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Raman scattering properties of amorphous As and Sb

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Raman scattering measurements on bulk amorphous As and thin-film sputter-deposited amorphous As and Sb indicate differences in the vibrational character of the systems. The polarization properties of amorphous As indicate quasimolecular character with differences between the bulk and sputtered material attributed to local variations in structure beyond nearest neighbors. The Raman spectra of sputtered amorphous Sb, in contrast, indicate nonmolecular character as in group-IV amorphous systems. A comparison of neutron-scattering measurements with the Raman spectra has been used to gain information about the frequency dependence of the Raman coupling parameter. The approximate form of the coupling parameter near the lowest peak in the density of phonon states, which is also found to hold for amorphous Se and Ge, is used to estimate the form of the density of states of amorphous Sb. The low-frequency phonon spectrum in amorphous Sb differs appreciably from the crystalline rhombohedral form reflecting changes in the second of higher neighbor distributions.

I. INTRODUCTION

The group-V systems As, Sb, and Bi when formed in a noncrystalline, amorphous state have electronic properties that differ appreciably from their common rhombohedral semimetallic forms. Amorphous (a-) As,[1] and Sb[2] are semiconducting while amorphous Bi is metallic.[3] This is in contrast to amorphous group-IV materials (a-C is an exception) and the amorphous group-VI systems which are semiconducting in their common crystalline forms. In a-Bi the structural change is associated with a different first-neighbor coordination while in a-As and a-Sb the first-neighbor coordination is unchanged on the average, but varies for second neighbors. It is useful to note that crystalline (c-) As also exists in an orthorhombic, metastable form[4,5] which is a narrow-gap semiconductor.[6,7]

The structure of a-As has been modeled by Greaves and Davis (GD),[7,8] whose results suggest a pyramidally threefold coordinated system with a local character that is layerlike over several interatomic distances on the average. The hand-built model and its refinements yield a density and radial distribution function (RDF) that is in reasonable agreement with the experimental density and RDF. In particular the model predictions are intermediate to the experimental results on two distinct forms of a-As.[9-11] Recent theoretical calculations using the GD model to determine the electron[12-14] and phonon[13-15] densities of states have suggested that the resulting spectra are sensitive to the local topology as reflected in the ring statistics. The electron and phonon spectra have, in addition, been suggested by Joannopoulos and Pollard[13-14] to be isomorphic as a result of the weak s-p hybridization in As. With increasing atomic number the s-p hybridization is expected to further decrease so that a-Sb is also expected to have an approximate isomorphism between the bonding p valence states and antibonding p' conduction states and the acousticlike (low frequency) and opticlike (higher frequency) phonon bands, respectively.

X-ray diffraction measurements,[9-11] as well as variations in density,[1] have suggested that a-As may exist in more than one metastable form depending on the conditions of preparation. Of basic interest both here, as well as for theories of the amorphous state, is the question of variations in local order and topology within a given amorphous material. Recent Raman scattering measurements in a-Sb,[16] and a-As,[17] have shown that the spectra are sensitive to preparation, particularly in a-As where thin-film and bulk samples have been compared. Appreciable differences in the optical properties of bulk and sputter deposited a-As have also recently been observed.[6] As will be discussed here, the similar RDF of a-As forms[10] suggests that the Raman scattering probes a range corresponding to second or further neighbors and as such is sensitive to the short-range order beyond nearest neighbors. The presence of extended structural correlations in a-As extending to $\gtrsim 5$ Å, as indicated in low-angle x-ray diffraction,[10,11,18,19] are relevant to the Raman spectra since these correlations are also a function of preparation.

In the present work the first-order Raman spectra of a-As and a-Sb are studied to gain information about the vibrational character, density of states, and the Raman coupling parameters. The availability in bulk a-As of an approximate density of states[18,19] allows information to be gained about the general form of the Raman scattering coupling parameters not possible in most amorphous systems studied to date. The neutron scattering measurements are, however, considerably broadened at higher frequency so that the Raman measurements provide additional information about the vibrational spectrum as well as its mode character. The mode character is reflected in the form of the two independent Raman components and their depolarization ratio.[20,21] Empirical information about the "effective" Raman coupling parameters may be useful in gaining information about the vibrational spectrum of thin-film amorphous materials for which neutron scattering measurements may not be possible.

In contrast to a-As, a-Sb has been found to exist only in relatively thin-film form so that the vibrational spectrum cannot be easily probed using neutron scattering. In the present work it will be suggested that an empirical, approximate determination of the phonon density of states of a-Sb may be obtained if knowledge of the frequency dependence of the Raman coupling parameter exists by analogy to the results in a-As. Constraints imposed on integrated portions of the spectra allow a boundary condition on the range of the average frequency-dependent coupling parameters. While the RDF of a-Sb (evaporated) indicates similar threefold coordination as in a-As,[10,22] there are differences in the distribution of second neighbors that are expected to influence the vibrational spectrum and Raman response. It has been observed that the degree of structural correlation as reflected in the low-angle x-ray scattering[22] is smaller in evaporated a-Sb relative to a-As. In addition, the Raman spectrum of a-Sb varies as the gaseous species changes.[16] An analysis of the depolarization ratio in films is employed here to provide further information about the molecular or nonmolecular character in a-Sb.

II. EXPERIMENT

Raman scattering measurements were performed using a third monochromator system with the approximate form of the stray light background estimated in thin-film a-As and a-Sb using an Al film. For the bulk a-As sample the irregularity of the surface prohibited use of the Al film method. The data were recorded on a multichannel counter, smoothed, and averaged for a number of runs. The thin-film a-As and a-Sb samples were prepared by dc sputtering in Ar at 2 kV at a pressure of ~20 mTorr onto substrates of ~300 and 100 K, respectively. For a-As a glass slide substrate was employed while for a-Sb a polished Si substrate of high conductivity was employed. The bulk a-As sample studied was obtained from Reichardt[23] who performed neutron scattering and diffraction measurements on this material. The bulk a-As is formed by AsH_3 thermal decomposition onto heated substrates. The density of the bulk material is 4.7 g/cm^3.

The two independent Raman components were obtained from measurements of I_{VH} and $I_{H'H}$, where H' is ~10° from being parallel to the surface in the scattering plane at 6471 Å, which was the primary laser line employed. Corrections to the true I_{HH} spectrum were estimated by measurements of I_{VU}, where U refers to the unanalyzed scattered light. The corrections were estimated to be $\lesssim 5\%$ in a-As. In a-Sb, for $\omega \gtrsim 110$ cm^{-1}, the depolarization ratio was determined from I_{VH} and I_{VV} measurements. The spectral resolution for the measurements was ~4 cm^{-1}.

The bulk a-As material has a similar density[23] and qualitatively similar form for the low-angle x-ray diffraction[18,19] as that of amorphous β-As prepared by evaporation onto a substrate of temperature, $T_s \simeq 200$ °C.[10] To allow for possible microscopic differences in the two preparations pending further work, the bulk material is not "labelled." Similarly, it is expected that the sputtered material may be related to evaporated γ-As ($T_s \simeq 100$ °C).[9,10] In an earlier report[17] the bulk and sputtered material were tentatively referred to for simplicity as β-As and γ-As, respectively.

III. RESULTS

In Fig. 1 a Raman spectrum of bulk a-As is shown with the scattered light unanalyzed (U). The figure clearly indicates the presence of relatively narrow bands superposed on a broad background. This indicates that the spectrum has quasimolecular as well as density-of-states features. By quasimolecular it is implied that the features are either narrow in frequency relative to the broad spectral bands, or have a spectral variation in the depolarization ratio, I_{VH}/I_{HH}.[21] Quasimolecular, however, does not in itself imply that a well-defined *simple* molecular unit exists. The two inde-

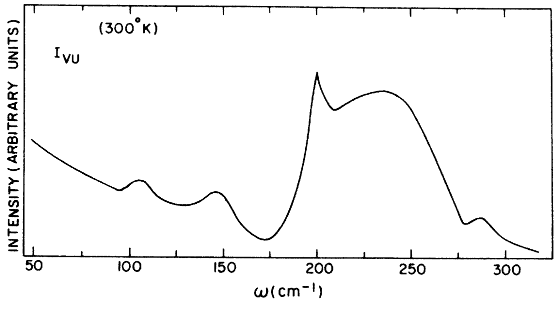

FIG. 1. Raman spectra of bulk a-As at 300 °K for I_{VU}, where U refers to the unanalyzed scattered light.

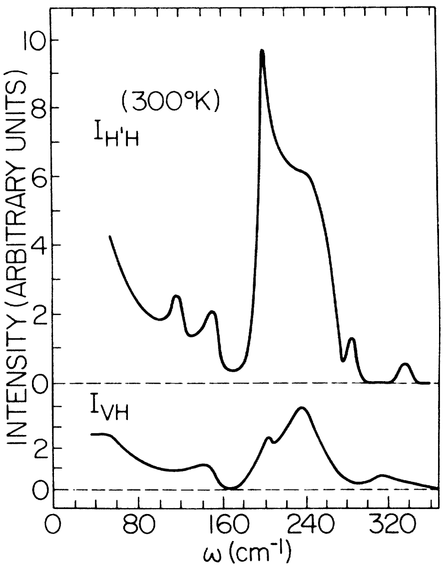

FIG. 2. Raman spectra of bulk a-As at 300 °K for I_{VH} and $I_{H'H}$ where H' refers to the incident refracted field ~ 10° from the plane of the surface. The dashed curves indicate the estimate zero levels.

pendent Raman components I_{VH} and $I_{H'H}$, where H' is within ~ 10% of the surface in the scattering plane in the present experiment, are shown in Fig. 2. The dashed lines indicate the approximate background level, which for the bulk a-As is primarily due to stray light. The two spectra differ appreciably in their narrow spectral features and further indicate the quasimolecular character of the system. The peaks at ~ 115, 283, and 340 cm^{-1} are not observed in the I_{VH} configuration. Infrared measurements[24] by Lucovsky and Knights for $\omega > 80$ cm^{-1} on similarly prepared bulk a-As also indicate a number of narrow spectral features, though the 200-cm^{-1} peak and the weak feature at 340 cm^{-1} are not observed. A rather weak infrared feature at 165 cm^{-1} is not observed in the Raman spectra. At lower frequency the stray light background prohibits a detailed resolution of the broad spectral band. However, the result in Fig. 2 for I_{VH} clearly indicates the presence of a peak or shoulder at ~ 50–60 cm^{-1}. The surface quality of the sample prohibited measurements at lower frequencies.

The Raman spectrum for the sputter deposited a-As with the scattered light unanalyzed does not indicate narrow spectral features below ~ 260 cm^{-1} in contrast to Fig. 1 for bulk a-As. A similar result has been obtained[25] in evaporated γ-As for I_{VU} for $\omega > 110$ cm. Figure 3, indicates, however, that the two independent Raman components when compared yield a variation of the depolarization ratio with frequency. This is particularly clear near 200 cm^{-1}, where the intensity of the I_{VH} component decreases more rapidly with frequency than does the $I_{H'H}$ component. In addition at higher energies above the broad main spectral band, differences in the weak spectral features indicate variations in the depolarization ratio qualitatively like that in bulk a-As. The weak feature at ~ 340 cm^{-1} in the latter is, however, not observed. While it is useful to plot the spectral variation of the depolarization ratio, in the present case this is complicated by the difficulty in estimating the true background level. In particular it is observed that the intensity at higher frequency in I_{VH} is above that at low and intermediate frequencies. The horizontal dashed line in Fig. 3 is an estimate of the maximum background level, while the zero level is that due to dark counts and as such indicates the minimum background for I_{VH}.

At lower frequency in sputtered a-As the stray light background in $I_{H'H}$, estimated using an Al film, has been subtracted to yield the approximate corrected spectrum. The low-frequency band is found to be similar to that observed in the I_{VH} configuration, where the background, though somewhat uncertain, does not appreciably change the form of the spectrum. Differences in the two components are within the experimental uncertainty in estimating the background form and in-

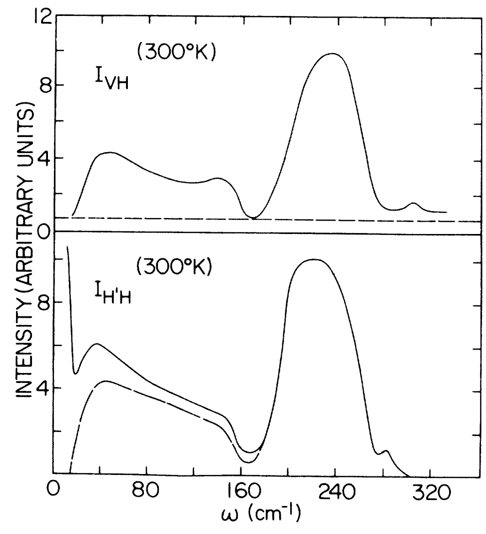

FIG. 3. Raman spectra of sputtered a-As ($T_s \simeq 300$ °K) for I_{VH} and $I_{H'H}$, where H' refers to the incident refracted field ~ 10° from the plane of the surface. The dashed curve in I_{VH} indicates the estimated (maximum) background, while the zero level corresponds to the phototube dark count (~ 10 counts/sec) and indicates the lower limit to the background. The intensity units are arbitrary for both components.

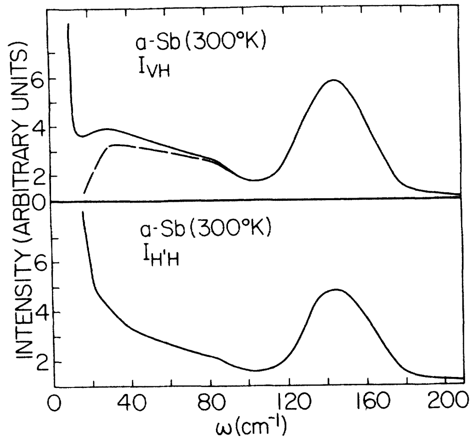

FIG. 4. Raman spectra of sputtered a-Sb ($T_s \simeq 100\,°K$) for I_{VH} and $I_{H'H}$. The dashed curve is that corrected for the estimated background.

tensity. The spectra of sputtered thin film a-As ($T_s \simeq 300$ K) indicates a quasimolecular character as reflected in the variation of the depolarization ratio with frequency. Qualitatively the spectra differ from that of bulk a-As in that they are broader with certain narrow spectral features, particularly in $I_{H'H}$, with the ~115- and 340-cm^{-1} peaks not observed within the experimental signal to noise. This clearly indicates that the Raman spectra are sensitive to preparation in contrast to nonmolecular group-IV systems.

In contrast to a-As the Raman spectra of a-Sb sputter deposited at lower temperature are similar for both Raman components and do not indicate any distinct features which are narrow in frequency. Figure 4 indicates the spectra taken at 6471 Å at room temperature with the zero level indicating the high-frequency background. A measurement of I_{VV} and I_{VH} at 4880 Å for $\omega \gtrsim 120$ cm^{-1} confirmed the constancy of the depolarization ratio equal to 0.36 ± 0.03. The background subtracted spectrum is shown for the I_{VH} configuration while for the $I_{H'H}$ spectrum the subtraction has not been made due to the relatively larger stray light contribution. It is, however, clear from the form of the $I_{H'H}$ spectrum that the low-frequency acousticlike features are present that are consistent with a similar form observed in I_{VH}. Previous measurements by Wihl *et al.*[16] on a-Sb prepared by evaporation from Sb and PtSb sources also yielded a relatively structureless higher-frequency band, although the depolarization ratio was not determined and the lower-frequency band was not studied. The results of Wihl *et al.*[16] did, however, indicate that the main higher-frequency peak position was sensitive to preparation and in the case of the Sb source shifted to higher frequency with increasing substrate temperature. For the PtSb source, which produces primarily Sb_1 gaseous species, versus Sb_4 for the Sb source, the peak occurs at a higher frequency, near to that of the sputter-deposited film. For the sputtered film the primary species is also expected to be Sb_1, though the incident energy of the atom species is on the average several orders of magnitude greater than in the evaporation case.

IV. DISCUSSION

A. Amorphous As

1. Comparison with neutron scattering

Information about the density of states and the Raman coupling parameters in a-As may be obtained by comparison of Raman and neutron scattering measurements. The Raman spectra require, however, consideration of frequency-dependent coupling parameters particularly for the low frequency acoustic-like regime[26-29] ($\omega \lesssim 100$ cm^{-1}). We define the frequency *weighted* reduced spectra for I_{VH} by the relation

$$\rho^R_{VH}/\omega^m = \omega^{1-m}(n+1)^{-1} I_{VH}(\omega)\,, \tag{1}$$

$$\frac{\rho^R_{VH}}{\omega^m} = \sum_b \frac{C^b_{VH}(\omega)}{\omega^m}\,\rho_b(\omega)\,, \tag{2}$$

where b labels the different modes of density ρ_b, and $C^b_{VH}(\omega)$ the coupling parameter.[30] Various choices of m, which for simplicity are taken as integers here, thus simulate the frequency dependence of the coupling parameter in a given frequency range. Figure 5 compares the neutron-determined density of states ρ^N of the Reichardt[18,31] in bulk a-As with the Raman results in sputtered a-As. Similar neutron results which yield the approximate density of states have recently been obtained by Leadbetter *et al.*[19] The I_{VH} component has been chosen as this is better resolved experimentally at low frequencies. The spectra are qualitatively similar with the choice $m=1$ yielding considerably better agreement than do $m=0$ or $m=2$ for the positions and relative intensities of the peaks in the low-frequency band. At higher frequency the various weighted reduced spectra yield a qualitatively similar form but with varying intensities; only the $m=1$ curve shown here.

Figure 6 compares ρ^R_{VH}/ω for both bulk and sputtered a-As with ρ^N. While the Raman spectra are similar there are differences at low frequency due to possible variations in $\rho(\omega)$ of the two forms of a-As or to the greater stray light contribution in the bulk material. At higher frequency the half width of the bulk spectrum is narrower than that of the sputtered a-As. The neutron broadening is

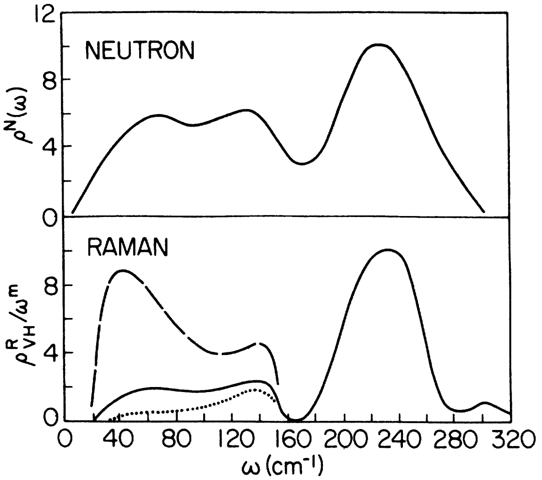

FIG. 5. A comparison of the neutron scattering determined density of states (Ref. 18) $\rho^N(\omega)$ in bulk a-As and the weighted reduced Raman spectra ρ^R_{VH}/ω^m of sputtered a-As. The dashed curve corresponds to $m=2$, the solid to $m=1$, and the dotted to $m=0$. At higher frequency only the $m=1$ curve is shown. The neutron and Raman spectra are normalized to the same peak intensity.

appreciable for the opticlike band with the resolution being ~20 cm^{-1} at 240 cm^{-1},[18,31] so that the 200-cm^{-1} Raman peak in bulk a-As is not observed. The linear decrease in resolution in ρ^N with frequency[18] results in an overestimate of $\rho(\omega)$ at high frequencies and in the minimum region between the low- and high-frequency bands. The essentially zero intensity in the weighted reduced Raman spectra in the minimum ~170 cm^{-1} results either from an overestimate of the background in this range or coupling parameter effects. The choice here of zero background to correspond to that in the minimum region precludes any discussion of the density of states for the I_{VH} component in this region. The nonzero intensity observed in $I_{H'H}$ and in the infrared absorption[24] indicates the lack of an actual gap in the spectrum. Second-order contributions to the spectra might contribute in this frequency range, however, Raman measurements at frequencies up to 500 cm^{-1} indicate that second-order scattering should be quite weak.

2. *Coupling parameter variations*

The results in Figs. 5 and 6 suggest an approximation linear variation of $C(\omega)$ for the low-frequency band. For frequencies below ~40 cm^{-1} use of this form does not however, yield the correct temperature dependence of the specific heat of evaporated a-As deposited on a room-temperature substrate.[32] This suggests a more rapid variation of $C(\omega)$ for the quasicontinuum modes. A detailed study was not made, however, to determine $C(\omega)$ in the quasicontinuum regime. Of interest here is that the most rapid variation of $C(\omega)$ in the quasicontinuum regime is $C \sim \omega^2$.[28] At higher frequencies $C(\omega)$ is physically expected to have a decreasing variation with ω for the broad, nonmolecular contributions to the spectra.[26]

Extrapolation of the lower-frequency form $C_{VH} = A\omega$, where $A=$ const, yields an opticlike peak whose intensity is too large relative to the neutron scattering[18,19] (Figs. 5 and 6) and theoretical results.[13,15] This indicates that the frequency dependence of the average coupling constant for the optic band must vary less rapidly with frequency than at lower frequencies if a simple monotonic form for $C(\omega)$ is assumed for the broad Raman spectral features. Thus, while the coupling to the higher-frequency modes is enhanced over those at lower frequency, the Raman and neutron results are consistent with a decrease in the frequency variation of the average coupling parameter with increasing frequency.[27] The requirement that the area of the low- and higher-frequency bands in $\rho(\omega)$ be equal in the limit of a gap between the bands is useful in estimating the decrease in the average coupling parameter. For simplicity, if it is assumed that an approximate gap between these bands exists then a form for the optic band, $C = B\omega$, with $B \simeq 2.5$ Å, would be required to yield the correct area ratio. Other variations of $C(\omega)$ would clearly be possible, such as a constant coupling parameter.[27] At present the neutron results are sufficiently broadened so that it is not possible to distinguish between these possible forms for $C(\omega)$ at higher frequencies.

It appears that $C \sim \omega$ also yields the approximate frequency of the lowest peak in the density of states of other systems. We have found, for example, that in both a-Ge,[27] and a-Se,[33] a similar

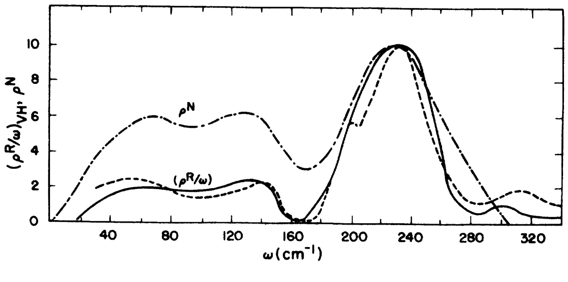

FIG. 6. Comparison of the weighted reduced Raman spectra ρ^R_{VH}/ω of sputtered (solid curve) and bulk a-AS (dashed curve) to the neutron determined density of states ρ^N in bulk a-As (Ref. 18).

variation in $C(\omega)$ is required to yield the lowest peak in position $\rho(\omega)$,[34-36] and a reasonable form for the low-frequency spectrum beyond the quasicontinuum regime. This suggests that it may be useful in other amorphous materials to estimate the lowest peak position in $\rho(\omega)$ using the Raman scattering data with $C \sim \omega$ as a first approximation. This would also be physically reasonable given the decrease in the frequency dependence of $C(\omega)$ for the broad features of the opticlike band and the more rapid variation for the quasicontinuum regime.[29-31]

3. *Comparison with theory*

Fundamental calculations of the *a*-As vibrational spectra have been made for the GD model by Joannopoulos and Pollard[13,14] and Beeman and Alben.[15] The results indicate structure in the density of states similar to that observed in the bulk *a*-As Raman spectra. In particular, both calculations indicate structure corresponding to the Raman peaks at 200 and 235 cm^{-1}. The cluster calculations of Joannopoulos and Pollard further indicate that the peak in the density of states ~200 cm^{-1} is sensitive to differences in local order as reflected in variations in bond angle and topology. This is qualitatively consistent with the variations in the Raman spectra of *a*-As prepared under different conditions. A calculation by Beeman and Alben[15] using a three-parameter polarizability model indicates qualitative agreement with the Raman results. The I_{VH} component for bulk *a*-As is found to yield a better representation of the form of the density of states than does $I_{H'H}$. This is expected due to the appreciable enhancement of polarized modes in $I_{H'H}$.

At lower frequencies the theoretical calculations[13-15] yield the peak in $\rho(\omega)$ at ~140 cm^{-1}, but do not compare as well with ρ^N or ρ^R_{VH}/ω for the lowest peak and form of the density of states. This is presumably due to the simplicity of the two-parameter models. Of interest for the lower-frequency band is the suggestion by Joannopoulos and Pollard[13,14] that certain features in the electronic density of states reflect the presence of five- and sevenfold rings not found in rhombohedral *c*-As. The sensitivity of the peak at the bottom of the *p* band to the presence of five- and sevenfold rings in *a*-As and the approximate electron-phonon isomorphism implies that the corresponding low-frequency vibrational modes would also be sensitive to ring statistics. Further Raman measurements in bulk *a*-As are in progress at lower frequency, to determine if this is the case.

At higher frequencies above the main opticlike band and above the limit of theoretical calculations a number of relatively narrow features are observed in both the sputtered and bulk *a*-As spectra as well as in the infrared absorption. One possibility is that a small fraction of the material has a local configuration similar to that of As_4 molecules with a 60° bond angle. This species which is present in both the vapor phase as well as in the solid phase as white or yellow As is normally unstable to visible light.[1] Where such units stabilized in the *a*-As matrix the three molecular vibrational frequencies would be somewhat depressed from their gaseous values of ~210, 252, and 342 cm^{-1}.[37,38] Only the highest peak in bulk *a*-As at 335 cm^{-1} which is polarized might correspond to the *A* mode of the As_4 molecule, the other features at 283 and 315 cm^{-1} do not. The presence of these narrow features beyond the main spectral band are thus not explained at present. It is possible that they represent some defect or local modes not accounted for in the theory.

4. *Molecular models*

In addition to more extensive first-principles calculations, the opticlike density of states of *a*-As has been considered using a four-atom pyramidally coordinated unit.[24] In a system such as *a*-As a molecular unit description will not in general be valid. Under certain conditions, however, such as weak bond bending force constants and geometrical constraints, such as an approximate 90° bond angle, it has been shown in binary systems that it may be possible to decouple the vibrations for various units.[39,40] A weak bond bending force constant in *a*-As and a 97° bond angle might allow vestiges of a decoupled model to hold. Were this the case, then the Raman modes particularly with quasimolecular character might have eigenvectors related to that of a molecular model. In the four-atom model there are four modes with Raman and infrared activity; ν_i, $i=1,2,3,4$ with two having *A* symmetry and two *E* symmetry.[20] For a two-parameter valence force model with bond stretching and bond bending force constants this yields $\nu_4(E) < \nu_2(A) < \nu_1(A) < \nu_3(E)$.[20,24] The symmetric *A* modes will be primarily polarized so that the identification $\nu_2 = 115$, $\nu_4 = 145$, $\nu_1 = 200$, and $\nu_3 = 238$ cm^{-1} could be made if one modifies the model to be three parameter by introducing a coupling of the bending and stretching modes.

The introduction of the third parameter is required if $\nu_2 < \nu_4$, as found experimentally. While the *A* modes are reasonably defined in this model the *E* modes are not and merely reflect the major nonpolarized features in the density of states. The lack of appreciably infrared activity for the 200-cm^{-1} peak implies that either a weak induced dipole moment for this symmetric, infrared allowed, approximate stretching-type mode or that the molecular model is not appropriate. Increasing the bond angle is found to increase the 200-cm^{-1} peak in the cluster calculations.[13,14] In contrast, in a molecular model decoupling is improved for a bond angle closer to 90°.

While the above model might in part explain the Raman results this does not necessarily imply that the true eigenstates corresponding to the various spectral features are related to the eigenvectors of the pyramidal unit. The observed quasimolecular behavior may imply the importance of a larger structure unit for example. It is interesting to note that second order Raman measurements[41] in rhombohedral As indicate structure in the density of states ~200 cm^{-1} as do theoretical calculations for the electronic structure[12] assuming an electron-phonon isomorphism.[13,14]

5. Structure

A major finding of this work is the sensitivity of the Raman spectra of a-As to preparation. This contrasts with nonmolecular group-IV systems where Raman spectra are essentially independent of preparation. It is useful, therfore, to inquire as to the structural origin of these differences. The x-ray data[10,18,19] in a-As suggest that a correlation may exist between the low-angle x-ray peak intensity and the degree of quasimolecular character of the Raman spectra. The more intense low-angle peak in the bulk amorphous material and the sharp and more intense Raman spectra particularly near 200 cm^{-1} are consistent with an increase in structural correlations relative to the sputtered and evaporated, low T_s material. Structural correlations involving second and higher neighbors might thus be expected to influence both the x-ray and Raman results. Moss's observation that the low-angle x-ray peak in sputtered a-As sharpens and increases in intensity with annealing[42] suggests a transformation to a more bulk or β-like form of a-As and is consistent with this picture.

The possible relation of Raman and x-ray results is also in accord with the sensitivity of the 200-cm^{-1} peak in the phonon density of states, $\rho(\omega)$, to bond angle and topology as noted theoretically.[13,14] The RDFs of amorphous β-As and γ-As are similar for the first peak and indicate a small increase in the second peak area from ~10 atoms in β-As to ~10.5 in γ-As.[10] The similar average first-neighbor distance and bond angle in β-As and γ-As thus suggest that the differences in the Raman spectra reflect longer-range variations in structure or differences in the statistical distribution of the local bond parameters. Longer-range effects relating to topological variations in ring statistics would be consistent with the suggested correlation between the Raman scattering and low-angle x-ray results.

Greaves *et al.* have recently[6] studied the optical properties of bulk and sputter-deposited a-As. Appreciable differences in the low-energy reflectivity, and optical constants were observed between the bulk and sputtered amorphous material. The possibility of the influence of H incorporated from the AsH_3 decomposition process was considered as a possible explanation for these differences.[6] The Raman and x-ray results point, however, to basic variations in the local structure of a-As with preparation that may explain, in part, the variation of the optical constants. In particular the approximate isomorphism between phonon and electron states might in general imply the sensitivity of the optical properties to preparation.

B. Amorphous Sb

In a-Sb sputter deposited at lower temperature the nonmolecular character of the Raman spectra is reflected in the lack of structure in the depolarization spectrum. This indicates that a discussion of the entire spectra in terms of the spectral density of states is reasonable with the assumption of smoothly varying coupling parameters. If the various frequency weighted reduced Raman spectra are considered, as in a-As, then it is possible to obtain information about the approximate density of states. Aside from differences in the two Raman components in sputtered a-As, the spectra are qualitatively similar to those of sputtered a-Sb in form. If, based on the results in a-As, Se, and Ge, it is assumed that the coupling parameter $C_{VH} \sim \omega^1$ for simplicity, then it might be expected that a reasonable representation for the form of the low-frequency peak might be obtained. Figure 7 indicates the resulting reduced spectrum, ρ^R_{VH}/ω, along with the neutron determined density of states of crystalline Sb of Salgado *et al.*[31] The minimum between the low- and higher-frequency bands in the crystalline spectrum is a result of resolution broadening since a gap in the density of states is expected.[43] For the amorphous material structural broadening due to fluctuations in short-range order results in a minimum rather than a gap.

The approximate separation of the low- and higher-frequency bands does, however, allow constraints to be placed on the relative areas of the bands which would be equal without broadening. The smaller area of the low-frequency band obtained using the simple form for $C_{VH} \sim \omega^1$ is similar to that obtained in sputtered a-As with the higher-frequency band having an area ~3 times that at

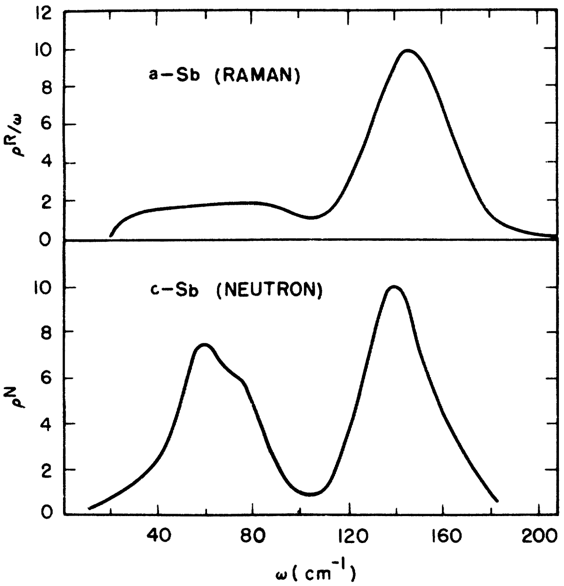

FIG. 7. Comparison of the weighted reduced Raman spectra ρ^R_{VH}/ω for sputtered a-Sb and the neutron determined density of states ρ^N of rhombohedral c-Sb (Ref. 31).

lower frequency. This indicates that the frequency dependence of the coupling parameter must vary less rapidly on the average for the higher-frequency band. The specific form of $C(\omega)$ will not in general appreciably change the predicted peak position and form for $\rho(\omega)$ for the higher-frequency band.

Figure 7 suggests differences in the density of states of c-Sb and a-Sb obtained from neutron[31] and Raman scattering, assuming $C_{VH} \sim \omega^1$. More detailed changes in the density of states of a-Sb relative to c-Sb may be obtained by comparison with second-order Raman measurements in[41] c-Sb which indicate sharp features in the density of states not observed in the lower resolution neutron results. While the highest optic modes in c-Sb have not been determined with certainty, the neutron dispersion[43] and second-order Raman results[41] indicate a maximum frequency at ~170 cm^{-1} with the highest peak in the density of state at ~150–155 cm^{-1}. While the a-Sb opticlike higher-frequency peak is shifted above that in c-Sb, the relative shift is considerably less than that in a-As relative to its rhombohedral form. The shift is in fact even smaller for a-Sb prepared by evaporation from an Sb source.[16] The smaller relative peak shift in a-Sb compared to that of a-As may reflect structural differences as indicated by the second-neighbor distribution.[10] In a-Sb a greater tendency toward metalliclike bonding is expected than in a-As which may influence the density of states and vibrational character. This would also be in accord with the nonmolecular character of the a-Sb spectra.

At lower frequency the spectrally weighted reduced Raman result and the density of states of c-Sb differ appreciably as was the case for a-As and rhombohedral As. The coupling parameter variation $C \sim \omega^1$ predicts a peak or shoulder in the a-Sb density of states roughly in the range of 35 ± 5 cm^{-1}. The predicted low-frequency enhancement in the density of states in a-Sb is again qualitatively similar to that in a-As and justifies, in part, the assumption for the approximate form for $C(\omega)$. Specific-heat measurements would be useful to confirm the prediction of an appreciable difference in the form of $C_p(T)$ in amorphous and crystalline Sb. At intermediate frequencies the minimum in $\rho(\omega)$ for a-Sb is near to the midgap in c-Sb. This differs from the results in a-As which indicate a shift to higher frequency of the minimum in the amorphous material relative to rhombohedral As.

The present results in sputter-deposited a-Sb indicate a nonmolecular character to the Raman spectra similar to that in group-IV amorphous systems. This does not necessarily imply that a-Sb prepared by other means, such as by evaporation or sputtering onto a higher-temperature substrate, will not have variations in the spectral form of the depolarization ratio that indicates some quasimolecular character. The increasing atomic number and the presence of ~1.5–2 neighbors[10] at closer relative distances than in a-As indicates the tendency toward a larger second or further neighbor interaction that tends to make a-Sb more nonmolecular. The presence of a weak low-angle x-ray peak in evaporated[22] a-Sb is suggestive that structural correlation effects cannot be fully neglected and may be such that this material may have some small quasimolecular character. Theoretical calculations of the density of states and Raman spectra in a-Sb using a modified GD-type model would thus be useful in this regard.

V. CONCLUSIONS

The Raman spectra of bulk and sputtered a-As have been compared to neutron scattering results to obtain further information about the density of states, mode character and frequency dependence of the Raman coupling parameters. The spectra of a-As are quasimolecular in character reflecting polarization properties differing from nonmolecular systems such as amorphous group-IV materials. The spectra of bulk a-As are similar to the theoretical calculations based on the GD model. For the lower-frequency modes the differences with theory presumably reflect the simplicity of the models employed.

The results in a-As suggest that differences in the Raman spectra of bulk and sputtered forms are related to local variations in structure beyond nearest neighbors. This is consistent with structural correlation effects observed in low-angle x-ray measurements. The results are in accord with theoretical calculations indicating the sensitivity of the vibrational and Raman spectra to topological features such as ring statistics. In contrast sputtered low-T_s a-Sb indicates nonmolecular spectra. Differences in the estimated form of the density of states from c-Sb have been suggested to also arise from changes in the second-neighbor distributions.

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