

Dynamical Structure Factor of Amorphous Germanium

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(Received 27 January 1986)

The dynamical structure factor of highly ordered and disordered states of amorphous Ge has been obtained from inelastic-neutron-scattering measurements. The results indicate significant changes in the phonon density of states, due to bond-angle-distribution variations. The modified structure factor, $G(Q, E)$, indicates damped oscillatory behavior that is in very good agreement with the bond-coherency model of Weaire and Alben. Low- Q deviations suggest coherency effects beyond first neighbors.

PACS numbers: 63.50.+x, 61.40.+b, 63.10.+a

Measurements of the dynamic structure factor $S(Q, E)$ provide basic information about the vibrational excitations of noncrystalline condensed matter; here E is the vibrational excitation energy and Q the neutron momentum transfer. In principle, dynamical correlations related to the structure and its vibrational eigenvectors are obtainable. In addition, the phonon density of states, $G(E)$, may be obtained under appropriate conditions of Q averaging in elemental systems. In amorphous solids previous $G(E)$ studies have been essentially confined to the study of averages over lower- Q , coherent-scattering conditions to obtain approximate densities of states, or to neutron-weighted partial densities of states for binary systems. It has been observed¹ that in bulk amorphous (*a*-)As at low Q , and more recently² over a wide Q range in *a*-SiO₂, coherency effects result in oscillations in $S(Q, E)$. A detailed theory for such oscillations has not been developed for the systems studied. For amorphous tetrahedral systems Weaire and Alben have suggested^{3,4} a simple analytic form for oscillations in the modified dynamical structure factor $G(Q, E)$ for the major low- and high-energy bands in the phonon spectrum. Their results suggest nearest-neighbor, bond-coherency oscillations.

In the present study $S(Q, E)$ is obtained for the important tetrahedral amorphous semiconductor Ge. In contrast to bulk glasses, the two independent Raman-scattering components in *a*-Si, *a*-Ge^{5,6} and other thin-film elemental amorphous solids⁷ are quite sensitive to variations in the conditions of formation or subsequent annealing.⁸ This has suggested that the phonon states are a valuable probe of modifications of intrinsic structural order of the noncrystalline network. In the case of *a*-Ge and *a*-Si the primary order parameter is the short-range, bond-angle distribution. Correlations observed between changes in the Raman spectra and the optical gap in *a*-Ge and *a*-Si suggest that both the

phonons and electrons in these systems are sensitive to short-range order variations.⁶

Although the Raman-scattering spectra of amorphous solids may be related under appropriate conditions to the approximate *form* of the density of states, important frequency-dependent coupling parameters, also common to infrared absorption and inelastic tunneling, exist. Neutron-scattering determinations of the phonon density of states are thus of basic interest in addressing the role of variable structural order. To this end two forms of *a*-Ge chosen to have a wide variation in structural order were prepared in large quantities for inelastic-neutron measurements. The results provide appropriately Q -averaged densities of states which indicate that significant changes occur with structural order. In addition, the form of $G(Q, E)$ is compared to the bond-coherency model of Weaire and Alben. Excellent agreement is obtained with this model, except at low Q values where correlation effects that extend beyond nearest neighbors are suggested to become important.

Two forms of *a*-Ge were prepared by sputtering so as to form samples with maximal degrees of intrinsic structural order and structural disorder, respectively. Depolarized Raman-scattering measurements were employed to determine this degree of order based on the high-energy phonon band width.⁶ At various stages of the deposition process Raman measurements confirmed that the thick-film nature and high deposition rates did not affect the homogeneity of *a*-Ge. The more ordered sample of 40 g was prepared by high-rate, triode magnetron sputtering from a 2¼-in. Ge target onto Al foil substrates at a temperature of 150°C. The disordered sample of 30 g was prepared by rf diode sputtering from a 5-in. target onto Al substrates at ~10°C. Sets of six films < 25 μm in thickness were prepared in each run. These were removed from the Al by dilute HCl. Pulsed neutron

measurements were performed at 15 K on the LRMECS time-of-flight instrument at the Argonne National Laboratory Intense Pulsed Neutron Source under incident energies of 56 meV. Instrumental resolution corresponded to $\sim 8\%$ of this value. Energy transfers from 6 to 44 meV and Q values up to $\sim 8 \text{ \AA}^{-1}$ were accessible. Multiple-phonon processes and other background and multiple-scattering contributions were subtracted to obtain $S(Q, E)$. Further discussion of the data analysis has been presented elsewhere.⁹

The modified dynamical structure factor $G(Q, E)$ may be used to study correlation effects as well as to obtain the phonon densities of states after appropriate Q averaging. $G(Q, E)$ is related to $S(Q, E)$ through the relation

$$G(Q, E) = S(Q, E) \{E/[n(E, T) + 1]\} \\ \times (2m/\hbar^2 Q^2) \exp(2\bar{W}),$$

where $n(E) + 1$ is the phonon population factor, \bar{W} the average Debye-Waller factor which is assumed independent of Q , and m the atomic mass. Figure 1 indicates the form of $G(E) = \langle G(Q, E) \rangle$ obtained after averaging over periods of $\Delta Q = 2\pi/r_1$, where r_1 is the first-neighbor distance. This average was performed at large values of Q between 4 and 7 \AA^{-1} as this yields an improved estimate of the density of states due to damping of coherency effects in $G(Q, E)$, noted in Fig. 2. The resulting neutron $G(E)$ spectra shown in Fig. 1 indicate three regions with the lowest and highest bands designated as "TA" and "TO" for correspondence with the crystalline Ge peaks in $G(E)$.¹⁰ The equality of the areas of the two spectra to within 2% supports the detailed analysis and the resulting $G(E)$ values. Although the two densities of states are similar, they clearly exhibit distinct differences, particularly for the TO band which has a more intense, narrower peak for the more ordered sample. This behavior parallels the results of theoretical $G(E)$ calculations,^{4, 11, 12} as well as trends in the Raman scattering

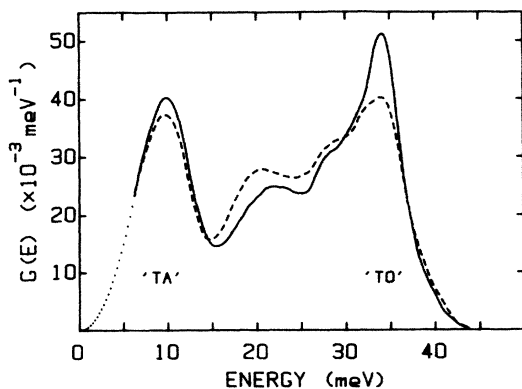


FIG. 1. $G(E)$ for highly ordered (solid line) and disordered (dashed line) a -Ge.

spectra.⁶ This confirms that changes in the latter involve variations in the phonon density of states as well as in Raman coupling parameters. At low energies the TA band also exhibits a small, but clearly resolved difference between variably ordered samples of a -Ge. These changes in the TO and TA band intensities and TO width, as well as the relatively small variations at intermediate energies, are qualitatively consistent with the trends observed in theoretical densities of states of a -Ge and a -Si as the tetrahedral bond-angle distribution $P(\theta)$ is increased in width. For the two a -Ge samples studied here the effective Gaussian bond-angle deviation is estimated^{6, 13} to change from approximately 9° to 11° , i.e., and $\sim 20\%$ variation.

At low energies $E < 6$ meV the $G(E)$ spectra of Fig. 1 have been extrapolated to $E = 0$ by a Debye-like form, $G(E) = AE^2$. Low-temperature specific-heat studies¹⁴ in a -Ge which indicate a T^3 variation, as well as low-frequency Raman spectra¹⁵ in a -Ge and a -Si, suggest Debye-like behavior in this energy range. The value of the constant A in Fig. 1 agrees with that obtained from specific-heat measurements¹⁶ on a -Ge prepared by evaporation onto a 300-K substrate, while sputtered a -Ge yields¹⁴ a factor of 2 smaller value. Clearly further specific-heat and lower-energy neutron measurements are required to determine possible variations with structural order. Broadening effects due to finite neutron resolution result in some increase in the value of A that also require further study.

Weaire and Alben have studied $G(Q, E)$ for quasicrystalline models of Ge and Si.^{3, 4} They have as well obtained simple analytic expressions for the Q dependence of the TA and TO peaks in a -Ge and a -Si. The theory assumes local tetrahedral order and correlated motions of first neighbors only. A comparison with their theoretical results for the ratio $G(Q, E_{TO})/G(Q, E_{TA})$

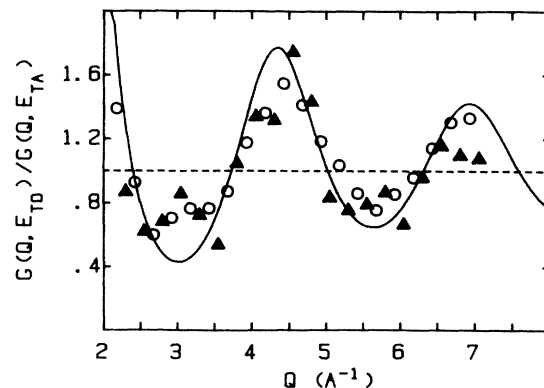


FIG. 2. $G(Q, E_{TO})/G(Q, E_{TA})$ comparison between theory (dashed line) and experiment in highly ordered (circles), and highly disordered (triangles) a -Ge. The results are normalized to oscillate about the high- Q density-of-states value indicated by the horizontal line.

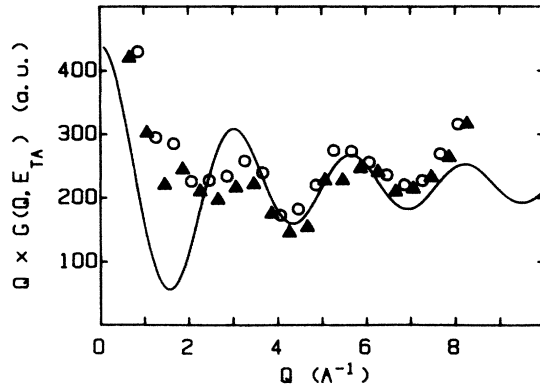


FIG. 3. $QG(Q, E_{TA})$, comparison of theory (line) and experiment for highly ordered (circles) and highly disordered (triangles) a -Ge.

E_{TA}) is shown in Fig. 2 for the two a -Ge samples. The values of $G(Q, E)$ at energies $E_{TA} = 9.5$ meV and $E_{TO} = 34.5$ meV were obtained by appropriate averaging over 1-meV intervals to reduce statistical noise. Both the experimental and theoretical ratios, oscillate about the very high Q value appropriate for $G(E)$ in the incoherent-atom approximation. The theoretical result is a damped trigonometric function dependent only on the product Qr_1 . It is predicted to be essentially independent of sample as r_1 has been found to have a very narrow thermally broadened, crystal-like distribution in a -Ge films. As Fig. 2 indicates, good general agreement is obtained between theory and the experimental data for highly ordered and disordered a -Ge, thus confirming the bond-coherency model. This model indicates that the incoherent-atom approximation is not satisfactory for obtaining $G(E)$ unless very high Q , $\geq 13 \text{ \AA}^{-1}$, are employed. A comparison of the results of the two samples in Fig. 2 does indicate some differences in $G(Q, E_{TO})/G(Q, E_{TA})$ not predicted by theory. Further measurements at higher Q and with improved statistics are necessary to resolve the sample order dependence of this ratio.

Although good agreement is observed in Fig. 2 for $Q \geq 2 \text{ \AA}^{-1}$, an analysis of the variation of $G(Q, E_{TA})$ indicates less satisfactory agreement with the analytic results at low Q values. This is shown in Fig. 3 where the theoretical results have been normalized in intensity to yield the best agreement with the two a -Ge values. The experimental data indicate the absence of a distinct minimum at $Q = 1.6 \text{ \AA}^{-1}$ predicted by theory. The experimental results also exhibit smaller amplitude than the theoretical oscillations of $G(Q, E_{TA})$. The differences between experiment and theory at low Q for the TA band are most logically a consequence of neglect of vibrational correlations beyond first neighbors for the phonon eigenvectors.

As the TA band is known to be primarily dependent of a bond-bending force constant, it is reasonable that second-neighbor correlation effects are significant at low Q values.

In conclusion, $S(Q, E)$ measurements have been employed to obtain both the density of states and its variation with structural order in a -Ge. The results confirm earlier suggestions that changes in $G(E)$ and in the Raman-scattering spectra are due to short-range bond-angle variations. The present $G(E)$ spectra now provide a means of obtaining the energy dependence of the Raman coupling parameters in a -Ge.¹⁷ Variations in $G(Q, E)$ confirm the general bond-coherency model of Weaire and Alben, although correlation effects beyond first neighbors are suggested to occur at lower Q values.

This work was supported at The Pennsylvania State University by National Science Foundation Grant No. DMR 8402894.

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