thermopower data is consistent with hopping conduction between spatially nearest localized states of a narrow band of width of the order of 0.01 eV. The thermopower is consistent with this model since it displays a temperature independent regime and a tail at lower temperatures. (An explanation for the reversal of the tail seen when N increases from 0 to 3 has already been given.[15]) The interpretation of the N dependence of the conductivity is consistent with nearest-neighbor hopping between sites which, when occupied, contain only one electron. The model uses the spin density as the carrier density ($kT>\Delta$), allows the physical value $\alpha^{-1}=4$ Å to be obtained, and easily explains the insensitivity of T_0 to hydrogenation. Although the narrow-band model may give new insight into the conduction mechanism, it is not a model for the electron-phonon interaction. Thus, the universal temperature dependence $\log\sigma \propto T^{-3/8}$, shown in Fig. 14, is an empirical, unexplained feature of the data.

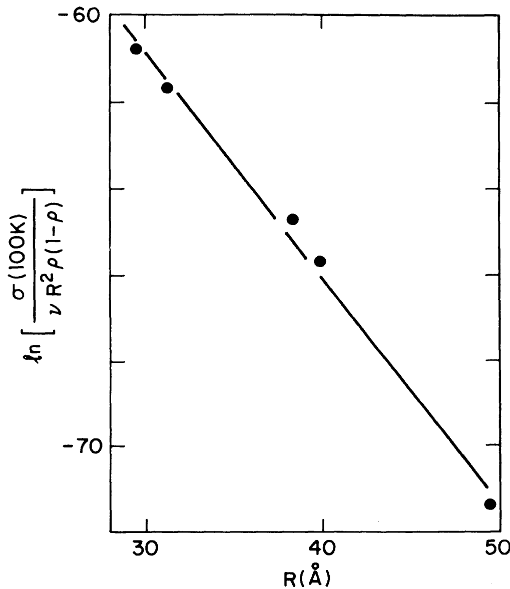

FIG. 13. Plot of the left-hand side of Eq. (10) against the intersite distance, as explained in the text, using the data listed in Table IV.

B. High-temperature regime

In the high-temperature regime, defined for each sample by the temperature range of Fig. 9, the conductivity should be given by the unipolar expression

$$\sigma(T)=\sigma_0\exp[-(E_s+E_\mu)/kT]. \qquad (11)$$

The problem is to determine how Eq. (11) can be reconciled with the data, including the knee near 420 K. Evidently, there are three quantities which may be temperature dependent, σ_0, E_s, and E_μ.

Attempts to fit all of the $\sigma(T)$ on Fig. 10 to the form of Eq. (11) with $\sigma_0 \propto T^{-x}$ and E_s, E_μ remaining constant were unsatisfactory since the data do not display the continuous curvature such a fit would require. Thus, the calculated conductivity for the best value of x, in the range 3–5, is always too small for 390 K<T<460 K, and too large otherwise.

The possibility that E_s may suddenly decrease by the necessary amount near 420 K can be ruled

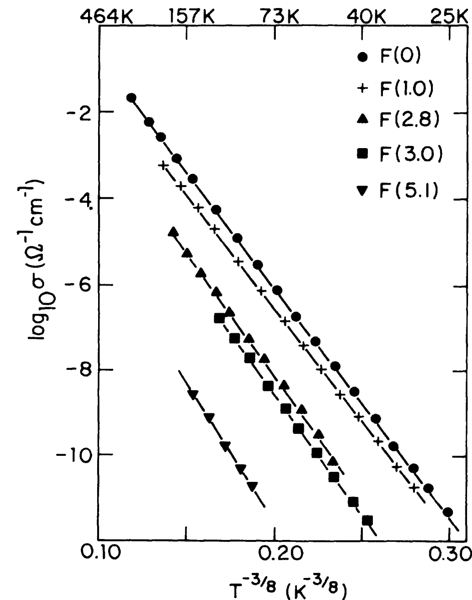

FIG. 14. Data of Fig. 4 replotted as the logarithm of the conductivity vs $T^{-3/8}$.

out since this would put a step shaped feature in the plot of S vs T^{-1} of order 150 μV/K, inconsistent with the data of Fig. 9.

If the conductivity and thermopower data are to be reconciled with Eq. (11), changes in the E_μ term must be allowed. Since a decrease in the prefactor is also required, the data suggest that if the mobility is written

$$\mu(T) = \mu_0 \exp(-E_\mu/kT) \quad \text{for } T<420 \text{ K},$$

then

$$\mu(T) \cong \tfrac{1}{10}\mu_0 \exp[-(E_\mu - 0.08 \text{ eV})/kT] \quad \text{for } T>430 \text{ K}.$$

If there are no reversible structural modifications in the Ge network near 420 K, a sudden decrease in the activation energy of the mobility is difficult to interpret. Nevertheless, the two available models for conduction by hopping can be compared to experiments to ascertain if one of them can be favored.

In models for conduction by hopping in a band tail of localized states, hopping occurs between sites whose energy difference is independent of temperature. This energy difference determines E_μ, and it is either temperature independent, as in the Cutler-Mott model developed by Weiser, Grant, and Moustakas,[16] or it increases with temperature, as in the variable-range-hopping model used by Grant and Davis.[33] Thus the transport data suggest it is unlikely that conduction occurs by hopping in a band tail of localized states.

A correlation which may be significant is that the knee occurs at nearly the temperature equivalent of the optical-phonon energy. These phonons, detected in infrared absorption and Raman scattering experiments[13,34] at about 0.035 eV, giving $T=\hbar\omega/k = 408$ K, are of dominant importance in the small polaron model of hopping conduction. But the prediction of this theory[35] is that

$$\mu(T) \propto T^{-3/2} \exp(-E_p/2kT),$$

where E_p is the small polaron binding energy. Although the prefactor term leads to a gradual decrease in slope in the plot of $\ln\mu$ vs T^{-1}, there is not yet an optical-phonon mechanism to account for a sudden decrease.

The model used to interpret the low-temperature transport data favors the small polaron interpretation since the existence of a band of width 0.01 eV would be inconsistent with a disorder energy of several tenths of an eV. In addition, the width of the $3d$ core level spectrum, determined by photoemission measurements,[36] is 0.45 ± 0.05 eV in both amorphous and crystalline Ge. Thus, there is no evidence that the disorder energy is larger than about 0.1 eV, another argument against there being a band tail of localized states of width 0.2 eV or greater.

To sum up, the model of conduction by small polaron hopping is favored over the model of hopping in a band tail of localized states, but as presently constituted,[35] does not explain the knee in the conductivity.

IV. CONCLUSIONS

The low-temperature conductivity and thermoelectric power measurements on hydrogenated a-Ge films are difficult to interpret within the framework of variable-range-hopping theory. Rather, the thermopower suggests that conduction takes place in a band of unpaired electrons of width 0.01 eV. Thus, the conductivity data at $T>70$ K are interpreted by assuming hopping conduction between sites which, when occupied, contain one electron. When the carrier density is equated to the spin density, the estimate for the localization length of the electron of 4 Å is deduced from the model. This model suggests that the disorder energy is small, of order or less than 0.01 eV.

In the temperature range where transport takes place a few tenths of an eV away from the Fermi level, the results, on balance, favor the small polaron model of conduction over the model of hopping in a band tail of localized states. Even if the disorder energy is as large as 0.1 eV, the maximum which can be consistent with photoemission results, small polaron hopping must still be preferred since the measured activation energy for the mobility is 0.2 eV.

The interpretations proposed here, the narrow band of states near E_F and small polaron hopping away from E_F, are self-consistent in that the disorder energy is necessarily small and a large electron-phonon interaction is therefore required.

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