Low-Temperature Heat Capacity of Amorphous Germanium*

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The heat capacity of amorphous germanium, measured between 2 and 30 K using a thermal-relaxation technique, is about 50% greater than that of crystalline germanium, but has a similar temperature dependence. We infer an amorphous phonon density of states at low frequencies given by the TA crystalline density of states, broadened, and with *all* modes reduced in frequency by a factor of 0.84. A re-examination of Raman measurements in amorphous germanium shows them to be consistent with this result.

Extensive studies of the phonon density of states in the oxide glasses[1] have shown a great similarity between the high-frequency modes in the vitreous and crystalline phases of a given material. More recently, Raman[2-4] and tunneling[5] measurements in amorphous silicon and germanium have produced similar results. These latter measurements are of particular importance since considerable progress can be made toward a theoretical understanding of the results by the use of a relatively simple structural model.[6]

In other solids the most marked differences between the amorphous and crystalline vibrational spectra occur at low frequencies. Raman data taken below 200 cm^{-1} in amorphous germanium has been used to suggest that the lowest peak occurs at a greater frequency than the corresponding TA mode in the crystal. However, there are uncertainties in the interpretation of the Raman data, while measurements of the low-temperature heat capacity provide a convenient and direct method for studying this part of the spectrum.[7] In this paper we present measurements of the heat capacity of amorphous germanium between 2 and 30 K, not only to extend the comparison of the spectra to lower frequencies, but also, through a comparison with the Raman absorption spectra in the region of overlap of the measurements, to investigate the weighting function which relates the Raman absorption to the phonon spectrum.

The samples were prepared by sputtering germanium onto a 0.010-in. sapphire substrate. A sputtering rate of 100 Å/min, with an argon pressure of 6 μm (and a base pressure of 10^{-3} μm) was used to deposit a 20-μm film on the room-temperature substrate. Films prepared in this way have both an oxygen and an argon content of approximately 2 at.%. The bulk density is about 10% smaller than the crystalline value, although x-ray diffraction patterns show an average nearest-neighbor separation only 1% larger than in crystalline germanium.

A thermal-relaxation technique, expressly developed for small samples, was used for the specific-heat measurements. The details have been given elsewhere[8]; sample temperature was monitored by a silicon bolometer, and a calibrated germanium thermometer was used to measure the absolute temperature T. The heat capacity of the film and substrate was measured, the germanium was then etched away using an HF/HNO_3 solution, and finally the heat capacity of the substrate was measured separately. This eliminated any uncertainties in the absolute values of the addenda or substrate heat capacity. The ratio of heat capacity of the 13.4-mg germanium film to that of the 153.4-mg substrate varied from 1, at 2 K, to 2 at 20 K. The resulting accuracy is about 5%; a second, lighter, film gave identical results within experimental error, as did a further film with an oxygen content of $\frac{1}{2}\%$. This provides significant evidence that the results are characteristic of pure amorphous germanium.

The results are shown, as C/T^3 against T^2, in Fig. 1, together with published results on crystalline germanium.[9] Before commenting on these results, it is helpful to review the salient features of such a plot.[7] The intercept at $T = 0$ gives a value for the Debye temperature Θ_0, and in the Debye approximation of a parabolic density of vibrational states, C/T^3 is independent of T. Any positive slope to the curve represents a density of states proportional to higher powers of fre-
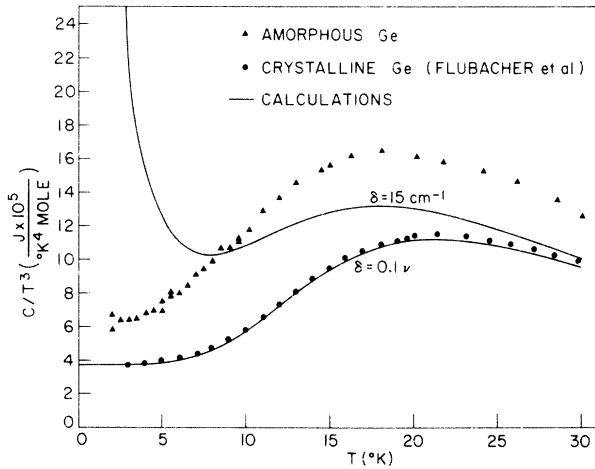
FIG. 1. Heat capacity C of amorphous and crystalline germanium, plotted as C/T^3, as a function of temperature. Solid curves, results of calculations described in the text.

FIG. 2. Effective Debye temperature $\Theta(T)/\Theta_0$, as a function of T/Θ_0.

quency, and a maximum in C/T^3 indicates a marked peak in the phonon spectrum. For example, the maximum at 22 K in crystalline germanium is due to the TA mode peak at about 85 cm^{-1}; a phonon of frequency ω makes a maximum relative contribution to the heat capacity at at a temperature $T \sim \hbar\omega/5k_B$.

From Fig. 1 it is clear that amorphous germanium has a higher heat capacity, although the temperature variation of C/T^3 is similar to that of the crystal. The intercept leads to a Debye temperature of 315 ± 5 K. The corresponding crystalline value is 374 ± 1 K, so that Θ_0 in amorphous germanium is reduced by a factor 0.84 with respect to crystalline germanium. The similarity of the temperature dependences of the two heat capacities is emphasized by replotting the data in terms of the effective Debye temperature $\Theta(T)$, normalized to Θ_0, against T/Θ_0.

Figure 2 illustrates that in both phases the minimum value of $\Theta(T)$ occurs at the same reduced temperature. In spite of the relative insensitivity of the heat capacity to fine detail in the phonon spectrum, this result implies an amorphous density of states closely resembling the (possibly smoothed) crystalline density of states, but with every frequency reduced by 16%. This is surprising: Most calculations of dispersion curves in crystalline germanium[10] indicate that a different combination of forces is important at low and high frequencies.

It is tantalizing that the sensitivity of our technique is not sufficient to give definite informa-
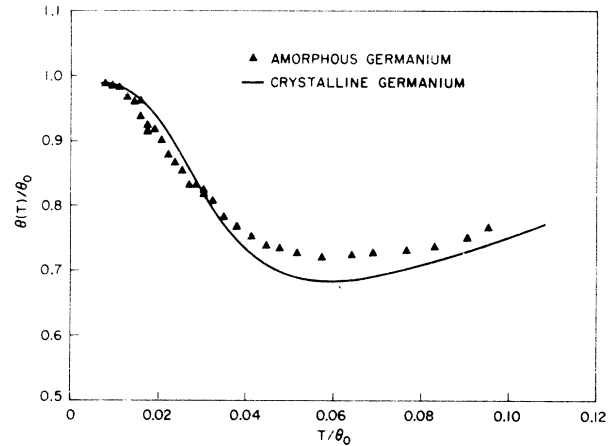
tion on a possible linear temperature dependence of the heat capacity. In other amorphous systems[11] such terms have magnitudes ranging from 1 to 25 μJ/g K: Our results indicate that such a term is less than 1 μJ/g K in amorphous germanium. It has been suggested that this term arises from the relatively "open" structure of many amorphous solids, and would not be expected in germanium.[12]

Raman scattering has given the most information on the phonon spectra of the amorphous elemental semiconductors, since the lack of translational symmetry causes all the modes to be Raman active. Shuker and Gammon[13] derived an expression for the Stokes intensity for first-order scattering:

$$I(\omega) = \sum_b C_b [1 + n(\omega, T)]\omega^{-1}g_b(\omega),$$

where C_b is a coupling constant for phonon branch b, $n(\omega, T)$ is the Bose-Einstein function, and $g_b(\omega)$ is the phonon density of states in branch b. Several authors[2-4] have used this equation to give a reduced Raman spectrum,

$$I_R(\omega) = \omega I(\omega)/[1 + n(\omega, T)],$$

proportional to $Cg(\omega)$. At high frequencies any slowly varying frequency dependence of C is not very important in determining the positions of peaks in the spectrum, and a good picture of the shape (but not the magnitude) of the phonon spectra has been obtained. However, the $I_R(\omega)$ analysis indicates that the lowest-frequency peak is shifted up in frequency relative to the same peak in the crystal, determined by inelastic neutron diffraction.[10] This is in direct contrast to our

results. We believe a consistent picture may be obtained through an examination of the effect of the frequency dependence of the coupling constant C, together with a re-examination of the crystalline phonon spectrum in the light of more recent neutron experiments.[14]

Smith et al.[2] compared their measured $I_R(\omega)$ spectrum with a Gaussian-broadened crystalline density of states and found the peak in $I_R(\omega)$ to be shifted up in frequency with respect to the broadened crystalline density. The lowest-frequency, TA, peak of the broadened spectrum occured at 78 cm^{-1}. However, this crystalline density of states, due to Dolling and Cowley,[10] was derived by fitting a shell model to dispersion curves obtained from neutron-diffraction experiments so that the results do depend to some extent on the validity of the model. Recently Nelin and Nilsson[14] have derived a phonon spectrum in germanium by direct interpolation between 500 measured frequencies within the irreducible volume of the first Brillouin zone. The direct interpolation leads to a greater density of states at higher frequencies within the TA branch, leading to significantly better agreement with the low-temperature heat capacity. By performing numerical calculations on Nelin and Nilsson's data we find a peak in the Gaussian-broadened spectrum at 85 cm^{-1} instead of 78 cm^{-1}.

The results of the previous analysis of the Raman data are further modified when the frequency dependence of the coupling constant C is included. Lannin[4,15] has recently found experimental evidence that C is proportional to ω^2 for low frequencies, so that it is $I_R(\omega)/\omega^2$ that is proportional to $g(\omega)$ rather than $I_R(\omega)$. An additional complication of the Raman data is the possible presence of background scattering intensities for small frequency shifts. It appears that Lannin has taken the most care in this region and so his results will be used for a comparison, although the conclusions are valid for the other data. The first peak in Lannin's[4] $I_R(\omega)$ spectrum occurs at 90 cm^{-1} as compared to 85 cm^{-1} in the broadened crystalline spectrum. However, the peak in $I_R(\omega)/\omega^2$ occurs at 75 cm^{-1} which represents a downward shift of 12%. This shift is in the right direction and of the correct magnitude to be in qualitative agreement with the specific-heat results.

Tunneling data[5] are liable to the same type of ambiguity that complicates the interpretation of Raman scattering, but are certainly consistent with the results presented here.

It has been suggested[3] that the changes in frequency of the amorphous spectra are associated with the changes in density through the Grüneisen constant γ. Clearly the numbers are appealing: A 16% change in Θ_0, together with a density change of 10%, implies the reasonable value of 1.6 for γ. However, the Grüneisen constant for the TA mode in crystalline germanium is known to vary from 0.75 for $\vec{q} = 0$ to -0.4 at the zone boundary,[10] certainly inconsistent with the observation that both Θ_0 and the position of the minimum are lower in frequency in the amorphous state.

It is possible that a smearing or broadening of the crystalline density of states could lead to changes in the measured heat capacity. An amorphous density of states $g_a(v)$ was calculated numerically using the crystalline form $g_c(v)$ from Ref. 14 together with a Gaussian weighting function in the form

$$g_a(v) = \frac{1}{(2\pi)^{1/2}\delta} \int_0^\infty g_c(v') \exp\left[-\frac{(v-v')^2}{2\delta^2}\right] dv'.$$

The parameter δ governs the width of the Gaussian, and was initially chosen to be independent of frequency. The resulting heat capacity could then be calculated using $g_a(v)$. For $\delta = 15$ cm^{-1} it was indeed found that the peak in C/T^3 was shifted by the observed amount, but the broadening also introduced a linear temperature-dependence term, which leads to the low-temperature divergence shown in Fig. 1. This additional term is certainly not present in the experimental results, and arises from the unphysical assumption of a frequency-independent δ. In the long-wavelength limit the broadening, which is due to local variations in bond angle or length,[6] should tend to zero as the phonon "averages" over larger regions of the solid.

A second calculation, using $\delta = 0.1v$, was performed to investigate the effect of a more realistic broadening. The precise numerical value is not very important, but was chosen to agree with the value deduced from the Raman data at higher frequencies. As shown in Fig. 1 this leads to C proportional to T^3 at low temperatures in agreement with the experimental data. However, this type of broadening does not lead to a larger value of C/T^3 at zero temperature nor a shift in the position of the peak of the curve. Therefore it appears that the differences in the low-frequency part of the phonon spectrum of amorphous and crystalline germanium are not due solely to broadening effects.

The calculation presented in Ref. 6 shows that translational symmetry is not required to obtain well-defined peaks in the vibrational density of states. Of necessity, a simplified potential was used for the elastic energy, involving only bond-stretching and bond-bending force constants. The density of states generated by this potential is separated into four branches, corresponding to the TA, LA, LO, and TO modes in the crystal, even in the presence of topological disorder. Of these branches, only the position of the TA peak is very sensitive to the magnitude of the bond-bending force constant. A decrease in this force constant would therefore reduce the frequency of the lowest-energy modes, while leaving the others almost unchanged, in agreement with observation. Unfortunately it is not easy to see why topological disorder should affect the bond-bending forces.

In summary, measurements of the low-temperature heat capacity have confirmed the general similarity between the vibrational spectrum of amorphous and crystalline germanium, although Θ_0 and the first peak occur at a slightly lower frequency in the amorphous phase. It is clear from the small size of the effect that a convincing explanation will require a detailed consideration of all possible differences between the amorphous and crystalline phases. These results also provide some additional evidence that the photon-phonon coupling constant is proportional to the square of the frequency in amorphous solids.

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