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Pressure dependence of the optic phonon energies in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$

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We have conducted an extensive Raman scattering study of the effects hydrostatic pressure has on $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloy phonons for $0 \leqslant x \leqslant 0.70$. The mode-Grüneisen parameter γ is found to depend on x. The variation is monotonic in dilution and increases by 30% over the range of x studied. We find that γ for GaAs-like and AlAs-like longitudinal-optic (LO) phonons correlates with Born's transverse dynamic effective charge on the respective alloy component. We suggest that this phenomenon is specific to alloys, and interpret it as a consequence of charge transfer on the cation sublattice. Pressure induced resonance Raman scattering is examined for $x = 0.40$. We observe strong enhancement for both LO phonons when in resonance with the direct energy gap. [S0163-1829(96)03736-8]

I. INTRODUCTION

The physical properties of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys have been studied in great detail because of their technological significance and because the full range of x can be achieved with great reproducibility. This makes the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ system an excellent arena for examining the results of alloying on the structural, electronic, optical, and vibrational properties.[1]

Raman scattering studies are important for examining long-range order and local structure in these alloys.[2–5] A two-mode behavior in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ is widely accepted. The optic-phonon branches do not overlap, producing AlAs-like transverse-optic (TO_2) and longitudinal-optic (LO_2) phonons and GaAs-like TO_1 and LO_1 phonons. In the GaAs optic branch, increasing x reduces both the LO_1 and TO_1 phonon energies. The LO_2 phonon in the AlAs optic branch increases in energy with x, with the TO_2 phonon showing a much smaller increase. For small x, the light Al atoms are sparsely populated on the cation sublattice and exhibit local vibrational mode behavior. For $x \approx 1$ the Ga atoms exhibit gap-mode behavior. For both these cases, long-range order is irrelevant in the dilute limit and there is no splitting between the LO and TO phonons.

Subsequent work[6,7] has challenged the spatial correlation model[3,8] as an explanation for the pronounced x dependence of the TO and LO phonons and the asymmetry of the LO phonons. In a recent paper,[7] the vibrational energy of the LO phonons and their line shapes were attributed to transfer of oscillator strength on the cation sublattice. This affects the vibrational energies of phonons (primarily LO but also TO) of both the GaAs and AlAs branches, as well as their line shapes, and interprets them without spatial correlation. Crystal momentum $\mathbf{k}$ remains a good quantum number, in agreement with Kash *et al.* This supports applicability of the virtual crystal approximation.[9] Brafman and Manor found strong contrasts between the results of alloying and those of ion implantation. The latter are known to create finite-size effects. Additionally, there are disorder activated Raman bands present in the alloys. This indicates violation of the single-crystal $\mathbf{k} \approx \mathbf{0}$ selection in first-order Raman scattering, but the results are not nearly as drastic as ion-implantation effects.[10]

Alloying effects on electronic band structure are also well known.[1] Pure GaAs is a direct-gap semiconductor (Γ symmetry point in the valence band to Γ point in the conduction band). With increasing x, the direct transition increases according to

$$E_g^\Gamma = \begin{cases} 1.424 + 1.247x & \text{if} \quad 0 \leqslant x \leqslant 0.45 \\ 1.424 + 1.247x + 1.147(x-0.45)^2 & \text{if} \quad 0.45 \leqslant x \leqslant 1 \end{cases} \tag{1}$$

room temperature.[1] We refer to this as the direct gap at any x. For $x \geqslant 0.45$, the conduction-band energy at the X symmetry point drops below the E_g^Γ in Eq. (1) and the alloy becomes indirect. The indirect transition (X conduction-band point to Γ valence-band point) varies with increasing x as

$$E_g^X = 1.900 + 0.125x + 0.143x^2, \tag{2}$$

which we will refer to as the indirect gap. Pure AlAs is an indirect-band-gap semiconductor.

Hydrostatic pressure studies are instructive because of the drastic changes they can cause on vibrational and electronic energy band structures. For cubic semiconductors, these perturbations do not alter the symmetry present within the specimen, and effects are primarily due to the increase pressure creates in the electronic charge density. Vibrational energies generally increase with increasing pressure, with several important exceptions.[11] The electronic band structure is also perturbed. The direct-gap energy splitting, which is a function of x, increases with pressure at a rate of 10.8 ± 0.3 meV/kbar in pure GaAs; the indirect gap decreases in energy with pressure, at a rate of -1.35 meV/kbar in pure GaAs.[12] Thus a powerful combination is the use of hydrostatic pressure to perturb the electronic transitions and create resonance-Raman conditions, while studying the vibrational properties.

TABLE I. Aluminum mole fractions x of the samples studied, mode assignments, zero-pressure vibrational energies (from fits to pressure data), pressure induced shift [quantity b in Eq. (4)], and mode-Grüneisen parameters [γ in Eq. (7)]. Both b and γ are dimensionless quantities.

x	Assignment	ν_0 (cm^{-1})	b	γ
0	TO$_1$	268.5±0.3	1.11±0.03	1.12±0.03
	LO$_1$	292.2±0.3	1	1.01±0.03
0.25	LO$_1$	283.5±0.5	1.10±0.05	1.12±0.08
	TO$_2$	359.8±1.4	1.01±0.05	1.15±0.07
	LO$_2$	367.0±0.6	1.12±0.04	1.14±0.06
0.40	LO$_1$	277.1±0.6	1.14±0.03	1.17±0.05
	TO$_2$	358.9±1.4	1.28±0.08	1.14±0.11
	LO$_2$	376.9±0.7	1.11±0.08	1.14±0.10
0.58	LO$_1$	267.6±0.3	1.18±0.03	1.22±0.06
	DALO$_2$	365.8±0.7	1.02±0.08	1.17±0.12
	LO$_2$	390.9±0.5	1.00±0.02	1.03±0.04
0.70	DALO$_1$	249.3±1.2	1.19±0.12	1.24±0.12
	TO$_1$	260.0±0.8	1.13±0.04	1.30±0.07
	LO$_1$	265.0±0.4	1.27±0.05	1.32±0.08
	TO$_2$	361.9±0.4	1.07±0.04	1.11±0.07
	LO$_2$	392.6±0.3	0.94±0.04	0.97±0.06
0.70 [a]	LO$_2$	390		0.93±0.08
0.92 [a]	LO$_2$	400		0.87±0.06
1.00 [a]	LO$_2$	404		0.86±0.08

[a] From Ref. 14.

We have undertaken a series of pressure experiments aimed at studying the effect it has on a disorder activated Raman band at 198 cm^{-1}. Evidently, it is observed for alloys with high aluminum mole fraction when the ambient-pressure band structure is indirect. In the course of this work, we have observed a *systematic* dependence of the optic-phonon pressure shifts with alloy content, which is the main focus of this paper. We have studied both TO and LO-phonon pressure dependences. This behavior was not noted[13,14] in prior experiments on Al$_x$Ga$_{1-x}$As, and is not explained by trends in the weakly varying bulk modulus. In this paper we discuss the observed effect and interpret it in terms of alloy mode softness. The remainder of this paper is organized into sections on the experimental details, followed by a discussion of the Raman spectra and their dependence on pressure, and a section discussing how the phonon pressure rates depend on x. We include a section on pressure tuned resonance-Raman results for the $x=0.40$ alloy. The results are then summarized.

II. EXPERIMENTAL DETAILS

The Al$_x$Ga$_{1-x}$As samples were grown by molecular-beam epitaxy on (001) substrates of pure GaAs. Sample thicknesses ranged between 0.2 and 1.0μm. Table I includes the aluminum mole fractions x for the samples studied. All results for $x=0$ were from Raman scattering by the substrate. In the spirit of the two-mode behavior, and for convenience, we define a quantity reflecting the mole fraction of either AlAs or GaAs:

$$\phi=\begin{cases} 1-x & \text{(AlAs)} \\ x & \text{(GaAs)}. \end{cases} \tag{3}$$

ϕ, therefore, is a measure of *dilution*. Small ϕ means that the alloy component in question is nearly pure or dominant, while increasing ϕ reflects increasing dilution by the other component. This is meant to facilitate interpretation of phonon behavior in terms of the presence (mole fraction) of that component of the alloy.

Raman scattering was stimulated using 514.5 nm, 488.0 nm, or 457.9 nm emission from an argon-ion laser. All experiments were performed with the samples at room temperature. A micro-Raman instrument was used to focus the light onto the sample and collect the scattered light. Standard optical components were used to control polarization conditions, when appropriate. The light was then passed through a holographic notch filter to discriminate against Rayleigh scattering, and dispersed by a 0.5 m monochromator. Gratings of 1200 and 1800 groove/mm were used, depending on the spectral coverage and resolution desired. A cooled charge-coupled device was used to detect the light. Integration times ranged from 0.5 to 10 min.

Hydrostatic pressures (to 70 kbar) were achieved using a diamond anvil cell. Samples were back thinned to ≈ 30 μm and cleaved into ≈ 100 μm square pieces. These were loaded into the cell with ruby for pressure calibration[15] and 4:1 methanol-ethanol as pressure transmitting medium. Backscattering from (001) surfaces in zinc-blende semiconductors exhibits allowed LO lines with weak (forbidden) scattering from TO phonons.[16]

It was found necessary to cleanly establish the pressure shift of the TO phonon. This was difficult from (001) backscattering experiments because the weak TO-phonon line overlaps disorder activated optic phonons. To overcome this, we examined our Al$_{0.70}$Ga$_{0.30}$As sample from the cleaved (110) surface in backscattering. In this geometry, scattering by TO phonons is allowed. A much thinner piece of the (001) sample was cleaved and stood *on edge* on the diamond anvil. The laser excitation was focused onto the epitaxial layer. At each pressure, we also measured the Raman spectrum of the substrate, giving us a clear determination of the TO-phonon pressure shift.

Pressure calibration by the ruby R_1 method was used primarily as a reference. We found that internal comparison with the GaAs substrate LO (or TO) phonon yielded more accurate pressure coefficients and facilitated our effort to compare pressure shifts with those observed in the pure compounds ($\phi=0$). Our relative pressure coefficients are dimensionless quantities

$$b(\phi)=\frac{\nu_{\mathrm{LO}}(0)}{\nu_{\mathrm{LO}}(\phi)}\frac{\partial\nu_{\mathrm{LO}}(\phi)}{\partial\nu_{\mathrm{LO}}(0)}=\frac{\dfrac{1}{\nu_{\mathrm{LO}}(\phi)}\dfrac{\partial\nu_{\mathrm{LO}}(\phi)}{\partial P}}{\dfrac{1}{\nu_{\mathrm{LO}}(0)}\dfrac{\partial\nu_{\mathrm{LO}}(0)}{\partial P}}, \tag{4}$$

where the phonon energies are in cm^{-1} and are evaluated at zero pressure. These are listed in Table I. To retrieve pressure shifts (i.e., in kbar^{-1}) one may use our pressure dependences of pure GaAs from an accumulation of 57 (LO) or 29

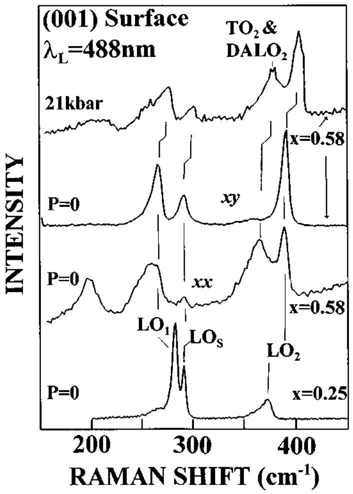

FIG. 1. Room-temperature Raman spectra from two of the samples studied. Backscattering from the (001) surface exhibits phonons of the GaAs-like (LO_1) and AlAs-like (LO_2) alloy components and the substrate (LO_S). Spectra are normalized to show spectral features and offset vertically.

(allowed TO) data points spanning the 0 to 70 kbar range. These exhibited linear pressure dependences. Least-squares analysis gives

$$\nu_{\mathrm{LO}}=(292.2\pm0.3)+(0.391\pm0.008)P \tag{5}$$

and

$$\nu_{\mathrm{TO}}=(268.5\pm0.3)+(0.401\pm0.007)P, \tag{6}$$

where ν is in cm^{-1} and P is in kbar. For the pure AlAs pressure shifts, we used the results of Reimann *et al.*[14]

III. RAMAN SPECTRA AND THE EFFECTS OF PRESSURE

In Fig. 1 we show Raman spectra from two samples, vertically scaled to exhibit the spectral features. The lowest spectrum is at ambient pressure for the $x=0.25$ sample. Clearly observed are the GaAs-like LO_1 phonon near 284 cm^{-1}, the substrate LO_S phonon at 292 cm^{-1}, and the weaker AlAs-like LO_2 phonon near 373 cm^{-1}. At Raman shifts just below each alloy LO line we see broader features corresponding to disorder activated scattering, with possible superposition of the TO bands. These are referred to as $DALO_1$ (GaAs-like) and $DALO_2$ (AlAs-like).[7]

The two middle spectra in Fig. 1 are taken at ambient pressure, both for the $x=0.58$ sample. The lower spectrum was collected under parallel (xx) polarization conditions, for which scattering by LO phonons is forbidden. The upper $P=0$ spectrum is taken with incident-light and scattered-light polarizations perpendicular (xy); in this geometry, scattering by LO phonons is allowed. Here, $x=(100)$ and $y=(010)$. In the xy spectrum, we again see three LO-phonon lines, the LO_1 has alloy downshifted to 268 cm^{-1}, the LO_2 has upshifted to 391 cm^{-1}, and the LO_S remains at 292 cm^{-1}. We also observe weak DALO bands. In the xx spectrum, we see weak scattering from the forbidden LO phonons and enhanced scattering from the DALO, which may be superimposed with the TO lines.

Additionally, a disorder related band is observed at 198 cm^{-1} in the xx spectrum (Fig. 1), which is not seen in the $x=0.25$ spectrum. This feature was observed in the $x=0.58$ sample when using 488.0 nm excitation, but was not present with 514.5 nm or 457.9 nm laser sources. This implies a resonance, possibly with $E_0+\Delta_0$. What is interesting is the observation that the sharp peak at 198 cm^{-1} quenches very rapidly with pressure, disappearing below 5 kbar. This does not permit us to determine a pressure coefficient. We attempted to pressure tune the apparent resonance to match the 457.9 nm laser line, assuming a pressure coefficient of ≈ 11 meV/kbar for the $E_0+\Delta_0$ gap, but were unable to observe the disorder band. Underlying the sharp band is another broad feature centered at 200 cm^{-1}. This feature shifted at a rate of 0.37 ± 0.05 cm^{-1}/kbar. The vibrational energy and pressure shift thus confirm that this underlying feature stems from zone-edge scattering by GaAs LA(L) phonons.[11]

When pressure is applied, we observe all the optic phonons to shift to higher vibrational energy. This is evident in the upper spectrum of Fig. 1. Because birefringence in the stressed diamond anvil scrambles the polarization, clean polarization dependent studies are not possible. Comparison of the 21 kbar spectrum with the $P=0$ spectra in Fig. 1 indicates that it is close to xx scattering geometry. From these spectra, we see that the $DALO_2$ band shifts with the LO_2 phonon. In Fig. 2 we show phonon shifts in the $Al_{0.58}Ga_{0.32}As$ alloy, as a representative, vs shift of the substrate LO phonon. The shifts were induced by pressure, which is included as the upper horizontal scale for reference. This shows the reliability of our pressure coefficients, which are listed in Table I. We will discuss the trends in pressure coefficients in the next section.

Figure 3 shows Raman spectra from the cleaved (110) surface at three different pressures. In strictly backscattering geometry, scattering by TO phonons is allowed, while the LO line is forbidden. Discussing first the AlAs-like vibrations, the TO_2 is readily followed with pressure, originating at 362 cm^{-1} when $P=0$. Additionally, we see scattering by the LO_2 phonon at 393 cm^{-1}. The strength of the LO_2 relative to the TO_2 is surprising, and may be present due to several factors: misorientation of the sample in the cell, forward scattering due to reflection off the back surface (the sample is transparent to the 514.5 nm light), or allowed right-angle scattering. Both TO_2 and LO_2 phonons blueshift with pressure, and these spectra conveniently permit us to examine them simultaneously under pressure.

All three spectra in Fig. 3, but especially the two at higher pressures, exhibit $DALO_1$ which pressure shift with the TO_1 band at 260 cm^{-1} ($P=0$). We believe that the broad linewidth of the TO_1 band stems from the close proximity of the LO_1 line at 265 cm^{-1} ($P=0$), measured by backscattering from the (001) surface. It is also possible that there is some scattering by the substrate TO_S phonon (268 cm^{-1} at $P=0$). By measuring TO_S from the ≈ 30 μm thick substrate, we were able to establish its position and subtract it from the $Al_{0.70}Ga_{0.30}As$ spectrum. This was done by fitting two Lorentzian bands in this range: one with the peak position and linewidth fixed to that of TO_S, the other determined by the fit. Results for the TO_1 were consistent and positions agreed well with ‘‘eyeball’’ estimates.

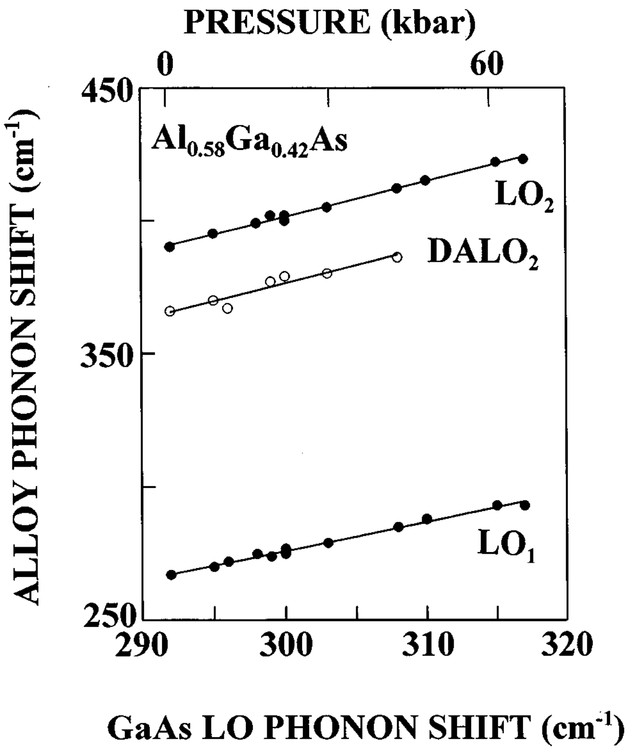

FIG. 2. Pressure induced shifts of the alloy phonon energies vs the substrate phonon energy. The latter was found to be more reliable than ruby as a pressure calibration due to its narrow linewidth and because it is an internal standard. Using Eq. (5), an approximate pressure scale is included at the top.

IV. PRESSURE DEPENDENCE OF THE OPTIC PHONONS

We wish to compare the effect pressure has on GaAs-like optic phonons in the alloys to the effect it has on pure GaAs, and likewise for AlAs. To do so, we examine the mode-Grüneisen parameter

$$\gamma = B_0 \frac{1}{\nu_0} \frac{\partial \nu}{\partial P_0}, \tag{7}$$

which is obtained from pressure coefficient b in Eq. (4) (Table I) and Eq. (5). The "0" subscript denotes that quantities are evaluated at $P=0$. For the bulk modulus

$$\frac{1}{B_0} = -\frac{1}{V_0} \frac{\partial V}{\partial P_0} \tag{8}$$

we use a linear interpolation between pure GaAs and pure AlAs.[1] It is possible to use direct pressure coefficients (from ruby), but the internal LO_S was found to be more precise. Either method produces the trends we report. In Fig. 4, we graph $\gamma_{LO_{1,2}}$ scaled to the pure-component mode-Grüneisen parameter versus ϕ. For pure GaAs we use our value of $\gamma_{LO} = 1.01 \pm 0.03$. For pure AlAs we use $\gamma_{LO} = 0.86 \pm 0.08$ (Ref. 14) and we include their results for $x = 0.70$ and 0.92 which agree with our trend. On the horizontal axis of Fig. 4, $\phi = 0$ corresponds to pure GaAs or pure AlAs, depending on which alloy component is being referred to. Increasing toward $\phi = 1$ means increasing dilution with the other alloy component.

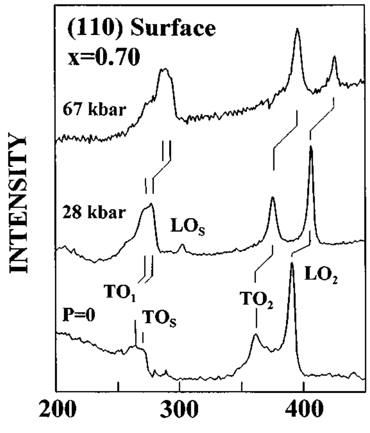

FIG. 3. Room-temperature Raman spectra for backscattering from the (110) surface of the $Al_{0.70}Ga_{0.30}As$ sample. The excitation wavelength was 514.5 nm, for which the sample is transparent at all pressures. In this case, scattering by the TO phonons is allowed. All phonon bands studied blueshift with pressure.

Two observations are intriguing about Fig. 4. First, both LO-phonon branches have pressure coefficients which increase with ϕ. We find no discussion of this effect in the literature. Second, when *internally* compared [$LO_1(\phi)$ to $LO_1(0)$—pure GaAs, and likewise $LO_2(\phi)$ to $LO_2(0)$—pure AlAs] the dependences follow the same trend.

There are several factors which need to be discussed regarding the higher-pressure coefficients measured in the alloys. First is the fact that pressure primarily enters through volume deformation described by the bulk modulus. This has already been taken into account, and does not explain the magnitude of the effect we observe. The bulk modulus varies from 755 kbar (GaAs) to 781 kbar (AlAs), i.e., by $\approx 3\%$ between pure GaAs and pure AlAs.[1] The pressure coefficients vary over a range of 30%. Thus bulk volume deformation does not explain the size of what we observe. Furthermore, increasing x means increasing stiffness through B_0, which should *decrease* the relative pressure coefficients. With increasing x we observe γ_{LO1} to increase, commensurate with "softening," while γ_{LO2} decreases. Therefore the directions of the variations in γ_{LO} are not predicted by the bulk modulus.

Another factor of concern is the presence of strain from the GaAs substrate. This is on the order of 0.1% for pure AlAs, and will increase with pressure to $\approx 0.2\%$ at 70 kbar. Over this same pressure range, the lattice constant of pure AlAs will shrink by 3%. The effect of strain is therefore small compared to the effect of hydrostatic pressure and compared to the magnitude of what we have observed. More convincing is the fact that the phonons in the alloy epilayer should experience a uniform effect, regardless of whether they are GaAs-like or AlAs-like. Thus pressure induced changes in the substrate strain do not explain our results.

The ϕ dependence of the mode-Grüneisen parameters is also not simply due to the decrease in the $LO_{1,2}$-phonon energies at $P=0$. These appear in the denominator of Eq. (7) and decrease with increasing ϕ. What we observe is also evident in both $(\partial\nu/\partial P)$ and $(1/\nu)(\partial\nu/\partial P)$.

Better insight into the ϕ dependent pressure coefficient is gained when we simultaneously analyze the dependence of

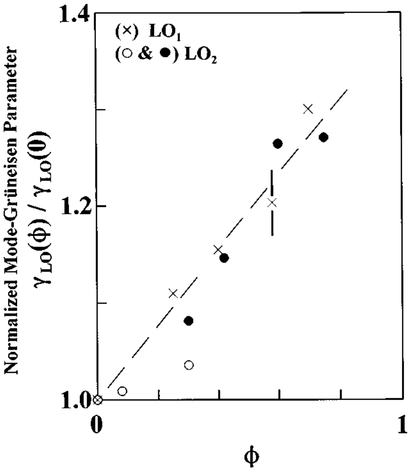

FIG. 4. Mode-Grüneisen parameter, normalized to that of the pure material, vs ϕ [Eq. (3)]. Filled in circles are from this work, open circles from Ref. 14. Shown is the $\approx$30% increase observed in γ_{LO}, and that when scaled, the AlAs and GaAs alloy components follow the same trend. The dashed line is a guide to the eye. A typical error bar is shown.

the vibrational energies with ϕ. Consider the GaAs alloy component. As ϕ increases, ν_{LO1} decreases or *softens*. Thus one would expect a higher-pressure coefficient and larger γ_{LO1} as observed in Fig. 4. Likewise, for the AlAs alloy component we see that increasing ϕ decreases (*softens*) ν_{LO2} beyond the initial softness of the phonon involved. Consequently, γ_{LO2} increases. Since neither the phonon nor bulk deformation properties (through B_0) explain our observations, these results also imply that phonon pressure coefficients in alloys are influenced by local alloy structure or charge transfer on the cation sublattice. This is consistent with the contention that phonon energies are determined by charge transfer between local structures within the alloy.[7] Evidently, pressure enhances the charge-transfer process from one alloy component to the other. We also point out that no comparable effect was seen in the mode-Grüneisen parameter of ion implanted GaAs, which exhibits clear evidence of finite-size effects.[17]

LO-phonon energies are often analyzed relative to the TO phonons in zinc-blende materials. LO-TO-phonon splitting enters through Born's effective dynamic charge e^* by

$$\nu_{\mathrm{LO}}^2-\nu_{\mathrm{TO}}^2=\frac{N_d/V}{c^2\pi\epsilon_\infty\mu}e^{*2} \tag{9}$$

in esu.[11] Here N_d/V is the density of cation-anion pairs (constant in the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ system), c is the speed of light, ϵ_∞ is the optical dielectric constant, and μ the reduced mass. For pure GaAs, Trommer *et al.* report a value of $e^*=2.18e$.[18] Using literature values for AlAs,[1,14,19] we find $e^*=2.28e$. Thus there is a 5% range in e^* when comparing the pure compounds. Since there is no LO-TO splitting in the dilute $\phi\approx1$ limit, e^* becomes 0. As ϕ increases the ratio $\gamma_{\mathrm{TO}}/\gamma_{\mathrm{LO}}$ decreases and approaches 1 (Table I). Thus "ionicity" (e^*) decreases with increasing ϕ as is evident in our γ_{TO} and γ_{LO} measurements. This is consistent with conclusions drawn from many compounds of varying e^*.[20] These arguments support the notion that charge transfer is the important factor in alloy phonon energies.

We have analyzed our γ_{LO} dependence on ϕ strictly using the alloy dependence of e^*. The latter was calculated assuming the two-mode approximation and using our measured phonon energies. In the spirit of two-mode behavior, we calculate e^* using the reduced mass of the alloy subcomponent (rather than the alloy average) and assume an average ϵ_∞. The latter assumption had a minor effect, while the reduced mass assumption was important. When using the average cation mass to calculate the reduced mass, we obtain no clear trend in γ_{LO} vs e^*. Our results are shown in Fig. 5. Again, previous measurements[14] are included for comparison. In this case, the mode-Grüneisen parameters are not scaled. What is interesting is that data sets for both alloy components exhibit the same trend, as in Fig. 4. e^* is approximately linear in ϕ over this range. This implies that e^* is an important factor in alloy pressure coefficients.

The splitting between the LO and TO phonons typically decreases with pressure. Considering first the GaAs-like modes, for pure GaAs the splitting decreases from $23.7\pm0.6\ \mathrm{cm}^{-1}$ at a rate of $-0.010\pm0.015\ \mathrm{cm}^{-1}$/kbar. Our most precise values for the alloy come from the $x=0.70$ sample, for which we measured allowed LO and TO phonons. For the GaAs-like mode we obtain splitting of $5.0\pm1.2\ \mathrm{cm}^{-1}$ which decreases with pressure at a rate of $-0.009\pm0.039\ \mathrm{cm}^{-1}$/kbar. The large error in determining the splitting pressure rate is due to the small splitting. For $x=0.70$, the LO_2-TO_2 splitting begins at $31.6\pm0.4\ \mathrm{cm}^{-1}$ and diminishes with pressure at $-0.030\pm0.011\ \mathrm{cm}^{-1}$/kbar. The latter is in good agreement with measurements on InP,[18] which has optic phonons in the same energy range. Although we expect to see the splitting collapse with increasing ϕ, along with the pressure dependence, the results are not definitive.

Figure 5 suggests that charge transfer *between* the cation sublattice components is an important factor in phonon energies and pressure coefficients. We propose that there are two consequences of increasing ϕ. The analysis of Brafman and Manor[7] would suggest that oscillator strength is transferred on the cation sublattice from weaker to stronger bonds. This tends to enhance higher phonon energies. Furthermore, charge may be shared between the alloy subcomponents. Pressure has first the effect of increasing vibrational energies due to increased valence charge volume concentrations. Apparently, pressure has the secondary effect in alloys of enhancing transfer of oscillator strength from the weaker (GaAs-like) to the stronger (AlAs-like) component of the alloy. The primary difference between the Ga and Al atoms is that the former possess $3d$ core electrons. It is suggested that pressure gradually pushes these electrons closer to the valence-band edge, i.e., into becoming more itinerant. This will also tend to push out the outermost valence electrons. Such a phenomenon would be observable in an alloy because of the presence of both a source (here, the Ga atoms) and a receptacle (the Al atoms with slightly higher electronegativity).[21] A discussion of such a charge-transfer mechanism appears in Ref. 22 regarding the pressure dependence of the direct gap in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. Thus one would expect to observe no effect at the alloy end points. It would be interesting at this stage to conduct a similar study of an

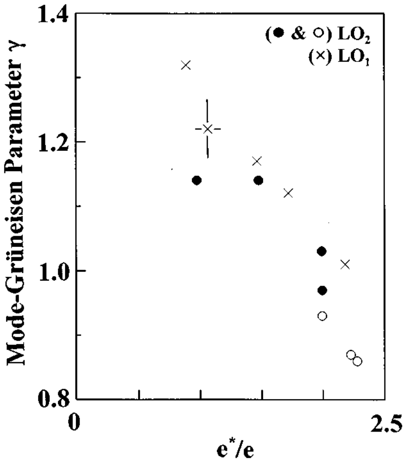

FIG. 5. Mode-Grüneisen parameters (not normalized) vs Born's transverse dynamic effective charge [Eq. (9)]. The latter is calculated using our phonon energies and assuming separate (two-mode) reduced masses for the alloy components. The error bars shown are typical. Symbols are the same as in Fig. 4.

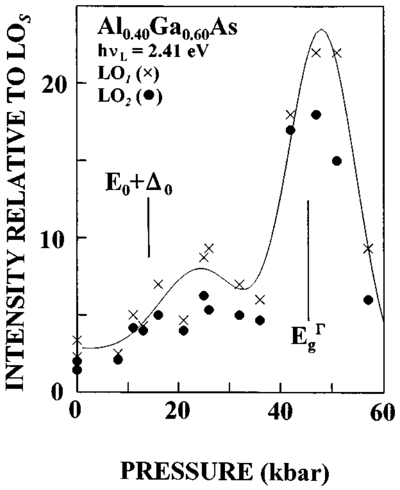

FIG. 6. Intensity of the LO_1 and LO_2 lines (relative to the substrate LO_S intensity) vs pressure. We see strong enhancement of both phonons near 47 kbar, consistent with unresolved ingoing and outgoing resonance of E_g^Γ A weaker enhancement is seen above 20 kbar, discussed in the text.

alloy series in which charge transfer is expected to be large (i.e., does not exhibit clean two-mode behavior in ambient vibrational properties).

We have also examined the literature concerning hydrostatic pressure studies of GaAs/AlAs superlattices, which include various periods and composition parameters (d_1 and d_2, the layer thicknesses of pure materials).[23,24] No similar effect is observed in the mode-Grüneisen parameters versus mole fraction, GaAs-like and AlAs-like phonons exhibited the same mode-Grüneisen parameters, and are not dependent on the quantity analogous to our ϕ. This may be because of the strict confinement of the optic phonons[25] and independent electronic energy band structures, which isolates the GaAs and AlAs components in the superlattices and minimizes mixing. In the superlattice, bulk modulus is a bulk concept within each component. In the alloys, there will be some local component to deformation parameters because of the range of neighborhoods possible even in the absence of clustering. Incidentally, this supports our argument that the GaAs substrate does not play a role, as the superlattices will experience the same effect of the substrate as the alloy epitaxial layers. More important, this further confirms that the phenomenon we observe is specific to alloying.

V. PRESSURE INDUCED RESONANCE-RAMAN SCATTERING

Pressure has a strong effect on the electronic energy band structure. This naturally leads us to ask if resonance was a factor. Resonance effects were observed, especially in the $\mathrm{Al}_{0.40}\mathrm{Ga}_{0.60}\mathrm{As}$ sample which has $E_g^\Gamma = 1.92$ eV at zero pressure. For this alloy, the direct gap will be tuned by pressure to equal the 2.409 eV (514.5 nm) excitation energy near $P = 50$ kbar. In Fig. 6 we graph the pressure dependence of the intensities for both LO_1 and LO_2 relative to the intensity of the substrate LO_S. For blueshifting energy gaps, increasing pressure corresponds to lower-energy transitions resonating with the fixed excitation energy.[23,26,27] Using LO_S as an internal reference is not ideal, because absorption of 2.409 eV light by the alloy surface layer depends on pressure. Also, the optical properties of pure GaAs will change with applied pressure. The bulk GaAs $E_0 + \Delta_0$ gap will be driven into resonance with the laser photon energy near $P = 60$ kbar.

Despite these obvious drawbacks to using LO_S as an internal standard, we see strong relative enhancement of both alloy LO phonons near $P = 47 \pm 3$ kbar. The solid curve in Fig. 6 is the sum of two Gaussian bands fit to the LO_1 data. A fit to the LO_2 measurements gives concurring results (central positions and linewidths) with the vertical scales adjusted. The value of 47 kbar is close to the pressure at which we expect to observe resonance with the direct gap. Averaging between ingoing and outgoing resonance,[5,28,29] this gives a linear pressure shift of $\partial E_g^\Gamma / \partial P = 10.8 \pm 0.7$ meV/kbar. This is in excellent agreement with the 11 meV/kbar value expected from a linear interpolation between GaAs and AlAs.[1] However, it is somewhat lower than the 12.2 ± 0.2 meV/kbar in Ref. 22. The pressure linewidth of the resonance is ≈ 15 kbar. This corresponds to ≈ 160 meV, which is large compared to the bulk-GaAs linewidth (80 meV).[26] This indicates that alloy mole fraction and subsequent broadening are important factors in optical-process linewidths.

At lower pressure (23 ± 4 kbar) we observe a weaker enhancement of both LO_1 and LO_2. This is most readily associated with the $E_0 + \Delta_0 = 2.27$ eV ($P = 0$) gap, but this identification is not as clean as the above argument. Mapping this onto our pressure scale (by assuming 11 meV/kbar as the pressure coefficient), we would expect the $E_0 + \Delta_0$ gap to be in resonance with 2.409 eV at a pressure of ≈ 15 kbar (Fig. 6). Prior examinations in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ ($x \leqslant 0.1$) (Ref. 4) and $\mathrm{Cd}_x\mathrm{Mn}_{1-x}\mathrm{Te}$ (Ref. 29) alloys show resonance enhancement for photon energies *above* $E_0 + \Delta_0$. This corresponds to enhancement at lower pressures than 15 kbar, conflicting with what we measure. This conflict can be reconciled in two ways. The first explanation to be considered is that the Δ_0 splitting is ≈ 190 meV, which is 100 meV too small. The second possible explanation is a rapid collapse of Δ_0 with pressure. It was also noted that this transition became weaker and broader with larger x.[4] The $E_0 + \Delta_0$ resonance study would be much more convincing with simultaneous optical properties studies, but these are extremely difficult with the substrate present. Cryogenic photoluminescence excitation combined with resonance-Raman experiments may be suitable to investigate this problem.

Delaney *et al.* have discussed subtle variations observed in the vibrational energies when measured under resonant-Raman conditions (ambient pressure).[5] These were observed when carefully comparing dipole allowed with forbidden scattering geometries. We did not observe any clear evidence of frequency shifting or oscillations as we pressure tune the E_g^Γ gap from below to above the laser photon energy. This is most likely due to the fact that clean polarization dependences are not achieved in the high-pressure experiment, causing us to measure a mixture of allowed and forbidden scattering. Furthermore, pressure shifting of the phonon lines introduces experimental deviations around the linear fit which obscure the ± 2 cm^{-1} oscillations. This null result is unfortunate, since hydrostatic pressure can be used to control the ''directness'' of a given alloy compound and mitigate the difficulties of comparing results from samples with different x.

VI. SUMMARY

We have performed a detailed study of the effect pressure has on alloy vibrational energies in the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ system. Optic phonons are found to blueshift with pressure. What is remarkable is the observation that $(\partial\nu/\partial P)$, $(1/\nu)(\partial\nu/\partial P)$, and γ show strong dependence on x (Figs. 4 and 5 and Table I). We believe that this effect is specific to alloys, and is not explained by variations in B_0, ν_0, or strain from the substrate. We argue that what we report stems from charge transfer on the cation sublattice which is influenced by hydrostatic pressure. This is supported by an observed correlation between γ_{LO} and e^*.

We attempted to investigate the effect pressure has on a disorder activated band at 198 cm^{-1} in indirect-band-gap materials (Fig. 1). Apparently, this is observed when the laser photon energy is in resonance with the $E_0+\Delta_0$ gap. This feature quenches rapidly with pressure and attempts to pressure tune the resonance with other laser lines were not successful.

For $x=0.40$ we studied resonance-Raman effects by pressure tuning the direct gap through the excitation photon energy. We see strong resonance in the LO_1 and LO_2 (Fig. 6) in approximate proportion to the mole fractions of the alloy components. This enhancement is convincingly related to the direct E_g^Γ gap. We see a somewhat weaker enhancement, which may be indicative of resonance with the $E_0+\Delta_0$ gap, but further examination is required.

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