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# Vibrational and Raman-scattering properties of crystalline $Ge_{1-x}Si_x$ alloys

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First- and second-order Raman-scattering measurements have been performed in the crystalline $Ge_{1-x}Si_x$ alloy series from low frequencies ($\sim 40$ cm$^{-1}$) to high frequencies ($\sim 1100$ cm$^{-1}$). The second-order optical-like spectra indicate appreciable structure in the phonon density of states not predicted by the coherent-potential-approximation theory, but are in accord with recent cluster calculations. The first-order low-frequency acoustic spectra provide a direct identification of one-phonon disorder-induced scattering in semiconductors resulting from mass disorder. The optical-mode first-order spectra are interpreted in terms of $k \simeq 0$ as well as density-of-states contributions. Comparison with the second-order spectra allows an estimate of the relative importance of the $k \simeq 0$ and density-of-states contributions. The results indicate that the first-order scattering from the Ge-derived optical mode is primarily associated with the $k \simeq 0$ component except at rather large values of $x$. Measurements at low frequencies and in the elastic continuum range also demonstrate an explicit frequency dependence of the Raman coupling parameter for the disorder-induced acoustic phonon scattering.

## I. INTRODUCTION

Binary and ternary crystalline alloys constitute a broad class of solids whose physical properties are not well understood from a fundamental point of view. Having a degree of disorder between mixed-crystal systems and amorphous solids, these materials pose a number of basic questions concerning the role of structural disorder and its local consequences on the electronic and vibrational properties of solids. While various rigid-band and effective-medium theories,[1,2] for example, have been proposed for alloy systems, they in general neglect the complex statistical effects associated with small clusters on an atomic scale.[3-6] Experimental evidence for such clusters has, however, been limited. Numerical studies of the vibrational properties of model systems have been the primary "data" for the discussion of cluster effects.[1,3,4] Recent experimental[7] and theoretical studies[8] in amorphous $Ge_{1-x}Si_x$ alloys have also pointed to the need for inclusion of clustering effects.

In the present study, Raman measurements were performed in crystalline $Ge_{1-x}Si_x$ alloys to gain information about the influence of disorder on the vibrational density of states and the coupling mechanisms for Raman scattering. $Ge_{1-x}Si_x$ alloys function as an almost model system with a complete range of solid solubility, a large mass ratio ($m_{Ge}/m_{Si} = 2.6$), similar force constants,[9] and end members whose phonon spectra have been extensively studied.[10,11] As the lattice dynamics of Ge and Si are primarily determined by local interactions,[9] this allows a comparison with experimental[7] and theoretical[8] studies of the corresponding amorphous alloys. Aside from smoothly varying matrix-element effects, the first-order Raman spectra of amorphous $Ge_{1-x}Si_x$ alloys reflect the phonon density of states.[7,8] In addition, the second-order spectra of crystalline Ge[12] and Si[13] also primarily reflect the form of the overtone density of states. Recent work in crystalline $Ge_{0.54}Si_{0.46}$ also suggests that overtone scattering predominates in the alloys.[14] Second-order measurements thus provide direct information about the form of the $Ge_{1-x}Si_x$ density of states.

The loss of translational symmetry with alloying modifies the pure-crystal selection rules for first-order Raman scattering. This yields additional allowed scattering from the entire density-of-phonon states as well as resonant or local modes. Of interest in $Ge_{1-x}Si_x$ alloys is the relative contribution of the $k \simeq 0$ and disorder-induced contributions. The major first-order alloy peaks[15-17] have been interpreted as reflecting either the $k \simeq 0$[18,19] or density-of-states terms in concentrated alloys.[16] In order to further determine the relative contribution of these scattering mechanisms, second-order as well as low-frequency first-order scattering has been studied. At low frequencies the scattering allows a more direct identification of disorder-induced scattering than has been obtained in crystalline semiconductors. In addition, the low-frequency region yields information about the matrix elements for the disorder-induced scattering through the coupling-parameter frequency dependence.[20,21]

Earlier Raman-scattering measurements in crystalline $Ge_{1-x}Si_x$ have primarily considered the dominant first-order modes[15-17] in the range of 280–521 cm$^{-1}$. Additional fine structure has also been discussed in terms of possible resonant, local, and density-of-states contributions. Second-order scattering has also been noted.[7,14,17]

For convenience of discussion and comparison, the paper is divided into different sections for the separate frequency ranges. The higher-frequency spectra are presented in Sec. III, followed by the lower-frequency results in Sec. IV and the intermediate range of frequencies in Sec. V.

## II. EXPERIMENT

Raman-scattering measurements at 4880 and 5145 Å were performed near room temperature on Syton polished polycrystalline samples previously employed in electroreflectance measurements.[22] Electron microprobe measurements indicated high compositional homogeneity in the samples. A third monochromator system in conjunction with a multichannel analyzer for improved signal-to-noise phonon counting was employed. The spectral resolution was ~4 $\mathrm{cm}^{-1}$.

The second-order spectra in the alloys were quite weak so that run times of the order of 4–8 h were employed for improved signal-to-noise. The incident argon laser power employed was ~500 mW and a cylindrical lens was employed to prevent appreciable heating. The thermal conductivity of the alloys is such that some heating, of the order of 30 K, was noted from a comparison of Stokes and anti-Stokes spectra. Selected measurements were also performed at $T \sim 100$ K in a cold finger dewar.

## III. HIGHER-FREQUENCY RANGE ($\omega \gtrsim 500\ \mathrm{cm}^{-1}$)

### A. Experimental results and discussion

Figure 1 indicates the Raman spectra for $\mathrm{Ge}_{1-x}\mathrm{Si}_x$ alloys for frequencies above ~500 $\mathrm{cm}^{-1}$, corresponding to second-order processes. The curves are arbitrarily normalized with the zero intensity indicated by the background value at 1050 $\mathrm{cm}^{-1}$. As shown by Weinstein and Cardona,[12] the spectrum in Ge is primarily associated with 2LO and 2TO overtones at ~480 and 560 $\mathrm{cm}^{-1}$, respectively. The sharp peak at ~597 $\mathrm{cm}^{-1}$ represents an additional contribution from resonant 2Γ phonon processes.[12] The Si spectrum shown in Fig. 1 is that of Temple and Hathaway[13] and is also overtone dominated. An exception is the peak at ~615 $\mathrm{cm}^{-1}$ which is attributed to combination optical-plus acoustical modes. A similar small peak is observed in Ge at lower frequencies.

For less concentrated alloys (≤12% additions), the spectra differ considerably from the end members, particularly in the Ge-rich end, where appreciable new structure is observed in the $x = 0.065$ and 0.11 samples. In addition, a broadening of the 2TO-like band for Ge is noted. The 2Γ peak, also seen for $x = 0.065$, is not observed at $x = 0.11$ with a laser excitation of 4880 Å. The addition of 8.5% Ge to Si similarly results in a broadening of the pure Si spectrum. A peak and shoulder observed at ~805 and ~855 $\mathrm{cm}^{-1}$ are new features, while the 2LO peak of Si is not distinctly observed. For more concentrated alloys (up to ~25% additions), the new features observed in the Si-rich

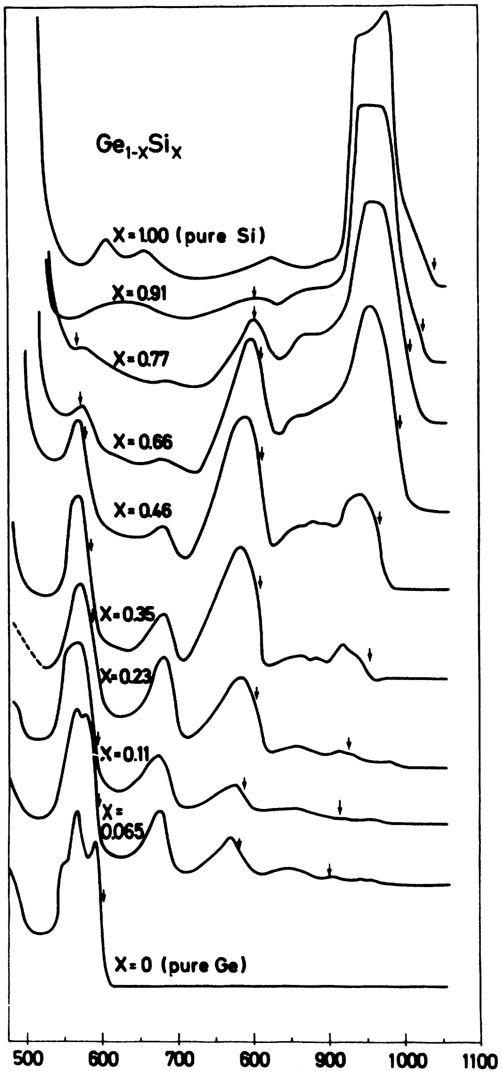

FIG. 1. Second-order Raman spectra in $\mathrm{Ge}_{1-x}\mathrm{Si}_x$ at $T \sim 330$ K. The zero level is the intensity at 1050 $\mathrm{cm}^{-1}$. The arrows indicate major first-order peak positions multiplied by 2. The $x = 1$ spectrum is from Ref. 13. The intensity scales are arbitrary and linear in counts/sec.

end grow in intensity, while there is a loss of the structure between ~590 and 670 cm$^{-1}$. In addition, new features are observed for $x=0.77$ at 575 and 686 cm$^{-1}$. In the highest-concentrated alloys, i.e., with $x=0.5\pm0.15$, there is a merging of the spectral features from the Si- and Ge-rich ends with a relative maximum intensity developing in the peak ~780 cm$^{-1}$ at $x=0.46$. Some shift of the peak derived from Si 2TO processes is observed, while only a relatively small shift of the band corresponding to 2TO in Ge is noted. In the neighborhood of $x=0.5$, no new structure is observed nor is there any noticeable sharpening of individual bands that might indicate a tendency toward ordering.[17] In addition to the three major bands at ~570, 800, and 930–970 cm$^{-1}$, less intense features between 670–680 and 850–900 cm$^{-1}$ are also observed to persist throughout the alloy series. Even at the smallest value of $x=0.065$ studied, the spectra indicate structure out to ~1000 cm$^{-1}$. Above ~890 cm$^{-1}$, the spectra are weak and vary in detail with composition for $x\lesssim0.2$. In addition, between $x=0.35$ and 0.46, the higher frequency Si-derived band develops a peak at ~920 cm$^{-1}$ which is observed at lower values of $x$.

The major peaks in the spectra of Fig. 1 are qualitatively similar to the first-order Raman results in amorphous $Ge_{1-x}Si_x$ alloys at one half the frequency.[7] Further evidence that the major and minor features in the second-order spectra reflect the overtone density of states is based on the observation of weak structure in the first-order scattering at lower frequencies (Figs. 4–7). This is discussed in Sec. V in terms of disorder-induced contributions that reflect the one-phonon density of states. Thus the weaker features ~680 cm$^{-1}$ and in the interval 860–900 cm$^{-1}$ indicate additional structure in the overtone density of states.

The results in Fig. 1, which primarily reflect the form of the one-phonon density of states with smoothly varying matrix elements, differ considerably from the calculations of effective-medium theories. This is seen, for example, if the spectrum for $x=0.11$ is compared with a single-site coherent-potential-approximation (CPA) calculation for $x=0.092$.[23] The Raman results indicate appreciable structure extending to high frequencies, as well as the lack of gap between the local and Ge-like modes, which is not predicted by the theory. These differences, even at low concentrations, are attributed to the average medium approach,[2] which neglects the details of small atom clustering. Thus the higher-frequency Raman tail, for example, indicates the presence of clusters of two or more Si atoms surrounded by a Ge matrix.[3-6,8] Similarly at $x\sim0.5$, the CPA theory predicts a relatively structureless density of states, with higher-frequency peaks at ~275 and 450 cm$^{-1}$.[24] In contrast, Yndurain[8] has employed a cluster-lattice method which yields good agreement with the Raman results for amorphous $Ge_{1-x}Si_x$ alloys. In addition, weak structure in the density of states has been noted at ~340 cm$^{-1}$ in the recent crystalline alloy calculations and attributed to specific Si cluster configurations.[25]

## IV. LOWER-FREQUENCY RANGE ($\omega \leqslant 340$ cm$^{-1}$)

### A. Experimental results and discussion

At lower frequencies the spectra encompass the vibrational modes of Ge and the alloy acoustic modes. In Ge, the spectrum below the highest mode at 301 cm$^{-1}$ is primarily composed of a second-order 2TA overtone band. For Si, this frequency range also encompasses most of the 2TA band. These are indicated in Fig. 2 with the Si data of Temple and Hathaway.[13] The 2TA band for Ge is similar to that of Weinstein and Cardona.[12] The stray light has been subtracted in an approximate manner at $x=0$ for purposes of clarity. The Raman spectra for $T\simeq 330$ K without the stray light subtracted is shown for the alloys between $x=0.11$ and 0.915.

The addition of 11% Si to Ge results in a Raman spectrum that differs appreciably from that of Ge. While the peak at 167 cm$^{-1}$ is related to the corresponding second-order peak in pure Ge at 162 cm$^{-1}$, the weak Ge shoulder at 130 cm$^{-1}$ is not observed, indicating a broadening of the acoustic band with increasing $x$. For compositions up to $x=0.46$, the major 2TA peak is distinctly observed. Of particular importance is the observation of a new band below 120 cm$^{-1}$. With increasing $x$, the low-frequency band is more clearly resolved due to a reduction in the stray light contribution which becomes relatively flat. The center of the low-frequency band occurs near one half the frequency of the 2TA peak and increases in frequency and relative intensity with increasing $x$. The peak of the low-frequency band is also found to vary approximately linearly with Si concentration up to $x=0.36$. This is in accord with inelastic tunneling data[26] and theoretical studies[2] of the variation of the one-phonon TA band if account is taken of the band-structure change with alloying.[27] The data thus demonstrate that the origin of the low-frequency scattering is associated with disorder-induced TA scattering. This is in qualitative agreement with the calculation of Xinh for the dilute case of 1% Si in Ge which predicts a weak disorder-induced acoustical-mode contribution to the scattering.[28] Comparison of the relative intensity of the TA to Ge-derived optic peak in Fig. 2 indicates a rapid increase in the disorder-induced scattering for

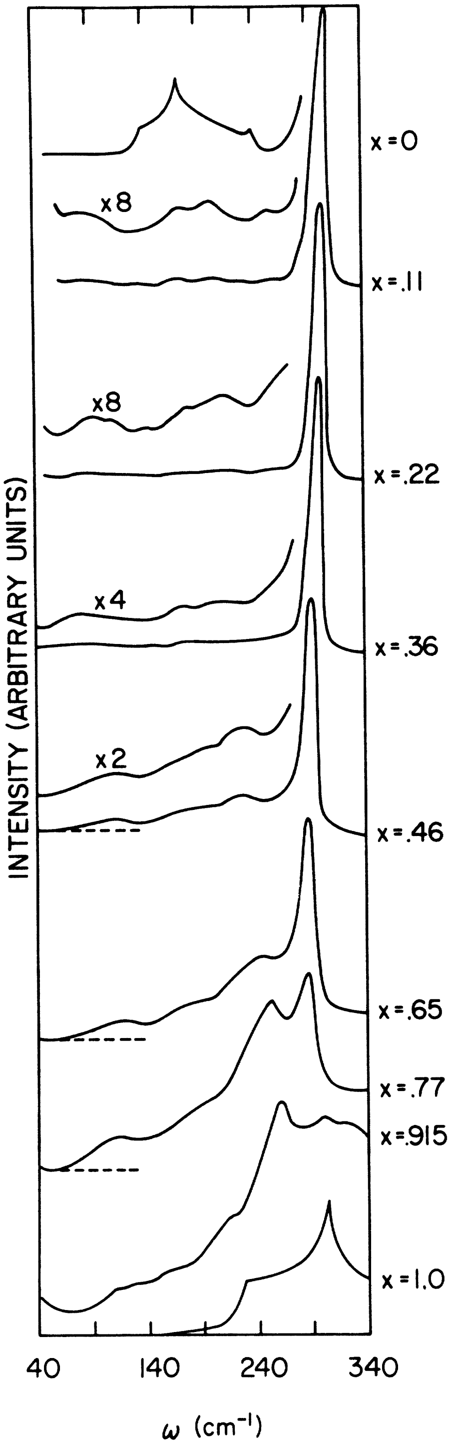

FIG. 2. First- and second-order Raman spectra for $Ge_{1-x}Si_x$ at $T\sim330$ K for $\omega\leq340$ cm$^{-1}$. The $x=0$ spectrum has the stray light background subtracted in an approximate manner. The intensity scales are arbitrary and linear in counts/sec. The horizontal dashed lines for $x\geq0.46$ indicate the approximate backgrounds at lower frequency.

$x\gtrsim0.4$.

Further direct evidence for disorder-induced scattering is shown in Fig. 2 for Si-rich alloys. For $x=0.915$, a peak and shoulder at 216 and 300 cm$^{-1}$ appear to be derived from the corresponding 2TA scattering in Si. Below ~170 cm$^{-1}$, however, a new band is observed with peaks or inflection points at 108 and 152 cm$^{-1}$. These features, at frequencies quite close to the corresponding second-order peaks, directly indicate disorder-induced first-order TA scattering. That the first-order spectrum does not decrease above ~160 cm$^{-1}$ reflects an overlap of first- and second-order Raman spectra. The intensity of the disorder-induced TA scattering for $x=0.915$ is quite small. For the spectral resolution of ~4 cm$^{-1}$ employed, the Si-derived optic peak is a factor of $\sim3.6\times10^2$ greater than the TA peak. At $x=0.77$, this ratio is reduced to $\sim7.8\times10^1$, while the Si linewidth is not appreciably changed.[16,17]

The identification of a low-frequency disorder-induced peak in $Ge_{1-x}Si_x$ alloys is *direct* detailed evidence for such scattering in semiconductors. While similar scattering has been observed in impure alkali halides[29] and, recently, in nonstoichiometric metallic carbides and nitrides,[30] only indirect evidence[31] has been presented to date for such scattering in semiconductors.[32-34] This arises from the modification of first-order $k\simeq0$ scattering with alloying as well as from resonant modes which may mask a density-of-states contribution. Thus, additional spectra features observed in mixed crystals as well as line-shape asymmetries do not necessarily reflect a disorder-induced density-of-states contribution.[31] Strahm and McWhorter have indicated that a weak peak was observed at one composition at low frequencies in the $GaAs_{1-x}P_x$ system which they interpret as disorder-induced scattering.[32] While this is suggestive of a density-of-states contribution, further low-frequency spectra for this alloy series as well as theoretical calculations are required to confirm this.

In contrast to the low-frequency acoustic modes, the peak at 256 cm$^{-1}$ for $x=0.91$ does not have a correspondence to features in Si. This suggests a resonant mode. In Fig. 3, the variation of the peaks between 195 and 256 cm$^{-1}$ is shown as a function of $x$ to ascertain their origin. The solid line is an aid to visualization, while the dashed line between $x=0.36$ and 0.46 indicates that a more rapid variation in peak position would be required if these peaks are to have a common origin. An alternative explanation is that for $x\gtrsim0.4$ the peaks reflect a resonant mode of the system, while for smaller $x$ they represent disorder-induced LA scattering. An extrapolation of the approximate

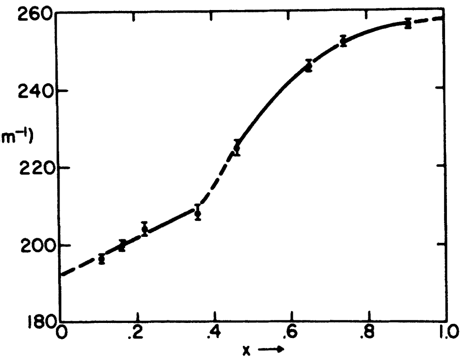

FIG. 3. Variation of the Raman peaks between 190–260 $\mathrm{cm}^{-1}$ as a function of $x$. The dashed curves indicate extrapolations for $x \rightarrow 0$ and $x \rightarrow 1$, while for $0.36<x<0.46$, the dashed curve indicates that the origin of the peak may change.

linear variation of the peak position to $x=0$ yields a value of 192 $\mathrm{cm}^{-1}$. This agrees with the peak position of the Ge LA band.[10] The results of Fig. 3, along with the observation of disorder-induced TA scattering at lower frequencies, thus indicate disorder-induced LA scattering at lower values of $x$. First-order Raman measurements in amorphous $\mathrm{Ge}_{1-x}\mathrm{Si}_x$ alloys[7] indicate structure near LA(Ge) that suggests a correspondence to crystalline LA modes.

The suggested resonant mode at 256 $\mathrm{cm}^{-1}$ for $x=0.915$ and the extrapolation of Fig. 3 to $x=1$ differs from the theoretical predictions for resonant modes of Ge in Si.[28,35] As is well known, resonant mode values are sensitive to the form of the density of states. For dilute additions of Ge to Si, earlier calculations were based on a density of states that is now known to be in error for portions of the spectrum.[8,13]

### B. Coupling parameter variation

As in amorphous solids, the disorder-induced density of states contribution can be written in the general phenomenological form[36] for first-order Stokes scattering:

$$I^\alpha(\omega)=\sum_b \omega^{-1}(n+1)C_b^\alpha \rho_b(\omega)\,, \qquad (1)$$

where $b$ labels the modes of density $\rho_b(\omega)$, $n+1$ is the statistical factor, and $\alpha$, the Raman tensor component. If the coupling parameters $C_b^\alpha$ are assumed for simplicity to be a smooth function of frequency with a similar value for all modes of the same frequency, then Eq. (1) yields

$$I^\alpha(\omega)=\omega^{-1}(n+1)C^\alpha(\omega)\rho(\omega)\,. \qquad (2)$$

$C^\alpha(\omega)$ thus functions as an effective coupling parameter with the simplifying assumption that it is a relatively smooth monotonic function of frequency. The total first-order Raman scattering is then assumed to be the sum of Eq. (2) along with a $k \simeq 0$ term. For simplicity in polycrystalline alloys, differences in the tensorial components are not considered. In dilute Ge alloys, only one Raman component $\Gamma_{25}$ yields first-order scattering.[28]

For the low-frequency TA regime contributions from the $k \simeq 0$ term are expected to be small[19] for $\omega \lesssim 130$ $\mathrm{cm}^{-1}$ so that information about the form of $C(\omega)$ may be obtained if $\rho(\omega)$ is known. In the quasi-continuum regime $\rho(\omega) \sim \omega^2$ and $I \sim C(\omega)$ for $\omega \ll T$. Estimates of the frequency range of this regime in $\mathrm{Ge}_{1-x}\mathrm{Si}_x$ alloys may be obtained using the weighted average mass[37] and the value of ~35 $\mathrm{cm}^{-1}$ for pure Ge.[10] While a detailed study of the quasi-continuum range was not made in the alloys, Raman-scattering measurements in the $x=0.46$, 0.65, and 0.77 alloys all indicated scattering above background at frequencies below the estimated cutoff of the quasi-continuum regime. The results directly demonstrate that $C(\omega)$ is a function of frequency for the disorder-induced scattering.

Information about $C(\omega)$ may also be obtained at higher $\omega$ by comparing the Raman TA-like peak position with that of the density of states. The latter may be estimated from inelastic tunneling measurements[26] or from Raman measurements in the amorphous alloys[7] with a reasonable choice for the coupling parameter.[38] The low-frequency Raman peaks in the measured intensities of Fig. 2 are found to occur at similar or higher frequencies than the predicted TA peak in the density of states. This is in contrast to amorphous $\mathrm{Ge}_{1-x}\mathrm{Si}_x$,[7] and suggests a more rapid variation of $C(\omega)$ in the crystalline materials. From Eq. (2), $C(\omega)$ is found to vary by order $\omega/(n+1)$ or faster in the crystalline alloys, that is between $\omega$ and $\omega^2$. In general, $C(\omega)$ may also change with composition, and the experimental results do indicate some variations from the predicted density-of-states peak. For $x=0.46$ and 0.65, the Raman peak is observed to be ~4–8 $\mathrm{cm}^{-1}$ above the estimated peak in $\rho(\omega)$, while for the other compositions the peaks are somewhat closer.

## V. INTERMEDIATE FREQUENCY RANGE

### ($280 \leqslant \omega \leqslant 525$ $\mathrm{cm}^{-1}$)

### A. Experimental results and discussion

The range of frequencies from ~280 to 525 $\mathrm{cm}^{-1}$, designated here as intermediate frequencies, overlaps somewhat the low- and higher-frequency range, but conveniently includes the major one-phonon Raman lines.[15-17] In addition to three major peaks, secondary spectral features have been

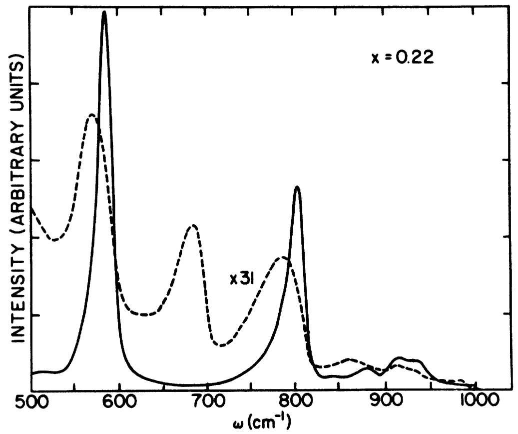

FIG. 4. Comparison of the first-order (solid) and second-order (dashed) Raman spectra for $x = 0.22$. The frequency scale of the former is multiplied by 2 for comparison.

noted by Ashkin *et al.*[39] and discussed by Brya.[17] In contrast to Renucci *et. al.*,[16] Brya[17] has suggested that the Si-derived mode has a linear variation with frequency between $x = 0.1$ to 0.9. Our measurements for $x = 0.065$ and 0.11 indicate, however, a derivation from linearity, with peaks at 450 and 455 cm$^{-1}$, respectively. A smooth extrapolation to $x = 0$ yields a value of $466 \pm 1$ cm$^{-1}$ for this mode which has been interpreted as a local Si-pair mode in Ge.[15]

Given the observation at lower frequencies of disorder-induced one-phonon acoustic scattering, it is useful to estimate the relative contribution of the disorder-induced one-phonon optical scattering. Renucci *et al.* have suggested from the line shape[16] and Gruniesen parameters[40] that the major peaks in concentrated alloys tend to reflect the vibrational density of states. In contrast, other calculations[18,19] consider only $k \simeq 0$ contributions to the Raman scattering.

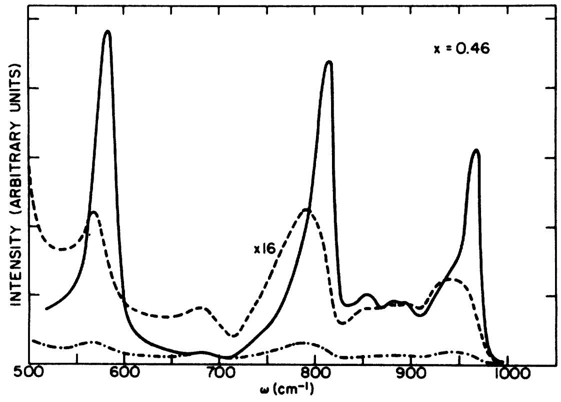

FIG. 5. Comparison of the first-order (solid) and second-order (dashed) Raman spectra for $x = 0.46$. The frequency scale of the former is multiplied by 2 for comparison. The broken curve is the second-order spectrum which has been scaled at 680 cm$^{-1}$ to the first-order spectrum.

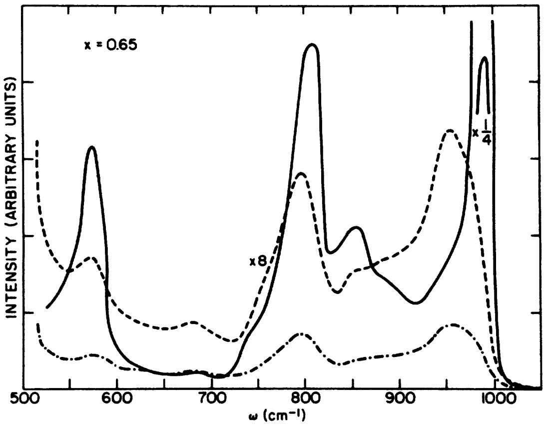

FIG. 6. Comparison of the first-order (solid) and second-order (dashed) spectra for $x = 0.65$. The frequency scale of the former is multiplied by 2 for comparison. The broken curve is the second-order spectrum which has been scaled at 680 cm$^{-1}$ to the first-order spectrum.

To ascertain the nature of the major peaks it is useful to note that in pure Ge and Si the optical modes occur at the highest frequency in the vibrational spectrum. A comparison of twice the frequency of the major Ge-derived, Ge-Si, and Si-derived peaks with the second-order overtone spectrum is indicated by arrows in Fig. 1. It is clear that only for relatively large concentrations do the first-order peaks occur near to those of the corresponding second-order spectra. A more detailed comparison of first- and second-order spectra for $0.22 \leq x \leq 0.77$ which demonstrates this point is indicated in Figs. 4–7.

In addition to the correspondence between major elements of the first- and second-order spectra, Figs. 4–7 indicate overlapping of the minor spectral features. Thus the peak observed (~680 cm$^{-1}$) in the second-order spectra has an analogous first-order peak at ~340 cm$^{-1}$ for $x \geq 0.46$. Similarly, structure observed at ~865 cm$^{-1}$ in second order tends to have a corresponding first-order peak approach it with increasing $x$. This is further evidence for the interpretation of weak second-order structure in terms of overtone processes.

Figures 1 and 4–7 thus indicate that the dominant contribution to the major first-order peaks for low or intermediate alloy concentrations is not due to density-of-states contributions, but rather the $k$

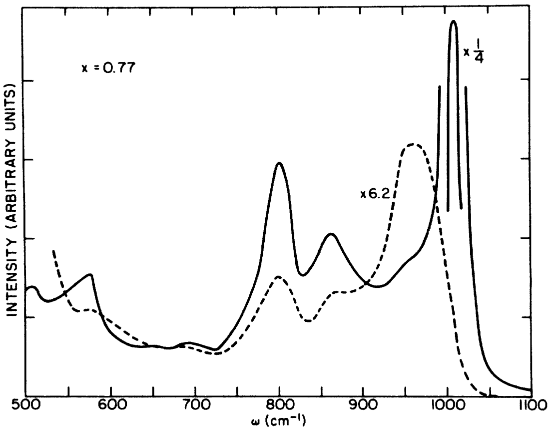

FIG. 7. Comparison of the first-order (solid) and second-order (dashed) Raman spectra for $x = 0.77$. The frequency scale of the former is multiplied by 2 for comparison.

$\simeq 0$ component of the spectral function.[1] In addition, the asymmetry to low frequencies, while reflecting disorder, is also to be associated with the $k \simeq 0$ contributions.[19,41] This is consistent with an appreciable asymmetry observed in the Ge-derived line for $x = 0.065$. At this concentration the disorder-induced density-of-states contributions to the Raman scattering is estimated to be quite weak.

### B. Estimates of the first-order optical contributions

At the present time there does not exist a theory that allows a separation of first-order Raman scattering in concentrated alloys into contributions that reflect the $k \simeq 0$ and density-of-states terms. The point of view pursued here is thus to give a rough estimate of these terms given the different interpretations of the origin of the major peaks in concentrated alloys.[16,18,19,40] The phenomenological separation into $k \simeq 0$ and density-of-states contributions is a simplifying approximation and neglects any additional "interference" terms.[41]

The qualitative importance of density-of-states contributions to the first-order scattering may be directly obtained by comparing the positions (Fig. 1) and widths of the corresponding first- and second-order peaks. This comparison indicates that only for $x \geq 0.46$ is the density-of-states contribution to the first-order peaks derived from Ge and Ge-Si modes appreciable. More quantitative estimates of the contribution of the density-of-states term may be obtained by either a scaling of the first- and second-order spectra or by extrapolation of the low-frequency TA scattering.

In order to scale the first- and second-order scattering, we consider a weak first-order feature that occurs only at high alloy concentrations and which can be interpreted as primarily arising from disorder-induced density-of-states contributions. Such a feature is observed at 340 cm$^{-1}$. Its position and width is similar to that of the corresponding second-order peaks and does not change with $x$. The first-order peak is superimposed on a background associated with the tails of the Ge-derived and Ge-Si peaks which may be estimated from the results at lower values of $x$. In Figs. 5 and 6, the broken curves indicate the first-order spectra at 340 scaled to the second-order spectra at 680 cm$^{-1}$. The zero intensity of the first-order spectra has been shifted to subtract the approximate background at 340 cm$^{-1}$. For the $x = 0.77$ spectra of Fig. 7, the scale choice of 6.2 yields an approximate normalization at 680 cm$^{-1}$.

For the $x = 0.77$ spectrum in Fig. 7, the second-order Ge-derived peak is enhanced by the high-frequency tail of the first-order Si-derived mode. Based on the first-order inelastic tunneling[26] and the first-order Raman spectra in the crystalline and amorphous material,[7] we estimate an overtone density-of-states contribution equal to $\sim\frac{1}{2}$ of the total intensity at 580 cm$^{-1}$. For $x = 0.77$, the density-of-states contribution to the first-order Ge-derived peak is then estimated with the scaling procedure to be of order $\frac{1}{2}$, while for $x = 0.65$ and $x = 0.46$, values of $\frac{1}{8}$ and $\frac{1}{23}$ are obtained, respectively. For the Ge-Si peak, the scaling procedure yields a somewhat larger density-of-states contribution than for the Ge-derived peak. As the Ge-derived peak may be expected to have a greater disorder-induced component, this suggests that the scaling procedure overestimates the Ge-Si peak, possibly due to the coupling parameter approximations or to background estimates. For the Si-derived density-of-states peak the scaling procedure clearly overestimates the possible contribution to the first-order shoulder between 470–480 cm$^{-1}$ as seen for $x = 0.77$.

An estimate of the density-of-states contribution to the Ge-derived first-order peak may also be obtained by extrapolating the approximate low-frequency form for $C(\omega)$. The density-of-states contribution may then be obtained using Eq. (2);

$$\begin{aligned} I(\mathrm{Op\text{-}Ge})/I(\mathrm{TA}) = {} & [\rho(\mathrm{Op\text{-}Ge})/\rho(\mathrm{TA})] \\ & \times \{[C(\mathrm{Op})/C(\mathrm{TA})](\omega_{\mathrm{TA}}/\omega_{\mathrm{Op}}) \\ & \times (n+1)_{\mathrm{Op}}/(n+1)_{\mathrm{TA}}\}, \end{aligned} \tag{3}$$

where $C(\mathrm{Op})$ and $C(\mathrm{TA})$ are the coupling parameters of the Ge-optical (Op) and TA peaks, respectively. As the density of states of the crystalline alloys is not known, the ratio $\rho(\mathrm{Op\text{-}Ge})/\rho(\mathrm{TA})$ may be estimated by assuming a similar variation with

$x$ as that calculated for the amorphous alloys.[8]

An extrapolation of the low-frequency variation of $C(\omega)$ from the TA peak frequency yields an approximate factor of unity for the second factor in braces in Eq. (3). For $x = 0.46$, 0.65, and 0.77, $\rho(\text{Op-Ge})/\rho(\text{TA})$ is also of order unity.[8] With these rough estimates, Eq. (3) then yields $I(\text{Op-Ge}) \approx I(\text{TA})$. This implies that the disorder-induced Op (Ge) density-of-states contribution will be of the same approximate magnitude as that of the low-frequency TA peak intensity of Fig. 2. For $x = 0.77$, this yields a contribution of $\frac{1}{5}$ of the total intensity of the Ge-derived peak, while for $x = 0.65$ a factor of $\frac{1}{20}$ is obtained. This is similar to the predictions based on the scaling of the first- and second-order spectra within a factor of 2–3. The results thus agree with the qualitative conclusions based on the widths and peak positions of the first- and second-order spectra. The density-of-states contribution is thus found to be considerably less than that of the $k \simeq 0$ spectral component except at rather high concentrations, where the Ge-derived peak tends to lose definition in the vibrational spectrum.

## VI. SUMMARY AND CONCLUSIONS

Second-order Raman measurements in $Ge_{1-x}Si_x$ have been interpreted in terms of primary overtone scattering and have thus yielded information about the variation of the phonon density of states in the alloys. The spectra are related to the experimental and theoretical density of states of amorphous $Ge_{1-x}Si_x$ alloys, but contain a number of additional features. The results indicate the importance of atomic clustering effects and do not agree with the results of the single-site CPA, but are in accord with recent cluster calculations. At lower frequency, the spectra indicate first-order disorder-induced acoustic scattering that reflect the one-phonon density of states as well as resonant-mode contributions. The data for the TA-like modes are direct evidence for a density-of-states contribution in semiconductors. In contrast to most Raman studies on disorder systems, the disorder in $Ge_{1-x}Si_x$ is attributed to "diagonal" or mass disorder rather than to "nondiagonal," or force-constant disorder. The low-frequency spectra also directly indicate that the coupling parameter for the disorder-induced scattering has an explicit frequency dependence. While scattering has been observed in the elastic continuum range, more detailed measurements are required to determine its precise form.[20,21]

A comparison of the first- and second-order spectra in regard to peak positions and widths indicate that the primary first-order modes are associated with the $k \simeq 0$ component of the scattering rather than the density-of-states term, except at rather high alloy concentrations. A semiquantitative estimate of the $k \simeq 0$ and density-of-states contributions to the first-order peak intensity was made for $x \geq 0.46$. The results indicate a dominant $k \simeq 0$ contribution to the first-order Ge-derived peak for $x \leq 0.65$, while for $x = 0.77$ the disorder-induced contribution may, however, be appreciable. Other probes such as infrared absorption in concentrated $Ge_{1-x}Si_x$ alloys[42] indicate a number of peaks that correspond to density-of-states structure observed here. This suggests an interpretation based on disorder-induced first-order infrared absorption.[43] The first-order Raman data point to a qualitative difference in the scattering contributions relative to that of amorphous solids. This is attributed to the intrinsic fluctuations in the local bond parameters in amorphous Ge or Si which are larger, for example, than those that arise in the crystalline alloys.

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