

Low-temperature magnetic properties of amorphous germanium and silicon*†

Stephen J. Hudgens‡

Department of Physics, The University of Chicago, Chicago, Illinois 60637

(Received 9 February 1976)

The absolute magnetic susceptibility χ of amorphous Ge (*a*-Ge) prepared by evaporation, rf sputtering, and glow discharge decomposition of GeH_4 and of amorphous Si (*a*-Si) prepared by rf sputtering and glow discharge decomposition of SiH_4 was measured in the range of $1.5 \leq T \leq 300$ K. The spin component χ_s of χ was fit to a Curie-Weiss law $\chi_s = C/(T + \Theta_N)$ for $T > 10$ K with Θ_N between 0 and 4 K depending on the sample's state of anneal. Before annealing all samples except glow discharge *a*-Ge deviate from Curie-Weiss behavior below 8 K suggesting antiferromagnetic ordering of most of the spins. As the annealing temperature T_A is increased above 50°C, the spin density N_s in sputtered and evaporated *a*-Ge decreases and the antiferromagnetic ordering temperature T_N is reduced to less than 1.5 K for $T_A \approx 200^\circ\text{C}$. The effect of hydrogen doping of sputtered *a*-Ge is to reduce T_N below 1.5 K. These results are discussed in terms of several theories of amorphous antiferromagnetism and the present understanding of spins in amorphous tetrahedral semiconductors.

I. INTRODUCTION

Of the many amorphous semiconductors studied in recent years, perhaps none have exhibited as many interesting magnetic properties as amorphous germanium (*a*-Ge) and amorphous silicon (*a*-Si). Both *a*-Ge and *a*-Si have diamagnetic susceptibilities much larger than their crystalline counterparts.^{1,2} Both contain large densities of free spins,^{3,4} and recently *a*-Ge has been reported to exhibit low-temperature antiferromagnetic ordering of its spins.⁵ In this paper we present additional low-temperature magnetic-susceptibility measurements on *a*-Ge and *a*-Si prepared in several ways.⁶ The effect of annealing and hydrogen-gas doping on magnetic susceptibility is studied and the results of these measurements are discussed within the framework of several models of amorphous antiferromagnetic systems. Comparisons are made to results for other systems of interacting spins in semiconductors.

II. MATERIALS PREPARATION

Amorphous Ge and Si (*a*-Ge and *a*-Si) can be prepared by a variety of techniques. Depending on the method of preparation employed many of the properties of the semiconductors are changed.⁷ Perhaps the three most widely investigated "types" of *a*-Ge and *a*-Si are those prepared by evaporation, radio frequency sputtering, and glow discharge decomposition of GeH_4 and SiH_4 . These methods were used to prepare samples for our low-temperature magnetic susceptibility measurements.

Evaporated *a*-Ge samples were prepared from crystalline Ge (resistivity $\approx 40 \Omega \text{ cm}$ at 300 K) by electron beam evaporation from a graphite crucible at a pressure $< 10^{-6}$ Torr at normal incidence

onto a 6-in.-square fused-quartz substrate located 25 cm from the source. Deposition rates were between 13 and 17 Å/sec. The substrate temperature was kept between room temperature and 50°C by depositing the Ge in a series of 3-min evaporations until the Ge in the crucible had been exhausted. Films with thicknesses of the order of 3 μm were obtained. The *a*-Ge was then scraped off the substrate with a Pyrex microscope slide. The material, in the form of small flakes with dimensions of the order of several millimeters, was sealed in fused-quartz ampoules. The ampoules contained 0.5 Torr of He to facilitate thermal equilibration during the susceptibility measurement.

Sputtered *a*-Ge and *a*-Si samples were prepared in a triode rf sputtering system in an argon plasma of 10^{-4} Torr pressure. The sputtering cathodes were hot pressed polycrystalline Si or Ge of 99.999% purity. In each case about 3 μm of semiconductor was deposited at a rate of ≈ 0.2 Å/sec on water cooled Pyrex substrates. The material was removed and encapsulated in the same manner as the evaporated sample.

Glow discharge *a*-Ge and *a*-Si were prepared by electrodeless radio frequency decomposition of GeH_4 and SiH_4 , at a gas pressure of ≈ 0.5 Torr. The material was deposited on the interior surface of a fused-quartz cylinder at room temperature. Deposition rates varied from 0.08 to 0.13 Å/sec. The deposited material was removed and encapsulated in the previously described manner.

III. MAGNETIC MEASUREMENTS

Magnetic susceptibility measurements were performed using the Faraday technique. The fused-quartz ampoules containing between 0.1 and 0.4 g of sample material were suspended by a quartz fiber

from an electrobalance. The apparatus was designed so that samples could be changed from above by removing the vacuum chamber covering the electrobalance, pivoting the electrobalance out of the way, and withdrawing the quartz fiber and ampoule using a wire and pulley attached to the ceiling. After the sample was changed and the new sample lowered back into the hangdown tube, the electrobalance was again precisely repositioned by locating pins. In this way, several samples could be measured without requiring the cryostat to warm up. The reproducibility of measurements of the Faraday force was $\pm 0.1\%$.

The samples were thermally coupled to the surrounding hangdown tube wall by helium exchange gas. The sample temperature was varied from 1.5 to 300 K using a Janis⁸ variable temperature cryostat which contains the hangdown tube. Temperature measurements were made in the range $4.2 \leq T \leq 300$ K with a Au (0.6 at.% Fe) vs Chromel thermocouple attached to the hangdown tube wall. In the range $1.5 \leq T \leq 4.2$ K, liquid He was allowed to flow around the outside of the hangdown tube. Temperature, in this range, was determined by measuring the vapor pressure above the liquid.

The balance was calibrated using a 0.5-cm cube of single-crystal Ge which previous measurements had shown to have a mass susceptibility $\chi = (1.06 \pm 0.01) \times 10^{-7}$ cm³/g. After completion of an annealing study the absolute magnetic susceptibility of the sample material was determined by subtracting the contribution of the quartz. This was done by breaking open the ampoule, removing the sample material and then, after glueing the ampoule back together with a negligible quantity of Duco cement, replacing and measuring the empty container in the apparatus. The absolute error of measurements done in this way is $\pm 2\%$.

Since extremely small amounts of ferromagnetic impurities can cause large errors in the measured susceptibility, χ for each sample was measured as a function of magnetic field in the range $1 \leq H \leq 8$ kG at room temperature, 4.2, and 1.5 K. Ferromagnetic contaminants produce a field dependent magnetic susceptibility which is linear in $1/H$ and thus easily detected. The importance of performing this test at low as well as at high temperatures, and after each annealing step, must be emphasized. In two samples of evaporated *a*-Ge, ferromagnetic contamination⁹ was discovered only after the sample had been annealed to $T_A = 275^\circ\text{C}$.

For the annealing studies, samples were placed inside a quartz tube in a temperature controlled furnace and heated to the specified temperature T_A for 3 h, a time sufficient for annealing processes to reach equilibrium.

IV. EXPERIMENTAL RESULTS

A. Amorphous germanium

The low-temperature magnetic susceptibility of amorphous semiconductors χ , can be written as the sum of a diamagnetic lattice component χ_L and paramagnetic component χ_S due to the presence of spin magnetic moments. χ_L is expected to be only weakly temperature dependent.¹⁰ For spin densities $N_S > 10^{18}$ cm⁻³, the low-temperature behavior of χ will be dominated by $\chi_S(T)$ which, for temperatures greater than the spin ordering temperature, T_N , will follow a Curie-Weiss law:

$$\chi_S = C / (T + \Theta_N). \quad (1)$$

Here Θ_N is the paramagnetic Néel temperature and C is the Curie constant which is proportional to N_S .

Thus a plot of χ_S^{-1} vs T will yield a straight line whose intercept with the temperature axis is $-\Theta_N$ and whose slope is the inverse of the Curie constant.

Figure 1 shows the low-temperature behavior of χ_S^{-1} for evaporated *a*-Ge which has been annealed to successively higher annealing temperatures T_A . Here $\chi_S = \chi - \chi_L$, where χ_L , the lattice diamagnetic component, is obtained by extrapolation of the high-temperature portion of the χ vs $1/T$ curve to $1/T = 0$.

The most striking feature in Fig. 1 is the deviation from the linear Curie-Weiss behavior exhibited by the $T_A = 50^\circ\text{C}$ and $T_A = 100^\circ\text{C}$ samples.

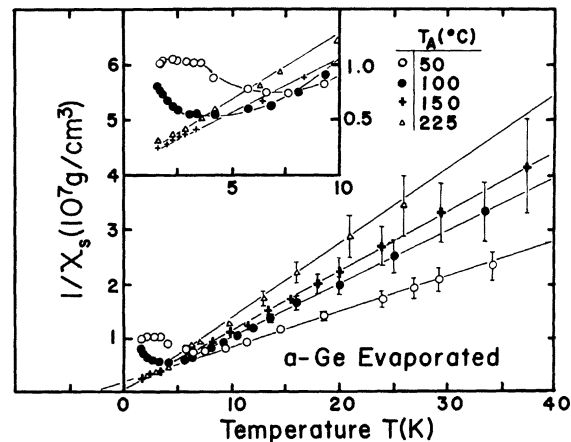


FIG. 1. Temperature dependence of the inverse of the paramagnetic component of the magnetic susceptibility χ_S^{-1} of evaporated *a*-Ge. χ_S is obtained from $\chi_S = \chi - \chi_L$ where χ_L is the nominally temperature-independent lattice diamagnetic component of the susceptibility. Curves are parameterized in T_A , the annealing temperature. Lines connecting data points are to serve as guides for the eye.

Similar behavior was seen by DiSalvo and co-workers⁵ in a room temperature annealed sample of evaporated *a*-Ge. The authors suggested this behavior resulted from a change in the *g* value of the spins, or from the presence of Cu impurities, or from an antiferromagnetic ordering of a fraction of the spins. Since, as will be seen, we have observed this behavior in samples prepared by different methods, it is unlikely that it is caused by impurities introduced by a particular preparation technique. Further, one sees in Fig. 2 the samples with $T_A = 50^\circ\text{C}$ and $T_A = 100^\circ\text{C}$ which deviate from Curie-Weiss law also have a positive Θ_N , indicating antiferromagnetic coupling between spins. This strongly suggests that the deviation is indeed due to antiferromagnetic ordering of the spin system.

Figure 3 shows the annealing dependence of the spin density N_S , obtained from the inverse of the slope of the linear portions of the χ_S^{-1} vs T curves for the evaporated *a*-Ge sample. Here we use $g = 2$, $S = \frac{1}{2}$, and we approximate the mass density of the sample with the crystalline Ge value. The decrease in N_S with increasing T_A is in good agreement with the results of Luby,¹¹ obtained from electron spin resonance (ESR). Our data are also in qualitative agreement with the ESR annealing study done by Agarwal,⁴ although we did not observe the 20% initial increase in N_S reported in this work.

ESR measurements were performed on a portion of the unannealed material used for the evaporated *a*-Ge magnetic susceptibility sample. Sample temperature was varied from 9 to 300 K using a Heli-Tran ESR Dewar. Sample temperature could not be determined accurately in the region $9 \leq T \leq 15$ K with this cryogenic system. We were, therefore, restricted to measuring ESR for $T > 15$ K. In the temperature region $15 \leq T \leq 70$ K,

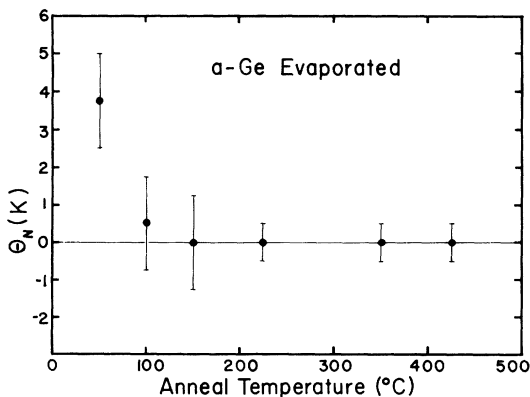


FIG. 2. Annealing dependence of the paramagnetic Néel temperature Θ_N in evaporated *a*-Ge.

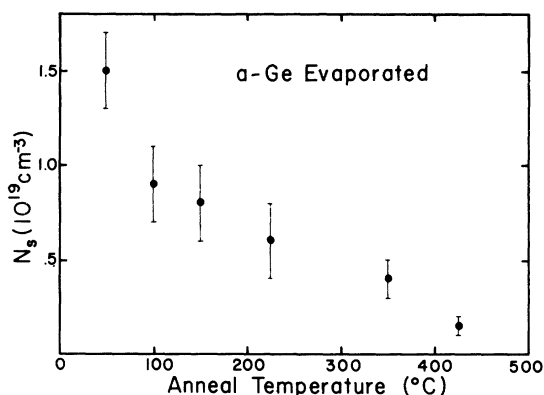


FIG. 3. Annealing dependence of the free spin density N_S in evaporated *a*-Ge.

a plot of the inverse of the resonance signal strength vs T yielded an extrapolated value of $\Theta_N = 3 \pm 1$ K in good agreement with $\Theta_N = 3.75 \pm 1.25$ K obtained from susceptibility measurements. The resonance was centered at $g = 2.022$ and had a temperature-independent width $W = 39 \pm 2$ G in agreement with the work of Agarwal.⁴ We did not attempt to determine N_S from the ESR measurements.

The inverse spin susceptibility of sputtered *a*-Ge, shown in Fig. 4, is quite similar to the evaporated *a*-Ge data. Although the dependence of N_S on annealing for this material is approximately the same as for the evaporated sample, one sees that spin ordering occurs in samples annealed to somewhat higher temperatures. The spin density of the unannealed sample, $N_S = (1.5 \pm 0.2) \times 10^{19} \text{ cm}^{-3}$, is in agreement with the recent magnetic susceptibility measurements of Pawlik *et al.*,¹² but almost an order of magnitude smaller than spin densities obtained earlier by Brodsky and Title from ESR

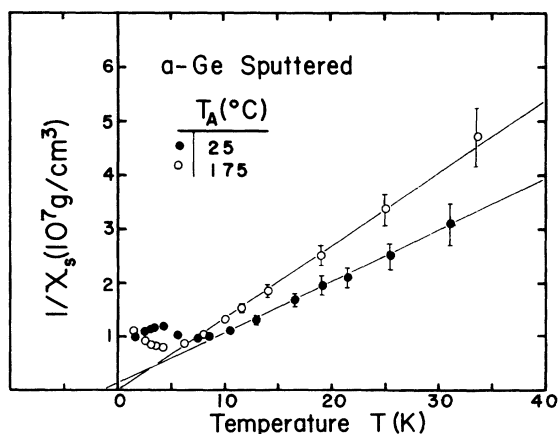


FIG. 4. Same figure caption as Fig. 1 except for sputtered *a*-Ge.

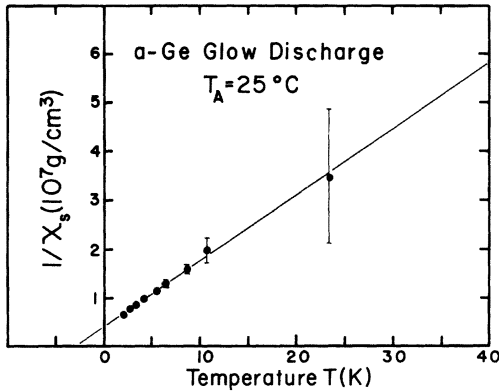


FIG. 5. Temperature dependence of χ_S^{-1} for glow discharge *a*-Ge.

measurements.¹³

Figure 5 show the temperature dependence of χ_S^{-1} for glow discharge *a*-Ge prepared at $T_A = 25^\circ\text{C}$. One notices that although Θ_N is nonzero there is no evidence of spin ordering for $T > 1.5$ K. Furthermore, the spin density is reduced from the sputtered and evaporated samples. Here $N_S = (6 \pm 1) \times 10^{18} \text{ cm}^{-3}$. Glow discharge *a*-Ge, however, is known to differ substantially in many of its physical properties from evaporated and sputtered *a*-Ge.¹⁴

It is thought that a principal cause of these differences is hydrogen incorporated in the material during its formation. Both *a*-Ge and *a*-Si prepared at 25°C by glow discharge decomposition contain up to 15 at. % hydrogen.¹⁵ Figure 6 shows the effect of intentional hydrogen doping on sputtered *a*-Ge. This sample was prepared in a manner identical to the previous sputtered *a*-Ge sample except 10^{-4} Torr of purified H_2 was admitted into the Ar plasma. Notice that for this sample Θ_N is also nonzero and also no spin ordering is

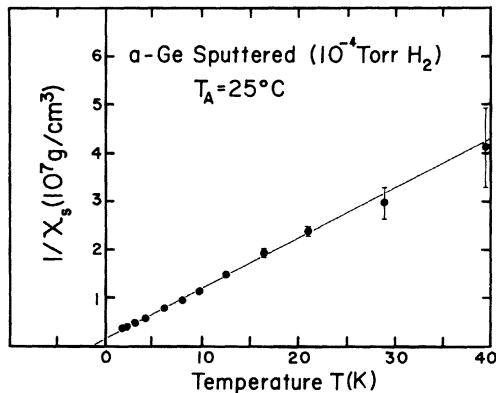


FIG. 6. Temperature dependence of χ_S^{-1} for *a*-Ge sputtered with 10^{-4} -Torr H_2 introduced into Ar plasma.

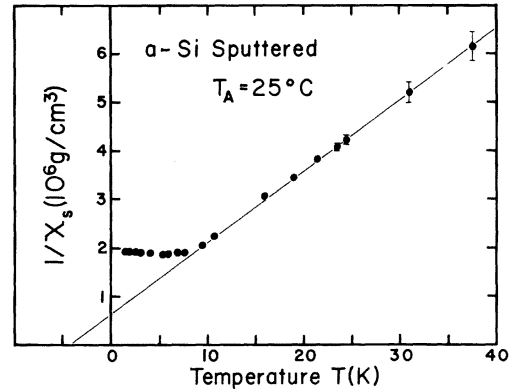


FIG. 7. Temperature dependence of χ_S^{-1} for sputtered *a*-Si.

observed. The spin density is reduced from the nonhydrogenated value to $N_S = (8 \pm 1) \times 10^{18} \text{ cm}^{-3}$. This is in agreement with the ESR work of Lewis¹⁶ in which it was found that the incorporation of approximately 6% hydrogen in sputtered *a*-Ge produces $N_S \approx 6 \times 10^{18} \text{ cm}^{-3}$.

B. Amorphous silicon

Figures 7 and 8 show the temperature dependence of χ_S^{-1} for unannealed samples of sputtered and glow discharge *a*-Si. In both of these samples spin ordering is observed in the vicinity of $T = 7.5$ K, and both have nonzero paramagnetic Néel temperatures: Θ_N (sputtered) = 4.25 ± 1.25 K; Θ_N (glow discharge) = 1.5 ± 1.25 K. Approximating the mass density of the amorphous material with the crystalline value one obtains $N_S = (2.6 \pm 0.2) \times 10^{19} \text{ cm}^{-3}$ for the sputtered material and $N_S = (6 \pm 1) \times 10^{18} \text{ cm}^{-3}$ for glow discharge. As in the case of sputtered *a*-Ge, N_S obtained from χ_S is found to be almost an order of magnitude smaller

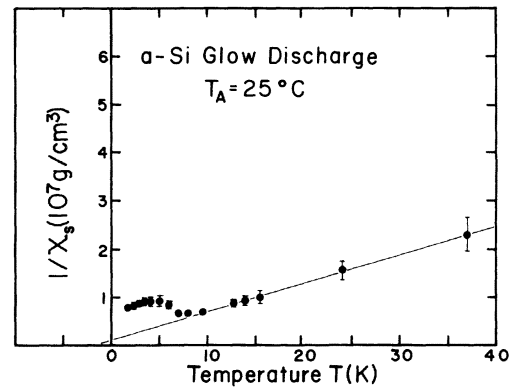


FIG. 8. Temperature dependence of χ_S^{-1} for glow discharge *a*-Si.

than the value $N_S = 2 \times 10^{20} \text{ cm}^{-3}$, obtained by ESR,¹³ for sputtered α -Si.

This discrepancy may be caused by differences in preparation conditions. The samples of sputtered α -Si measured by Brodsky and Title¹³ were deposited at rates between 3 and 10 Å/sec. These rates are between 15 and 45 times larger than the rates at which our samples were prepared. Although the effect of changes in deposition rate on N_S in sputtered α -Si has not been studied, Bahl and Bhagat¹⁷ recently investigated the dependence on deposition parameters of ESR spin density in evaporated α -Si. They find that N_S varies from 10^{19} cm^{-3} to $\approx 3 \times 10^{20} \text{ cm}^{-3}$ as the evaporation rate is increased from 0.4 Å/sec to ≈ 10 Å/sec.

On the other hand, the spin density for the glow discharge material is much larger than published values. LeComber and co-workers¹⁸ were unable to detect an ESR signal in samples of glow discharge α -Si. They place an upper limit of $N_S < 5 \times 10^{17} \text{ cm}^{-3}$. Their samples were, however, deposited on heated substrates and were found to contain very little hydrogen. In contrast, our samples, deposited on room temperature substrates, evolved enough hydrogen upon annealing to $T_A = 150^\circ\text{C}$ to burst the quartz ampoules containing them. As mentioned earlier these samples were found to contain up to 15 at. % hydrogen. ESR measurements¹⁹ made on the glow discharge α -Si at 77 K and at room temperature, showed a single resonance at $g = 2.005 \pm 0.001$ with a temperature-independent linewidth, $W = 6.2 \pm 0.6 \text{ G}$. For comparison, ESR measurements reported by Brodsky and Title¹³ on sputtered and evaporated α -Si samples were characterized by $g = 2.0055 \pm 0.005$ and $W = 4.7 \text{ G}$, in excellent agreement with these results. Clearly, further studies on the effect of prepara-

tion conditions, in particular, substrate temperature and deposition rate, on the magnetic properties of glow discharge α -Si are needed.

The experimental data for each of the samples are summarized in Table I. T_N , the ordering temperature, is taken to be the temperature at which the minimum in the cusp in χ_S^{-1} occurs.

V. DISCUSSION

Various types of amorphous antiferromagnetic systems have been reported in the literature. These include, for example, disordered rare-earth oxide-ferric oxide materials,²⁰ iron and cobalt phosphate glasses,²¹ dilute magnetic alloys of, for example, Mn in Cu,²² and phosphorus-doped Si.^{23,24} The amorphous antiferromagnetic system represented by α -Si and α -Ge differs from these systems in two fundamental ways. First, the magnetic moments in the previous systems arise from either unfilled atomic d or f levels or from unionized donor electrons associated with impurity atoms imbedded in a nonmagnetic matrix. The magnetic moments in α -Ge and α -Si are intrinsic to the materials and are thought to be caused by broken bonds. One is led to this belief by the observation of Brodsky *et al.*³ that the g values and linewidths of the ESR signals from α -Ge and α -Si are identical to those observed on mechanically damaged surfaces of the respective crystalline materials. Second, the magnetic moments in the previous system are homogeneously distributed in a random manner throughout the nonmagnetic matrix. The moments in α -Ge and α -Si, however, are distributed inhomogeneously. Some fraction is thought to lie on the surfaces of an internal network of cracks

TABLE I. Summary of experimental data.

Material	Method of preparation	Anneal temp. T_A (°C)	Spin density N_S (10^{19} cm^{-3})	Ordering temp. T_N (K)	Paramagnetic Néel temp. Θ_N (K)
α -Ge	evaporated	50	1.5 ± 0.2	7.5 ± 1	3.75 ± 1.25
		100	0.9 ± 0.2	4.5 ± 1	0.5 ± 1.25
		150	0.8 ± 0.2	< 1.5	0 ± 1.25
		225	0.6 ± 0.2	< 1.5	0 ± 0.5
		350	0.4 ± 0.1	< 1.5	0 ± 0.5
		425	0.15 ± 0.05	< 1.5	0 ± 0.5
		500	0.15 ± 0.05	< 1.5	0 ± 0.5
	sputtered	25	0.8 ± 0.2	7.5 ± 1	1.25 ± 1.25
		175	0.7 ± 0.1	5.0 ± 1	0 ± 1.25
		25	0.6 ± 0.1	< 1.5	2.5 ± 1.75
α -Si	glow discharge	25	0.8 ± 0.1	< 1.5	1.75 ± 1.25
	sputtered in 10^{-4} Torr partial pressure H_2	25	0.8 ± 0.1	< 1.5	1.75 ± 1.25
α -Si	sputtered	25	2.6 ± 0.2	7.5 ± 1	4.25 ± 1.25
	glow discharge	25	0.6 ± 0.1	8.0 ± 1	1.5 ± 1.25

or microvoids which are observed in films prepared on low-temperature substrates. As a consequence of these differences, theoretical models developed to treat other amorphous antiferromagnetic systems may not be applicable to α -Ge and α -Si without modification. In the following sections we will consider in detail three approaches: the spin-cluster method, the spin-glass approach, and the Hubbard band model.

A. Spin-cluster method

The spin-cluster method treats a distribution of N_S spins as a collection of N_S/n noninteracting clusters of n spins. Within the cluster the spins are considered to interact via exchange energies $J_{ij}(R)$, which are determined from a probability distribution of interspin distances R , and an assumed functional form of $J_{ij}(R)$. The simplest form of this model²⁵ is the system composed of a random spatial distribution of noninteracting spin pairs, all of which have the same J_{ij} . The exchange interaction results in a singlet two-electron ground state and a triplet excited state. At elevated temperatures the triplet state is populated resulting in a paramagnetic contribution to the magnetic susceptibility which follows a Curie-Weiss law. As the temperature is lowered the susceptibility begins to deviate from Curie-Weiss behavior because of the temperature dependence of the population of the triplet state. When $kT \approx J_{ij}$, the triplet state is rapidly becoming depopulated, sharply reducing the effective number of magnetic moments and causing χ_S^{-1} to diverge as $T \rightarrow 0$, as shown in Fig. 9. This minimum in χ_S^{-1} is similar to the behavior of χ_S^{-1} in crystalline antiferromagnets and may easily be mistaken for evidence of long-range antiferromagnetic ordering. It is, of

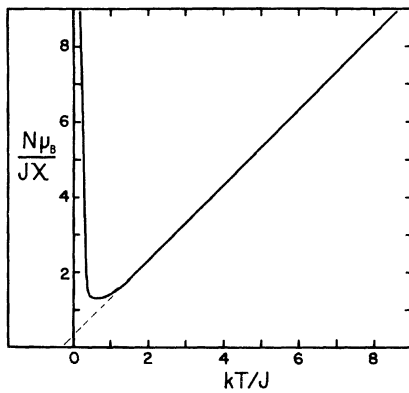


FIG. 9. Inverse magnetic susceptibility in reduced units versus temperature in reduced units for $\frac{1}{2}N$ two spin clusters with exchange energy J . The minimum occurs at temperature T_N , where $kT_N = 0.6J$. Extrapolation to $T \rightarrow 0$ gives $\Theta_N = 0.4T_N$.

course, not the consequence of a cooperative interaction and is indicative only of a short-range magnetic ordering.

Such a spin = 1 center has in fact been observed experimentally²⁶ in ESR studies of neutron-irradiated crystalline Si, and has been associated with a neutral divacancy containing two weakly interacting $\langle 111 \rangle$ dangling bonds separated by about 5 Å. Although the detailed temperature dependence of this resonance was not studied, its presence at 77 K and absence at 4.2 K allows one to infer that the singlet-triplet splitting for this state lies between 0.4×10^{-3} and 6.2×10^{-3} eV.

A more realistic form of the two-moment-cluster model is obtained by replacing the single value of J_{ij} with a Gaussian distribution centered at a mean energy J_0 with a standard deviation σ . One finds that the behavior of χ_S^{-1} for this system is essentially unchanged from the previous example for $\sigma \leq 0.1J_0$. For increasingly broader distributions T_N shifts slightly towards lower values so that for $\sigma = 0.4J_0$, $kT_N = 0.55J_0$, while Θ_N is unchanged.

Of course neither of these two systems (single exchange energy, or Gaussian broadened distribution of exchange energies) represents a random spatial distribution of single spins. In this case one obtains the distribution of J_{ij} from the probability distribution $P(R)$ of interspin distances, R ,

$$P(R) dR = 4\pi NR^2 dR \exp(-\frac{4}{3}\pi NR^3), \quad (2)$$

and from an assumed form of $J_{ij}(R)$. Sonder and Schweinler,²³ using this approach, showed if $J_{ij}(R) = A \exp(-BR_{ij}^3)$, then $\chi_S = C/T^{1-\epsilon}$. Here ϵ and C are constants proportional to the spin concentration. This expression is not of the Curie-Weiss form at elevated temperatures, nor does it exhibit a cusp in χ_S^{-1} at low temperature.

This result is not, however, a general consequence of the application of the spin-cluster method to a random distribution of spins, but rather the result of a particular choice of $J_{ij}(R)$. Slater²⁷ has shown that the exchange energy between hydrogenic

TABLE II. 2-spin-cluster systems.

System	T_N/Θ_N
Single exchange energy	1.5
Gaussian broadened exchange energy distribution $\sigma = 0.4J_0$	1.38
Random spatial distribution of spins:	
$B = 1.7 \times 10^{-1}$	1.024
$B = 8.5 \times 10^{-2}$	0.975
$B = 4.2 \times 10^{-2}$	0.543
$B = 1.7 \times 10^{-2}$	0.220

atomic states is $J(R) = J_0(R)e^{-\alpha R}$. Since $J_0(R)$ varies slowly with R compared to the exponential function we can assume $J_0(R) = J$, a constant. One then obtains $\chi_S^{-1}(T)$ by a numerical integration. The results of this calculation are shown in Fig. 10, parameterized in terms of the dimensionless quantity, $B = 4\pi N/3\alpha^3$. χ_S^{-1} has a cusp at low temperature and is Curie-Weiss-like at higher temperatures. Both T_N and Θ_N depend on B .

For $N = 3 \times 10^{19} \text{ cm}^{-3}$, $B \leq 1.7 \times 10^{-1}$ corresponds to a localization radius $1/\alpha \leq 11 \text{ \AA}$ and for $N = 3 \times 10^{18} \text{ cm}^{-3}$, $1/\alpha \leq 24 \text{ \AA}$. Since one may reasonably assume that dangling bond wave functions are no larger than 11 \AA , this range of B covers the physically significant region for a -Ge and a -Si. In this region one sees in Table II this model predicts $T_N/\Theta_N \leq 1.0$, while one sees in Table I that experimentally T_N exceeds Θ_N for every sample in which ordering is observed. One therefore concludes that the spin system in a -Ge and a -Si is not correctly represented in the spin-pair approach by a homogeneous random distribution of spins.

This conclusion is further substantiated by observing that for the unannealed samples of sputtered and evaporated a -Ge and for the sample of glow discharge a -Si there is a downward turn in χ_S^{-1} at temperatures below T_N . This indicates the presence of noninteracting spins which contribute a Curie susceptibility component to χ_S which begins to dominate at low temperature. This will be discussed later, but for now it is sufficient to observe that it is conceptually difficult to introduce a noninteracting spin component into a random spin distribution. The random distribution already con-

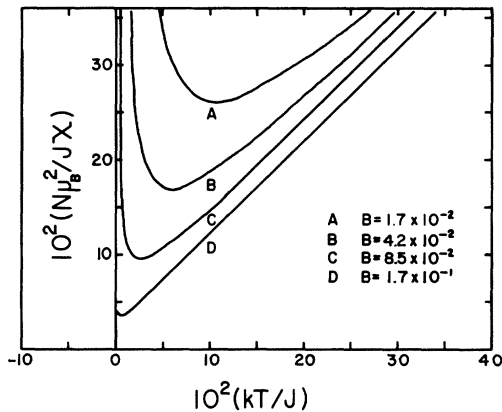


FIG. 10. Inverse magnetic susceptibility in reduced units versus temperature in reduced units for a random spatial distribution of N spins per unit volume. Exchange interaction occurs pair-wise between spins according to: $J(R) = J e^{-\alpha R}$. B is the volume fraction occupied by the spin wave function $B = 4\pi N/3\alpha^3$.

tains spins which are noninteracting. On the other hand, one can easily visualize noninteracting spins in a system in which the remaining spins have clustered.

B. Spin-glass method

Spin glasses are a class of dilute magnetic alloys with randomly competing exchange interactions.²⁸ They are characterized by having a frozen-in local moment, but without any overall moment or simple sublattice antiferromagnetic structure. They show a sharp cusp in χ_S^{-1} at the spin-glass transition temperature T_{sg} when one measures the susceptibility at low field.²² This cusp is smoothed as the field is increased. Most theoretical work on these materials treats only the case in which the distribution of interspin exchange energies has a mean value of zero. One finds for these systems that Θ_N extrapolated from the high-temperature behavior of χ_S^{-1} is zero. Recently, Southern²⁹ has presented a treatment of the spin-glass phase from the standpoint of molecular-field theory in which the distribution of J_{ij} is allowed to have a nonzero mean. For this system he finds

$$k\Theta_N = \frac{1}{3} S(S+1) \bar{J}(0), \quad (3)$$

where $\bar{J}(0)$ is the mean of the exchange energy distribution, k is Boltzmann's constant, and the ordering temperature is given by

$$kT_{sg} = [S(S+1)/3] \left\langle \sum_{ij} (J_{ij}^2)^{1/2} \right\rangle_{av}. \quad (4)$$

The spin-glass phase is stable provided that $T_{sg} > \Theta_N$. If one assumes that $\langle \sum_j J_{ij}^2 \rangle_{av}$ scales as the concentration N of magnetic moments, then T_{sg} will vary as $N^{1/2}$. At the ordering temperature

$$\chi_S(T_{sg}) = Ng^2 \mu_B^2 S(S+1)/3kT_{sg}. \quad (5)$$

For $T < T_{sg}$ the local susceptibility at a given site can be considered in terms of its component along the field direction and perpendicular to the field direction. $\chi_{||}$ decreases to zero as $T \rightarrow 0$, while $\chi_{\perp}(T) = \chi_S(T_{sg})$ for $T \leq T_{sg}$. Consequently, the average susceptibility at zero temperature is

$$\bar{\chi}_S(T=0) = 0.67 \bar{\chi}_S(T_{sg}). \quad (6)$$

This is exactly the result one obtains for a powder average with a crystalline antiferromagnet, as shown in Fig. 11. Presumably by choosing the distribution of J_{ij} correctly, one could introduce noninteracting spins in this system which would result in the observed downward turn in χ_S^{-1} discussed earlier.

In principle one can distinguish the spin-glass phase from, for example, the spin-cluster system

described earlier in terms of the magnetic-field dependence of the cusp in χ_S^{-1} . As mentioned earlier we saw no variation in χ_S as a function of field in the range $1 \leq H \leq 8$ kG. However, measurements might have to be performed at fields much below 1 kG in order to observe the field dependence of the cusp one expects in the spin glass phase. Such low-field measurements are difficult to perform with a Faraday balance and are perhaps more suited to the use of a vibrating sample magnetometer.

It should be mentioned at this point that fundamental problems can arise in the application of conventional molecular field theory to dilute magnetic systems. In an early paper, Sato, Arrott, and Kikuchi³⁰ object to the mean-field theory prediction of a finite Néel temperature for infinitesimally small magnetic-moment concentrations. To remedy the problem they treat the antiferromagnetically interacting disordered spin system by the cluster-variation method of Takagi³¹ and Kikuchi.³²

In this model the magnetic moments can be non-interacting, belong to an isolated pair, or belong to a pair adjacent to other pairs. This model predicts $\Theta_N = 0$ for concentrations of magnetic moments $c < 1/(Z - 1)$, where Z is the number of nearest neighbors. For Ge and Si this requires $c < \frac{1}{3}$. However, the samples of *a*-Ge and *a*-Si observed to have nonzero Θ_N all have $c < 5.0 \times 10^{-4}$. Thus in this model as in previous models, the assumption of a homogeneous random distribution of spins leads to a prediction inconsistent with experiment.

C. Hubbard band model

All of the preceding models include exchange interactions but neglect electron correlation effects. If the states giving rise to χ_S in *a*-Ge and *a*-Si lie energetically among a large density of localized gap states, then correlation effects will be important. Models³³⁻³⁵ which treat correlation in the Hubbard approximation lead to two contributions to the susceptibility. The first is a temperature independent Pauli term, $\chi_P = \mu_B^2 N(E_M)$, arising from a finite density of states, $N(E_M)$, at the energy E_M , where $E_M = E_F - \Delta E$: E_F is the Fermi energy, and ΔE is the average Hubbard energy over a localized state. Second, there is a Curie-Weiss term proportional to the number of singly occupied states with Θ_N nonzero only if exchange is included.^{34,35} At $T = T_N$ antiferromagnetic ordering of the magnetic moments occurs, in the system which includes exchange. The exact temperature dependence has not been calculated but will clearly depend on the nature of the localized orbitals and

distribution of interspin distances.

The Pauli-like temperature-independent component predicted by the Hubbard band models is small compared to the lattice diamagnetism. Even for values of $N(E_M)$ as large as 10^{20} eV⁻¹ cm⁻³ it amounts to only a few tenths of a percent of χ_L . Thus changes in this term reflecting the decrease in localized state density with annealing will go undetected in measurements of the room temperature magnetic susceptibility of *a*-Ge and *a*-Si. This is consistent with the experimental observation of Hudgens.¹

VI. CONCLUSION

As we have seen, one cannot, on the basis of magnetic-susceptibility measurements alone, distinguish between long-range cooperative antiferromagnetic ordering and the short-range ordering of a system of noninteracting spin pairs or clusters. Heat-capacity measurements which could provide additional information have been performed on sputtered *a*-Ge films,³⁶ but were not sufficiently sensitive to detect the anomaly which would result from antiferromagnetic ordering of $\approx 10^{19}$ spins.

Not being able to experimentally distinguish between these two types of systems makes it difficult to derive quantitative information from the measurements. One can, nevertheless, draw several qualitative conclusions about the magnetic moments in *a*-Ge and *a*-Si.

We have seen that, in all of the models, the assumption of a random distribution of exchange energies leads to predictions in disagreement with experiment. We can thus conclude that the magnetic moments in unannealed *a*-Ge and *a*-Si are, for the most part, arranged in clusters throughout the material. These clusters may be as small as a divacancy or as large as a uniform distribution of spins on the surface of a microvoid. It is also clear that unannealed sputtered and evaporated *a*-Ge and *a*-Si contain a fraction of essentially noninteracting spins. These result in the appearance of a low-temperature maxima in χ_S^{-1} . However, these noninteracting spins must comprise a small fraction of the total number of spins in the system.

Figure 12 is a plot of χ_S^{-1} obtained from the crystalline molecular-field theory curve shown in Fig. 11. Here the powder average of χ_S is used and the effect of a Curie component due to a fraction of noninteracting spins is included. Figure 12, while not an exact representation of Southern's theory²⁹ is correct for $T > T_N$ and for $T \leq T_N$ in the limit $T/T_N \rightarrow 0$ and $T/T_N \rightarrow 1$. Here one sees that for a fraction of noninteracting spins, $\eta = 0.1$, there is very little evidence of an upturn in χ_S^{-1} .

In the spin-cluster models a slightly larger fraction ($\eta \approx 0.2$) of noninteracting spins is required to obscure the minima in χ_S^{-1} , but for either model to reproduce the experimental data it is clear that the majority of spins in the system must be interacting.

One can view the primary effect of annealing on sputtered and evaporated *a*-Ge as a shifting downward in energy of the mean of the interaction energy distribution resulting in a reduced T_N and Θ_N . This effect might occur physically from the removal at random of spins from the uniform distribution on microvoid surfaces.

Agarwal⁴ has suggested the temperature-independent linewidth $W = 37$ G of the ESR resonance in evaporated *a*-Ge could be due to dipole-dipole interaction between spins. The observation that W is not changed on annealing, even though the spin density is reduced, is explained by assuming that the spins, thought to lie on void surfaces, are removed as the voids are reduced in such a way as to leave the spin-spin distance unaltered. The observation of the strong annealing dependence of T_N and Θ_N in this paper is inconsistent with this suggestion. Furthermore the fact that $W \approx 4$ G in *a*-Si¹³ and the observation that T_N and Θ_N for *a*-Si are approximately equal to the *a*-Ge values also suggests that the linewidth of the ESR resonances is caused by mechanisms other than dipole-dipole broadening. The same arguments rule out exchange narrowing as the predominant cause of the observed linewidths.

Hydrogen doping and glow discharge preparation reduce N_S in *a*-Ge from the sputtered or evaporated values, but in a manner different from annealing. One sees in Table I that these procedures re-

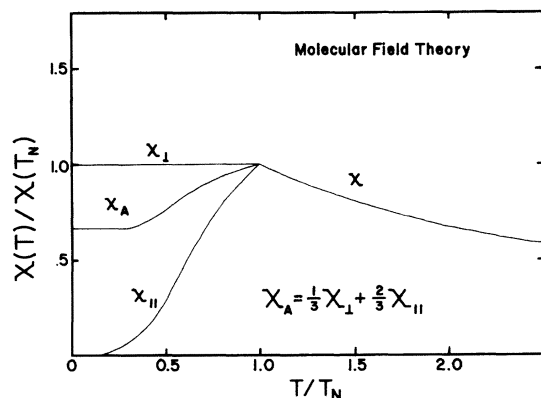


FIG. 11. Magnetic susceptibility as a function of temperature for an antiferromagnetic bcc lattice of $S = \frac{1}{2}$ spins in the absence of next nearest-neighbor interactions. Curve is the prediction of molecular-field theory and is plotted in reduced units. [A. B. Lidiard, Rep. Prog. Phys. 17, 201 (1954).]

sult in material with spin densities appropriate to evaporated *a*-Ge which has been annealed to $T_A > 300$ C but with paramagnetic Néel temperatures Θ_N similar to unannealed sputtered and evaporated *a*-Ge, and with no indication of spin ordering.

The observation that hydrogen doping and annealing affect the magnetic properties of *a*-Ge in such different ways is surprising in light of the work of Lewis *et al.*¹⁶ where it was found that these two procedures change the conductivity and thermopower in essentially the same way. One must conclude that either these properties are insensitive to the details of spin-spin interaction and depend only on N_S , or that the states responsible for the transport phenomena in *a*-Ge are different from those giving rise to magnetic moments. It is also surprising that sputtered and evaporated *a*-Ge should have similar spin systems. Shevchick and Paul³⁷ have concluded from small angle x-ray scattering experiments that evaporated *a*-Ge contains voids up to 30 Å in radius. Sputtered *a*-Ge, on the other hand, contains some voids of no larger than 5 Å, while most of them are of atomic size.

Glow discharge *a*-Si is similar to glow discharge *a*-Ge in that it has a spin density which is smaller than the sputtered material even though Θ_N is approximately the same. In contrast, however, the glow discharge *a*-Si spin system orders at the same T_N as the sputtered material. This difference might be better understood through studies of the effect of deposition parameters, notably substrate temperature, on the magnetic properties of glow discharge *a*-Ge and *a*-Si.

The present work represents the first report of the presence of magnetic moments in *a*-Ge and *a*-Si prepared by the glow discharge technique. During the removal of one of the glow discharge *a*-Ge films from its quartz substrate, explosive

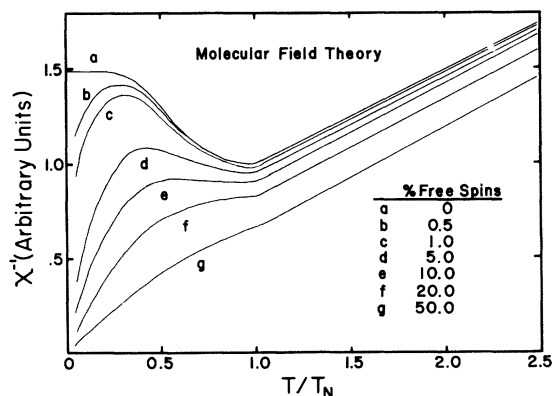


FIG. 12. χ_S^{-1} vs reduced temperature for an anisotropic $S = \frac{1}{2}$ antiferromagnetic system where a fraction of the spins is noninteracting and follows a Curie law.

recrystallization of the film was observed. This phenomena has previously been observed in films of *a*-Ge prepared by evaporation and by sputtering, and is thought to result from the high internal stress observed in these films.³⁸ The internal stress has, in turn, been associated with the presence of voids.³⁹ The observation of the mechanically induced recrystallization coupled with the observation of spins in these glow discharge prepared materials suggests that, under certain preparation conditions, these materials contain voids of mechanical inhomogeneities which may be

similar to those found in their sputtered or evaporated counterparts.

ACKNOWLEDGMENTS

The author wishes to acknowledge useful discussions with Professor P. Horn and Professor M. Kastner. He would also like to thank P. Gaczi for permission to quote results from ESR measurements still in progress. He is especially grateful to his thesis advisor Professor H. Fritzsche for his many helpful suggestions and encouragement throughout all phases of this work.

*Work supported by the U. S. AFOSR, Office of Aerospace Research, under Contract No. AFF44620-71-C-0025. We have also benefited from support of the Materials Research Laboratory by the NSF.

†Submitted in partial fulfillment of the requirements for the Ph.D. in Physics at the University of Chicago.

‡Present address: Dept. of Physics, Bldg. 13-2138, MIT, Cambridge, Mass. 02139.

¹S. Hudgens, *Phys. Rev. B* **7**, 2481 (1973).

²H. Fritzsche and S. Hudgens, *Proceedings of the Sixth International Conference on Amorphous and Liquid Semiconductors* (Nauka, Leningrad, 1975).

³M. H. Brodsky, R. S. Title, K. Weiser, and G. D. Pettit, *Phys. Rev. B* **1**, 2632 (1970).

⁴S. C. Agarwal, *Phys. Rev. B* **7**, 685 (1973).

⁵F. J. DiSalvo, B. G. Bagley, and A. H. Clark, *Bull. Am. Phys. Soc.* **19**, 316 (1974).

⁶A preliminary report was given by S. Hudgens and H. Fritzsche, *Bull. Am. Phys. Soc.* **20**, 392 (1975).

⁷N. F. Mott and E. A. Davis, *Electronic Properties in Noncrystalline Solids* (Clarendon, Oxford, 1971), Chap. 8.

⁸Model 8 DT Super-Vari-Temp liquid He Dewar for Faraday susceptibility measurements manufactured by Janis Research Company.

⁹The origin of the ferromagnetic contamination was traced to stainless steel parts in the electron beam evaporation system. After these parts were covered with a Ta sheet, no further difficulty was encountered.

¹⁰S. Hudgens, M. Kastner, and H. Fritzsche, *Phys. Rev. Lett.* **33**, 1552 (1974).

¹¹S. Luby, *Thin Solid Films* **8**, 333 (1971).

¹²J. R. Pawlik, G. A. N. Connell, and D. Prober, *Proceedings of the Sixth International Conference on Amorphous and Liquid Semiconductors* (Nauka, Leningrad, 1975).

¹³M. H. Brodsky and R. S. Title, *Phys. Rev. Lett.* **23**, 581 (1969).

¹⁴P. G. LeComber, A. Madan, and W. E. Spear, *J. Non-Cryst. Solids* **11**, 219 (1972).

¹⁵A. Triska, D. Dennison, and H. Fritzsche, *Bull. Am. Phys. Soc.* **20**, 392 (1975).

¹⁶A. J. Lewis, G. A. N. Connell, W. Paul, J. R. Pawlik, and A. J. Temkin, *Proceedings of the Conference on Tetrahedrally Bonded Amorphous Semiconductors* (A.I.P., New York, 1974), p. 27.

¹⁷S. K. Bahl and S. M. Bhagat (unpublished).

¹⁸P. G. LeComber, R. J. Loveland, W. E. Spear, and R. A. Vaughan, *Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors*, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974).

¹⁹P. Gaczi (unpublished).

²⁰A. W. Simpson and J. M. Lucas, *Proc. Br. Ceramic Soc.*, **18**, 117 (1970).

²¹T. Egami, O. A. Sacli, A. W. Simpson, A. L. Terry, and F. A. Wedgewood, *J. Phys. C* **5**, L261 (1972).

²²V. Canella and J. A. Mydosh, *Phys. Rev. B* **6**, 4220 (1972).

²³E. Sonder and H. C. Schweinler, *Phys. Rev.* **117**, 1216 (1960).

²⁴J. R. Marko and J. D. Quirt, *Phys. Status Solidi B* **64**, 325 (1974).

²⁵A. B. Lidiard, *Rep. Prog. Phys.* **17**, 201 (1954).

²⁶W. Jung and G. S. Newell, *Phys. Rev.* **18**, 648 (1963).

²⁷J. C. Slater, *Quantum Theory of Molecules and Solids*, (McGraw-Hill, New York, 1963), Vol. 1.

²⁸P. W. Anderson, *Amorphous Magnetism*, edited by H. O. Hooper and A. M. de Graaf (Plenum, London, 1973), p. 1.

²⁹B. Southern, *J. Phys. C* **8**, L213 (1975).

³⁰H. Sato, A. Arrott, and R. Kikuchi, *J. Phys. Chem. Solids* **10**, 19 (1959).

³¹Y. Takagi, *Proc. Phys.-Math. Soc. Jpn.* **23**, 44 (1941).

³²R. Kikuchi, *Phys. Rev.* **81**, 988 (1951).

³³T. A. Kaplan, S. D. Mahanti, and W. Hartmann, *Phys. Rev. Lett.* **27**, 1796 (1971).

³⁴N. F. Mott, *Philos. Mag.* **23**, 935 (1971).

³⁵N. F. Mott, *Adv. Phys.* **21**, 785 (1972).

³⁶C. N. King, W. A. Phillips, and J. P. de Neufville, *Phys. Rev. Lett.* **32**, 538 (1974).

³⁷N. S. Shevchik and W. Paul, *J. Non-Cryst. Solids* **8-10**, 381 (1972).

³⁸M. A. Paesler, *Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors*, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974).

³⁹M. A. Paesler, S. C. Agarwal, S. Hudgens, and H. Fritzsche, *Proceedings of the Conference on Tetrahedrally Bonded Amorphous Semiconductors* (A.I.P., New York, 1974), p. 37.