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Raman coupling-parameter variation in amorphous germanium

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Inelastic neutron and Raman scattering measurements on amorphous Ge are combined to obtain the frequency variation of the depolarized and fully polarized Raman coupling parameters, $C^\alpha(\omega)$. These measurements were obtained on two forms of a-Ge chosen so as to maximize differences in the degrees of local short-range order. For both highly ordered and highly disordered forms of a-Ge the variation of $C^\alpha(\omega)$ is found to be qualitatively similar in overall form, although quantitative differences exist, particularly at low frequencies. The results provide a means of determining the phonon density of states of other forms of a-Ge thin films for which neutron measurements are not feasible. Qualitatively similar variations in $C^\alpha(\omega)$ for a-Si are also predicted.

INTRODUCTION

Dynamical probes of amorphous solids provide basic information on the vibrational excitations and the role of interatomic interactions. In addition, these methods provide a means of ascertaining changes in the local structural order with nonequilibrium conditions.[1–4] The simplest dynamical quantity, the phonon density of states, is often difficult to obtain experimentally. This is in part due to sample size constraints on inelastic neutron measurements on amorphous films as well as conditions of neutron momentum transfer. Raman scattering, as well as infrared absorption and inelastic tunneling spectroscopy, often provides a simpler means of probing spectral response functions that are related to the phonon density of states.

Phenomenologically these response functions are related to the density of states by frequency-dependent coupling parameters that are, in general, not known. Under appropriate conditions changes in the form of a spectral response function may be related to approximate changes in the phonon density of states. The extent to which this is the case has not, however, been determined experimentally.

Limited work to date has been performed to determine the frequency variation of the Raman and other spectral response coupling parameters. Low-frequency measurements in a-Si (Ref. 5) and a-Ge (Ref. 6) have shown that the two independent Raman coupling parameters, $C^\alpha(\omega)$, vary approximately as ω^2 in the Debye-like regime. Theoretical analysis[7] and experimental studies of a-GeS$_2$ (Ref. 8) in this often inaccessible regime indicate that this behavior is an approximation to the more general form of the coupling parameter given by

$$C(\omega)=A\omega^2[B\exp(-a\omega^2)+C\exp(-b\omega^2)] , \qquad (1)$$

where A, B, C, a, and b are constants that depend on the longitudinal and transverse velocities of sound and various correlation lengths in the material. Beyond this regime the Raman and infrared coupling-parameter variation has only been experimentally obtained for bulk a-Se.[9] Here, clear changes occur in the form of $C^\alpha(\omega)$, particularly between the high-frequency opticlike band and lower-frequency bands. For bulk a-As inelastic neutron scattering measurements[10] indicate a less rapid variation of $C^\alpha(\omega)$ for the lowest peak in the acousticlike band in the density of states.[11] Similar results are suggested from specific-heat[12] and limited inelastic neutron scattering measurements in a-Ge (Ref. 13) at low frequencies.

In the present study the two independent Raman coupling parameters were obtained on two forms of a-Ge that were chosen to have large differences in short-range, bond-angle disorder.[2] Significant changes have been predicted in the phonon density of states due to these differences[2] and have recently been confirmed by neutron studies in a-Ge.[14] Of importance to such studies of variable local order is the extent to which the coupling parameter is itself a constant or a function of local order.

EXPERIMENT

Two forms of a-Ge were deposited by dc and rf sputtering at Ar pressures of 5 and 7 mTorr, respectively. One sample was deposited by high-rate triode magnetron sputtering of 2.25-in. Ge cathodes onto Al foil held at 150 °C to yield highly ordered a-Ge. The target-substrate separation was 2 in., and the system base pressure for the depositions was 3×10^{-7} Torr. Raman measurements at various stages of deposition confirmed the amorphous character and degree of order of the sample. Highly disordered a-Ge was rf sputtered from a 5-in. target onto Al foil cooled to 5 °C. A series of runs was made in each case to obtain large amounts of a-Ge samples. The sputtered material was removed from the Al foil by dissolving in dilute HCl. Neutron activation analysis indicated 1–2% Ar content in both samples and negligible amounts (less than 0.05%) of Al and Cl.

About 40 g of the highly ordered material and 30 g of the highly disordered material were used for the inelastic neutron scattering measurements, which were performed at 15 K. The experiments were carried out on the LRMECS instrument at the Argonne Intense Pulsed Neutron Source facility. Instrumental resolution was 4.5 meV (36 cm^{-1}) for the incident energy of 56 meV. Details of the background analysis of multiphonon scattering and the appropriate Q averaging required to obtain the density of states are discussed elsewhere.[14,15] Depolarized (VH) and polarized (HH) Raman scattering measurements at 5145 Å Ar excitation were performed at 300 K on a Spex third-monochromator system in a pseudobackscattering configuration. The instrumental resolution for the Raman measurements was 4 cm^{-1}. The stray light background was estimated from previous studies of metal films. The background uncertainty, which is larger at lower frequencies, is estimated to be less than 10% for the low-frequency TA phonon peak. Differences in the Raman and neutron measurement temperatures are estimated to be of secondary importance for the broad amorphous bands whose peaks are relatively insensitive to temperature.

RESULTS AND DISCUSSION

The VH and HH-($\frac{4}{3}$)VH Raman spectra of *a*-Ge are compared in Fig. 1 to the corresponding neutron densities of states for highly ordered (HO) and highly disordered (HD) samples. The fully polarized, HH-($\frac{4}{3}$)VH, component is of importance in that the current theory of this Raman component in amorphous solids is a function of one parameter.[16] To obtain the Raman coupling parameter for component α the approximate relation

$$C^{\alpha}(\omega) \sim I_{\alpha}(\omega)\omega(n+1)^{-1}/G(\omega) \, , \tag{2}$$

where $(n+1)$ is the Stokes population factor, $I_{\alpha}(\omega)$ is the Raman intensity, and $G(\omega)$ the neutron-determined density of states, was employed. The coupling parameters for the VH component obtained from Eq. (2), and shown in Fig. 2, do not take account of the considerably higher Raman resolution in $I_{\alpha}(\omega)$ relative to the neutron-determined $G(\omega)$. The coupling-parameter spectra are obtained directly from the Raman and neutron spectra of Fig. 1 which are normalized to the same areas.

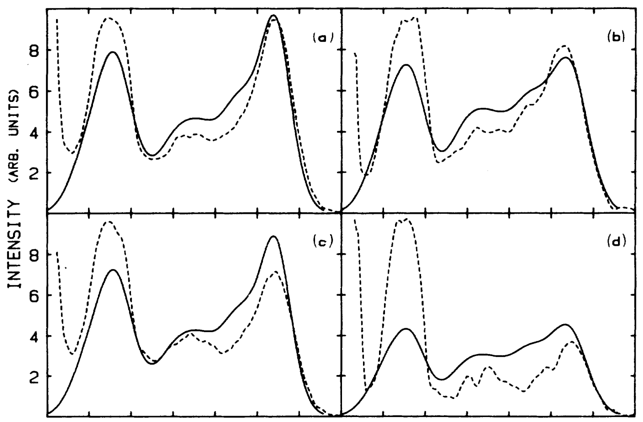

FIG. 1. Comparison of room temperature (a) VH and (c) HH-($\frac{4}{3}$)VH Raman (dashed lines) and neutron scattering spectra (solid lines) for the HO sample; (b) and (d) show the same results for the HD sample.

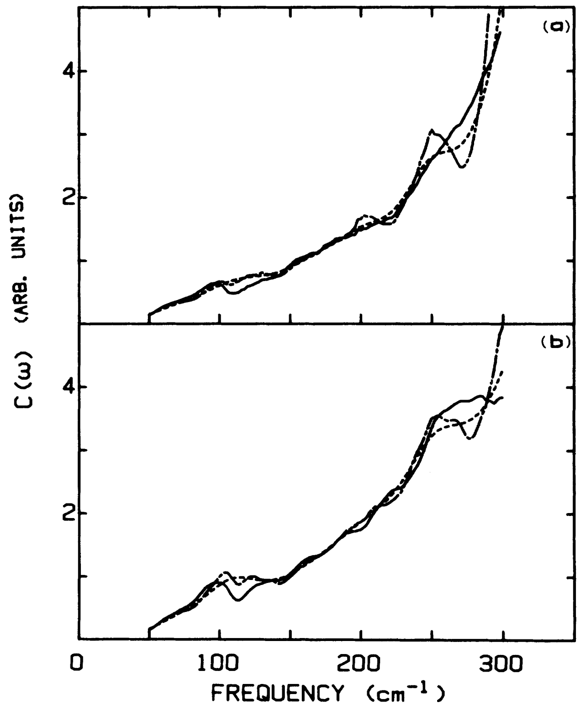

FIG. 2. Coupling parameter for the VH Raman component for (a) HO and (b) HD samples determined from as-measured Raman and neutron (solid lines), broadened Raman and as-measured neutron (dashed lines), and as-measured Raman and deconvolved neutron (dotted-dashed lines) scattering data.

An alternative estimate of the coupling parameter employs Raman spectra broadened to have a resolution equal to that of the neutron scattering data. The coupling parameters obtained by replacing $I_{\alpha}(\omega)$ in Eq. (2) by the broadened Raman spectra place both measurements on comparable footing. The resulting form of the coupling parameter, $C_b^{\mathrm{VH}}(\omega)$, is also shown in Fig. 2. A third measure that attempts to estimate the true coupling parameter corrected for limited neutron resolution employs a deconvolution procedure. While the latter is not unique and may introduce additional features into the neutron spectra, it does provide an estimate of the effects of resolution semiquantitatively. The coupling parameter obtained from this procedure, $C_{\mathrm{dec}}^{\mathrm{VH}}(\omega)$, is also shown in Fig. 2.

The different forms of $C^{\mathrm{VH}}(\omega)$ in Fig. 2 are very similar, exhibiting only small variations between the different methods for obtaining them. Noticeable differences occur only at high frequencies, where the largest differences between the deconvolved neutron estimates and those of Eq. (2) are ~20%. Figure 3 compares the results based on the as measured VH and HH-($\frac{4}{3}$)VH Raman components and neutron results using Eq. (2) for HO and HD samples. Except for oscillations about a monotonically increasing form, the coupling parameters are rather similar for the two samples. This monotonic behavior confirms previous discussions,[2,3] which predicted a qualitatively similar form to the room-temperature Raman spectra as the densities of states. This is also seen clearly in Fig. 1. Differences in the intensities of $C^{\mathrm{VH}}(\omega)$ between samples may increase somewhat for the high-frequency TO phonon band due to limitations of neutron resolution on the narrower ordered sample. The deconvolution procedure indicates that an ~20% greater coupling may occur for the ordered sample in this range.

The coupling parameters for the fully polarized HH-$(\frac{4}{3})$VH spectra of Fig. 3 also indicate similar forms, although somewhat larger differences are seen at low frequencies. At frequencies above ~100 cm^{-1} Fig. 3 shows that the form of $C(\omega)$ is similar for the two samples of a-Ge. The minor oscillations in Figs. 2 and 3 indicate the level of the combined noise in the Raman and neutron measurements.

The availability of $G(\omega)$ for two forms of a-Ge implies that it is now possible to also obtain the coupling-parameter variations for infrared absorption and inelastic tunneling spectra. In the case of infrared absorption in a-Ge there exist variations in the forms of the spectra between different studies[17–20] that may be associated with intrinsic as well as extrinsic structural effects. The latter refer here to the influence of impurities, such as oxygen, which may form ionic bonds, for which the static dipole moments may be significant.[19] Differences in the low-frequency behavior of the infrared absorption coefficient may in part be due to this effect. In addition, it is to be noted that in contrast to Raman scattering the infrared absorption spectra require a more detailed analysis of transmission and reflectance spectra as well as inclusion of geometrical interference effects. The present results clearly suggest sensitivity of the infrared spectra to modifications in structural order through changes in the density of states as well as possibly in the matrix element variations with structural order.

Inelastic tunneling methods have been employed in a very thin a-Ge film prepared by the reduction of GeO_2.[21] The phonon spectrum calculated on the basis of tunneling theory differs from those of the present measurements in the width of the TO peak as well as in the relative intensity of the TA to TO peaks. This suggests that $M(\omega)$, the coupling parameter for the inelastic tunneling spectra, has a somewhat more rapid variation with frequency than that obtained from theory to account for the more than 30% difference in the TA-TO ratio in $G(\omega)$ between experiment and theory. It is possible, however, that some of this difference is due to the nature of the very thin film which results in possible increased local strains at the interfaces[22] as well as possible GeO_2 contributions if full reduction was not achieved in film formation.

In summary, the coupling parameters for the two independent Raman components have been obtained for a-Ge. The forms of $C(\omega)$ indicate relatively monotonic behavior with increasing frequency, with local variations also observed. The behavior is consistent with a more rapid variation in $C(\omega)$ observed earlier in the Debye-like regime at low frequencies. The study of two samples of a-Ge of widely differing degrees of short-range order indicates qualitative as well as quantitative similarities in the forms of $C(\omega)$. At low frequencies in the TA band more substantial variations are observed with structural order. Similarities[2,3] in the Raman spectra of a-Si and a-Ge suggest that similar effects may be expected for the coupling parameter and density of states variations in a-Si with changes in bond-angle disorder. Simple scaling is not expected, however, as differences exist in the low-frequency spectra that are due to a reduction of the relative strength of the bond-bending forces in a-Ge.[23] Other coupling parameters, such as that of infrared absorption and inelastic tunneling spectra, may also now be estimated, although extrinsic contributions to these spectra require more careful analysis.

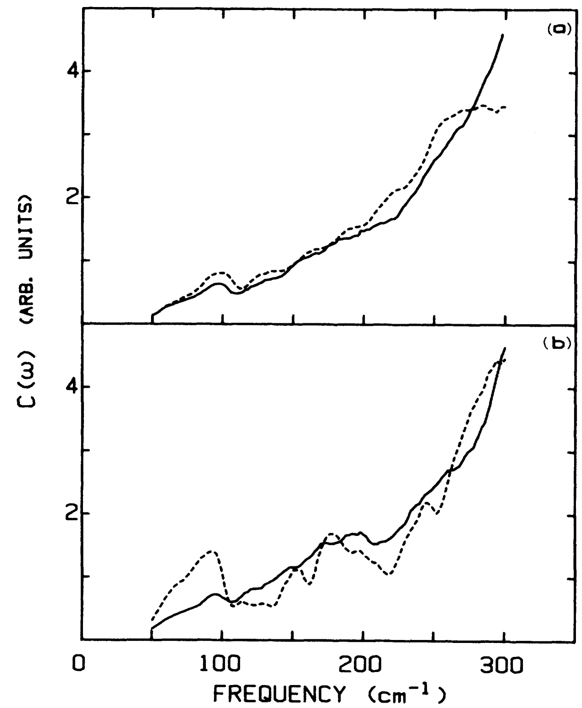

FIG. 3. Comparison of (a) $C^{VH}(\omega)$ and (b) $C^{FP}(\omega)$ for the HO (solid lines) and HD (dashed lines) samples.

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