

rent theoretical picture of n textures across the entire B -phase regime of the phase diagram of superfluid ^3He .

Application of these methods to lower temperatures and to flowing superfluid ^3He - B is underway.

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Specific Heat of Amorphous Germanium at Very Low Temperatures

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A specific-heat study of a tetrahedrally bonded amorphous semiconductor at very low temperatures (0.08–2.5 K) is reported. Through an investigation of as-evaporated and annealed amorphous Ge films it can be shown that the contribution by low-energy excitations considered akin to the amorphous state is at least six times smaller than in vitreous silica. The specific heat observed below 1 K is mainly attributed to localized unpaired electronic states (“dangling bonds”) situated in clusters.

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Amorphous solids exhibit a number of interesting low-temperature properties. One of the most prominent features is a roughly linear specific-heat contribution of nonelectronic origin.¹ The underlying excitations are commonly interpreted as two-level systems (TLS) arising from tunneling of atoms or groups of atoms between two nearly degenerate local energy minima.^{2,3} It has been suggested³ that the number of TLS should be much less in tetrahedrally bonded amorphous semiconductors than in, say, vitreous silica because of their rather “closed” structure which might inhibit atomic motion. Hence these materials provide a unique opportunity to test this model.

Previous specific-heat measurements^{4,5} on a -Ge were limited to temperatures above 1 K and could thus give no decisive answer concerning this question. The thermal conductivity κ of a -Ge films⁶ resembles that of other amorphous materials and hence indicates phonon-TLS scatter-

ing.⁶ However, the interpretation is complicated by the presence of boundary scattering in a -Ge films. Very recent measurements of κ down to 50 mK showed a T^3 dependence below 0.2 K while no well-defined T^2 regime indicative of resonant phonon-TLS scattering was found.⁷ From acoustic measurements on a -Si films with use of surface waves⁸ it was concluded that their interaction with TLS is at least 12 times smaller than in a -SiO₂ films. In view of these conflicting results it is highly desirable to directly check the existence of TLS-like excitations in a -Si or a -Ge with specific-heat measurements below 1 K.

Another important motivation for our work comes from the long-standing problem of the spatial distribution of and interactions between localized unpaired electrons (“dangling bonds”) in a -Ge and a -Si. From magnetic susceptibility measurements above 1 K, some evidence for spin interactions⁹ and even spin ordering¹⁰ has been reported, but this is not universally accept-

ed.¹¹ Our results below 1 K provide valuable information as to the presence and type of spin interaction, as well as to the number of spins involved.

In this Letter, we present the first measurements of the specific heat of a tetrahedrally bonded amorphous semiconductor, a -Ge, at very low temperatures. We observe an important contribution to C in addition to the T^3 term. Our results on as-evaporated and annealed films suggest, however, that low-energy excitations contribute only little to the specific heat, with a linear term $a_{\text{TLS}} \lesssim 2 \times 10^{-7}$ J/g K² which is at least 6 times smaller than in vitreous silica. Concerning the second point, the specific heat of a -Ge films indicates the onset of magnetic correlations in exchange-coupled clusters (comprising less than 10% of the total number of spins) at very low temperatures.

The a -Ge films were prepared by electron-beam evaporation of 99.999% Ge from a graphite crucible onto a Si substrate (2×3 cm², 0.02 cm thick) located 25 cm away, at normal incidence at a rate of ≈ 100 Å/s. The base pressure was 2×10^{-7} mbar, rising to 10^{-6} mbar during evaporation. The temperature of the Si substrate was kept below ≈ 100 °C. The samples were checked to be fully amorphous by x-ray diffraction. The

Si substrate with the a -Ge film was glued with a small amount of Apiezon N grease to a Si sample holder with an evaporated Au heater and a doped Si thermometer. The total heat capacity C_T was determined by the standard heat-pulse technique, as described in detail by Albert *et al.*¹² The heat capacities of the sample holder, the Apiezon N grease,¹³ and the Si substrates all were previously determined in separate runs and the specific heat of a -Ge was finally obtained by subtraction. The specific heat of one sample was remeasured after it had been annealed in high vacuum (10^{-6} mbar) at 350 °C for 5 h.

We present our results in Figs. 1 and 2 in the "raw data" form, total heat capacity C_T versus temperature T , in order to facilitate an estimate of the relative contributions of sample and addenda. Above 1.5 K the specific heat of a -Ge exhibits an enhanced T^3 term with respect to crystalline Ge, in quantitative agreement with previous observations^{4,5} although our experimental setup is somewhat imprecise in that temperature region because of the large addenda heat capacity. The main result inferred from Fig. 1 is the large specific-heat contribution below 1 K observed in all our as-evaporated samples. Figure 2 shows that this contribution is strongly reduced upon annealing. It is only near 0.1 K that a sizable

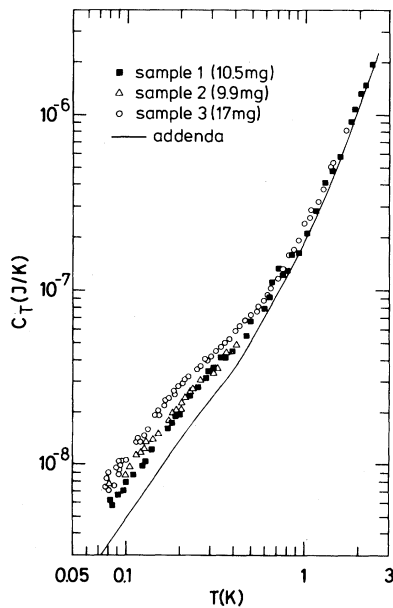


FIG. 1. Heat capacity C_T of three different a -Ge films including addenda as a function of temperature T . The solid line indicates the heat capacity of the addenda.

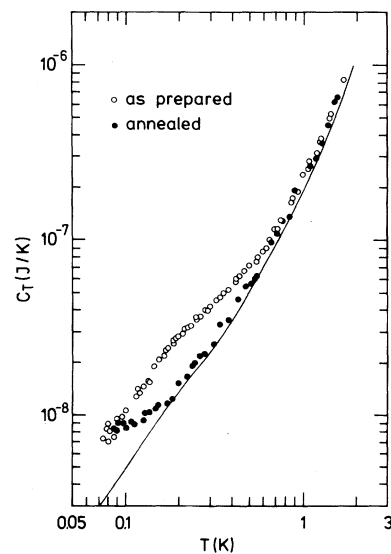


FIG. 2. Heat capacity C_T of a -Ge film (sample 3, before and after annealing) including addenda as a function of temperature T . Annealing was done in high vacuum at 350 °C for 5 h. The solid line indicates the heat capacity of the addenda.

specific heat is observed for the annealed film. Finally Fig. 3 shows the specific heat ΔC of a -Ge with the T^3 contribution^{4,5} subtracted. Between 0.08 and 0.3 K ΔC is proportional to T with a coefficient $a = 3.9 \times 10^{-6}$ J/g K² for samples 2 and 3. Sample 1 has a slightly smaller coefficient, $a = 2.9 \times 10^{-6}$ J/g K² (data not included in Fig. 3 for clarity). At higher temperatures, ΔC levels off and exhibits a shallow maximum near 0.4 K. For the annealed sample ΔC is very much reduced and appears to exhibit a maximum near 0.1 K, although this is near the lower end of our accessible temperature range.

The first important conclusion to be drawn from our data is that the large specific heat in the as-evaporated samples is *not* due to TLS for two reasons: (i) In insulating glasses their number can hardly be affected by heat treatment,¹⁴ (ii) the T dependence of ΔC with a maximum at 0.4 K is quite different from the linear behavior observed up to $T > 1$ K in other glasses. The small specific-heat contribution in the annealed sample above 0.2 K is compatible with a coefficient of the linear term of $a_{\text{TLS}} \approx 2 \times 10^{-7}$ J/g K², i.e., at least 6 times smaller than that in vitreous silica. This supports the original idea³ that TLS are less numerous in "closed" structures such as a -Ge than in vitreous silica, while being compatible with some phonon scattering by these excitations.⁶ It is interesting to note that the above number compares favorably with an estimate of the linear specific heat due to one-atom tunneling sites, based on computer simulations.¹⁵

Hence the major contribution to ΔC in the as-

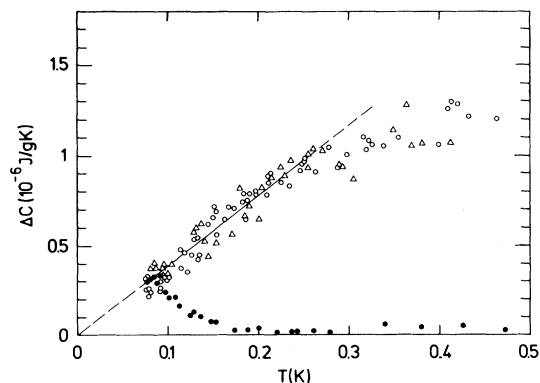


FIG. 3. Specific heat ΔC of a -Ge films (T^3 contribution subtracted) as a function of temperature T . Symbols denoting the samples are the same as in Figs. 1 and 2. The line indicates a linear dependence of ΔC on T .

evaporated films (and also that below 0.2 K in the annealed film) must have another origin than the structurally induced TLS well known from glasses. We suggest that these contributions are of intrinsic magnetic origin. Impurity contributions can be ruled out because of the good vacuum (better than high vacuum) and the high evaporation rate. It is well known that vapor-deposited a -Ge and a -Si films contain unpaired electrons up to a density of $N \approx 10^{19}$ to 10^{20} cm⁻³ as evidenced by electron-spin resonance^{11,16} and susceptibility measurements.^{9,10} Electron-spin resonance measurements performed on our sample 1 are in agreement with these values. As mentioned above, it is unresolved at present (and, in fact, will be partly answered in this Letter) where exactly these spins are located and if they are distributed at random or form clusters. In the former case, only the dipolar interaction between spins or the hyperfine interaction¹⁷ can lift the spin degeneracy. The corresponding energy splittings divided by k_B are less than 1 mK and a few millikelvins, respectively,¹⁷ i.e., at least one order of magnitude below our lowest accessible temperature. We conclude that the observed specific heat is not due to isolated spins but must be attributed to exchange-coupled clusters. The shallow maximum of ΔC at the rather low temperature of 0.4 K suggests that the exchange interaction is quite small, $J/k_B \approx 0.5$ K, in agreement with susceptibility data on a -Ge which can be interpreted with $J/k_B \approx 1$ K (Ref. 9) and also with a study by Thomas *et al.*¹¹ on UHV-evaporated a -Si films for which $J/k_B < 1$ K was found. Our results are in contrast to earlier studies¹⁰ reporting spin ordering as inferred from a susceptibility maximum at temperatures as high as 7.5 K.

From the entropy change associated with the low-temperature specific heat ΔC , we can estimate the number of spins in clusters. For the as-evaporated film we obtain $S = 2.5 \times 10^{-6}$ J/g K and hence $N_s = S/(k_B \ln 2) = 1.4 \times 10^{18}$ cm⁻³ (taking the density as that of crystalline Ge). Taking $N \approx 1 \times 10^{19}$ cm⁻³ as a lower limit for the spin density in a -Ge films^{9,10} evaporated near room temperature, we conclude that less than about 10% of free spins are in clusters while more than 90% are isolated. To our knowledge, this is the first time a definite assessment of the clustering of unpaired spins in a -Ge can be made.

The reduction of the specific heat upon annealing is obviously due to the reduction of the spin density generally observed in annealed a -Ge films.^{14,16} The indication of a maximum of ΔC

at ≈ 0.09 K suggests that ΔC starts to decrease below that temperature. If one assumes the same linear coefficient as for the as-evaporated film, the number of spins in clusters is estimated from the measured entropy to be $N_s = 2.6 \times 10^{17} \text{ cm}^{-3}$ for the annealed film. This reduction by a factor of 5 is somewhat larger than the reduction of the total number of spins after similar heat treatments,^{10,11} indicating that spins in clusters recombine somewhat more easily than isolated spins.

As a final point we want to discuss the linear temperature dependence of ΔC below the maximum. This can be attributed to a superposition of Schottky anomalies with a constant distribution of their energy splittings. Because of the disordered structure a broad distribution of exchange interactions of clusters of localized spins is very plausible. Of course, there will be a natural high-energy cutoff because dangling bonds coming too close will recombine. We believe that this is the origin of the shallow specific-heat maximum. In this picture, annealing could lead to a recombination of free spins slightly further apart, i.e., those which are just stable at room temperature. Hence the maximum of ΔC is shifted to lower temperature in agreement with the experiment.

In conclusion, the specific heat of as-evaporated *a*-Ge below 1 K is largely due to localized unpaired electrons in exchange-coupled clusters demonstrating the importance of spin correlations. The contribution of low-energy excitations generally considered genuine to the amorphous state is considerably smaller than in glasses obtained by quenching from the melt. Our analysis suggests that the number of spins in clusters is a small fraction ($\approx 10\%$) of the total number of free spins. It is hoped that our findings challenge measurements of the magnetic susceptibility of *a*-Ge and *a*-Si films below 1 K in order eventually to observe clustering and possible blocking of clusters¹⁸ by the intracluster dipolar interaction. With the availability of SQUID magnetometry such experiments should be possible.

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