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INELASTIC NEUTRON SCATTERING FROM AMORPHOUS GERMANIUM*

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ABSTRACT

Inelastic neutron scattering has been used to study vibrational spectra of amorphous germanium. For large momentum transfers, i.e. several times that of the first maximum in the amorphous x-ray scattering pattern, neutron energy loss spectra should become insensitive to further changes in momentum transfer and are then simply related to the vibrational density of states. This incoherent limit neutron scattering method in principle avoids the matrix element uncertainties which enter interpretations of infrared absorption and Raman scattering experiments. Preliminary results, obtained with a 5 gram sample of evaporated amorphous germanium, indicate that the lowest energy peak in the density of states is broadened, and its center of gravity is shifted to somewhat lower energy than the corresponding TA phonon peak in the crystalline density of states.

Ge and Si are attractive candidates for the study of vibrational excitations in the amorphous state. Both possess reasonably simple structures and the vibrational excitations (phonons) in the respective crystalline phases have been extensively studied and are reasonably well understood.¹ Of the various possible characteristics of the vibrational properties of a nearly harmonic solid, perhaps the most useful is the vibrational density of states function $g(\omega) = 1/3N \sum_{\lambda} \delta(\omega - \omega_{\lambda})$, where ω_{λ} is the vibrational eigenfrequency of the λ 'th normal mode of the solid. Infrared,^{2,3} Raman^{2,3} and electron tunneling spectroscopy⁴ have been used to derive effective densities of states

$$g_{\alpha}(\omega) = \frac{1}{N} \sum_{\lambda} |\alpha_{\lambda}|^2 \delta(\omega - \omega_{\lambda}) \quad (1)$$

for amorphous Group IV semiconductors. The behavior of the matrix elements α_{λ} appropriate to the particular experiment are calculable⁵ but are model dependent. It is therefore desirable to have a reliable measurement of $g(\omega)$ upon which to test various model assumptions, with the hope of then understanding the distortions that matrix elements have on the spectroscopic measurements discussed above.

The measurement of the inelastic scattering spectrum of a one-component amorphous harmonic solid also yields an effective density of states of the form of Eq. (1) with

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$$\alpha_{\lambda} = \sum_{\mathbf{k}} (\vec{Q} \cdot \vec{\xi}_{\mathbf{k}}(\lambda)) e^{-i\vec{Q} \cdot \vec{r}_{\mathbf{k}}} e^{-W_{\mathbf{k}}(Q)} \quad (2)$$

where $\vec{Q} = \vec{k}_f - \vec{k}_i$ is the transferred momentum and $\vec{\xi}_{\mathbf{k}}$, $\vec{r}_{\mathbf{k}}$ and $W_{\mathbf{k}}$ are respectively the vibrational eigenvector (suitably normalized), equilibrium position, and Debye-Waller factor of the $\mathbf{k}$ 'th atom. At large Q coherent processes are unimportant and Eq. (1) reduces to

$$g'(\omega) = Q^2 e^{-2W} \frac{1}{3N} \sum_{\lambda} \delta(\omega - \omega_{\lambda}) \quad (3)$$

Thus, in contrast to other spectroscopic methods discussed, inelastic neutron scattering at fixed and large values of Q measures directly the vibrational density of states. One difficulty that arises is that in arriving at Eq. (3) scattering processes involving more than a single vibrational quantum (multi-"phonon" processes) have been neglected. This is increasingly difficult to justify as Q becomes large. Thus in a given experiment one must try to select a value of Q large enough that the scattering is largely incoherent but at the same time small enough to insure that the "multiphonon" scattering is acceptably small.

We report here some preliminary results of inelastic neutron scattering experiments on amorphous Ge carried out at the Brookhaven AFR reactor using a triple-axis spectrometer. Amorphous Ge for neutron scattering measurements was prepared by evaporation of 99.999% polycrystalline Ge from a resistance heated, boron nitride crucible (2cm diam., 2.5cm deep) onto water cooled, glass substrates ($\sim 100^\circ\text{C}$) in an oil diffusion pumped vacuum system ($P=10^{-5}$ - 10^{-6} Torr during evaporation). A total of 5.3g of amorphous germanium was collected from 14 different evaporations; evaporation times were from 2 to 7 hr. Some evaporations employed a 225cm² substrate, 25cm from the crucible; others used a 530cm² substrate 32cm from the crucible. The source temperature was adjusted to give 5A/sec evaporation rates. Final film thicknesses were between 4 and 13 μm . The films were removed from glass substrates by scraping, under distilled H₂O, and the scrapings were washed in acetone and were dried by storage at 10^{-6} Torr for 24 hr. Scrapings from each evaporation were checked for crystallinity by large-angle x-ray scattering before being mixed together. More quantitative x-ray measurements on a representative sample produced a reduced interference function nearly identical to that reported by Temkin et al.⁶ for sputtered amorphous Ge films.

The room temperature inelastic neutron scattering spectrum was obtained by constant " Q " scans with a fixed final energy, $E_f=41\text{meV}$. The data were taken in 1meV intervals with counting times ~ 2 hrs per point. The measurements were restricted to energy transfer $< 20\text{meV}$ because of intensity limitations. The results are shown in Fig. 1. The results were put on an absolute basis by scaling the experimental $g(\omega)$ to give the experimental heat capacity⁷ at $T=30^\circ\text{K}$. At this temperature modes with energies $< 10\text{meV}$ are most heavily weighted. Another independent normalization based upon a comparison with the elastic neutron scattering intensity gave a scale factor higher by ~ 1.5 . We believe the difference between the two scaling methods gives

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Fig. 1. Comparison of density of vibration states of crystalline and amorphous Ge at room temperature. Vertical error bars represent the combined effect of counting statistics and background subtraction. Horizontal error bars represent approximate energy resolution. The solid curve is the Nelin-Nilsson density of states for crystalline Ge (Ref. 1) convoluted with a smoothing function of ~ 2 meV width to simulate the effect of instrumental resolution.

some indication of the importance of multiphonon contributions. At the value of Q we chose, $7.2 \text{ \AA}^{-1}$, we estimate that about 23% of the inelastic scattering is "multiphonon," but extra high frequency contributions to the scattering cause a disproportionately large error in the density of states. The data, being preliminary, have not been corrected for this effect. At $Q=7.2 \text{ \AA}^{-1}$ the total scattering as measured by x-rays⁶ differs by $\sim 20\%$ from the incoherent limit, but this may be of minor importance for the inelastic scattering.

Included for comparison in Fig. 1 are data taken under similar conditions for polycrystalline Ge at room temperature, normalized in the same way to the crystalline heat capacity. Finally we include a "theoretical" density of states for crystalline Ge at 80°K, which was obtained from the experimental density of states of Nelin and Nilsson¹ by convoluting with a smoothing function of ~ 2 meV width to simulate the effect of instrumental resolution. The principal features of the TA peak, including a vestige of the shoulder at ~ 14 meV show up clearly in our experimental data for polycrystalline material. The only serious disagreement is the failure to achieve the low pre-

dicted minimum at ~ 18 meV. Discrepancies of this sort are characteristic of most comparisons of theoretical densities of states with those determined by incoherent neutron scattering.

Our data show a definite "TA-like" peak in amorphous Ge but somewhat broadened and with a center of gravity shifted to lower energies as compared with crystalline Ge. The subsequent minimum is also shifted to lower energy and is much less pronounced. One measure of this shift in weight to low frequencies in amorphous Ge is that whereas the Nelin and Nilsson $g(\omega)$ has $\sim 36\%$ of its weight below 20 meV, the corresponding fraction for amorphous Ge from Fig. 1 is 46%.

To carry these measurements to higher energies requires additional intensity. More intensity could be obtained by relaxing the momentum resolution of the spectrometer. This also has the beneficial effect of averaging over a larger sample of Fourier components of the vibrational spectrum, assuring a result closer to the true density of states. Unfortunately, it is impossible to relax the momentum resolution of a triple-axis spectrometer without simultaneously broadening the energy resolution to an unacceptable level. This type of independent control of energy and momentum resolution is much better accomplished with a multidetector time-of-flight spectrometer. We are presently collaborating with H. A. Mook of Oak Ridge National Laboratory on further experiments using such a spectrometer system.⁸ Based upon preliminary experiments it appears that it will be possible to measure the entire density of states of amorphous Ge with accuracy comparable to the present measurements a preparation for such experiments are under way. Further experiments to elucidate the Q-dependence of $S(Q, \omega)$ are also clearly of interest⁵ and would appear feasible given a modest (~ 5 fold) increase in sample size.

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