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Nature of Localized States in Amorphous Semiconductors—A Study by Electron Spin Resonance*†

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The paramagnetic behavior of localized states in amorphous chalcogenide alloys and the tetrahedrally coordinated amorphous germanium has been studied by ESR experiments. No signal has been detected in any of the chalcogenide glasses, prepared by quenching from the melt, with a sensitivity of about 10^{11} spins/G near $g=2$. This enables us to estimate 10^{14} spins/cm^3 as an upper limit to the density of unpaired spins. In some samples a small signal is detectable whose magnitude is $\approx 10^{15}$ spins/cm^3 and depends sensitively on heat treatment. In contrast, and in agreement with Brodsky and Title, thin films of evaporated amorphous germanium (a-Ge) are found to yield a large ESR signal at $g=2.022\pm0.001$, corresponding to a spin density of approximately 10^{20} spins/cm^3. In a-Ge, the temperature dependence of the linewidth indicates that two relaxation mechanisms are operative. For temperatures below $T\approx 200$ K, the width is temperature independent, probably due to spin-spin relaxation. One obtains a spin-spin relaxation time $T_2\approx 10^{-9}$ sec. Above 200 K the linewidth is proportional to $1/T$ in accordance with a direct relaxation process. It is suggested that this direct relaxation process is associated with the high density of low-energy excitations which may be responsible for large linear specific heat in amorphous materials at low temperatures observed by Zeller and Pohl.

I. INTRODUCTION

One feature common to all models so far proposed to understand the nature and properties of amorphous semiconductors is the assumption of the existence of localized gap states.[1] The deeper gap states are expected to be singly occupied because of the Coulomb repulsion between localized electrons. These states should therefore be paramagnetic and observable by electron spin resonance (ESR).

It is convenient to group covalent amorphous semiconductors into two major classes.[2]

(i) The so-called glassy semiconductors, such as the chalcogenide-based compounds (As_2S_3, As_2Se_3, etc.), alloy glasses ($Ge_{16}Te_{82}S_2$, etc.), and elemental semiconductors like selenium, can be obtained in the amorphous bulk form by rapid quenching from the melt. Upon heating, these glasses show a glass transition temperature, which manifests itself by an increase in the specific heat of the glass. At that temperature additional degrees of freedom become available to the system.

(ii) The tetrahedrally coordinated semiconductors, such as Ge and Si, cannot be made amorphous by quenching from the melt, but have to be quenched from vapor phase. Furthermore, they do not show a glass transition prior to crystallization.

Amorphous Ge, Si, and SiC have been found to give large ESR signals (10^{20} spins/cm^3)[3-6] in contrast to the chalcogenide glasses,[4] where a small signal (less than 10^{15} spins/cm^3) was detectable only after a heat treatment. We shall therefore discuss our ESR studies in two separate sections. Section II A deals with glassy semiconductors, and Sec. II B deals with tetrahedrally coordinated semiconductors.

II. RESULTS AND DISCUSSION

A. Glassy Semiconductors

The samples were prepared by rapid quenching from the melt and were kept in bulk form in quartz ampoules. The ampoules were repeatedly flushed with an inert gas before sealing in a residual inert gas pressure of about 10^{-4} Torr. To detect the ESR signal, an X-band microwave spectrometer (operating at ≈ 9 GHz) was used which has a spin detection sensitivity of 10^{11} spins/G.[7] The chalcogenide-glass compositions studied are listed in Table I. None of these showed an ESR signal at room temperature or at 77 K within g value range of 1.5–2.5. Powdering the samples in order to increase their surface to volume ratio, or exposing them to atmosphere, had no effect.

These findings enable us to put an upper limit on the concentration of paramagnetic centers in these materials at 10^{14} spins/cm^3.[8] This upper limit to the density of unpaired localized electrons is considerably smaller than 2×10^{18}/cm^3, the density of localized states in the gap estimated from the optical-absorption data by Tauc *et al.*,[9] in a-As_2S_3 and a-As_2Se_3. One might conclude then that most of these localized states are doubly occupied, and hence not detectable by ESR absorption. However, if there is a continuous density of states at the Fermi level, as in the Mott-CFO[1] model, the materials should show a spin paramagnetism at finite magnetic fields and temperatures even if there are no unpaired electrons at zero field and temperature.[10]

TABLE I. List of the chalcogenide glasses studied for the ESR absorption.

1.	Se
2.	As_2Se_3
3.	As_2S_3
4.	$Se_{92}Te_8$
5.	$Ge_{16}As_{35}Te_{28}S_{21}$
6.	$Ge_7Si_8As_{38}P_2Al_{10}Te_{35}$
7.	$Ge_{15}As_2S_2Te_{81}$
8.	$Ge_{15}Sb_2S_2Te_{81}$
9.	$Ge_{16}Sb_2Te_{82}$
10.	$Ge_{13}As_{25}Te_{62}$
11.	$Ge_{13}As_{27}V_{10}Te_{24}S_{26}$
12.	$(GeTe)_{20}(As_2Te_3)_{80}$
13.	$(GeTe)\ (As_2Te_3)$

It would thus seem that the states near the valence band edge are doubly occupied and the density of states near the Fermi level $g(E_F)$ is less than N_{UL}/kT (or $N_{UL}/\mu B$, whichever is smaller), where $N_{UL}=10^{14}/\text{cm}^3$ is the upper limit to the concentration of spin centers. This gives at room temperature $g(E_F)\leq 4\times 10^{15}\ \text{eV}^{-1}\,\text{cm}^{-3}$. If that is so it should be possible to increase the density of unpaired electrons by disturbing the equilibrium distribution of the electrons by illuminating the sample with strong electron-hole-pair-producing light. Materials 1–9 in Table I were exposed at various temperatures to light from a 500-W mercury lamp during the ESR measurements. This illumination is expected to create a nonequilibrium distribution of unpaired electrons over localized states. No ESR signal could be detected. These electrons should be fairly long lived at low temperatures, as evidenced by the long time constant (several hours) of decay of photoconductivity at 77 K (frozen-in photoconductivity), observed by Fagen and Fritzsche.[11] Further, thinking that a short relaxation time might render the ESR absorption undetectable by broadening the ESR line, we tested some chalcogenides for ESR at 1.5 K. Here again all attempts to detect the ESR signal with or without optical excitation failed.

The limit on the density of states at the Fermi level obtained above is several orders of magnitude smaller than the estimates obtained from ac conductivity data in similar materials.[12] We wish to point out, however, that this is not necessarily a contradiction, since extremely short temperature-independent relaxation times may make it impossible to observe them by ESR. Moreover, there may exist a wide distribution of g values, such that the resonance becomes too broad for detection.

Since mechanically damaged surfaces and structural defects are known in many cases to give rise to ESR absorption, experiments were also done on thin films of chalcogenides 5 and 8 (see Table I) which were prepared by radio-frequency sputtering onto quartz rods. Again no ESR signal was observed. However, since the quantity of material in these thin-film experiments was much less than those on the bulk samples, the upper limit to the density of paramagnetic centers is placed at 10^{17} spins/cm^3 in this case.

Materials 1–3 (Table I) were subjected to several different heat treatments with fast and slow cooling. No effect was observed. However, a small signal could be seen in materials 5–9 (Table I) after a heat treatment (a) which consisted of annealing the sample for a few minutes at temperatures somewhat above the melting point and subsequent quenching in air or water. The spin density after annealing was typically of the order of 10^{15} spins/cm^3. The signal height was found to increase upon increasing the length of annealing but the signal width and the g value remained unchanged. This is illustrated in Fig. 1. Slow cooling after annealing and vibration of the sample during annealing were found to result in a reduction or even a complete loss of the ESR signal. A heat treatment (b) consisting of annealing to 750 °C or higher, a temperature several hundred degrees above the melting temperature, and subsequent quenching in air or water, caused the ESR signal to disappear. This last heat treatment (b) is nearly that experienced by the glassy semiconductors when they were originally prepared, which explains why no signal was detected in the untreated samples. The ESR signal could then be recovered by a subsequent heat treatment (a) slightly above the melting point and cooling without shaking the sample. Sometimes a very broad signal was also observed (about

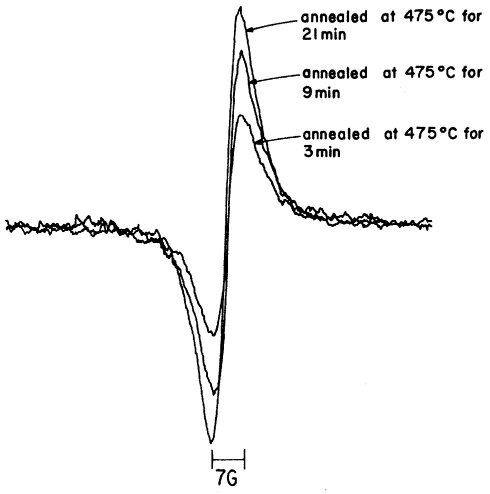

FIG. 1. Effect of annealing on the ESR of a chalcogenide glass, with composition $Ge_{15}Te_{81}S_2Sb_2$. The g value is 2.021 ± 0.001.

1 kG wide). However, the treatment required to observe this very broad signal reproducibly could not be established.

The nonreproducibility of the broad signal and the similarity of the annealing behavior of the narrow signals in different composition chalcogenides suggest that these signals might be associated with some impurities common to all compositions which exhibited these effects. Impurities are likely to play an important role at concentration levels as low as $10^{15}/\text{cm}^3$. The study of ESR in amorphous selenium exemplifies this point. Here a broad and large ESR signal similar to the one described above was found to be due to the presence of some hydrocarbon impurities in the samples.[13] A very small concentration of impurities was sufficient to produce the observed signal. This can be seen from the fact that they were unintentionally introduced into the 99.9999%-pure selenium by merely storing the Se pellets in plastic bottles. Furthermore, Miller and Haneman[14] found that in several of their materials hydrocarbons from the oil of a diffusion vacuum pump gave rise to narrow signals upon annealing. This will be further discussed in Sec. II B, where the ESR absorption in amorphous germanium is described.

Although the question of origin of these ESR signals in the glassy semiconductors is far from settled, we are left with the ineradicable result—the concentration of unpaired spins in the glasses studied is at the most 10^{15} spins/cm^3, irrespective of whether the signals are attributable to localized states in the amorphous chalcogenide itself or to trace impurities.

The latest paramagnetic-susceptibility measurements on amorphous As_2S_3 are in agreement with the above results[15] by setting an upper limit to the density of paramagnetic centers at $2\times10^{16}/\text{cm}^3$.

B. Tetrahedrally Coordinated Semiconductors

Tetrahedrally coordinated amorphous semiconductors like *a*-Ge, *a*-Si, and *a*-SiC have previously been studied by ESR, and were found to contain approximately 10^{20} unpaired spins/cm^3 (see Table II). Their *g* values and the resonance linewidths are similar to those of unpaired electrons on the freshly cleaved surfaces of the respective crystals. Brodsky *et al.*[16] found that in the case of *a*-Si the signal decreases upon annealing.

In the following we present some further work on the behavior of ESR in *a*-Ge as a function of annealing and measuring temperatures.

Amorphous germanium films were prepared either by electron-beam evaporation from a graphite boat or by resistance heating from a tungsten boat in a vacuum of better than 10^{-6} Torr onto a quartz substrate at room temperature. The temperature of the substrate monitored by a thermocouple rose to approximately 50 °C during a typical evaporation. Multiple evaporations were used for thicker films so as to avoid excessive heating of the substrate above this temperature. The films were of thicknesses ranging from a few thousand angstroms to several microns. The evaporation rate, monitored by an oscillating-quartz-crystal microbalance, ranged from 500 to 3000 Å/min. The source-substrate separation was about 20 cm.

Two kinds of substrates were used. In some cases the film was deposited on a 6×6-in. quartz plate. The *a*-Ge film was then removed by scraping with a microscope slide, and collected in quartz ampoules in the form of flakes and powder. The ampoules were then flushed repeatedly with argon gas and sealed off in an argon pressure of about 10^{-4} Torr. In other cases *a*-Ge was deposited directly on quartz rods of suitable size so that the ESR spectra could be taken, without having to remove the film from the substrate. Both methods of preparation gave similar results. The number of spins scaled with the thickness of the film. The amorphous nature of the film was ascertained by taking x-ray-diffraction photographs.

A quartz Dewar with flowing exchange gas was used to make ESR measurements down to 175 K. For measurements at 77 K, sealed quartz tubes holding the samples were directly immersed in liquid nitrogen. The *g* value was determined by comparison with the known value of diphenyl picryl hydrazyl (DPPH). The number of spins was ascertained by comparing the signal with that of a standard 3×10^{-4}%-weak-pitch sample supplied by Varian Associates, which is made by diluting the pitch derived from coal with KCl.[17] The reproducibility of successive insertions of samples into the microwave cavity was found to be good. The accuracy of the "strength measurement" was limited mainly by the difference in the filling factor and dielectric constant of our sample and the standard sample. Thus the relative strengths of the signals after various anneals can be determined rather accurately, although the absolute strength of the signal can be calibrated in terms of spin density only within a factor of 10. The number of spins in freshly prepared samples of *a*-Ge was estimated to be 10^{20} spins/cm^3 in agreement with previous workers.[3-6]

The line shape was found to be very nearly Lorentzian in all cases. Figure 2 shows a comparison of the observed line shape with Lorentzian and Gaussian. The *g* value remained unchanged through the experiment and was found to be 2.022 ± 0.001, which is somewhat larger than the free-electron value of 2.00023.

It has been claimed[18] that *g* values larger than free-electron values imply that the paramagnetic centers are holes rather than electrons. Yafet,[19]

TABLE II. Summary of the ESR results in tetrahedrally coordinated amorphous semiconductors.

Material	Physical form	Preparation method	Density of spins (cm^{-3})	g value	Width (g)	Temp. (K)	Ref.
a-Ge	Film	rf sputtering	10^{20}	2.021 ± 0.001	39	77	a
	Powder	Evaporation	10^{19}	2.021 ± 0.003	83	300	b
	Film	Evaporation	10^{20}	2.022 ± 0.001	37	77	c
	Powder	Evaporation	10^{20}	2.022 ± 0.001	37	77	c
a-Si	Film	Evaporation	3×10^{18}	2.006 ± 0.001	15	77, 293	d
	Film	rf sputtering Evaporation	2×10^{20}	2.0055 ± 0.0005	4.7	300, 77, 4	a, e
	Film	Glow discharge of SiH_4	none				f
a-SiC	Film	rf sputtering	3×10^{20}	2.003 ± 0.001	6	77	a

[a] M. H. Brodsky and R. S. Title, Phys. Rev. Letters 23, 581 (1969).

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however, explains that this contention originates from a rule in spectroscopy where the spin-orbit constant is positive for less than half-filled shells and negative for shells filled more than half. This rule does not hold in general because the wave functions in solids can be quite different from those of atoms. Yafet, for example, quotes cases in crystalline germanium and silicon where a g shift opposite to that expected from the above rule is observed. Thus one cannot infer the sign of the paramagnetic center from the sign of the g shift, unless the tight-binding approximation can be shown to be valid. This is not likely to be the case for amorphous germanium.

Figure 3 shows the strength of the signal as a function of annealing temperature T_A for various temperatures of measurement. The anneals were carried out in steps of 25 °C and were 6 h long each. The resistivity of a-Ge was also monitored by using a sample with molybdenum electrodes, which was prepared along with the ESR sample, and annealed in the same furnace in inert atmosphere. As T_A is raised the room-temperature resistivity increases continuously, in agreement with previous workers.[20] The ESR signal, however, first increases as T_A is raised to 75 °C and then decreases monotonically upon subsequent

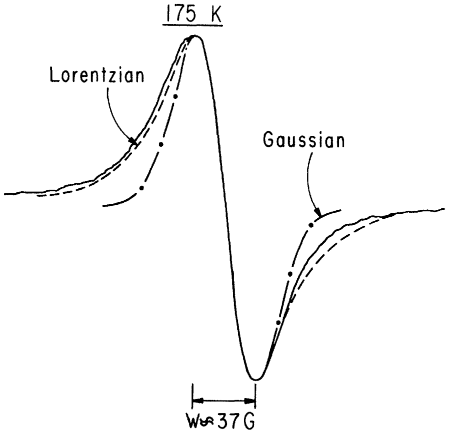

FIG. 2. Comparison of the observed ESR line shape in a-Ge, measured at 175 K, with Lorentzian and Gaussian line shapes.

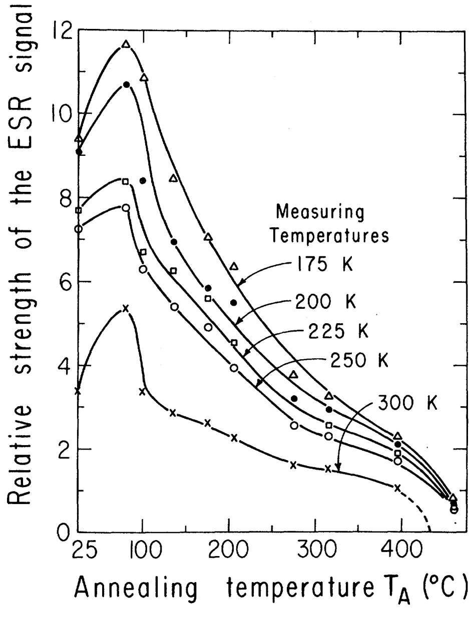

FIG. 3. Effect of annealing on the strength of ESR absorption in a-Ge. Each anneal is 6 h long.

annealing. Such a behavior has previously been observed in amorphous silicon by Brodsky *et al.*[15] and in crushed crystalline silicon by Haneman *et al.*[21]

As the annealing temperature is raised above 400 °C, a new narrower signal begins to appear. This is shown in Fig. 4. The new signal grows as the original signal at $g = 2.022$ gets reduced. After annealing beyond the crystallization temperature of germanium (i.e., greater than 500 °C), the original signal becomes undetectable, and one observes only the new narrow signal of about 1-G width and $g = 2.0027$, independent of the temperature of measurement. This narrow signal disappears when the sample is exposed to air.

It is instructive at this point to compare these findings with the results obtained on crystalline germanium surfaces. Walters and Estle[22] reported an ESR signal from crushed crystalline germanium, which is quite similar in g value and width to the $g = 2.022$ signal observed in amorphous germanium. The latest results of Haneman[23] have confirmed this observation. It is believed that the signal arises from the dangling bonds on the surface of freshly cleaved germanium crystals.[22] Upon annealing the strength of the signal decreases. However, as the annealing temperature is raised to 400 °C and above, one obtains a signal about 1 G wide and $g = 2.0027$, the same as that of the narrow signal in amorphous germanium. This narrow signal rises to a maximum upon annealing near $T_A = 550$ °C and becomes undetectable upon exposure to air. Miller and Haneman[14] showed that not only crushed germanium but also crushed Si, GaAs, GaSb, Pyrex, and quartz all show exactly the same behavior upon annealing, and that this behavior is quite similar to carbonaceous materials. They contend that the signal is not due to crushed germanium but is due to carbon impurities which may come from sources like oil of the diffusion pump in the vacuum system. They were unable to prepare samples which did not show this signal at higher annealing temperatures. Thus, we conclude that whereas the $g = 2.022$ signal may well be a property of amorphous germanium, the narrower signal at $g = 2.0027$, which appears on annealing beyond crystallization, is quite likely caused by carbon impurities.

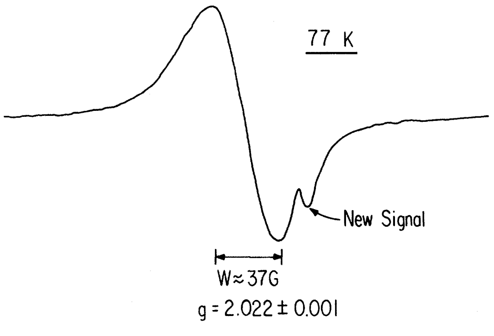

FIG. 4. Appearance of a new ESR signal at $g = 2.0027$ after annealing a-Ge at 420 °C.

In the following we shall confine ourselves to the discussion of the broader $g = 2.022$ signal. The fact that the strength of the signal scales with the thickness of the sample indicates that it arises from the bulk of amorphous germanium. This led Brodsky and Title[3] to postulate a large density of internal voids, thereby giving rise to dangling bonds on the internal surfaces, which show ESR. Moss and Graczyk[24] arrived at the same conclusion from their low-angle electron-diffraction data. The existence of such voids inside the bulk of a-Ge films has now been confirmed by the electron microscopy studies of Donovan and Heinemann.[25] Upon annealing, a reduction in the number of dangling bonds might result in the observed reduction of the ESR signal. Kastner and Fritzsche[26] have shown the internal surfaces to be sensitive to ambient gases, as evidenced by an increase in the electrical conductivity when films of a-Ge are exposed to moisture. Keeping this in view, ESR measurements were made after exposing the a-Ge to moist air. Surprisingly, no change in signal was observed. The moisture can affect the surface either by interacting with the paramagnetic centers on the surface or by altering the surface-charge density, thereby changing the space-charge region near the surface. The effect of 35% relative humidity on amorphous germanium is to increase the conductivity by about 20%. In contrast, an exposure to as high as 100% relative humidity had no detectable effect on the ESR signal. This shows that the resonance might arise from the surface, because if it were due to internal centers, the change in their occupational probability in the space-charge region would result in a change in the ESR absorption.[27] However, in order to establish the surface origin of these centers firmly, one must show that the ESR signal is proportional to the surface area. Since we are assuming the films to contain voids and thereby to have internal surfaces, such an estimate is difficult to make.

The samples were also illuminated, during the ESR measurement, at low temperatures, with a 2000-W high-pressure Xe arc lamp. Again, no change in signal resulted.

The insensitivity of the ESR signal to moisture and its initial increase upon annealing are taken to be an indication that the electrons that contribute to the ESR are not taking part in the electrical conduction, in contrast to the conclusion drawn by Luby.[5]

Now we turn to the study of the relaxation mechanism. The fact that the line shape is Lorentzian tells us that the line broadening is homogeneous; i.e., the line is broadened by processes like spin-lattice interaction, dipole-dipole interaction between like spins, interaction of the spins with the radiation field, etc., rather than hyperfine interactions, or anisotropy of the splitting of spin levels or inhomogeneities in the applied field, etc. The signal did not saturate upon increasing the microwave field. This means that the relaxation times are too short to be measured by this technique.

The temperature dependence of the width W of the signal[28] before and after annealing at $T_A = 400\ ^\circ\mathrm{C}$ is shown in Fig. 5. We find that before annealing the width is proportional to the temperature of measurement down to $T = 200$ K. Below 200 K the width is $W = 37$ G, independent of temperature. We think that the temperature-dependent width is caused by the spin-lattice relaxation time (T_1). Further, $T_1 \propto T^{-1}$ implies that the relaxation occurs through transfer of energy from a single spin to a single excitation mode of the lattice, which has essentially the same frequency as the splitting of the levels. This is known as the *direct process*. This result is quite unexpected because at these "high" temperatures, two phonon processes (i.e., Raman process) are known to dominate. For these the relaxation time is $T_1 \propto T^{-7}$.[29] The fact that $T_1 \propto T^{-1}$ is observed above 200 K might be an indication that there is an abundance of excitation modes of the proper energy, about 10^{-6} eV in our case, far in excess of acoustic phonons. This would cause the direct relaxation process to be more probable than the two-phonon processes. Fritzsche[30] suggested that these excitation modes might be the same as those which give rise to the anomalous specific-heat term which was observed by Zeller and Pohl[31] in all amorphous materials studied so far. This anomalous low-temperature specific-heat term is linear in temperature. Its magnitude, which is about one-quarter of the electronic specific heat of copper, implies a large and constant density of excitation states between zero and about 10^{-4} eV.

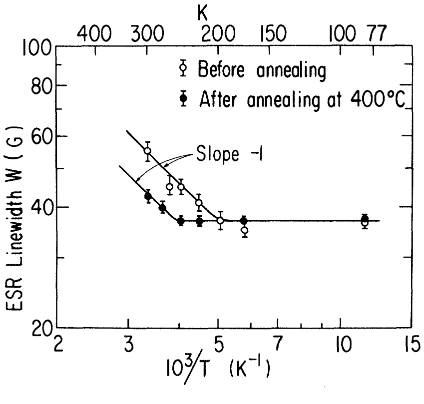

FIG. 5. Temperature dependence of the linewidth in a-Ge, before and after annealing. The lines drawn do not represent the best fit to the data, but are intended to show the slope -1.

Anderson, Halperin, and Varma[32] have proposed a model in which these low-energy excitations arise from tunneling transitions between energetically nearly identical configurational states of the amorphous material. It is then likely that the density of these configurational levels is affected by annealing. This might explain the observed decrease of the temperature-dependent linewidth upon annealing as shown in Fig. 5.

The temperature-independent linewidth might arise owing to dipolar spin-spin interaction. A 37-G-wide line can be explained by assuming the average distance between the spins to be approximately 10 Å. The uncertainty principle yields the spin-spin relaxation time $T_2 \approx 10^{-9}$ sec.

III. CONCLUSIONS

Our experiments have thus shown that the ESR divides the amorphous semiconductors into two distinct classes. The glassy semiconductors, which include the chalcogenide alloys, show very little or no ESR. The tetrahedrally coordinated amorphous semiconductors, like a-Ge and a-Si, show a large spin resonance. Since the resonance in the amorphous germanium and silicon seems to arise from the dangling bonds in the void structure, it is perhaps reasonable to expect that in void-free amorphous materials like the true glasses there is no resonance. This also agrees well with the assumption in the Mott–CFO model that most atoms in these glasses are in sites satisfying their valence requirements, and correspondingly there are few dangling bonds. The lack of signal in glasses, at first sight, also seems to imply that the density of localized states in these materials is very small, which is contrary to the assumption made in the Mott–CFO model and to the optical-absorption data. Further, the upper limit obtained on the density of states at the Fermi level is $4\times10^{15}\ \mathrm{eV}^{-1}\,\mathrm{cm}^{-3}$, which is several orders of magnitude smaller than the estimates obtained from the ac conductivity data in similar materials. However, regions of localization may possibly be large enough to allow double occupancy of these states, thereby making them unobservable by ESR. Furthermore, extremely short temperature-independent relaxation times might be responsible for not observing a signal from the states near the Fermi level. The fact that the illumination of the samples with electron-hole-pair-producing light fails to give rise to an ESR signal casts some doubt on the presence of large densities of double-occupied and unoccupied localized gap states. This, again, is possible if singly occupied states created by shining light have a short enough relaxation time so that they are undetectable by ESR, even at liquid-helium temperatures. Also, even if the relaxation times are long enough, a spread in g values may broaden the resonance and make it unobservable. A good experiment to test this hypothesis would be to measure the Curie paramagnetic contribution to the susceptibility in amorphous materials at low temperature as a function of light intensity which creates a nonequilibrium distribution of electrons over the localized states.

The linewidth in amorphous germanium was found to be proportional to temperature of measurement for $T > 200$ K. One does not expect direct relaxation processes to persist to such high temperatures. It has been suggested that this anomalous behavior may be caused by direct relaxation via excitations which give rise to the observed linear temperature dependence of the specific heat at low temperatures observed in many amorphous materials. The decrease in the temperature-dependent linewidth upon annealing may then simply be due to the change in the density of such excitations by annealing. The linewidth below 200 K is found to be temperature independent and constant with annealing. This may arise from the spin-spin relaxation with $T_2 \approx 10^{-9}$ sec. Since the strength of the signal changes upon annealing, it may seem surprising at first that the temperature-independent width remains unchanged, because it depends on the distance between the spins. This can however be understood if one realizes that upon annealing the voids may coalesce and thus the reduction in strength of signal is due to the reduction in the total internal surface area, although the density of spins per unit area remains the same, thereby leaving the distance between the neighboring spins unchanged.

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[29] Although one cannot rule out other processes, like the Orbach process, we shall confine ourselves to these simple processes, in view of the fact that the data at present are not precise enough to warrant such a detailed analysis.

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