Conductivity and thermoelectric power of amorphous germanium and amorphous silicon*

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A series of amorphous germanium (a-Ge) and amorphous silicon (a-Si) films was prepared by rf sputtering. For the a-Ge samples the temperature dependence of the conductivity measured down to 25 K is in general agreement with the earlier results of Knotek and Hauser. The thermoelectric power measured down to 40 K is negative ($\sim -80\ \mu V/K$) and virtually temperature independent for 70K $< T <$ 300 K. For $T <$ 70 K, it becomes rapidly more negative with decreasing temperature. The temperature dependence of the conductivity in the a-Si samples is similar to that found in a-Ge but the thermopower, which is negative and changes by little from 200 to 300 K, becomes more positive as the temperature is decreased. An attempt is made to interpret these data using the variable-range hopping theory and three simple density-of-states models. The attempt is unsuccessful. However, the Ansatz that conduction occurs in a narrow band (width ~ 0.01 eV) does explain the features of the thermopower data and suggests that for these samples conduction at $T >$ 70 K is by hopping between nearest-neighbor sites.

I. INTRODUCTION

Films of amorphous germanium (a-Ge) and amorphous silicon (a-Si) prepared by evaporation or sputtering onto room-temperature substrates generally exhibit a conductivity below room temperature that cannot be attributed to a single activation energy,[1-3] lack the sharp optical-absorption edge of the corresponding crystal,[1,2] contain a bulk distribution of voids,[4] and have an electron-spin-resonance signal.[5,6] It has been demonstrated[7] that the electrons on the void surfaces are responsible, at least in large part, for these electronic properties. By bonding these electrons to hydrogen atoms, Connell and Pawlik[8] determined that the spin resonance signal is given by only 1% of the total number of surface electrons. The vast majority of them have paired up because it is energetically favorable, presumably because of lattice distortion, for them to do so. These data show that there are two kinds of surface electron states, one with paired electrons and one which is singly occupied, but leave open the question as to which state requires the smaller energy for promotion of one electron to a higher-energy state. The unpaired-dangling-bond state is the parental state of all subsequent surface electron states, and so it is conceivable that the singly occupied state lies the higher in energy (perhaps because, for it, the energy lowering distortions are not strong enough to overcome the effects of the correlation energy associated with the pairing). If so, then the unpaired electrons will control the properties of the material associated with the states at the Fermi level, such as the low-temperature dc transport. It will be shown below that this speculation is supported by a detailed analysis of the thermopower data.

Theories for the low-temperature conductivity in a-Ge and a-Si have been inspired by Mott's idea of variable-range hopping between localized states.[9] It is assumed that disorder induces a spatial fluctuation in the electron potential (the disorder energy). The disorder energy and hence the bandwidth are assumed to be larger than kT. Mott argues that at low-temperature conduction by hopping to a nearest neighbor is less favorable than longer-range hopping. By maximizing the hopping probability, he derived the relation

$$\ln\sigma = A - (T_0/T)^{1/4}, \tag{1}$$

which has since been rederived in several ways.[10-12] The measured temperature dependence of the dc conductivity in a-Ge is consistent with Eq. (1) from 25 to 120 K over a range in σ of ~ 7 orders of magnitude.[13,14] On the other hand, there are few experimental data of other transport properties in the range $T <$ 120 K with which the theory can be checked. In this paper, measurements of the dc conductivity and thermoelectric power of a-Ge and a-Si will be presented. These measurements extend into the temperature regime below liquid-nitrogen temperature.

The temperature dependence of the conductivity below room temperature is similar to that measured by Hauser[13] and Knotek.[14] The thermopower data, however, are difficult to interpret within the framework of variable-range hopping theory, but can be straightforwardly interpreted if conduction occurs in a narrow band of order 0.01 eV in width. If this interpretation is correct, kT becomes greater than the bandwidth at a lower temperature than has been generally realized. The use of variable-range hopping theory to explain the conductivity data of a-Ge and a-Si at and above liquid-nitrogen temperature would therefore have to be questioned.

II. EXPERIMENTAL PROCEDURES

The samples used in this study were prepared by rf sputtering in 5 mTorr of (99.9995%-pure) argon after first dry pumping the system to a base pressure of 4×10^{-7} Torr. The 5-in.-diam targets were "optical grade" polycrystalline Si and Ge obtained from Exotic Materials, Inc. The substrates (Corning 7059 float glass) were ultrasonically cleaned and subsequently plasma etched at 500 V and 50 W *in situ* for 5 min just prior to deposition. Stainless-steel masks, placed on the substrates, defined the rectangular sample geometry. The target was supplied with 250 W of rf power at about 2 kV. Material was deposited onto substrates, nominally at room temperature, at rates of ~1.5 Å/sec (a-Si) and ~3 Å/sec (a-Ge). Film thicknesses are 11–31 μm. These films are amorphous, as determined by x-ray diffraction.[15]

Two films, prepared under slightly different conditions, were also studied. An a-Si film (Si *S*2) was deposited in the presence of an air leak of 2×10^{-6} Torr and an a-Ge film (Ge *S*48) was prepared at half the deposition rate of the others but at the standard base pressure of 4×10^{-7} Torr.

After deposition of the amorphous layer, nichrome electrodes, ~1000 Å thick, were evaporated onto the samples in a separate system. The samples were then mounted in a cryostat where they were allowed to relax, actually in a vacuum and in the dark, for at least 24 h before measurements were made. The samples were annealed in the measurement cryostat (vacuum ~ 1×10^{-5} Torr at 250 °C) except for one sample (Ge *S*43) which was annealed at 325 °C for 6 h at 1×10^{-5} Torr in a separate system. Since x-ray diffraction measurements[15] showed that this film was still amorphous, it was assumed that the other annealed films were also amorphous.

The configuration for the four-probe conductivity measurements is shown in Fig. 1. The sample was cemented[16] to a copper block. Care was

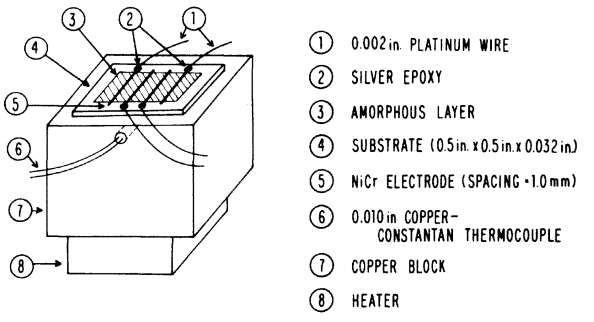

FIG. 1. Scheme of the conductivity specimen. A copper radiation shield (not shown) covers the sample.

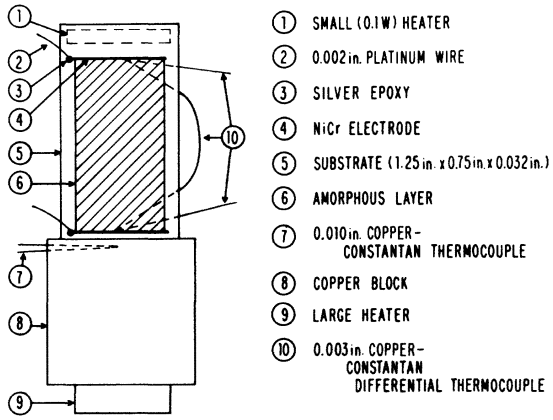

FIG. 2. Diagram of the thermopower arrangement. A copper radiation shield (not shown) surrounds the sample.

taken to minimize heat flow through the sample by heat sinking the thermocouple to the block, by supporting the block only near the heater, and by covering the sample with a copper radiation shield. In order to assess the accuracy of the temperature measurements, the copper-constantan thermocouple was measured several times against a calibrated platinum resistance thermometer over the temperature range of measurements (25–525 K). The thermocouple voltage deviated from the published values[17] only at the lowest temperatures. As an additional test, a differential thermocouple (0.003-in. diameter, 6-in. connecting leg) was placed between the thermocouple junction and the top of a cemented down substrate (with electrical leads attached), and the temperature difference between the top of the substrate and thermocouple was measured several times in the range 25–525 K. This temperature difference was <1 K for $25<T<460$ K and reached only 1.8 K at $T=525$ K. As a consequence of applying both corrections to the raw-thermocouple reading, the determination of the sample temperature is in error by at most ±0.5 K.

Conductivity measurements were carried out using four-probe techniques. A 1.35-V mercury battery and Keithley 602 electrometer used as an ammeter were floated above ground on Teflon standoffs within a shielded enclosure. Voltages were measured with a Cary 401 vibrating-reed electrometer. Leakage resistances were large enough that sample resistances of ~10^{12} Ω could be measured for a field strength of only 5 V/cm.

Guarded triaxial cable was used in the thermopower setup, allowing measurements at a sample resistance of 10^{12} Ω using the vibrating-reed electrometer (measured input resistance $>10^{16}$ Ω). The sample arrangement for these measurements is shown in Fig. 2. A small heater and differen-

tial thermocouple were cemented[16] to the uncoated side of the glass. The substrate was cemented[16] into a slot in the copper block whose temperature was controlled by a larger heater. Care was taken in making these bonds to ensure that the isotherms were parallel to the electrodes.

The thermopower of the platinum lead wires was measured relative to thermocouple-grade copper wire. The thermovoltages of the platinum-copper thermocouple agreed with handbook values. The raw thermoelectric power of the platinum-a-semiconductor couple was corrected for the thermopower of platinum using Huebener's[18] data. The values reported in this work for a-Ge and a-Si are thus absolute.

After establishing a temperature in the copper block with the small heater turned off, the temperature gradient along the sample was less than 1 K at temperatures below 400 K. When the temperature gradient was actually zero, the sample voltage was less than 200 μV with respect to a short circuit at the electrometer input. The sample voltages were measured by connecting a digital voltmeter of $\pm 0.1\%$ accuracy to the output voltage (linearity of $\pm 0.1\%$) of the electrometer. After applying power to the small heater, the thermopower of the sample was calculated from

$$S = -\Delta V/\Delta T + S_{Pt},$$

where ΔV and ΔT are the differences in voltage and temperature with the small heater off and on. By convention, S is negative when the hot end develops a positive voltage. Typically, $\Delta T \sim 5$–10 K over the 2-cm length of the sample. The reading of the thermocouple (item 7 in Fig. 2), which measures the (constant) temperature of the cold end, is appropriately adjusted to give the average temperature for the measurement. This average temperature is estimated to be accurate to less than 1 K over the range investigated (40–525 K).

The random error in the thermopower data is typically less than 1% except when $R > 10^{10}$ Ω ($\sigma < 10^{-7}$ Ω^{-1} cm^{-1}) or $|S| < 100$ μV/K where the error may be somewhat larger. As a result of remounting the same sample several times and measuring S at one temperature, a systematic error of 5% is estimated. It is attributed to slight misalignments of the differential thermocouple with respect to the electrode-sample junction.

Finally, it should be noted that even though the conductivity and thermopower samples were co-deposited during one preparatory run, two-probe conductivity measurements were performed on the thermopower samples as a check and were consistent with the four-probe measurements on the conductivity samples, the comparison being limited to $R < 10^{10}$ Ω. This was also found to be true for annealed samples.

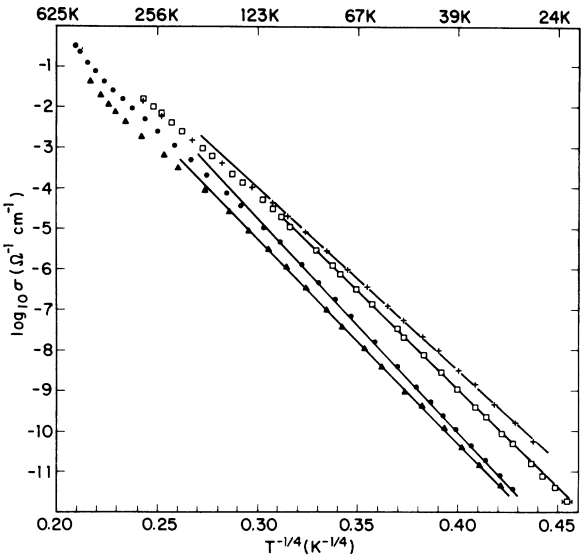

FIG. 3. Logarithm of the conductivity plotted against $T^{-1/4}$ for the as-deposited a-Ge films Ge $S48$(+) and Ge $S65$(□) and for the annealed a-Ge films Ge $S70$ (250 °C, 1 h) (●) and Ge $S43$ (325 °C, 6 h) (▲). The error in $T^{-1/4}$, corresponding to an error in T of ± 0.5 K, is shown on the lowest temperature data point. For $T^{-1/4} < 0.40$ the data points are large enough to include this error.

III. RESULTS

Typical conductivity data for a-Ge are shown plotted against $T^{-1/4}$ in Fig. 3. Results for as-deposited films prepared under the standard conditions, represented by the open squares, are within 10% of each other. For the more slowly deposited film (Ge $S48$), the slope at low temperature is ~30% smaller than for standard films. Thus the more slowly deposited film is only quantitatively, not qualitatively, different.

In detail, the plot of $\log\sigma$ against $T^{-1/4}$ shows three features. At the lowest temperatures there is a regime, extending up to 110 K, where Mott's law [Eq. (1)], gives a good description of the data. In as-deposited films, the data give $T_0 \sim 1.5\times10^8$ K while in annealed films the value of T_0 has increased to $\sim 2.0\times10^8$ K. For $110 < T < 300$ K, the conductivity does not increase as rapidly as it does at lower temperatures. This over-all temperature dependence for $T < 300$ K is similar to that found for a-Ge by Knotek[14] and Hauser[13] for evaporated and sputtered films, respectively. Finally, above room temperature, the conductivity begins to rise rapidly, as though another conduction mechanism is setting in.

The conductivity of a-Si is quite similar, as shown in Fig. 4. Again there is a $T^{-1/4}$ regime at low temperature ($T < 140$ K) with $T_0 \sim 1.4\times10^8$ K in as-deposited films, which increases to $\sim 2.1 \times 10^8$ K in annealed films. Above room tempera-

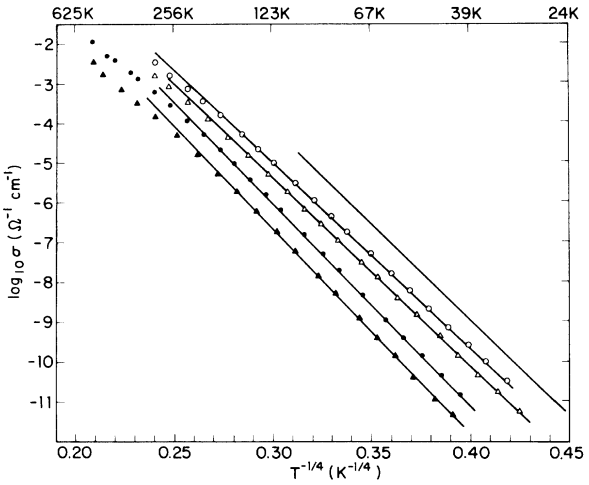

FIG. 4. Logarithm of the conductivity plotted against $T^{-1/4}$ for the as-deposited a-Si films Si $S2$(△) and Si $S3$(○) and for the annealed a-Si films Si $S2$ (250 °C, 1 h) (▲) and Si $S3$ (250 °C, 1 h) (●). The solid line represents the $T^{-1/4}$ regime for an as-deposited a-Ge film.

ture, however, the conductivity does not rise rapidly, suggesting that the low-temperature mechanism is dominant to higher temperatures than in similarly annealed a-Ge films. Note that the oxygenated film[8] (Si $S2$) has a smaller conductivity, as expected on the basis of hydrogenation studies[7] and oxygen-incorporation studies[19] on a-Ge. At the low level of incorporation used in this work, the oxygenation did not change the temperature dependence of σ.

The similar temperature dependences of the

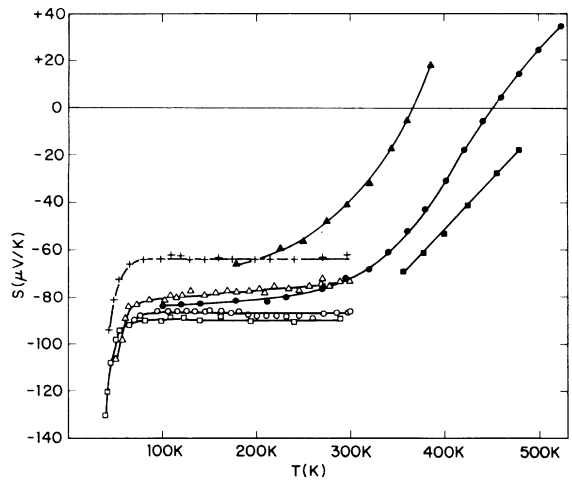

FIG. 5. Thermoelectric power vs temperature for the as-deposited a-Ge films Ge $S43$ (△), Ge $S48$ (+), Ge $S65$ (□), and Ge $S70$ (○) and for the annealed a-Ge films Ge $S43$ (325 °C, 6 h) (▲), Ge $S65$ (200 °C, $2\frac{1}{2}$ h) (■), and Ge $S70$ (250 °C, 1 h) (●). For $T > 75$ K, the random error in each data point does not exceed ± 2 μV/K.

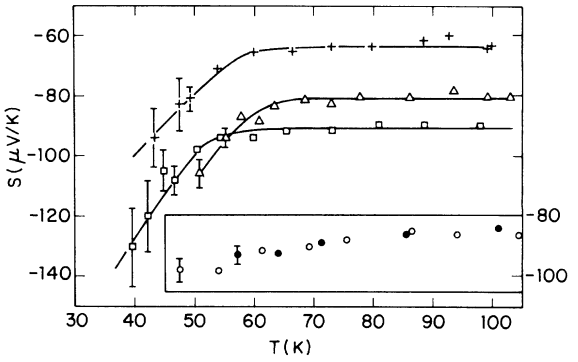

FIG. 6. Thermoelectric power vs temperature in the low-temperature regime for the as-deposited a-Ge films Ge $S43$ (△), Ge $S48$ (+), and Ge $S65$ (□). The insert shows the data for the film Ge $S70$ in the as-deposited condition (○) and after annealing at 250 °C for 1 h (●), using the same temperature scale as for the other films but a shifted vertical scale. Error bars are shown if the random error in the measurement exceeds ± 2 μV/K.

conductivity in a-Ge and a-Si contrasts with the different temperature dependences of the thermopower data, shown in Figs. 5–7. The thermopower at the lowest temperatures becomes more negative in a-Ge but more positive in a-Si. The opposite is true, however, at the highest temperatures. Between these two temperature extremes, S in a-Ge is virtually temperature independent, at least in as-deposited films. A nearly constant thermopower in a-Ge has been reported by other workers, but none of the measurements extended below about 120 K.[19–22] On the other hand, S has some temperature dependence in as-deposited a-Si, but it does show a tendency to level off.

Despite these differences, there are some similarities which are significant. It is clear, for example, that there is no correlation between the

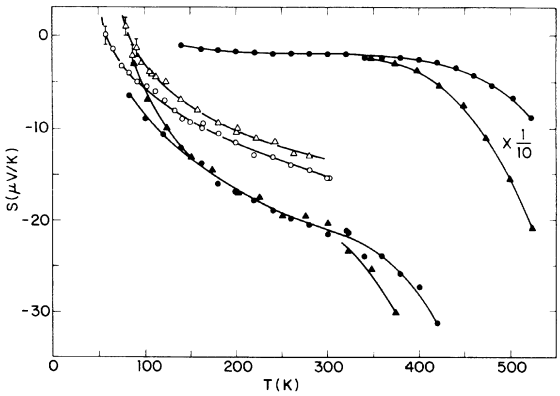

FIG. 7. Thermoelectric power vs temperature for a-Si for the same films and notation as in Fig. 4. Error bars are shown if the random error in S exceeds ± ½ μV/K.

temperature dependence of the thermopower data and the temperature at which the conductivity deviates from the $T^{-1/4}$ behavior. This will be taken up in the discussion. There is also the important observation that the data are not described by the metallic formula[23]

$$S = -\frac{\pi^2 k^2 T}{3|e|} \left.\frac{\partial \ln\sigma(E)}{\partial E}\right|_{E_F}, \tag{2}$$

which predicts $S \propto T$, or by the formula for unipolar conduction at a band edge[23]

$$S = \pm(k/|e|)[(E - E_F)/kT + A], \tag{3}$$

which predicts $S \propto T^{-1}$. Finally, it should be noted that, in contrast with the conductivity, annealing at 250 °C for 1 h has no effect on the thermopower of a-Ge at the lowest temperatures (Fig. 6, insert). A similar trend can be noted in the a-Si data of Fig. 7, in that the difference in S before and after annealing gets smaller as T gets smaller.

It is clear from the presentation of the results that some questions are raised. Given the similar temperature dependences of the conductivity in a-Ge and a-Si, is there a model which can explain qualitatively and quantitatively the different temperature dependences of the thermopower? Can the model be used to give a quantitative explanation for the temperature dependence of the conductivity? In the discussion that follows, a new model for the density of states near the Fermi level will be proposed. Using this model, it will be shown that the first question can be answered affirmatively but that the second involves considerably greater difficulty.

IV. INTERPRETATION OF RESULTS

The data for a-Ge show that the rapid increase in σ at the highest temperatures is correlated with a rapid increase in S above room temperature. This increase in both σ and S has been interpreted in many places[19,21,22,24] as being due to the onset of a bandlike conduction mechanism. The present thermopower data can therefore provide an experimental criterion for the temperature T_c below which bandlike conduction can be ignored. Assuming that there is a high-temperature activated process acting in parallel with the low-temperature process in both a-Ge and a-Si, the measured thermopower can be written

$$S = (\sigma_L S_L + \sigma_H S_H)/(\sigma_L + \sigma_H), \tag{4}$$

where L and H designate low and high temperature, respectively. In a-Ge and a-Si, the high-temperature process is activated by several tenths of an eV, and one finds $S_H \sim 1$ mV/K near room temperature.[19] Using this value in Eq. (4) together with the requirement that $\sigma_H \leq 0.02\sigma_L$ gives $|S - S_L| \leq 20\ \mu$V/K. This last inequality is used to define

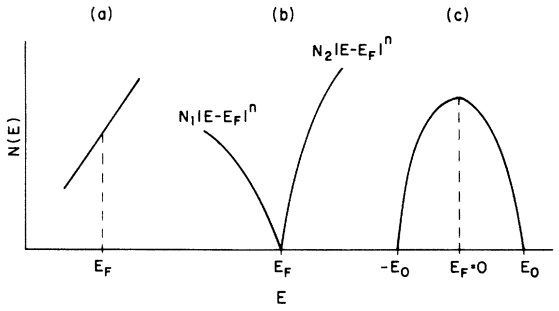

FIG. 8. Sketch of three density-of-states models vs energy for which some transport properties can be predicted as discussed in the text.

T_c and only data below T_c will be considered in the remainder of this paper. This criterion gives $T = 300$ K for all as-deposited films as well as annealed Ge $S65$ and Ge $S70$. For the other annealed samples, the values 250 (Ge $S43$), 350 (Si $S2$), and 400 K (Si $S3$) are deduced.

In this low-temperature region, the variable range hopping theory has been used to describe the detailed temperature dependence of the conductivity in both [25]a-Ge and [26]a-Si. Thermopower data, however, have not been generally available below about 120 K. As a result, the thermopower has received less theoretical consideration and only recently has the percolation treatment of variable range hopping been applied in detail to experimental results.[26] Since the thermopower data in this work extend down to 40 K, the theory can be subjected to a stiffer test. It will be argued below that the data are not interpretable with the simple density of states models sketched in Fig. 8 for which some semiquantitative predictions can be made.

An approximate expression for the thermopower when conduction is by variable range hopping about the Fermi level was obtained by Zvyagin.[27] Calling W the most likely hopping energy and $N(E)$ the density of states, he derived

$$S \approx -\frac{k}{|e|}\int_{-W}^{W} \frac{E}{kT} N(E)\,dE \Big/ \int_{-W}^{W} N(E)\,dE\,. \tag{5}$$

In writing Eq. (5), the zero of energy is E_F and $N(E)$ is assumed nonzero in the interval $-W \rightarrow W$.

For a linear density of states, Eq. (5) gives

$$S = -\frac{k}{3|e|} \frac{W^2}{kT} \left.\frac{\partial \ln N(E)}{\partial E}\right|_{E_F}. \tag{6}$$

In the $T^{-1/4}$ hopping regime, we have

$$W \sim g(T_0/T)^{1/4} kT, \tag{7}$$

where g is a constant.[11] Using Eq. (7) in (6) gives

$$S = -\frac{k^2}{3|e|} g^2 (T_0 T)^{1/2} \left.\frac{\partial \ln N(E)}{\partial E}\right|_{E_F}. \tag{8}$$

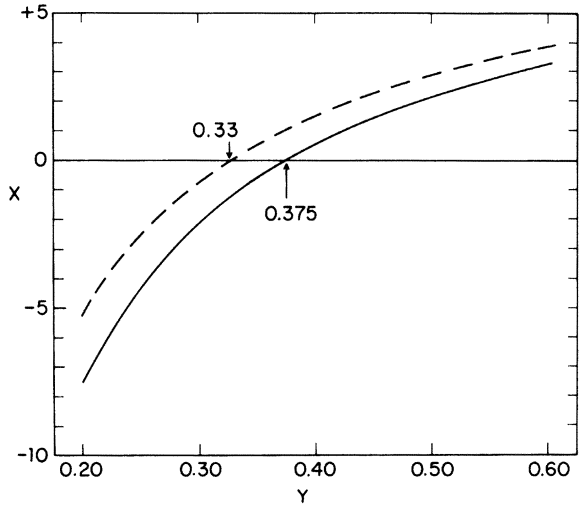

FIG. 9. Plot of x against Y obtained by fitting the conductivity data shown in Figs. 3 and 4 to Eq. (12) of the text for $T < T_c$. The dashed line characterizes the data taken on as-deposited films of a-Si. The solid line is for the data on annealed a-Si, as-deposited a-Ge and annealed a-Ge films.

This is Zvyagin's result; but, more recently, Overhof,[26] using a more rigorous percolation theory treatment and fewer assumptions, also found $S \propto T^{1/2}$ for a linear density of states. Since the a-Ge data are clearly incompatible with $S \propto T^{1/2}$ at all temperatures, the linear density of states shown in Fig. 8(a) can be ruled out.

Consider next a density of states which has a minimum near E_F, as shown in Fig. 8(b). For the symmetric case ($N_1 = N_2 = N_0$),

$$N(E) = N_0 |E - E_F|^n , \tag{9}$$

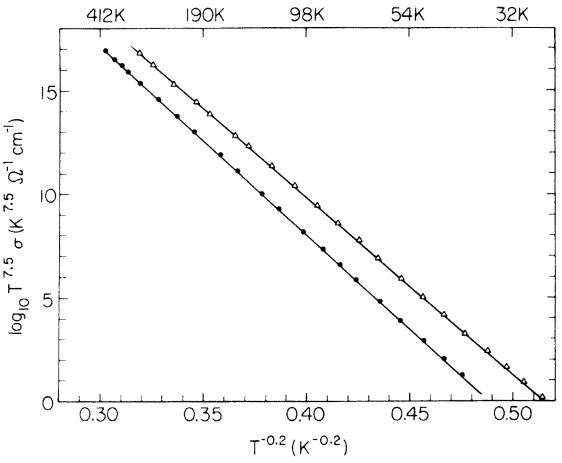

FIG. 10. Plot of the conductivity times $T^{7.5}$, on a logarithmic scale, vs $T^{-0.20}$ for the as-deposited a-Ge film Ge S43 (Δ) and for the annealed a-Si film Si S3 (250 °C, 1 h) (●).

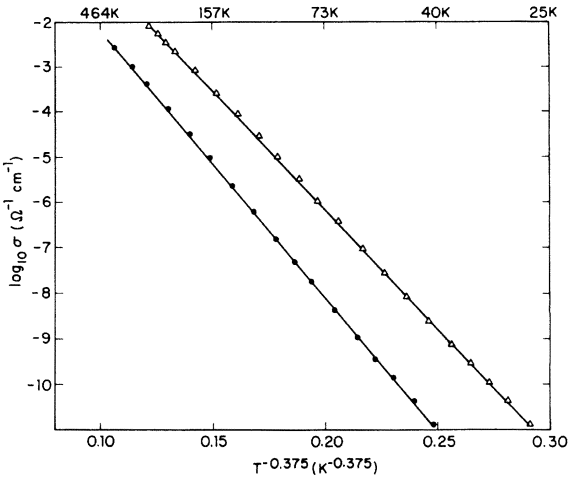

FIG. 11. Logarithm of the conductivity vs $T^{-0.375}$ for the same films and notation as in Fig. 10.

with $n \geq 0$, Pollak[11] finds

$$\log\sigma \propto T^{-Y} , \tag{10}$$

where

$$Y = (n+1)/(n+4) . \tag{11}$$

This same temperature dependence was also derived by Hamilton[28] using Mott's maximization procedure. Allowing for some temperature dependence in the pre-exponential term, the present conductivity data of a-Ge and a-Si for all $T < T_c$ were fit to the expression

$$\sigma = A T^x \exp[-(T_0/T)^Y] , \tag{12}$$

where A, x, and T_0 are temperature independent. For each value of Y, at least-squares computer routine fit A, x, and T_0 to the data. The range $0.05 \leq Y \leq 0.40$ gave good fits to the data, nearly independent of Y. The variation of x with Y is given in Fig. 9, which demonstrates quantitatively that the temperature dependence of the conductivity is the same for as-deposited a-Ge, annealed a-Ge and annealed a-Si and is only slightly different for as-deposited a-Si. The data for two films are plotted in Figs. 10–12 for the (Y, x) combinations (0.20, −7.50), (0.375, 0.0), and (0.55, 2.75), respectively. For $Y = 0.55$, the data show oscillatory behavior around the best straight line which becomes more severe for larger values of Y. The value $Y = 0.55$ is judged the very highest value which can be consistent with the error in the data. The allowable range of n is then $0 \leq n \leq 3$.

The thermopower for the symmetric density of states (9) is zero, according to (5). It can be made nonzero by the modification of moving E_F from the minimum. According to Eq. (8), however, this modification should result in $S \propto T^{1/2}$ at low enough temperatures. Since $S \propto T^{1/2}$ is

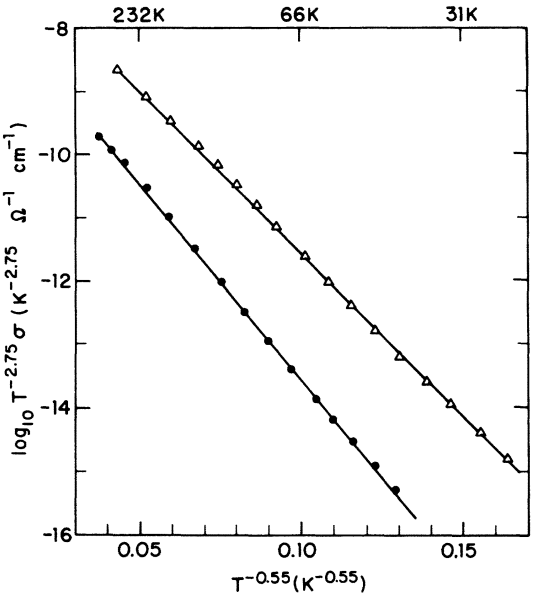

FIG. 12. Plot of the conductivity times $T^{-2.75}$, on a logarithmic scale, vs $T^{-0.55}$ for the same films and notation as in Fig. 10.

incompatible with the a-Ge data down to 40 K, the symmetric density of states will be modified by assuming, in Fig. 8(b), that N_2 is slightly larger than N_1, but E_F remains at the minimum. Using (5), the thermopower is given by

$$S \approx -\frac{k}{|e|}\left(\frac{n+1}{n+2}\right)\left(\frac{N_2-N_1}{N_1+N_2}\right)\frac{W}{kT} . \tag{13}$$

For $N_1 \sim N_2$, Mott's maximization technique gives[28]

$$W \propto T^{3/(4+n)} . \tag{14}$$

So for the nearly symmetric density of states shown in Fig. 8(b), $\log\sigma$ and S are expected to vary as

$$\log\sigma, \quad S \propto T^{-Y} , \tag{15}$$

where Y is given by (11). Since the σ data require $0 \leq n \leq 3$, a minimum decrease of 30%, corresponding to $n = 0$, is expected for S between 70 and 300 K. The maximum change observed in as-deposited films of a-Ge amounts to only 12% for the sample Ge S43. (Mathematically, the experimental variation of S with T in a-Ge requires $0 \leq Y \leq 0.09$ but the theory requires $Y \geq 0.25$.) Therefore, the nearly symmetric density of states sketched in Fig. 8(b) is unlikely, if conduction is by variable range hopping that is described by the presently available theories.

Using Pollak's percolation theory[11] for variable range hopping, Pollak *et al.*[25] have calculated the temperature dependence of the conductivity for the density of states model shown in Fig. 8(c) and described by

$$N(E) = \begin{cases} N_0[1-(E/E_0)^2] & \text{for } |E| < E_0 , \\ 0 & \text{for } |E| > E_0 . \end{cases} \tag{16}$$

These authors point out that a proper choice of bandwidth and bandheight can be made so that their low-temperature conductivity data for a-Ge and the small optical absorption below 0.6 eV reported by Donovan *et al.*[29] can be interpreted consistently without invoking special matrix element effects for optical transitions. The deviation of $\log\sigma$ from $T^{-1/4}$ behavior near 110 K was attributed by them to the cutoff in hopping energy which results from the density of states going to zero at $|E| = E_0$. The full width of the band depends in detail on the temperature at which the slope changes and on the exact shape of $N(E)$, but is estimated[25] to be of order 0.3 eV. If there is a cutoff in $N(E)$, the average energy of the charge carriers Π, the Peltier coefficient, will approach a constant value with increasing temperature. [Since $\Pi = ST$, Π = constant implies $S \propto 1/T$. Crudely speaking, this comes about because the integration limits in (5) are changed from $\pm W$ to $\pm E_0$, so asymptotically $S \propto 1/T$.] As a result, a change in the temperature dependence of S is expected at the temperature where the conductivity is affected by the cutoff in $N(E)$. Further, the thermopower at lower temperatures is expected to be temperature dependent (or zero), according to (5). The conductivity of a-Ge films shows the deviation at 110 K ($T^{-1/4} \sim 0.31$) but S is constant from 70 to 300 K ($0.24 < T^{-1/4} < 0.35$ $K^{-1/4}$), which runs counter to both expectations. It is concluded that the feature in the conductivity data near 110 K is not due to a cutoff in the energy of the charge carriers. Therefore, the thermopower and conductivity data, taken together, do not support the model sketched in Fig. 8(c) if E_0 is a few tenths of an eV.

So far it has been argued that variable range hopping theory applied to the density-of-states models shown in Fig. 8, with the limitations and approximations discussed above, does not give an adequate description of the thermopower data of a-Ge. If a fit to the data by percolation theory is to be achieved, then a more sophisticated analysis, such as that used by Overhof,[26] must be attempted. Unfortunately, as pointed out by Overhof, an exact treatment is very tedious and, furthermore, can be carried out analytically only for the simplest density-of-states models.

It is clear that the temperature-independent part of the thermopower of a-Ge is the most difficult feature to interpret in the variable range hopping theory. On the other hand, a temperature independent thermopower can be readily understood[30] if the *Ansatz* is made that transport takes place in a band whose width Δ is less than kT. This is clearly a break from traditional models

for the density of pseudogap states. Nevertheless, the *Ansatz* can be used to interpret the thermopower data, at least.

Consider a narrow band at $E=0$. For $kT \gg \Delta$, all states have an equal probability of occupancy ρ, which is the Fermi factor $f(0)$. Thus,

$$E_F(T) = -kT \ln[(1-\rho)/\beta\rho], \tag{17}$$

where β is the degeneracy factor.[31] When conduction occurs by electrons at a fixed energy, the Peltier coefficient is just

$$\Pi = -(E - E_F)/|e| \tag{18}$$

and the thermopower is, for $E=0$,

$$S = (k/|e|)E_F/kT, \tag{19}$$

which, using (17), can be rewritten

$$S = -(k/|e|)\ln[(1-\rho)/\beta\rho]. \tag{20}$$

If all other bands are so far away in energy that electrons are not excited into or out of the narrow band, then ρ and therefore S are temperature independent. In addition, S changes sign as a function of ρ at $\rho = (1+\beta)^{-1}$ and *does not depend significantly on the details of the conduction mechanism.*[32] At the lowest temperatures ($kT \ll \Delta$), the usual wideband conditions are recovered. Here, S will depend on the details of the conduction mechanism and should be given by a relation similar to either (2) or (8). However, the derivative term $[\partial \ln N(E)/dE]_{E_F}$ and therefore S will be very large compared to a normal metal. At high temperatures ($kT \gg \Delta$) the thermopower, given by (20), will be positive for $\rho > (1+\beta)^{-1}$ and negative for $\rho < (1+\beta)^{-1}$. Assuming $N(E)$ to be symmetric, the overall temperature dependence of S is sketched in Fig. 13 and discussed below. Note that the temperature is measured in units of kT/Δ.

For $\rho \lesssim \frac{1}{2}$ and $kT \ll \Delta$, S is negative since S is proportional to $[\partial \ln N(E)/\partial E]_{E_F}$ which is positive and $\partial S/\partial T$ is large and negative. As the temperature is increased for $kT \lesssim \Delta$, S peaks negatively but now $\partial S/\partial T > 0$ since the Peltier coefficient tends to a constant value as a function of temperature. Finally, when kT exceeds Δ, E_F tends to the value given by (17) and S is given by (20). Observation of the $\partial S/\partial T > 0$ region becomes less likely as ρ decreases below $\frac{1}{2}$ because of the increase in $|S|$ given by (20) coupled with the fact that (17) becomes operative at somewhat lower temperatures. The other curves in Fig. 13 are derived similarly. Note that only certain values of β apply to certain curves.

The curve labeled $[\rho < (1+\beta)^{-1}$ and $\rho \lesssim \frac{1}{2}]$ reproduces the essential features of the a-Ge data and the curve $[\rho < (1+\beta)^{-1}$ and $\rho > \frac{1}{2}]$ most resembles the a-Si data. Of the possible values $\beta = \frac{1}{2}$, 1, 2 only $\beta = \frac{1}{2}$ satisfies all these inequalities.[33] This

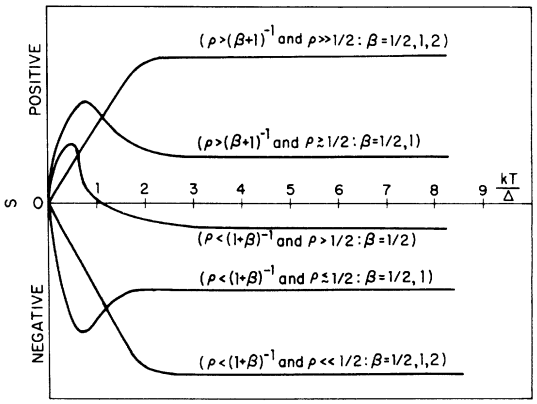

FIG. 13. Sketch of the thermoelectric power vs kT/Δ for a narrow band of width Δ and fractional occupancy ρ. The first inequality is determined by Eq. (20) and the sign of S at high temperatures. The second is determined from the sign of $\partial \ln N(E)/\partial E|_{E_F}$, as discussed in the text. The value of β, the degeneracy factor, is obtained by solving the inequalities subject to the restriction $\beta = \frac{1}{2}$, 1, or 2.

degeneracy factor applies when there is one electron per site (e.g., neutral donor in a crystalline semiconductor[31]). Now, since the low-temperature transport properties of a-Ge are determined by the surface electrons on voids[7] and since the present thermopower data are consistent with conduction via singly occupied sites, it is reasonable to infer that the unpaired electrons (which give rise to the paramagnetic spin signal) are the electrons responsible for the low-temperature dc transport. This assignment supports the speculation given in Sec. I that the unpaired electron states lie higher in energy.

Using $\beta = \frac{1}{2}$ and Eq. (20), the temperature-independent part of the thermopower of a-Ge (−64 to −90 μV/K) gives $\rho = 0.49$–0.41. For a-Si, the data (−13 to −21 μV/K) give $\rho = 0.63$–0.61. In a-Ge, the bandwidth Δ is estimated to be of order 0.01 eV on the basis that S is temperature independent for $T \gtrsim 70$ K. For a-Si, the value of Δ is more difficult to estimate from the data, but on the basis that the expected peak in (positive) S is at $T \leq 80$ K, the estimate $\Delta \lesssim 0.01$ eV is obtained.

A temperature-independent S requires ρ to be temperature independent. This assumption can be examined by calculating E_F from (19). The result for a-Ge is $E_F \sim -kT$ and for a-Si is $E_F \sim -\frac{1}{4}kT$. The assumption, then, is equivalent to assuming that all other bands are more than a few kT away and is therefore not obviously unreasonable.

As mentioned above, the thermopower due to conduction in a narrow band will depend significantly on the conduction mechanism only at the lowest temperatures ($kT \ll \Delta$). The thermopower

measurements presented in this paper do not extend to such low temperatures. Rather, they indicate only that conduction could take place in a narrow band. Nevertheless, this alone has implications for the interpretation of conductivity data. One premise of variable range hopping theory is that the disorder energy, and hence the bandwidth, are both larger than kT. Since $\Delta \lesssim kT$ for $T \gtrsim 70$ K, variable range hopping should predominate only at the lowest temperatures. It is therefore interesting to note that the conductivity of a-Ge films, measured to 6 K by Bahl and Bluzer,[34] is interpreted by them in terms of Mott's original formulation of the $T^{-1/4}$ theory, i.e., with realistic values of the model parameters, but only for $T \lesssim 10$ K. At 10 K, where their conductivity data noticeably deviates from the $T^{-1/4}$ behavior seen at lower temperatures, they estimate the hopping energy W to be 7 meV. The hopping energy cannot exceed the average energy between nearest-neighbor hopping sites and therefore must be of the order or less than the bandwidth. Thus, Bahl and Bluzer's estimate $W \sim 7$ meV is not inconsistent with the estimate $\Delta \sim 10$ meV obtained from the present thermopower data. In fact, if their data deviate from $T^{-1/4}$ behavior because nearest-neighbor hopping starts to contribute, then $W(10\text{ K}) \sim \Delta$ is to be expected, since the asymptotic limit of W as a function of temperature is the average energy between nearest-neighbor hopping sites.

For $70\text{ K} < T < T_c$, the conductivity should be determined primarily by the hopping rate between nearest-neighbor sites because the available thermal energy is now comparable to the energy difference between sites. But even in this situation the conductivity need not have a temperature dependence displaying a single activation energy. According to Emin,[35] acoustic multiphonon processes, which can give complex temperature dependences to σ, are important at all but the very lowest temperatures. In addition, temperatures in the range $70\text{ K} < T < T_c$ are high enough that optical phonon processes must be considered. In the range $10 < T < 70$ K, the conductivity should depend on both nearest-neighbor and variable-range hopping. Since the same electron can be involved in both mechanisms and since Emin's point still holds, $\sigma(T)$ should again have a complex temperature dependence.

These arguments imply that the fit of $\sigma(T)$, for $25\text{ K} < T < T_c$, to

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{3/8}] \tag{21}$$

is just a mathematical description of the data. Although it seems likely that conduction in this temperature range is by hopping between localized states, no one of the present simplified approaches appears to be adequate to describe the data. On the other hand, the conductivity in a-Ge and a-Si could easily have the same temperature dependence for $25\text{ K} < T < T_c$ but, as already shown, a different temperature dependence and sign for S.

On a different point, it could be noted that the S data of a-Ge at the lowest temperatures are reminiscent of some data on Ge crystals[36] which have been interpreted by Herring[37] in terms of the phonon-drag effect. It seems unlikely, however, that the a-Si data can be interpreted by invoking this effect. The reason is that a negative S in crystalline Si becomes more negative as T is lowered to the temperature at which the phonon drag effect causes S to peak.[36] The data for a-Si actually becomes more positive as T is lowered, counter to the expectation of the phonon-drag theory.[37] The absence of phonon-drag effects in a-Si and, by implication, in a-Ge is to be expected if momentum is not conserved in transitions between localized states.[27] The *Ansatz* that conduction occurs in a narrow band provides a straightforward explanation for the opposite curvature in the thermopower of a-Ge and a-Si at $T < 100$ K.

So far it has been argued that the thermopower data are interpretable with a model in which transport occurs in a narrow, partially filled band which is effectively thermally isolated from other bands. The most novel feature of this model is, of course, the assertion that the bandwidth is only of order 0.01 eV. It is difficult to argue, *a priori*, that such a narrow band exists. In fact, it is often suggested that potential fluctuations are a few tenths of an eV. But there is experimental evidence to suggest that the actual fluctuations, if any, can be smaller than this. In an extensive photoemission study of amorphous III-V and II-VI compounds, Shevchik, Tejeda, and Cardona[39] found that the width of the cation core levels is the same, within their resolution of 0.1 eV, as in the corresponding crystals. They conclude that the lack of additional broadening in the core level spectra of these amorphous materials rules out the fluctuating potential model.[40] In photoemission studies on Ge, Eastman, Freeouf, and Erbudak[41] found that the $3d$ core level linewidth is the same in both the amorphous and crystalline phases and is 0.45 ± 0.05 eV. Obviously, these results do not prove that the disorder energy is as small as 0.01 eV but they do show that there is no evidence for it to be larger than about 0.1 eV. Furthermore, the magnitude of the expected disorder energy may be reduced by, for example, a strong electron-phonon interaction which permits atomic rearrangements.

Small values of the disorder energy have already been suggested in more complex systems.

Seager, Emin, and Quinn[42] measured the dc transport properties of a series of chalcogenide glasses containing both As and Te and they concluded that there is no evidence for the disorder energy to be larger than kT. Also, Austin and Mott[43] have noted that the transport data in vanadium glasses are evidence that the spread of electron energies on vanadium sites is at most kT. For completeness, however, it should be mentioned that disorder energies larger than kT have been estimated in some other semiconducting glasses, for example those containing Fe and Cu.[43,44]

V. SUMMARY

New measurements of the dc conductivity and thermoelectric power of a-Ge and a-Si have been presented. In the temperature range $25 < T < 300$ K, the conductivity can be described by (21),

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{3/8}],$$

where σ_0 is temperature independent. But the thermopower of a-Ge is independent of temperature in the range $70 < T < 300$ K, an observation which cannot easily, if at all, be interpreted with the variable range hopping theories. On the other hand, if it is assumed that conduction takes place in a very narrow band, of order 0.01 eV wide, then all the features of the thermopower data can be explained. No detailed interpretation of the temperature dependence of the conductivity is attempted since, in the temperature range investigated, the thermopower does not depend significantly on the conduction mechanism. The proposed scheme of conduction in a narrow band does suggest, however, that conduction above liquid-nitrogen temperature should be dominated by hopping between spatially nearest localized states of the narrow band.

This new model is consistent with Bahl and Bluzer's[34] liquid-helium-range conductivity data and is not inconsistent with the results of recent photoemission studies which suggest that disorder energies in some amorphous materials are smaller than about 0.1 eV.

The low-temperature conductivity of a-Ge is known to be dominated by the electrons on the internal void surfaces.[7] A comparison of the present thermopower data with the expectation of the narrow band model suggests that the electron degeneracy factor is $\frac{1}{2}$ and that therefore the same electrons responsible for the spin resonance signal are responsible for the conductivity. Indeed, the qualitative correlation between the two has been known for some time.[2]

Note added in manuscript. After submission of this manuscript, an article by Emin[45] appeared in which he considers the thermopower for conduction by variable-range hopping. In particular, he points out that a density of states which is symmetric about the Fermi level need not give a zero value for S. However, in the $T^{-1/4}$ hopping regime he finds $S \propto T^{1/2}$ for symmetric hopping. Thus this new work further supports the contention that variable range hopping is unlikely for $T > 40$ K.

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