Raman-scattering probe of anharmonic effects due to temperature and compositional disorder in III-V binary and ternary alloy semiconductors

C. Ramkumar, K. P. Jain, and S. C. Abbi
Department of Physics, Indian Institute of Technology, New Delhi, 110 016, India
(Received 12 January 1996)

Anharmonicity due to temperature and compositional fluctuations in ternary alloy semiconductors has been investigated. A comparative Raman-scattering study of temperature and compositional-fluctuation-induced anharmonic effects for various phonon modes in GaP, $GaAs_{1-x}P_x$, and $In_xGa_{1-x}As$ is presented. In binary semiconductors, anharmonicity is found to increase with increasing temperature, whereas, in ternary alloys, it is found to increase with increasing compositional fluctuations and increasing temperature. Temperature-induced anharmonicity introduces changes in the linewidth and line center position, while compositional-fluctuation-induced anharmonicity, not only introduces changes in the linewidth and line center position, but also changes the line shape. [S0163-1829(96)07619-9]

I. INTRODUCTION

Experimental and theoretical studies of epitaxial layers of ternary III-V alloy semiconductors have become a subject of considerable interest because of the wide range of applications in different fields of science and technology. Vibrational properties contain information about many parameters which are essential to an understanding of semiconductor device operation as well as of the physics of the materials themselves. Raman spectroscopy is a powerful nondestructive technique to understand the vibrational properties of solids, necessary for their characterization. Binary III-V semiconductors provide only fixed energy gap values in the spectral region from 0.17 eV (InSb) to 2.78 eV (GaP) and fixed lattice constants. A solid solution of two binary semiconductors has energy-band gaps and lattice constants intermediate to those of the two constituent binary semiconductors.[1] This makes it possible to tailor their properties intermediate to those of the constituent binaries, making them attractive candidates as device materials.

III-V ternary alloy semiconductors of the form $A_xB_{1-x}C$, where A and B are either anions or cations, are formed when a group-III or -V atom is substituted with another atom of the same group. In a semiconductor alloy, atoms of the constituent binary semiconductors are randomly distributed, leading to fluctuations in the masses and force constants in the neighborhood, and therefore resulting in compositional disorder. This leads to a violation of translation symmetry, but, nevertheless, the concepts of crystal band theory may be applied to these mixed crystals, since deviation from perfect periodicity is usually rather small.

The Raman spectra of ternary alloy semiconductors show changes of various phonon modes with a change in compositional disorder. The alloy-induced compositional disorder introduces changes in the vibrational properties including a shift in phonon frequency and changes in the linewidth, asymmetry, and appearance of disorder-activated modes even at room temperature. The change in linewidth and asymmetry may be understood in terms of the spatial correlation model[2,3] based on the finite correlation length of a propagating phonon[4,5] due to alloy potential fluctuations. This model, however, cannot describe the shift in the phonon frequency. Recently coherent-potential approximation (CPA) (Ref. 6) calculations have been performed based on Taylor's[7] notation, to obtain the difference in phonon energies and broadening between an isotopically enriched crystal of ^{70}Ge and a germanium crystal of natural isotopic composition, and good agreement between calculated and experimentally observed values has been found. In addition, an increase in crystal temperature also introduces changes in the vibrational properties, which are reflected in a softening of phonon frequencies, a broadening of line shapes, and a decrease in intensity. There are two processes which induce lifetime broadening of optical phonons in alloy semiconductors—one due to anharmonic decay of an optical phonon into lower-energy phonons, and the other due to scattering by compositional disorder. Fuchs *et al.*[8] investigated the anharmonic decay time, isotopic scattering time, and inhomogeneous line broadening of optical phonons in different isotopes of germanium, in which they observed two types of lifetime broadening of optical phonons: (i) spontaneous anharmonic decay into lower-energy phonons (τ_{decay}), and (ii) elastic scattering due to isotopic disorder (τ_{disorder}). Also, they found that isotopic disorder influences the lifetime of phonons, measured by the inverse of the phonon linewidth in Raman spectra, as well as causes an asymmetry of the line shape and a shift of the phonon frequency.

Optical phonons decay into two or more lower-energy phonons due to anharmonic processes, which decrease their lifetime. Relaxation of carriers is often dominated by the decay of optical phonons, which interact strongly, into weakly interacting phonons.[9,10] The temperature dependence of Raman scattering in silicon has been studied by many authors,[11–13] who reported that both the line center and linewidth of optical modes at the Brillouin-zone center change with temperature due to anharmonicity. The Klemens[11] model assumes that the contribution to the linewidth arises only from the decay of the Raman optical phonon into two acoustical phonons of the same frequency and opposite momentum. Later, the work of Hart, Aggarwal, and Benjamin[12] on silicon found good agreement with the predictions of the

Klemens model. The Klemens model fits the experimental data well when the temperature of the sample is below the Debye temperature. In order to obtain a good fit at high temperature, Balkanski, Wallis, and Haro[13] assumed that the decay processes involve three phonons of the same frequency belonging to the same branch in the phonon-dispersion curve. Menéndez and Cardona[14] have shown that the number of decay channels with $\omega_1(\mathbf{q},\mathbf{j}_1)\neq\omega_2(-\mathbf{q},\mathbf{j}_2)$ is much higher than the number of overtone decay channels especially for Si and Ge, and, at the same time, they obtained a very good fit for α-Sn using the Klemens model. These authors also mentioned that because of the analogy with Si and Ge, the combination decay channel also exists for α-Sn. Thus one should look at the phonon-dispersion curve and find all the possible decay channels. For GaP, Bron, Kuhl, and Rhee[15] have shown that of all the possible interactions, only the decay of LO phonon into acoustic phonons needs be considered. Recently, Verma, Abbi, and Jain[16] carried out a comparative study of anharmonic effects in various structural forms of GaAs, and found that the dominant decay channel in this material is into two acoustical phonons of the same frequency. However, no detailed work has been reported on the anharmonic effect in ternary alloy semiconductors. Jusserand and Sapriel[5] have, to some extent, investigated the anharmonic effect on a GaAs-like LO phonon in $Al_xGa_{1-x}As$ epitaxial layers with $x=0.27$, and they observed that anharmonicity is not affected by substitutional disorder, which differs from our results. We have studied the anharmonic effect as a function of a wide range of compositional variation, and found that the anharmonicity increases with an increase in substitutional disorder.

Changes in the linewidth of the phonon in Raman and infrared spectra can be used for estimating the lifetime of strongly interacting optical phonons. These results can be compared with the direct lifetime measurements of the optical phonons in time-resolved spontaneous Raman scattering (TRSRS) and picosecond laser measurements.[16–19] Using TRSRS, Von der Linde, Kuhl, and Klingenberg[17] estimated the lifetime of the nonequilibrium incoherent LO phonon generated during the interaction of photoexcited hot electrons and holes with the lattice in GaAs grown by molecular-beam epitaxy. They found a decrease in the lifetime of the LO phonon with an increase in temperature. Also, Bhat, Kim, and Stroscio[18] estimated the lifetime of the LO phonon as a function of lattice temperature for GaAs bulk samples, and also found a decrease in lifetime with increasing temperature. Kuhl, Rhee, and Bran[16] investigated the temperature dependence of the LO phonon in GaP and ZnSe single crystals using a picosecond laser system. They compared the results to the traditional (indirect) determination of the lifetime of both LO and TO phonons from spontaneous Raman linewidths.[20,21] The results for the temperature dependence of the first-order LO-phonon lifetimes in GaAs as determined by Raman scattering agree fairly well with those determined by TRSRS.[16]

The purpose of this paper is to investigate anharmonic effects due to temperature in GaP, and due to both temperature and compositional disorder in lattice-matched $GaAs_{1-x}P_x$ ($x=0.90$, 0.65, and, 0.59) and $In_xGa_{1-x}As$ ($x=0.05$, 0.12, 0.19, 0.24, and, 0.53). It is then possible to make a comparative study of anharmonic effects in binary and ternary alloy semiconductors. Raman-scattering measurements in these samples were carried out between 295 and 10 K to determine the temperature dependence of the line center and linewidth of the first-order LO-phonon modes at the Brillouin-zone center which gives the anharmonicity. The experimentally obtained values are fitted by a simple expression obtained from terms which represent the decay of the Raman optical phonon into two acoustical phonons[11] of the same frequency with opposite momentum. The effect of compositional disorder on the Raman optical modes is qualitatively discussed using the CPA formalism.[6,7,22] Second-order transverse-acoustic-phonon [2TA(X)] scattering in GaP and $GaAs_{0.1}P_{0.9}$ is reported at different temperatures, and a comparison is made between the two. The temperature dependence of the dipole-forbidden first-order GaP-like TO-phonon mode is also discussed. The relaxation time of the first-order optical-phonon modes is estimated in this paper from linewidth measurements in Raman experiments.

Our results show a decrease in the linewidth and a shift in the line center position toward the high-frequency region for the first-order optical-phonon modes in the Raman spectra of GaP, $GaAs_{1-x}P_x$, and $In_xGa_{1-x}As$ with decreasing temperature. In ternary alloy systems, anharmonicity is introduced due to compositional disorder and temperature, leading to the decay of a strongly interacting optical phonon into weakly interacting acoustic phonons.[15] A comparative study between binary and ternary systems indicates that the anharmonicity increases with increasing temperature in binaries, while it increases with increasing compositional disorder and increasing temperature in ternary alloys. The temperature-induced anharmonicity gives rise to a shift in the phonon frequency and changes in linewidth and intensity. On the other hand, anharmonicity due to compositional disorder not only introduces a shift in the phonon frequency and changes in linewidth and intensity, but also changes phonon line shapes. This suggests that the temperature-induced anharmonicity and the compositional-disorder-induced anharmonicity may not be additive in nature due to their different characters. However, the two components of the anharmonicity could be separated out at low temperatures by comparing the anharmonicity-induced effects in binary and ternary systems, since, for the latter, at low temperatures anharmonicity is mainly due to compositional disorder. The strong temperature dependence of the dipole-forbidden GaP-like TO-phonon mode suggests that, for a low value of alloying, the thermal anharmonicity is dominant whereas, for a high value of alloying, the compositional-disorder-induced anharmonicity predominates. A two-mode behavior is observed for the anharmonicity in $GaAs_{1-x}P_x$, one for the first-order GaP-like LO phonon, and the other for the first-order GaAs-like LO phonon. The degree of anharmonicity for the first-order GaP-like LO phonon is found to increase, while that for the GaAs-like LO phonon is found to decrease with decreasing phosphorous concentration. Furthermore, the degree of anharmonicity for these two modes is found to be different for a given value of phosphorous concentration, greater for the first-order GaP-like LO phonon, which is attributed to the difference in the masses of GaP and GaAs. The density of phonon states for the 2TA(X) mode in GaP is found to decrease with decreasing temperature, while that for the mode in $GaAs_{0.1}P_{0.9}$ is found to be independent of temperature,

indicating that the compositional-disorder-induced effect compensates for the temperature-induced effect in $GaAs_{0.1}P_{0.9}$. Finally, the lifetimes of the first-order optical-phonon modes are measured from the broadening of the Raman lines, and they are found to decrease with increasing anharmonicity.

II. EXPERIMENTAL PROCEDURE

The basic Raman spectroscopic setup consists of a RAMANOR double monochromator (HG2S), a HAMAMATSU R943-02 photomultiplier tube, and an amplifier and discriminator, a photon counter, a chart recorder, and a light source (argon-ion laser, COHERENT, INNOVA 90-5). The Raman experiments were carried out in a back-scattering geometry at different temperatures. The different discrete lines of the argon-ion laser were employed to avoid resonance effects in the temperature dependence of the various phonon modes. The samples of GaP and $GaAs_{1-x}P_x$ with $\langle 100 \rangle$ orientation and 60-μm epitaxial layer thickness, grown by liquid-phase epitaxy, were obtained from Society Radio Technique Complec, Caen, France, and the $In_xGa_{1-x}As$ samples with $\langle 100 \rangle$ orientation and 2.0 ± 0.4-μm epitaxial layer thickness, grown by molecular Vapor-phase epitaxy (MVPE), were obtained from Université Pierre et Marie Curie, Paris, France. The concentration x in these materials were determined to better than 3% accuracy from electron microprobe analysis and photoluminescence. Low-temperature Raman-scattering experiments were performed by fixing the samples on the cold finger of a cryostat using silver paste and the temperature of the order of 10 K was achieved using a HELITRON closed-cycle liquid-He cryostat. The temperature of the sample was accurately measured by keeping a thermocouple on the cold finger. The cryostat was evacuated to 1×10^{-6} torr by a typical ALCATEL rotary-diffusion pump combination in order to avoid condensation near the sample during the low-temperature experiments. The double monochromator was calibrated with the strong plasma lines of the argon-ion laser, and the slit width was kept between 50μ and 75μ for the first-order modes in order to improve the resolution of the monochromator. The instrumental error, calculated from the optical specifications and geometry of the double monochromator, is between ± 0.4 and ± 0.6 cm^{-1} at this slit-width level. Each spectrum was recorded three times in order to obtain the average values of the line center position and linewidth. Also, the instrumental linewidth was deconvoluted from the experimentally obtained values of the linewidth in order to obtain the true intrinsic linewidth of the phonon modes. The true Raman line shape is represented by a Lorentzian function, and a Gaussian line shape is assumed for the spectrometer which comes from the diffraction limit due to very narrow opening of the slit. Therefore, the recorded Raman line will have a convoluted line shape for the two distributions. The convolution of a Lorentzian and a Gaussian distribution can be represented by

$$I(\omega_1)=\int_{\omega}\frac{1}{(\omega-\omega_0)^2+\left[\frac{\Gamma_1}{2}\right]^2}\,e^{[-4(\omega_1-\omega)^2]/\Gamma^2}d\omega, \quad (1)$$

where ω_0 is the frequency of the Raman modes, and Γ_1 is the width of the Lorentzian distribution. The instrumental linewidth (Γ) can be estimated experimentally by allowing a strong plasma line of the Ar^+ laser (the linewidth of the plasma line is much smaller than the slit width) to pass through the spectrometer, and its line shape is considered to be the line shape of the instrument. The value of Γ_1 is properly chosen so that the convoluted line shape matches exactly with the experimentally observed line shape. This value of Γ_1 will be the true linewidth of the Raman modes. For second-order TA scattering, the slit width was kept at 500 μm, at which the resolution of the monochromator was ± 4 cm^{-1}.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. First-order optical phonon mode

The temperature dependence of the optic modes can be attributed to anharmonic terms in the vibrational potential energy, which leads to a decay of the optical phonon into two, three, or more low-energy phonons, respectively, from cubic, quartic, or higher-order anharmonicities. The decay processes should include all the possible interactions by which an optical phonon could decay into lower-energy phonons. A close examination of the phonon-dispersion curve and the calculated two-phonon combined density of states[14] would identify the decay channel from which the contribution arises. For GaP, the interaction in which the zone-center LO phonon decays into acoustic phonons should be considered out of all the possible interactions. Furthermore, combination of a zone-center LO phonon with an acoustic phonon is not possible because that would lead to a phonon with frequency greater than $\omega_{LG}(q\approx 0)$.[15] Similarly for GaAs, the same process fits the experimentally observed data very well.[16] Based on this discussion, it could be concluded that the decay of the optical phonon into acoustic phonons prevails in our samples, since the samples investigated in this study are phosphorous-rich $GaAs_{1-x}P_x$ and gallium-rich $In_xGa_{1-x}As$ ternary alloy semiconductors. The temperature dependence of the line center and the linewidth of the first-order optical modes at the Brillouin-zone center, taking into account the contributions form cubic and quartic anharmonic terms, is given by[11,13]

$$\omega(T)=\omega_0+\Delta(T), \quad (2)$$

where

$$\Delta(T)=C\left[1+\frac{2}{e^x-1}\right]+D\left[1+\frac{3}{e^y-1}+\frac{3}{(e^y-1)^2}\right] \quad (3)$$

and

$$\Gamma(T)=A\left[1+\frac{2}{e^x-1}\right]+B\left[1+\frac{3}{e^y-1}+\frac{3}{(e^y-1)^2}\right], \quad (4)$$

where $y=\hbar\omega_0/3k_BT$ and $x=\hbar\omega_0/2k_BT$. The constants A and C are related to three phonon processes, while the constants B and D are related to four phonon processes and ω_0 is the intrinsic frequency of the optical phonon at the Brillouin-zone center in the harmonic approximation.

At temperatures much below the Debye temperature, the contribution from higher-order anharmonic terms (quartic) is

negligible. In this case, the important contribution is from the cubic anharmonic terms, so that

$$\Delta(T)=C\left[1+\frac{2}{e^{x}-1}\right] \tag{5}$$

and

$$\Gamma(T)=A\left[1+\frac{2}{e^{x}-1}\right]. \tag{6}$$

Off-resonant Raman experiments were carried out on GaP, $GaAs_{1-x}P_x$, and $In_xGa_{1-x}As$ well below the Debye temperature (GaP, 446 K; GaAs, 344 K, and InAs, 249 K), so that Eqs. (5) and (6) can be used to describe the temperature dependence of the line center and linewidth of the first-order optical phonons at the Brillouin-zone center.

Compositional disorder introduces changes in the phonon energies, linewidths, and line shapes of Raman-active modes. Fuchs and co-workers[6,8] investigated the effect of isotopic disorder on phonon energies, widths, and shapes of Raman lines using the CPA formalism,[22] where the effects of differences in isotopic masses are taken into account and the isotopes are randomly distributed in the lattice site rather than clustered. In a similar way, the effect of compositional disorder on vibrational properties in ternary alloy semiconductors could be understood in terms of CPA calculations.[6,8,22] In ternary alloy semiconductors also, there exists a difference in reduced masses due to the isoelectronic substitution and the atoms of the constituent binary semiconductors are randomly oriented on the lattice site. The alloy semiconductors could be considered as an effective medium characterized by a dimensionless ''self-energy'' $\tilde{\varepsilon}(\omega)$, where ω is the phonon frequency with respect to the virtual crystal (VC). The CPA condition for zero average scattering at a single site in this medium is given by

$$\sum_{i=1}^{2}\frac{x_i\{\mu_{\rm VCA}\omega^2[1-\tilde{\varepsilon}(\omega)]-\mu_i\omega^2\}}{1-\{\mu_{\rm VCA}\omega^2[1-\tilde{\varepsilon}(\omega)]-\mu_i\omega^2\}G_M(0,0;\omega^2)}=0, \tag{7}$$

where x_1 and x_2 are the fractional concentrations of constituent binary semiconductors which sum to 1, μ_1 and μ_2 are their respective reduced masses, and the virtual reduced mass is $\mu_{\rm VCA}=x_1\mu_1+x_2\mu_2$. G_M is the site Green's function in the effective medium given by

$$G_M(0,0;\omega^2)=\frac{1}{N\mu_{\rm VCA}}\sum_{qj}\frac{1}{\omega^2[1-\tilde{\varepsilon}(\omega)]-\omega_{qj}^2}, \tag{8}$$

where N is the number of unit cells in the VC. Equations (7) and (8) must be solved self-consistently for the complex self-energy $\tilde{\varepsilon}(\omega)$, the real part of which would give the shift in the phonon frequency and the imaginary part the broadening. The detailed calculations of the CPA equations will be published separately later.

The analysis of the linewidth broadening in the Raman measurements can be used as an indirect measurement for estimating the lifetime of the first-order optical phonon at the Brillouin-zone center. Assuming a Lorentzian function for the deconvoluted line shape of the natural Raman line, the lifetime of the optical phonon can be calculated using a simple relation

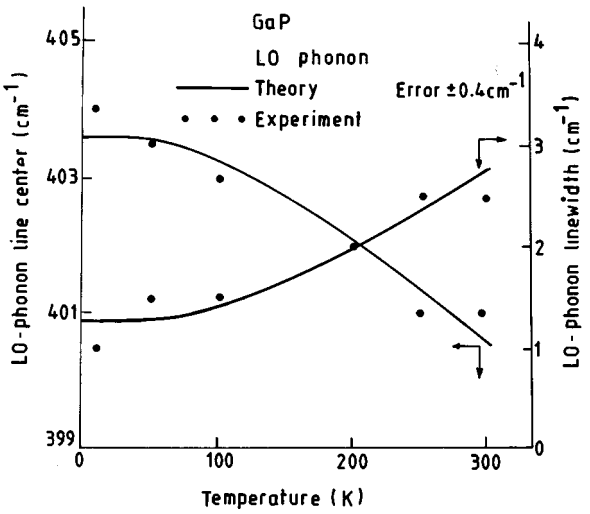

FIG. 1. Temperature dependence of the LO-phonon line center and linewidth in GaP.

$$\tau=\frac{1}{\pi c\Gamma}, \tag{9}$$

where c is the velocity of light and Γ is the linewidth of the first-order optical mode from the Raman measurements. Equation (9) is used to calculate the lifetime of the first-order optical-phonon modes in GaP, $GaAs_{1-x}P_x$, and $In_xGa_{1-x}As$.

1. Gallium phosphide

The temperature dependence of the line center and linewidth of the first-order LO-phonon mode in GaP is discussed in this section. Experiments were performed at five different temperatures with the 4880-Å line of the argon-ion laser. The slit width of the monochromator was kept at 50 μm, which gave a resolution of ± 0.4 cm^{-1}. Figure 1 gives the variation in the line center and linewidth with temperature, showing, as expected, a decrease in the linewidth and a shift in the line center toward higher frequencies as the temperature is lowered. Equations (5) and (6) are used to fit the experimentally observed changes in the line center and linewidth by properly choosing the constants C, A and ω_0. Good agreement is obtained between theory and experiment for GaP with $C=-2.457$ cm^{-1}, $A=1.266$ cm^{-1}, and $\omega_0=406.024$ cm^{-1}. Furthermore, the lifetime of this mode, estimated using Eq. (9), is $\tau=4.24$ ps at 295 K, 5.30 ps at 200 K, and 10.61 ps at 10 K.

2. The alloy $GaAs_{1-x}P_x$

(i) $GaAs_{0.1}P_{0.9}$. The changes in the line center and linewidth of the first-order GaAs- and GaP-like LO-phonon modes were recorded with the 5145-Å line of the argon-ion laser at various temperatures, again with a slit width of 50 μm. The Raman spectrum of $GaAs_{0.1}P_{0.9}$ consists of two prominent peaks, one corresponding to the first-order GaAs-like LO-phonon mode and the other corresponding to the first-order GaP-like LO-phonon mode. At room temperature, the first-order LO phonon in GaP appears at 401 cm^{-1} with a linewidth of 2.5 cm^{-1}. On the other hand, the first-order GaP-like LO-phonon mode in $GaAs_{0.1}P_{0.9}$ appears slightly shifted toward low frequency at 398 cm^{-1} with a linewidth

TABLE I. Best-fit values of the anharmonic constants for the first-order GaAs-like and GaP-like LO-phonon mode in $GaAs_{1-x}P_x$.

	GaAs-like LO phonon				GaP-like LO phonon			
x	A (cm^{-1})	C (cm^{-1})	ω_0 (cm^{-1})	Γ_a/Γ_b	A (cm^{-1})	C (cm^{-1})	ω_0 (cm^{-1})	Γ_a/Γ_b
1.00					1.266	−2.457	406.024	1.00
0.90		−2.311	282.927		1.551	−2.985	404.759	1.00
0.65	3.053	−1.950	289.852	1.83	2.558	−3.668	398.017	1.50
0.59	2.670	−1.752	290.564	1.50	3.127	−3.899	396.581	1.80

of 3.0 cm^{-1}. The first-order GaAs-like LO-phonon mode at 276 cm^{-1} is not resolved from the first-order GaAs-like TO-phonon mode, because of the high degree of disorder experienced by this mode, and, therefore, the linewidth of this mode could not be measured. Furthermore, the ratio of the intensity of the first-order GaAs-like LO-phonon mode to the TO-phonon mode is small. These modes show a shift in the line center toward the high-frequency region, and a decrease in the linewidth with decreasing temperature. Also, the ratio of the intensities of the first-order GaAs-like LO-phonon mode to the TO-phonon mode increases with a decrease in temperature. Equations (5) and (6) are used to fit the experimentally observed changes in the line center and linewidth of these two modes. The values of the anharmonic constants, which are used to obtain the best fit between the theory and experiment, are given in Table I. The lifetime of the first-order GaP-like LO phonon in this alloy is then obtained by using Eq. (9), and is given in Table II.

(ii) $GaAs_{0.35}P_{0.65}$. A similar series of experiments were done on this sample with the 4880-Å line of the argon-ion laser to ascertain the effect of increasing arsenic content. In this sample, at room temperature, the first-order GaAs-like LO-phonon mode appears shifted toward higher frequency at 284 cm^{-1}, compared to its counterpart in the 90% phosphorous sample with a linewidth of 8.5 cm^{-1} which is clearly resolved from the first-order GaAs-like TO-phonon mode. Conversely, the first-order GaP-like LO-phonon mode appears further shifted toward lower frequency at 390 cm^{-1} with a linewidth of 5.0 cm^{-1}. Furthermore, as expected, the intensity of the first-order GaAs-like LO-phonon mode increases, and that of the first-order GaP-like LO-phonon mode decreases as the concentration of phosphorous decreases from 0.9 to 0.65. The GaP- and GaAs-like first-order LO-phonon modes show line-shape asymmetry with a tail on the low-energy side, which is reflected in the asymmetry parameter (Γ_a/Γ_b), where Γ_a is the half-linewidth on the low-energy side, and Γ_b is the half-linewidth on the higher-energy side. The asymmetry parameter Γ_a/Γ_b (Table I) for the first-order GaP-like LO-phonon mode increases as the concentration of phosphorous changes from 0.90 to 0.65, which is reflected in the increase in the tail on the low-energy side. An investigation of the temperature dependence of the line center and linewidth of these modes indicates a decrease in the linewidth and a hardening of the first-order LO-phonon mode as the temperature is decreased. The experimentally observed line center and linewidth are fitted to Eqs. (5) and (6). Good agreement between theory and experiment is observed, and the best obtained values of the anharmonic constants are given in Table I. The lifetime for the two modes is estimated using Eq. (9), and is given in Table II.

TABLE II. Lifetime of the first-order GaAs-like and GaP-like LO-phonon mode in $GaAs_{1-x}P_x$.

Temp. (in K)	GaAs-like LO-phonon lifetime (ps)			GAP-like LO-phonon lifetime (ps)		
	$x=0.90$	$x=0.65$	$x=0.59$	$x=0.90$	$x=0.65$	$x=0.59$
295		1.25	1.42	3.54	2.12	1.52
250		1.42	1.63	3.54	2.12	1.77
200		1.77	1.93	4.24	2.65	2.12
150		2.12	2.65	5.31	3.03	2.36
100		2.65	3.22	5.31	3.54	3.03
50		3.03	3.54	7.07	4.24	3.54
10		3.03	3.54	7.07	4.24	3.54

(iii) $GaAs_{0.41}P_{0.59}$. In this sample, at room temperature, a hardening of the first-order GaAs-like LO-phonon mode, which appears at 285.5 cm^{-1} with a linewidth of 7.5 cm^{-1}, is observed compared to $GaAs_{0.35}P_{0.65}$. The first-order GaP-like LO-phonon mode, on the other hand, shifts toward low frequency and appears at 388 cm^{-1} with a linewidth of 6.0 cm^{-1}. The intensity of the first-order GaAs-like LO-phonon mode further increases, and that of the first-order GaP-like LO-phonon mode decreases as the phosphorous concentration changes from 0.65 to 0.59. The asymmetry parameter Γ_a/Γ_b (Table I) is observed to decrease for the first-order GaAs-like LO-phonon mode, and increases for the first-order GaP-like LO-phonon mode as the concentration of phosphorous changes from 0.65 to 0.59. A decrease in the linewidth and a shift in the line center toward high frequency is observed for these two modes with decreasing temperature. Equations (5) and (6) are used to fit the experimentally observed changes in the line center and linewidth, and the best-fit values of the anharmonic constants are given in Table I. Equation (9) is used to calculate the lifetime of these two modes which is given in Table II.

3. $In_xGa_{1-x}As$

$In_xGa_{1-x}As$ ternary alloy semiconductors exhibit a partial two-mode behavior, one mode at the gallium-rich end and the two modes for indium-rich samples. The scattering volume of these samples is rather small because of their opaque nature and small penetration depth. The scattered signal was

TABLE III. Best-fit values of the anharmonic constants for the first-order GaAs-like LO-phonon mode in $In_xGa_{1-x}As$.

x	A (cm^{-1})	C (cm^{-1})	ω_0 (cm^{-1})	Γ_a/Γ_b
0.05	0.986	−2.298	298.520	1.20
0.12	1.266	−2.331	295.768	1.57
0.19	2.134	−2.350	292.153	1.74
0.24	2.472	−2.369	289.247	2.00
0.53	3.144	−2.312	281.243	2.25

collected at each frequency for 3 s to improve the quality of the spectrum. At the same time, the error in the measurement of the line center and linewidth is minimized to less than 0.6 cm^{-1} by keeping the slit width at 70 μm. Raman studies of MVPE-grown ⟨100⟩-oriented $In_xGa_{1-x}As$ ($x=0.05$, 0.12, 0.19, 0.24, and 0.53) were investigated with the 5145-Å line of the argon-ion laser at various temperatures. The $In_xGa_{1-x}As$ compounds investigated in this work are gallium-rich samples in which only the GaAs-like LO-phonon mode is prominent. The first-order InAs-like LO-phonon mode appears for $x \geqslant 0.19$, but it is too weak for changes in the line center and linewidth to be measured. A softening of the first-order GaAs-like LO-phonon mode and an increase in its linewidth at room temperature is observed with an increasing concentration of indium. Furthermore, the asymmetry parameter Γ_a/Γ_b (Table III) increases for the first-order GaAs-like LO-phonon mode with an increasing concentration of indium. As the temperature is decreased, this mode shows similar behaviors for all $In_xGa_{1-x}As$ samples: the line center of this mode shifts toward high frequency and its linewidth decreases. Equations (5) and (6) are again used to fit the experimentally observed changes in the line center and linewidth of this mode. The best-fit values of the anharmonic constants are given in Table III. Equation (9) is used to obtain the lifetime of the first-order GaAs-like LO-phonon mode for different indium concentrations, and is given in Table IV.

4. Comparative study of anharmonic effects

The effect of anharmonicity on Raman spectra of GaP, $GaAs_{1-x}P_x$, and $In_xGa_{1-x}As$ has been discussed in the previous sections. Softening of phonons, an increase in the linewidth with increasing temperature, and increasing compositional disorder is observed. As the temperature is lowered, hardening of phonons and a decrease in the linewidth is observed. Experimentally observed changes in the line center and linewidth may be understood in terms of three-phonon processes in which an optical phonon decays into two acoustic phonons for temperatures much below the Debye temperature of the sample. At low temperatures, the thermal anharmonicity in the sample is reduced, and the phonon modes become sharp and narrow. Equations (5) and (6) are used to fit the experimentally observed changes in the line center and linewidth, and the best-fit values of the anharmonic constants are given in Tables I and III.

TABLE IV. Lifetime of the first-order GaAs-like LO-phonon mode in $In_xGa_{1-x}As$.

Temp. (in K)	GaAs-like LO-phonon lifetime (ps)				
	$x=0.05$	$x=0.12$	$x=0.19$	$x=0.24$	$x=0.53$
295	3.22	2.36	1.93	1.77	1.41
220	5.31	3.03	2.36	1.93	1.77
160	7.07	4.24	3.03	2.65	2.12
120	7.07	5.31	3.79	3.22	2.36
70	10.61	7.07	4.24	4.24	3.54
15	10.61	10.61	5.31	4.24	3.54

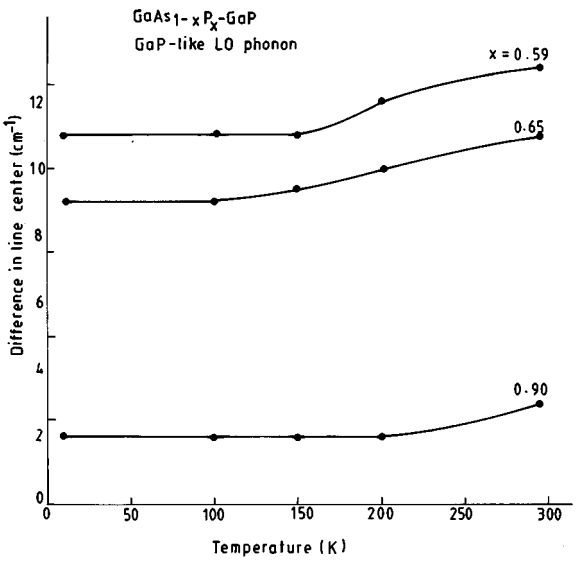

FIG. 2. Temperature dependence of the difference in the line center between $GaAs_{1-x}P_x$ and GaP for the first-order GaP-like LO-phonon mode.

A comparative study of the values of the anharmonic constants of GaP and $GaAs_{1-x}P_x$ reveals that the degree of anharmonicity experienced by the first-order GaP-like LO-phonon mode in $GaAs_{1-x}P_x$ is greater than that of the LO-phonon mode in GaP. In GaP, the anharmonicity depends only upon the temperatures, and increases with increasing temperature. In ternary alloys, on the other hand, there are two components of anharmonicity, one corresponding to temperature and the other to compositional disorder. There is a qualitative difference between these two different kinds of anharmonicities: temperature-induced anharmonicity gives rise to a shift in the phonon frequency and a change in the linewidth. Compositional-fluctuation-induced anharmonicity, on the other hand, yields, in addition, changes in the phonon line shapes which can be described by an asymmetry parameter (Γ_a/Γ_b). This observation indicates that the temperature-induced anharmonicity and compositional-fluctuation-induced anharmonicity are not additive in nature due to their different characters. However, at low temperatures, one can qualitatively separate out the two components of the anharmonicity by comparing the anharmonicity-induced effects in binary and ternary systems, since, for the latter, at low temperatures, anharmonicity is mainly due to compositional disorder. Furthermore, the values of the anharmonic constants increase with increasing compositional disorder in ternary alloys. Figures 2 and 3 show the difference

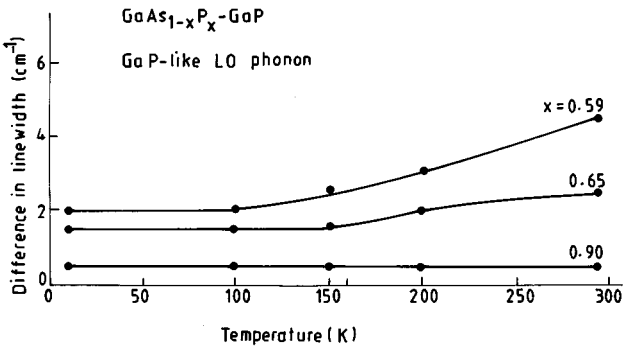

FIG. 3. Temperature dependence of the difference in the linewidth between $GaAs_{1-x}P_x$ and GaP for the first-order GaP-like LO-phonon mode.

in the line center and linewidth between $GaAs_{1-x}P_x$ and GaP for the first-order GaP-like LO-phonon mode as a function of temperature. From the figures, one can see sharp changes in the difference with the decrease in phosphorous concentration, which indicates that the degree of anharmonicity increases with the increase in compositional disorder. Similarly, Figs. 4 and 5 give the difference in the line center and linewidth between $In_xGa_{1-x}As$ and $In_{0.05}Ga_{0.95}As$ for the first-order GaAs-like LO-phonon mode as a function of temperature, which also shows a steep increase in the difference with an increase in indium concentration. It can also be seen from these figures that the effect of anharmonicity prevails even at low temperatures with increasing compositional disorder. The values of the anharmonic constants C and A also increase with increasing compositional disorder, which can

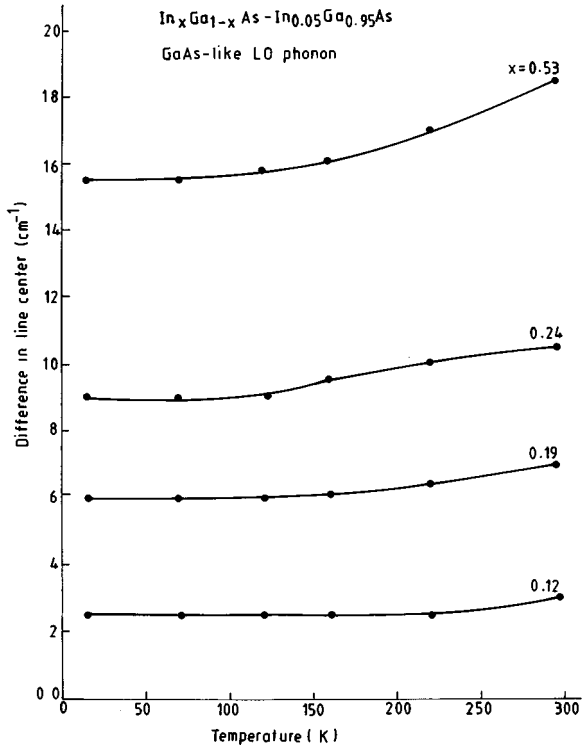

FIG. 4. Temperature dependence of the difference in the line center between $In_xGa_{1-x}As$ and $In_{0.05}Ga_{0.95}As$ for the first-order GaAs-like LO-phonon mode.

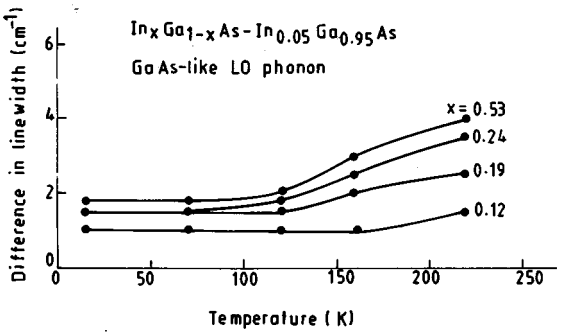

FIG. 5. Temperature dependence of the difference in the linewidth between $In_xGa_{1-x}As$ and $In_{0.05}Ga_{0.95}As$ for the first-order GaAs-like LO-phonon mode.

be seen from Tables I and III.

Another salient feature of the alloy spectrum is that anharmonicity due to compositional disorder distorts the phonon line shapes, leading to a tail on the low-energy side. This is in sharp contrast to temperature-induced anharmonicity, where the phonon line shapes do not change. Figures 6 and 7 show the effect of compositional-disorder-induced anharmonicity on the line center and linewidth of the first-order GaP-like LO phonon in $GaAs_{1-x}P_x$ at 10 K, and the first-order GaAs-like LO phonon in $In_xGa_{1-x}As$ at 15 K. At these temperatures, anharmonicity is mainly due to compositional disorder. The changes in the line center and linewidth with the increase in compositional disorder are not quantitatively explained by self-consistently solving the CPA equations for the self-energy $\overline{\varepsilon(\omega)}$. However, from these figures one can observe large changes in phonon energy and width with an increase in compositional disorder. It can also be seen that these changes are more pronounced than temperature-induced effects.

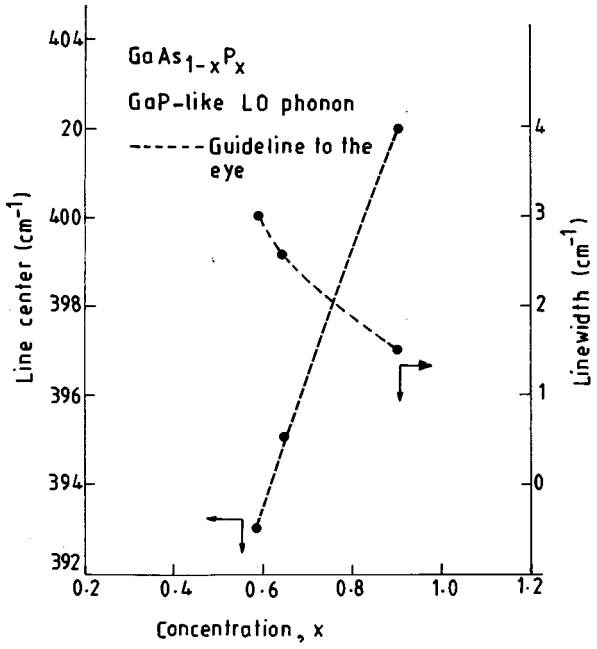

FIG. 6. Concentration dependence of the line center and linewidth for the first-order GaP-like LO phonon in $GaAs_{1-x}P_x$ at 10 K.

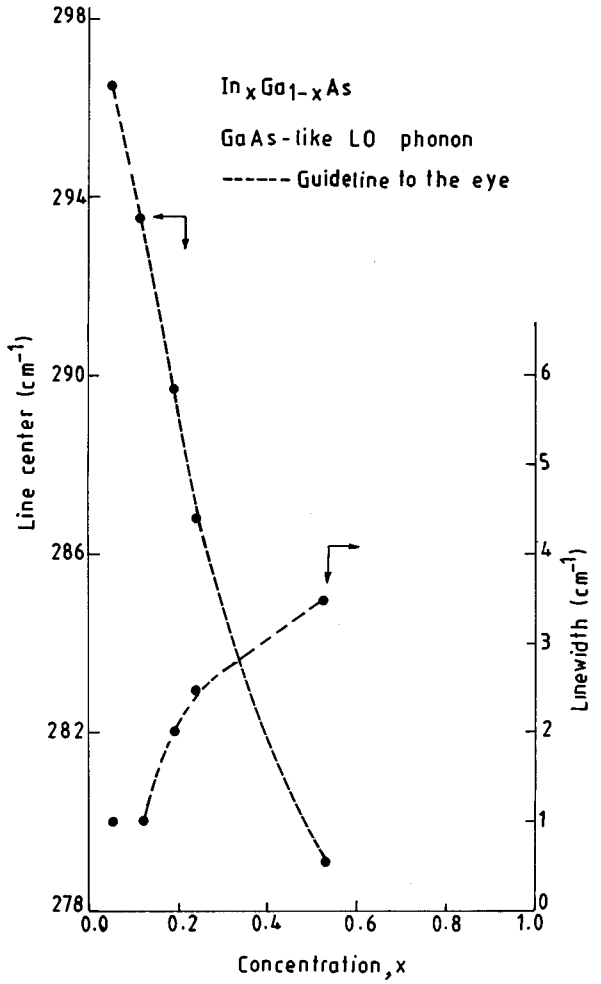

FIG. 7. Concentration dependence of the line center and linewidth for the first-order GaAs-like LO phonon in $In_xGa_{1-x}As$ at 15 K.

In $GaAs_{1-x}P_x$ ternary alloys, a two-mode behavior is observed for anharmonicity, one corresponding to the first-order GaAs-like LO-phonon mode, and the other corresponding to the first-order GaP-like LO-phonon mode. It is therefore pertinent to explore the effect of anharmonicity on both these types of phonons in this alloy system. It is found that the degree of anharmonicity of the GaP-like LO-phonon mode increases, whereas the corresponding effect in the GaAs-like LO-phonon mode decreases with a lowering of the phosphorous concentration. Furthermore, the first-order GaP-like LO phonon has a greater anharmonicity than the GaAs-like LO phonon for a given x. Even in phosphorous-rich samples, the GaP-like LO phonon has greater anharmonicity than the GaAs-like LO-phonon, whereas one might expect the reverse, since the GaAs-like LO phonon experiences a high degree of disorder in phosphorous-rich samples. This feature is attributed to the difference in the masses of phosphorous and arsenic.

Finally, our results show that the lifetime of first-order optical phonons in GaP decreases with increasing temperature and, in $GaAs_{1-x}P_x$ and $In_xGa_{1-x}As$, it decreases with increasing temperature and increasing compositional disorder, making the strongly interacting optical phonons decay into weakly interacting acoustic phonons. The greater the

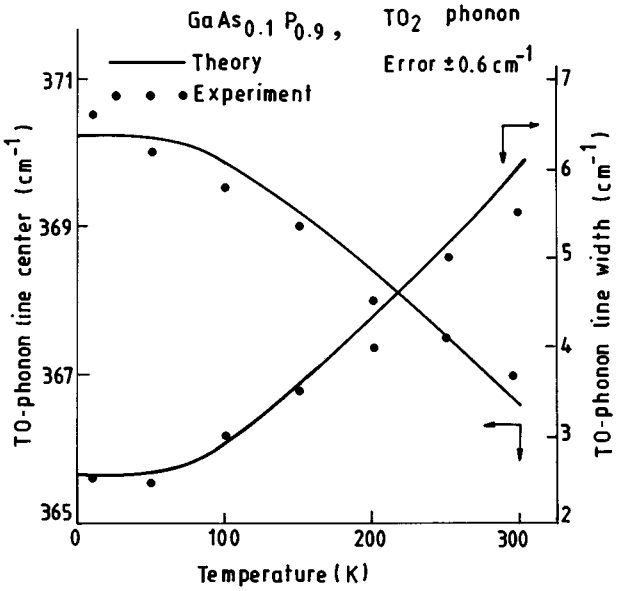

FIG. 8. Temperature dependence of the first-order GaP-like TO-phonon line center and linewidth in $GaAs_{0.1}P_{0.9}$.

degree of anharmonicity, the faster the decay of the optical phonons.

B. First-order TO phonon

The first-order TO-phonon mode is dipole forbidden in the Raman spectrum of the ⟨100⟩-oriented sample in the backscattering geometry configuration. But, in the Raman spectrum of $GaAs_{0.1}P_{0.9}$, the GaP-like first-order TO-phonon mode appears as a prominent peak. This is attributed to the presence of compositional disorder in ternary systems due to alloying. For this mode, Raman experiments were recorded with the 5145-Å line of the argon-ion laser at different temperatures. The slit width of the double monochromator was kept at 75 μm, which gave a resolution of ± 0.6 cm^{-1}. One would normally expect that this mode, which is a disorder-activated one, would not have any temperature dependence. However, as the temperature is lowered, the line center is observed to shift toward high frequency and the linewidth is found to decrease as shown in Fig. 8. Equations (5) and (6) describe the temperature dependence of allowed modes. The temperature dependence of the disorder-activated modes is not clear. However, when Eqs. (5) and (6) are used to fit the experimentally observed changes in the line center and linewidth of this mode, good agreement between theory and experiment is obtained for $C=-2.601$ cm^{-1}, $A=2.538$ cm^{-1}, and $\omega_0=372.816$ cm^{-1}. Equation (9) is used to estimate the lifetime of this mode as a function of temperature, which gives $\tau=1.93$ ps at 295 K, 3.54 ps at 100 K, and, at 10 K, $\tau=4.24$ ps. From the strong temperature dependence of this mode, we can conclude that the anharmonicity due to temperature is dominant in ternary systems with a lesser degree of disorder, whereas the anharmonicity due to disorder is predominant in ternary systems with a higher degree of disorder.

C. Second-order transverse-acoustic mode

In first-order Raman scattering, acoustic-phonon modes are not allowed. However, for second-order scattering, the

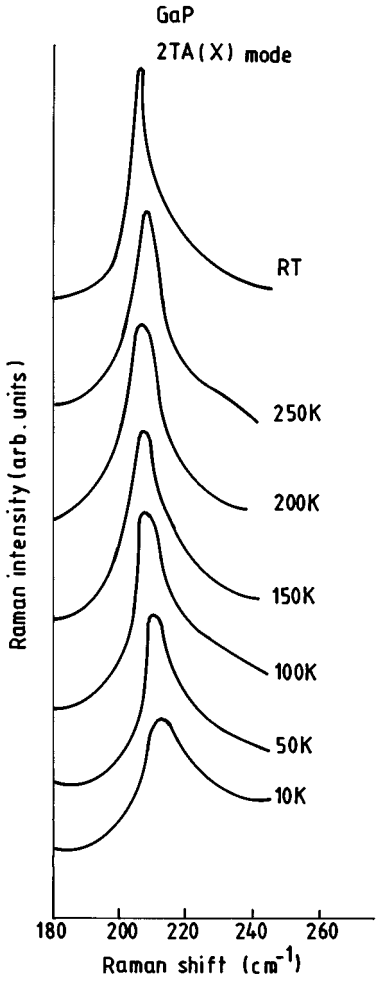

FIG. 9. Temperature dependence of the second-order transverse-acoustic-phonon structure in GaP.

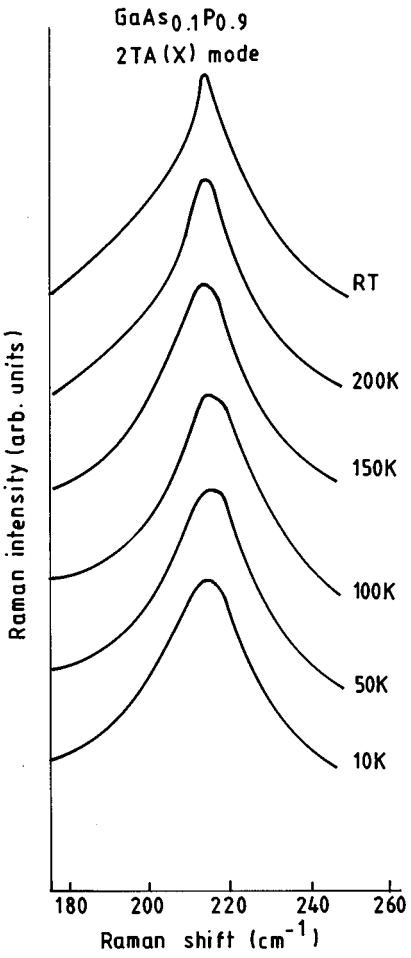

FIG. 10. Temperature dependence of the second-order transverse-acoustic phonon structure in $GaAs_{0.1}P_{0.9}$.

selection rules are relaxed. This mode is very weak compared to the first-order LO-phonon mode. The slit width of the double monochromator was maintained at 500 μm, which gave a resolution of ± 4 cm^{-1}, to improve the signal. The temperature-induced shift in the line center and a change in the linewidth is difficult to be observed at this resolution level. Figure 9 shows the second-order transverse-acoustic phonon structure, 2TA(X), at various temperatures in GaP. The 2TA(X) mode appears at around 212 cm^{-1} at 295 K in the Raman spectrum of $\langle 100 \rangle$-oriented GaP. From Fig. 9, one can see that this mode becomes broad, and its intensity decreases as the temperature is decreased. The temperature dependence of this mode was recorded using the 4765-Å line of the argon-ion laser to avoid resonance effect at the X point.

For a sharp mode, the number of phonons taking part in the scattering process can be determined by the intensity of the mode. However, if the mode is broad, the number of phonons taking part in the scattering process will also depend upon the width of the mode. The number of phonons taking part in the scattering process for the mode, shown in Fig. 9, is proportional to the area under the mode structure. At any finite temperature, the total number of phonons taking part in the scattering process will be proportional to their occupation number, because of the creation and annihilation of phonons. The occupation number of phonons taking part in any scattering process at finite temperature is given as

$$n = 1 + n_B , \tag{10}$$

where n_B is the Bose-Einstein function given as

$$n_B = \frac{1}{e^{\hbar\omega_0/k_B T} - 1} , \tag{11}$$

where ω_0 is the mean position of the mode and T is the temperature. The occupation number indicates that the density of phonon states for the second-order transverse-acoustic phonon decreases with a decrease in the temperature.

Figure 10 shows the 2TA(X) mode structure for $GaAs_{0.1}P_{0.9}$ at various temperatures. In the Raman spectrum of $GaAs_{0.1}P_{0.9}$ at 295 K, this mode appears as a weak and broad structure at around 207 cm^{-1}. This mode, which appears at around 212 cm^{-1} in the Raman spectrum of GaP, shifts toward low frequency and becomes weak and broad as the phosphorous concentration decreases from 1.0 to 0.9. The oscillator strength of the 2TA(X) mode structure does not change as the temperature is lowered, which is evident from Fig. 10. In the case of GaP, the overall structure of the 2TA(X) mode changes with a decrease in the temperature. This is explained on the basis of occupation number, which indicates that the density of phonon states for this mode de-

creases with a decrease in temperature. But, in the case of $GaAs_{0.1}P_{0.9}$, this mode does not undergo any appreciable change as a function of temperature. This could be due to the suppression of the temperature dependence of this mode by the disorder-induced effect. The decrease in the density of phonon states for this mode with a decrease in temperature is compensated for by disorder activation.

IV. CONCLUSION

A comparative study of anharmonic effects in binary and ternary systems shows two components for anharmonicity in ternary alloys: one due to temperature and the other due to compositional disorder. The anharmonicity in binary systems increases with increasing temperature and, while in ternary alloys, it increases with increasing temperature and increasing composition fluctuations. Both thermal and compositional-disorder-induced anharmonicities introduce a shift in the phonon frequency and a change in the linewidth, and, in addition, the latter contributes significantly to the phonon line shapes which indicates the nonadditive nature of the two components of the anharmonicity due their different characters. Anharmonicity at low temperatures, in ternary alloys, is due mainly to compositional disorder, because of which the components of anharmonicity could be separated out by comparing the anharmonicity-induced effects in binary and ternary systems. The strong temperature dependence of the dipole-forbidden GaP-like TO phonon in $GaAs_{0.1}P_{0.9}$ indicates that thermal anharmonicity is dominant for low values of alloying, while compositional-disorder-induced anharmonicity predominates for high values of alloying. In $GaAs_{1-x}P_x$, a two-mode behavior is observed for anharmonicity, one for the first-order GaAs-like LO phonon and the other for the first-order GaP-like LO phonon. The degree of anharmonicity for the GaP-like LO phonon increases, whereas the corresponding effect in the GaAs-like LO phonon decreases with a lowering of phosphorous concentration, indicating that the degree of anharmonicity increases with an increase in disorder. Furthermore, the degree of anharmonicity is different for these two modes, greater for the GaP-like LO phonon, for a given value of phosphorous concentration, and this is attributed to the difference in the masses of phosphorous and arsenic. The density of phonon states for the $2TA(X)$ mode in GaP is found to decrease with decreasing temperature, while its counterpart in $GaAs_{0.1}P_{0.9}$ is independent of temperature, indicating that the compositional-disorder-induced effect compensates for the temperature-induced effect in $GaAs_{0.1}P_{0.9}$. Finally, the lifetime of the first-order optical modes is found to decrease with increasing anharmonicity.

[1] V. B. Gera, Rita Gupta, and K. P. Jain, J. Phys. Condens. Matter **1**, 4913 (1989).

[2] K. K. Tiong, P. M. Amirtharaj, and F. H. Pollack, Appl. Phys. Lett. **44**, 122 (1984).

[3] P. Parayanthal and F. H. Pollack, Phys. Rev. Lett. **52**, 1822 (1984).

[4] H. Richter, Z. P. Wang, and L. Ley, Solid State Commun. **39**, 625 (1981).

[5] B. Jusserand and J. Sapriel, Phys. Rev. B **24**, 7194 (1981).

[6] H. D. Fuchs, C. H. Grein, C. Thomsen, M. Cardona, W. L. Hansen, E. E. Haller, and K. Itoh, Phys. Rev. B **43**, 4835 (1991).

[7] D. W. Taylor, Phys. Rev. **156**, 1017 (1967).

[8] H. D. Fuchs, C. H. Grein, R. I. Devlen, J. Kuhl, and M. Cardona, Phys. Rev. B **44**, 8633 (1991).

[9] S. Das Sarma, in *Hot Carriers in Semiconductor Nanostructures: Physics and Applications*, edited by J. Shah (Academic, Boston, 1992), pp. 53–85.

[10] S. Das Sarma, V. B. Campos, M. A. Stroscio, and K. W. Kim, Semicond. Sci. Technol. B 60, **7** (1992).

[11] P. G. Klemens, Phys. Rev. **148**, 845 (1966).

[12] T. R. Hart, R. L. Aggarwal, and Benjamin Lax, Phys. Rev. B **1**, 638 (1970).

[13] M. Balkanski, R. F. Wallis, and E. Haro, Phys. Rev. B **28**, 1928 (1983).

[14] José Menéndez and Manuel Cardona, Phys. Rev. B **29**, 2051 (1984).

[15] W. E. Bron, J. Kuhl, and B. K. Rhee, Phys. Rev. B **34**, 6961 (1986).

[16] Prabhat Verma, S. C. Abbi, and K. P. Jain, Phys. Rev. B **51**, 16 660 (1995).

[17] D. Von der Linde, J. Kuhl, and H. Klingernberg, Phys. Rev. Lett. **44**, 1505 (1980).

[18] A. R. Bhat, K. W. Kim, and M. A. Stroscio, J. Appl. Phys. **76**, 3905 (1994).

[19] J. Kuhl and W. E. Bron, Solid State Commun. **49**, 935 (1984); Physica **117B/118B**, 532 (1983).

[20] B. Kh. Bairamov, D. A. Parshin, V. V. Toporov, and Sh. B. Ubaidullay, Pis'ma Zh. Tekh. Fiz. **5**, 1116 (1979) [Sov. Tech. Phys. Lett. **5**, 466 (1979)].

[21] B. Kh. Bairamov, Yu. E. Kitaev, V. K. Negoduiko, and Z. M. Khashkhozhev, Fiz. Tverd. Tela (Leningrad) **16**, 2036 (1974) [Sov. Phys. Solid State **16**, 1323 (1975)].

[22] P. Soven, Phys. Rev. **156**, 809 (1967).