Second-order Raman scattering in the group-V_b semimetals: Bi, Sb, and As

J. S. Lannin

Max-Planck-Institut für Festkörperforschung, Stuttgart, Federal Republic of Germany and Argonne National Laboratory, Argonne, Illinois 60439*

J. M. Calleja[†] and M. Cardona

Max-Planck-institut für Festkörperforschung, Stuttgart, Federal Republic of Germany (Received 3 March 1975)

Second-order Raman scattering has been observed in the group-V_b semimetals Bi, Sb, and As. Comparison of the spectra in Bi and Sb, which are primarily of even A_{1g} symmetry, with neutronscattering measurements indicate a predominance of overtone scattering. Variations in the form of the second-order spectra are attributed to differences in the phonon density of states within the group-V_b system. In contrast to Bi and Sb, the optical modes at Γ in As are shifted to relatively higher frequency so that the $E_g(\Gamma)$ mode no longer occurs at the minimum of the optic branch. Differences in the vibrational spectra near Γ between As and Bi or Sb are attributed to a decrease in second- or further-neighbor interactions. From the ratio of the second- to first-order scattered intensities the corresponding ratios of average electron-one-phonon to electron-two-phonon deformation potentials are determined.

INTRODUCTION

The semimetals As. Sb. and Bi constitute an interesting class of materials whose electronic and vibrational properties are largely determined by the simple cubic distorted rhombohedral structure and the resulting mixture of metallic and covalent bonding.¹ Many of the physical and chemical properties of these materials suggest, as in the group-IV elements Si, Ge, Sn, and Pb, that with increasing atomic number the fraction of metallic to covalent bonding increases. This is reflected as a decrease in the s-p hybridization as well as in the overlap energy so that Bi, which has the smallest number of free carriers, tends toward p^3 metallic bonding¹; the common valence +3 of Bi in most compounds is a manifestation of this tendency. In contrast, As has an internal displacement parameter u, which is larger than in Bi and Sb so that the tendency is toward that of a covalent layered crystal with weaker bonding between double layers.²

The relative importance of covalent and metalliclike bonding has at the present time not been explored in detail, though Golin and Stocco³ have calculated the charge density in As. They find covalent bonding with a small bond charge between nearest neighbors. The importance of short-range covalent bonding interactions in As and Sb is seen, for example, by comparison with the electronic and vibrational properties of their amorphous (*a*) semiconducting counterparts. Photoemission measurements in *a*-As and *a*-Sb (Ref. 4) indicate that the primary effect of structural disorder is to broaden the crystalline valence bands. Raman

585

scattering in⁵ a-As and^{5, 6} a-Sb when compared to the results presented here, as well as neutron scattering measurements in a-As,⁷ also indicate the importance of covalent-bonding effects. The influence of metalliclike bonding effects on the phonon dispersion in Bi and Sb has been suggested by several workers.⁸⁻¹⁰ The rapid rise of the lowest optical $E_{e}(\Gamma)$ mode with wave number in Bi and Sb has been suggested by Sharp and Warming⁹ to be a consequence of long-range forces and associated free-carrier screening effects. Macfarlane⁸ has similarly indicated the need for long-range forces to account for the behavior of the dynamical matrix in Bi. He has also pointed to the possible importance of long-range screening effects, though noted that free-carrier screening alone could not account for the phonon dispersion.

Raman-scattering measurements in semimetals and metals up to this time have been essentially confined to first-order spectra and therefore only yield information about $k \simeq 0$ modes. Recent second-order Raman measurements in the group-IV systems Si (Ref. 11) and Ge (Ref. 12) have given useful information about the single-phonon density of states. This result is a consequence of the Raman scattering in these materials being primarily due to overtone scattering processes involving two phonons of the same branch of equal and opposite wave vector, rather than combination modes from different branches. In addition the coupling constant appears to be a smoothly increasing function of phonon frequency. The microscopic reason for primary overtone scattering in these systems is not known, however, Weber et al.¹³ have successfully obtained this result with

a phenomenological model for the second-order Raman process which involves bond polarizabilities. The goal of the present work was the observation of second-order Raman scattering in the group-V_b semimetals, to gain information about the vibrational spectrum and to ascertain whether overtone processes primarily determine the spectra as in Si and Ge. While the phonon dispersion in Bi and Sb has been studied experimentally and theoretically,^{8, 9} similar studies have not been performed in As. The results presented here for As are rather interesting and indicate qualitative differences from the spectra of Bi and Sb which bear on questions of bonding and interatomic forces in these systems.

Concurrent with a preliminary report of this work,¹⁴ Salgado *et al.*¹⁵ have reported neutron scattering from polycrystalline semimetals using the technique of Oskotskii *et al.*¹⁶ for coherent neutron scatterers. Their results, which yield the approximate density of phonon states, are of limited resolution for the optic modes and as such do not indicate the detailed features reported here.

Considerable attention has also been paid recently to the resonant behavior of first- and second-order Raman scattering near energy gaps in semiconductors.¹⁷ These studies vield information about electron-two-phonon deformation potentials and show that the electron-two-phonon interaction in many semiconductors is anomalously large. Resonant behavior in the first-order scattering of As, Sb, and Bi has been recently reported.¹⁸ In the present work we were not able to study in detail the corresponding resonant behavior of the second-order scattering of As, Sb, and Bi. By making the necessary assumptions we were able, however, to obtain from the observed ratios of first- to second-order scattering average values of the corresponding deformation potentials.

EXPERIMENT

The Raman-scattering measurements were performed with a Spex third monochromator system employing photon counting and the use of a multichannel counter to improve signal to noise. The following laser lines were primarily used: for Bi the krypton 6471-Å, for Sb the argon 5145-Å, and for As the 5145-Å line. Measurements at other laser frequencies, Bi (argon 5145Å) and Sb (argon 4880 Å) did not indicate any qualitative change in the second order spectra associated with resonant Raman effects.

The crystals employed were grown at the Max-Planck-Institut by Dr. E. Schönherr using the Bridgman technique. The data reported here were taken on cleaved trigonal faces. Attempts to cut and polish other faces of Bi and Sb using $0.05-\mu m$ alumina plus Syton polish (Monsanto Corp., St. Louis, Mo.) were not successful in that the resulting firstorder Raman spectra did not satisfy the expected selection rules, a result attributed to selection rule breakdown induced by some form of surface disorder. Electropolish was not successful either. The As sample was cleaved and maintained in a high-purity low-humidity environment of less than 1-ppm H_2O to prevent oxidation. Removal of the As sample from this environment for several hours did not, however, indicate an oxide associated darkening or a degradation of the signal. This suggests that the As crystal was of sufficient purity that the usual fast oxidation to As₂O₃ did not occur. In spite of the breakdown in selection rules for first-order scattering, the form of the second-order spectra on the polished (110) faces was similar to that of the cleaved trigonal faces indicating that the Raman tensor components¹⁸ are similar in form. For primary overtone scattering this is what would be expected.

EXPERIMENTAL RESULTS

A. Bismuth

The first- and second-order Raman-scattering measurements for Bi at 300 K obtained with no analyzer in the scattered beam are shown in Fig. 1. The dashed curve indicates a rough estimate of the stray-light background. Polarization measurements indicate that the second-order spectrum is primarily composed of the A_{1g} symmetry component with $A_{1g}/E_g \simeq 3-4$ and has similar shape for both components. The ratio A_{1g}/E_g corresponds to a^2/c^2 , where a and c are the Raman tensor elements of A_{1g} and E_g symmetry, respectively.¹⁸



FIG. 1. Smoothed first- and second-order Raman spectrum of a cleaved (001) face of Bi at 300 K. The dashed curve indicates the estimated background.

586

Overtone scattering is likely to occur in the A_{1e} component of the spectrum since the square of a given representation always contains the symmetric representation A_{1g} ; this is, however, only to be considered as a plausibility argument. The ratio of the area under the second-order to that under the first-order peaks is given in Table I. To compare the measured spectra to neutron scattering measurements it is useful to define a reduced second order Raman spectrum obtained by multiplying the intensity above background by the factor $\omega^2/$ $(n_B + 1)^2$, where $n_B + 1$ is the Bose-Einstein factor for Stokes scattering and ω the frequency or wavenumber Raman shift. For overtone scattering the reduced second-order intensity yields the spectral density of states, i.e., the density of states weighted by the coupling constants for the various modes. Thus if the coupling constant is independent of phonon frequency and wave number, the reduced intensity yields the density of overtone phonons at 2ω , i.e., the density of one phonon states with the horizontal scale expanded by a factor of 2.

Figure 2(a) indicates the reduced Raman intensity for Bi using the estimated background shown in Fig. 1. The phonon dispersion determined by inelastic neutron scattering⁸ taken at 80 K is shown in Fig. 3, with the frequency scale multiplied by 2 for comparison. First-order Ramanscattering measurements of Grant et al.¹⁹ and neutron measurements of Salgado et al.¹⁵ indicate an approximate shift of $\sim 2 \pm \frac{1}{2}$ cm⁻¹ to lower frequency between 80 and 300 K. This corresponds to a temperature shift of 4 ± 1 cm⁻¹ in the 80-K curves of Fig. 3 with respect to room temperature. The lowest feature labeled I in Fig. 2(a) occurs as an inflection at ~173 cm⁻¹ (see Fig. 1 also) and is $\sim 1 \text{ cm}^{-1}$ below the lowest zone boundary phonon of X_3 symmetry. This small difference is consistent with an X_3 assignment to feature I, in particular, since the neutron measurements at Γ of Macfarlane⁸ are 1.3 and 2.3 ± 0.5 cm⁻¹ high relative to the Raman measurements at the same temperature.¹⁹ The relatively flat dispersion in the neighborhood

TABLE I. Ratios $I^{(2)}/I^{(1)}$ of second- to first-order scattered intensities in As, Sb, and Bi and corresponding ratios of electron-two-optical-phonon to electronone-phonon deformation potential. The numbers in parentheses indicate the laser wavelength employed in Å.

	As (5145)	Sb (5145)	Bi (6471)	Bi (5145)	Sb _{0.92} Bi _{0.08} (4880)
$I^{(2)}/I^{(1)}$	0.024	0.031	0.031	0.036	0.030
D /d	40	49	49	53	48

of X in the directions ΓX and $\Lambda' X$ is consistent with structure in the density of states and thus indicates overtone scattering at this frequency. Similarly feature II, the main peak, occurs at a frequency common to that of a large number of flat bands and is also suggestive of overtone processes. Somewhat surprisingly, no further distinct features are observed above II since the neutron results indicate several branches contacting the zone



FIG. 2. (a) Reduced Raman spectrum in Bi obtained from Fig. 1 (resolution ~4 cm⁻¹). (b) Theoretical optical-phonon density of states (Ref. 20). (c) Theoretical optical-phonon density of states for coherent neutron scatterers (Ref. 15). (d) Optical-phonon density determined by neutron scattering (Ref. 15) (resolution ~ 27 cm⁻¹) (b, c, and d frequency scales have been multiplied by 2 for comparison with the second-order Raman data.)

boundary at higher frequency. The cutoff of the spectrum at ~220 cm⁻¹ corresponds to the highest frequencies in the dispersion relations observed at Λ' , *T* and other points in the Brillouin zone.

In Fig. 2, the reduced Raman intensity is compared to the results of neutron scattering on polycrystalline Bi by Salgado et al.,¹⁵ Fig. 2(d), and to theoretical calculations of the density of states of the optic branches.^{15, 20} The onset of the reduced Raman intensity occurs $\sim 16 \text{ cm}^{-1}$ above the theoretical onsets, a result possibly due to the difficulty in estimating the background. The neutron curve of Fig. 2(d) was obtained by subtracting a constant background from the experimental results so as to yield a gap between acoustic and optic modes and to eliminate a high-frequency tail. The neutron results indicate a single main peak $\sim 5 \text{ cm}^{-1}$ above and somewhat broader than that observed in the reduced Raman intensity. Note that according to Fig. 3 the lowest optic mode occurs at Γ . The lack of the additional structure in the neutron measurements, which is, however, observed in the theoretical calculations shown and in Figs. 2(b) and 2(c), and the extended tail reflect the limited resolution of $\sim 13.5 \,\mathrm{cm}^{-1}$ (or 27 cm⁻¹ for the second-order comparison). This is in constrast to the Raman resolution of $\sim 4 \text{ cm}^{-1}$. The limited neutron scattering resolution also explains, at least in part, the smaller width observed in the Raman measurements. The weaker shoulder obtained in the theoretical calculation at ~170 cm^{-1} of Fig. 2(c) is, for example, not seen in the neutron measurements. The calculation of Fig. 2(c) was obtained with a Born-von Kármán model employing a root sampling technique so as to fit the measurements for coherent polycrystal neutron scattering: under a number of assumptions this technique should yield the phonon density of states.^{15,16}



FIG. 3. Optical-phonon dispersion curves of Bi at 80 K (Ref. 8). The solid lines are not a theoretical fit, but merely an observational aid (frequency scale multiplied by 2 for comparison).

Also shown in Fig. 2(b) is the histogram density of optic phonons calculated by Czochar *et al.*²⁰ using a five-neighbor Born-von Kármán model. While the gross features of the reduced Raman intensity are similar to those of the theoretical calculations and thus indicative of overtone processes, the lack of distinct structure and the relative weak intensity above 200 cm⁻¹ cannot be explained with a frequency-independent coupling constant. The observation of appreciable structure in the theoretical calculations and in the phonon dispersion suggests a decrease in the Raman coupling parameter at higher frequency.

B. Antimony

Figure 4 shows the first- and second-order Raman scattering for Sb with no analyzer in the scattered beam. As in Bi both symmetry components were found to have similar shape with $A_{1g}/E_{g} \simeq 3$. In addition to the main structural band between ~ 235 and 320 cm⁻¹, weak reproducible structure is also observed at ~190 cm⁻¹. The reduced Raman intensity calculated with the assumed background of Fig. 4 is shown in Fig. 5(a). While the phonon dispersion in Sb has not been studied in the same detail as in Bi, measurements in the ΓX , ΓL , and ΓT directions have been performed by Sharp and Warming.⁹ Comparison of the reduced Raman intensity with these measurements indicates that feature I at ~268 cm⁻¹ corresponds to the lowest zone-boundary mode which occurs at X. In Bi the lowest optic X mode is of symmetry X_3 while the higher modes X_1 and X_4 assigned in Fig. 3 are nearly degenerate. In Sb, a detailed branch separation comparable to that of Fig. 3 for Bi has not been performed, however, the qualitatively similar dispersion in Sb makes it reasonable to assign feature I to X_3 . The



FIG. 4. Smoothed first- and second-order Raman spectrum of a cleavage (001) face of Sb at 300 K. The dashed curve indicates the estimated background.

588

Raman peak II at ~286 cm⁻¹ occurs, as was the case in Bi, at a frequency corresponding to a number of phonon branches and cannot be assigned to a single region of the Brillouin zone. The weaker higher-frequency feature at ~304 cm⁻¹ occurs, within the experimental uncertainty of the neutron measurements (± 2 cm⁻¹), at the frequency of the highest X mode and the lowest T mode. Comparison with Bi suggests that other zoneboundary modes may also contribute to this frequency. Weak reproducible structure at ~280 cm⁻¹ also occurs at a frequency corresponding to that of several bands.

In Fig. 5 the reduced Raman intensity is compared to the neutron polycrystal measurements of Salgado *et al.*¹⁵ and to the theoretical density of states of Sosnowski *et al.*²¹ calculated with a model similar to that used to determine Fig. 2(b) for Bi. Of the two models calculated by these authors we have chosen their least-square-fit model since distinct peaks occur near to features I and II in the reduced Raman spectrum. The fit of this model to the lowest-lying optical branches is poor, however, and does not reproduce the sharp rise at low wave vectors. This results in a larger the-



FIG. 5. (a) Reduced Raman spectrum in Sb obtained from Fig. 4 (solid curve) and optical-phonon density determined by neutron scattering (Ref. 15) (dashed curve). (b) Theoretical optical-phonon density of states (Ref. 21). (Neutron scattering and theoretical frequency scales multiplied by 2 for comparison.)

oretical density of states at the lower region of the band similar to the situation in Bi. The other model of Sosnowski *et al.*,²¹ using an algebraic approach yields a lower density of states in this region but does not yield agreement with features I and II.

The neutron measurement shown as a dashed curve in Fig. 5(a) has its main peak near peak II of the Raman spectrum. A constant has been subtracted from the neutron data in order to eliminate an extended tail at higher frequencies and to introduce the gap expected between acoustic and optic branches.⁹ Due perhaps to a resolution limit of ~18.5 cm⁻¹ (37 cm⁻¹ in second order) the neutron data do not have any well-resolved structure.

The experimental band width of the Raman results and its correspondence to the theoretical calculations and the neutron data clearly suggests the dominance of overtone processes. The relative intensity of features I and II in both Bi and Sb when compared to theory strongly corroborate this conclusion. A further argument for dominant overtone rather than combination processes is based on the position of the lowest zone-boundary combination and overtone modes which, based on the neutron results,⁹ involve X phonons. In particular, zone boundary combination process involving two optical X phonons can be seen from Fig. 3 and in the results of Sharp and Warming,⁹ to have their onset at frequencies considerably above the lowest overtone modes. Weak structure at 190 cm⁻¹ may reflect weak combination acoustic plus optic modes and again suggest dominant overtone scattering. As found in Bi, the intensity of feature III does appear low relative to the theoretical calculations and the neutron scattering results, suggestive of a possible decrease in the coupling parameter at higher frequency.

C. Arsenic

Figure 6 illustrates first- and second-order scattering in As for unanalyzed scattered light. The relatively weak signal intensity made polarization measurements rather difficult and time consuming, so that by analogy with Bi and Sb we assume primary A_{1g} scattering. In Fig. 7 the reduced Raman intensity is compared to the neutron results of Salgado *et al.*¹⁵ on polycrystalline As. The main Raman features have been labeled I, II, III based on the general qualitative similarity to the spectrum in Sb. The neutron resolution is $\sim 20 \text{ cm}^{-1}$ (40 cm⁻¹ in second order), while the Raman spectrum has $\sim 5 \text{ cm}^{-1}$ resolution. An extended high-frequency tail in the neutron results has been subtracted for purposes of comparison. An important difference, with respect to Sb and Bi,

is the observation in As that the $E_{\mathfrak{s}}(\Gamma)$ mode occurs above the minimum in the optical band of the second-order spectrum. Comparison with the neutron-scattering results also indicate this qualitative difference. As neutron-scattering measurements suggest a gap between acoustic and optic modes as in Bi and Sb, the onset of the optic branch must occur either within or at the boundary of the Brillouin zone. Since the lowest mode is no longer at Γ , appreciable contributions to the density of states might be expected from the lowestlying zone-boundary mode. The feature labeled 0 might, for example, correspond to a flat branch at or near a zone boundary. In addition, the estimated onset of the Raman spectrum $\sim 40 \text{ cm}^{-1}$ below $2E_{g}$ indicates a dispersion of at least 10% in certain modes.

The qualitative differences between As and Sb or Bi make a symmetry assignment of the As peaks somewhat tentative, so that the features labeled I, II, and III may not correspond to the same symmetry points in the three materials. The structural difference between As and Sb or Bi results in an increase in the ratio of the next-nearestto-nearest-neighbor distance. A calculation of Yarnell et al.²² for Bi has shown that in the trigonal direction the problem is similar to that of pseudo-one-dimensional chain. Decreasing the interaction between next-nearest neighbors in this model results in a depression of the T point modes such that the lowest mode occurs below $E_{\varepsilon}(\Gamma)$. One might therefore speculate that feature 0 to I would correspond to the T point TO mode. In Bi and Sb feature I was shown to correspond to overtone scattering from modes near X. The relative intensity of feature I in As relative to that of Sb suggests a tentative labeling of X_3 in As.

The single peak in the neutron results of Fig. 7 in As occurs between feature I and II, in contrast to its position in Sb and Bi, and probably reflects resolution broadening. Feature II, which occurs as a shoulder, by analogy with Sb and Bi is expected to correspond to the frequency of an appreciable number of bands and cannot be assigned to a single region of the zone. Feature III, which is broader and has more integrated strength than in Sb, would correspond to the highest-lying modes. The appreciable asymmetry in the neutron measurements at higher frequencies is clearly consistent with the relative strength of feature III and with the implicit assumption we have made, based on the results in Bi and Sb, of primary overtone scattering. The estimated termination of the secondorder spectrum in Fig. 6 occurs near to $2A_{1e}(\Gamma)$ while in Bi and Sb it takes place at considerably lower frequency. In Bi, and possibly in Sb, the highest-lying zone-boundary modes occur near T. Decreasing the range of interactions in the model of Yarnell *et al.*²² results in a change in the form of the dispersion of the highest-lying (LO) modes along T, with the resulting zone-boundary modes occurring at a lower frequency than $A_{1g}(\Gamma)$. Similar results have been observed by Smith for other directions in the Brillouin zone.²³ It is thus possible that the maximum optical modes in As occur at or near Γ in frequency. Single-crystal neutronscattering measurements of the phonon dispersion



FIG. 6. Smoothed first- and second-order Raman spectrum of a (001) cleavage face of As at 300 K. The dashed curve is the estimated background. Note the horizontal scale change at $\omega = 300$ cm⁻¹.



FIG. 7. Reduced Raman spectrum of As obtained from Fig. 6 (solid curve) and optical-phonon density of states obtained by neutron scattering (frequency scale multiplied by 2 for comparison) (dashed curve) (Ref. 15).

in As are clearly required to test the tentative assignments made here.

DISCUSSION

While detailed theoretical calculations are required in the semimetals, comparison of the reduced Raman spectra indicate a number of tendencies. In Sb and As the reduced Raman intensity at lower frequencies (peak I) increases relative to that in Bi. This suggests a relative increase in the density of states at lower frequencies as do the limited theoretical calculations. Contributions of the coupling constant to this variation cannot be excluded. Measurements in Sb, both above and below the optical gap E_2 ,²⁴ suggest that resonant Raman effects do not influence the shape of the spectrum, i.e., the spectral dependence of the coupling constant. Similar results were drawn from measurements in Bi near to and above E_2 .

Comparison of the second-order spectra with neutron scattering data for single and polycrystalline samples has established the dominance of overtone scattering, a result common to other elemental materials with two atoms per unit cell (Si, Ge). The relative intensity of the secondorder Raman spectra at higher frequencies in Bi and possibly in Sb is lower than the neutron scattering and theoretical densities of overtones states. This suggests a possible decrease of the coupling parameter at higher frequencies. An explanation for such a decrease in the coupling constant with frequency is at present lacking. Further experimental and theoretical determinations of the density of states are required to confirm the present data. It is, for example, possible that off symmetry directions are not appropriately weighted in the Born-von Kármán models so that the density of states is lower than predicted at higher frequencies. The reduced Raman spectra also indicate an increase in the scattering intensity at higher frequencies in the series Bi, Sb, As, which are most reasonably interpreted as an increase in the density of states.

Perhaps the most interesting result of this study is the observation that the $k \simeq 0$ modes in As are shifted to higher frequencies relative to their position in Bi and Sb. The observation that the $E_g(\Gamma)$ modes in As are no longer the lowest modes of the optic branch is a distinct difference which bears on questions of the range and form of the interatomic interactions. In Bi and Sb the minimum at $E_g(\Gamma)$ and in particular its relatively rapid increase with increasing wave vector requires, in a Born-von Kármán model, the need for longrange interactions extending beyond second-nearest neighbors.^{8, 9} Macfarlane⁸ has noted that the

quantity $\sum_{i} \omega_{i}^{2}(\vec{k})$, which is equal to the trace of the dynamical matrix, $T(\vec{k})$, deviates appreciably from a constant in Bi, especially near Γ . The index i refers here to the band index. The results of Sharp and Warming⁹ indicate a very similar variation of $T(\vec{k})$ in Sb. Rosenstock²⁵ has shown that variations of $T(\vec{k})$ from a constant value, independent of \vec{k} , cannot arise from crystallographically unlike nearest-neighbor interactions or interactions which have a "classical electromagnetic" representation. Variations of $T(\vec{k})$ with \vec{k} must therefore arise from interactions between second or further neighbors which are not classical electromagneticlike in their representation. This result follows from the fact that for nearest neighbors the k-dependent part of the interaction appears only in off-diagonal elements of $T(\vec{k})$ and thus does not contribute to the trace.²⁶ In addition. the vanishing of the diagonal Coulomb terms is a consequence of the electrostatic nature of the interaction which, due to Laplace's equation, yields a zero contribution to $T(\vec{k})$. The results in As point to an increase in the relative value of T(0)and thus suggest that second-neighbor (or further) interactions are less important than they are in Bi and in Sb. The change in T(0) and in the suggested form of the phonon dispersion is indicative of the more covalent nature of As. A decrease in the second-neighbor interaction in As relative to Bi and Sb is also consistent with the decrease in the ratio of nearest- to next-nearest-neighbor distance and the resulting increase in compressibility in the trigonal direction.²

Resonance Raman-scattering measurements in semiconductors show that the second order processes are due to the direct electron-two-phonon interaction renormalized so as to include electron-one-phonon terms with nonresonant intermediate states.^{17,27} Under these conditions the shape of the second-order resonances is similar to that of the first order. A detailed analysis requires precise knowledge of the symmetries of the states involved in the resonances. Such information is not available for the materials under consideration.

The simplest expression for the ratio of the second to the first-order scattered integrated intensities, however, $is^{17,27}$

$$\frac{I^{(2)}}{I^{(1)}} = \left(\frac{\delta^{(2)} \mathcal{S}_0}{\delta^{(1)} \mathcal{S}_0}\right) \frac{\langle \xi_1^2 \rangle \langle \xi_2^2 \rangle}{\langle \xi_2^2 \rangle} \frac{N}{2} , \qquad (1)$$

where $\delta^{(1)}\mathcal{E}_0$ and $\delta^{(2)}\mathcal{E}_0$ are changes in electronic energies produced by the phonon displacements to first and second order in these displacements, respectively, N is the number of unit cells, $\langle \xi_i^2 \rangle$ are for classical oscillators the average phonon am592

12

plitudes. For quantum-mechanical oscillators, they must be replaced by the average square of the appropriate matrix element between neighboring oscillator states:

$$\langle \xi_i^2 \rangle = (h/4MN\omega_i)(1+n_B) , \qquad (2)$$

with M the atomic mass, ω_i is the phonon frequency, and n_B is the Bose-Einstein statistical factor. The subindex 0 of ξ_0 refers to first order scattering while 1 and 2 refer to the two phonons participating in the second order scattering. The terms $\delta^{(1)}\mathcal{S}_0$ and $\delta^{(2)}\mathcal{S}_0$ have dimensions of eV/cm and eV/cm², respectively. For simplicity in calculation, Ω_i is taken as the average frequency of the corresponding band. In order to convert them to the standard deformation potentials we multiply them by the "quasicubic" lattice constant a_0 and a_{00}^2 , respectively,

$$d = a_0 \delta^{(1)} \mathcal{E}_0, \quad D = a_0^2 \delta^{(2)} \mathcal{E}_0.$$
(3)

We should point out that a number of numerical factors of the order of unity are possible in the definitions of Eqs. (1) and (2). We take them equal

to one for the sake of simplicity. The ratios D/d obtained from the experimental data by this procedure for As, Sb, Bi, and a polycrystalline Bi-Sb alloy are listed in Table I. These ratios are very large, a fact already noted for the tetrahedral semiconductors.^{17, 28} First-order deformation potentials have normal values, of the order of a few eV, at least for Bi.²⁹ Thus, we conclude that the semimetals As, Sb, and Bi also possess an anomalously large electron-two-phonon interaction which may manifest itself in processes such as the temperature dependence of the lattice contribution to the carrier mobility.³⁰

ACKNOWLEDGMENT

We wish to thank Dr. E. Schönherr for the growth of the single crystals and Dr. W. Reichardt, Dr. W. Richter, and Professor M. H. Cohen for helpful discussions. The use of experimental unpublished data of Dr. J. Salgado, Dr. F. Gompf, and Dr. W. Reichardt is very gratefully acknowledged.

*Present address.

- †Present address: Universidad Autonoma de Madrid.
- ¹M. H. Cohen, L. M. Falicov, and S. Golin, IBM J. Res. Devel. <u>8</u>, 215 (1964).
- ²N. G. Pace, G. Saunders, and Z. Sümengen, J. Phys. Chem. Solids 31, 1467 (1970).
- ³S. Golin and J. A. Stocco, Phys. Rev. B <u>1</u>, 390 (1970).
- ⁴L. Ley, R. A. Pollak, S. T. Kowalczyk, R. McFeely, and D. A. Shirley, Phys. Rev. B <u>8</u>, 641 (1973).
- ⁵J. S. Lannin, in *Proceedings of the Conference on Tetrahedrally Bonded Amorphous Semiconductors*, edited by D. Weaire and S. Kirkpatrick (AIP, New York, 1974), p. 260; and Bull. Am. Phys. Soc. <u>20</u>, 379 (1975).
- ⁶M. Wihl, P. J. Stiles, and J. Tauc, in *Proceedings of* the Eleventh International Conference on the Physics of Semiconductors (Polish Scientific, Warsaw, 1972), p. 484.
- ⁷W. Reichardt, German Physical Society Mtg., Freudenstadt, Germany 1972, and Inst. für Angewandte Kernphysik, Kernforschungszentrum, Karlsruhe, Federal Republic of Germany, Progress Report, 1974 (unpublished).
- ⁸R. E. Macfarlane, in *Physics of Semimetals and Narrow-Gap Semiconductors*, edited by D. L. Carter and R. T. Bate (Pergamon, New York, 1971), p. 289.
- ⁹R. I. Sharp and E. Warming, J. Phys. F 1, 570 (1971).
- ¹⁰D. Weaire and A. R. Williams, in *Physics of Semimetals and Narrow-Gap Semiconductors*, edited by D. L. Carter and R. T. Bate (Pergamon, New York, 1971), p. 35.
- ¹¹P. A. Temple and C. E. Hathaway, Phys. Rev. B <u>7</u>, 3685 (1973).
- ¹²B. Weinstein and M. Cardona, Phys. Rev. B 7, 2545

(1973).

- ¹³W. Weber, S. Go, K. G. Rustagi and H. Bilz, in Proceedings of the Twelfth International Conference on the Physics of Semiconductors, edited by M. Pilkuhn (Teubner, Stuttgart, 1974), p. 194.
- ¹⁴J. H. Calleja, J. S. Lannin, M. Cardona, and E. Schönherr, Bull. Am. Phys. Soc. <u>19</u>, 227 (1974).
- ¹⁵J. Salgado, F. Gompf, and W. Reichardt, German Physical Society Mtg., Freudenstadt, Germany, 1974, and Inst. für Angewandte Kernphysik, Kernforschungszentrum, Karlsruhe, Federal Republic of Germany, Progress Report, 1974 (unpublished).
- ¹⁶V. S. Oskotskii, Fiz. Tverd. Tela <u>9</u>, 550 (1967) [Sov. Phys.-Solid State <u>9</u>, 2 (1967)]; N. Breuer, Z. Phys. 271, 289 (1974), and references therein.
- ¹⁷M. A. Renucci, J. B. Renucci, R. Zeyher, and M. Cardona, Phys. Rev. B <u>10</u>, 4309 (1974), and references therein.
- ¹⁸J. B. Renucci, W. Richter, M. Cardona, and E. Schönherr, Phys. Status Solidi 60, 299 (1973).
- ¹⁹W. B. Grant, S. Hüfner, H. Schulz, and J. Pelzl, Phys. Status Solidi B 60, 331 (1973).
- ²⁰A. Czochar, A. Rajca, J. Sosnowski, and A. Pindor, Acta Phys. Polonica A <u>43</u>, 37 (1973).
- ²¹J. Sosnowski, A. Czochar, and E. Maliszewski, in *Fifth IAEA Symposium on Inelastic Neutron Scattering* (IAEA, Vienna, 1972), p. 61.
- ²²J. I. Yarnell, J. L. Warren, R. G. Wengel, and S. H. Koening, IBM J. Res. Devel. <u>8</u>, 234 (1964).
- ²³D. B. Smith, Los Alamos Scientific Report (1967) (unpublished).
- ²⁴M. Cardona and D. L. Greenaway, Phys. Rev. <u>133</u>, A1685 (1964).

- ²⁵H. B. Rosenstock, Phys. Rev. <u>129</u>, 1959 (1963).
 ²⁶H. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., New York, 1954), p. 68.
 ²⁷B. Weinstein and M. Cardona, Phys. Rev. B <u>8</u>, 2795 (1973).
- ²⁸J. B. Renucci, R. N. Tyte, and M. Cardona (unpublished).
- ²⁹A. A. Lopez, Phys. Rev. <u>175</u>, 823 (1968).
 ³⁰K. L. Ngai, in Ref. 13, p. 489.