Raman investigation of anharmonicity and disorder-induced effects in $Ga_{1-x}Al_xAs$ epitaxial layers

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Raman scattering measurements between 20 and 450 K are reported in $Ga_{1-x}Al_xAs$ single crystals for the range $0 \le x \le 1$. Peak-frequency and linewidth variations versus temperature and composition of the first-order modes are studied in the light of disorder and anharmonicity. The asymmetry of the LO mode is tentatively explained with the help of an elementary model, chiefly based on the knowledge of the general form of the dispersion curves in the zinc-blende structure. A detailed analysis of the anharmonic effects is carried out in the case of GaAs and the calculated cubic contribution is found to be dominant with respect to the quartic one. It is shown that the anharmonicity is not affected by the substitutional disorder in $Ga_{1-x}Al_xAs$. A resonant Raman study of an aluminum-rich composition (x = 0.75) allows an accurate observation of disorder-induced modes corresponding to the Brillouin-zone edges X and L of the acoustic branches. Disorder-activated longitudinal- and transverse-acoustical structures exhibit the same resonance behavior as the first-order lines and are chiefly Γ_1 polarized.

I. INTRODUCTION

A great deal of theoretical and experimental study has been carried out on the lattice dynamics of ternary alloys, especially on III-V semiconductors with the zinc-blende structure,¹ which are often used as basic materials for laser device technology. Raman scattering is a versatile and efficient tool for probing long-wavelength and shortwavelength lattice vibrations in such systems.

One can generally distinguish two kinds of Raman lines in the III-V semiconductors. The first corresponds to the longitudinal (LO) and transverse (TO) Brillouin-zone center optical modes. The second kind arises from second-order Raman scattering in which two phonons are involved. In the case of $Ga_{1-x}Al_xAs$, the long-wavelength optical phonons display a two-mode behavior^{2,3} throughout the whole composition range. Thus, there are two couples of LO and TO modes, one "GaAs-like" and the other "AlAs-like" (GaAs-like phonons have frequencies which approach those of the phonons in GaAs as x approaches zero).

Although many studies have been devoted to the compositional dependence of these modes in ternary crystals, to our knowledge no detailed work on their linewidth and profile has yet been published. A large part of this paper will be devoted to these generally neglected features. Until now the second-order Raman effect has only been inves-

tigated in detail for the end members of the $Ga_{1-x}Al_xAs$ system (i.e., GaAs single crystals^{4,5} and AlAs polycrystals⁶). The low-energy part of the Raman spectra (below 250 cm^{-1}) contains mostly overtones of transverse-acoustical phonons. For the alloys investigated in this work, this energy range is dominated by other lines whose energy and temperature dependence cannot be explained within the frame of Raman scattering theory for perfectly ordered materials. We attribute these lines to one-phonon scattering events by shortwavelength acoustical phonons $(k \neq 0)$ which become Raman active as a consequence of the disorder. This disorder is believed to result from substitutions of Ga by Al in the gallium atomic sublattice. Kawamura et al.7 have observed singlephonon scattering events in $Ga_{1-x}Al_xAs$ which they interpret as a disorder-activated longitudinalacoustical mode. Our study emphasizes the existence of several short-wavelength modes in the low-frequency part of the Raman spectra, the assignment being performed for most of them. A similar study on disorder-induced modes in $InP_{1-x}As_x$ alloys and in mechanically-perturbed InAs crystal samples has been carried out by Carles et al.8

It should be pointed out that for the region x < 0.45, $\text{Ga}_{1-x}\text{Al}_x\text{As}$ is a direct-gap material.⁹ At $x \simeq 0.45$ the Γ and X minima cross and the gap becomes indirect. Thus for x > 0.45 the troublesome luminescence effects can be avoided. As we shall see later, advantage will be taken of this feature to perform resonant Raman scattering in a $Ga_{0.25}Al_{0.75}As$ crystal. This technique enhances appreciably the weak structures which can then be resolved.

The paper is divided into two parts. The first part presents the experimental results, where the frequencies and profiles of the LO modes are reported as a function of composition and temperature. The contribution of the short-wavelength phonons is observed both in the second-order Raman scattering and through the disorder-induced lines. The discussion which follows (Sec. III) gives an interpretation of the experimental work of Sec. II in the light of the anharmonicity theory and as a consequence of the substitutional disorder. A brief conclusion summarizes the paper's contents and points out areas that we feel require further work.

II. EXPERIMENTAL

The investigated samples were layers of several micrometers thickness which had been grown by liquid-phase epitaxy (LPE), molecular-beam epitaxy (MBE), or vapor-phase epitaxy (VPE) on (001)-oriented GaAs substrates. The $Ga_{1-x}Al_xAs$ crystals were of the *n* or *p* type, the carrier concentration being less than 5×10^{17} cm⁻³ in order to avoid the observation of the LO-phonon-plasmon modes¹⁰ characteristic of heavily doped materials.

A Coherent Radiation CR4 År⁺ laser was used chiefly on the 5145, 4880, and 4765 Å exciting lines. About 300 mW of the laser beam were directed on the samples at the Brewster incidence to maximize the power transmitted into the film. The samples were observed under vacuum or under a circulation of ⁴He gas in order to prevent surface degradation of aluminum-rich alloys and to suppress spurious low-frequency Raman lines from atmospheric N₂ and O₂ rotational vibrations. The temperature ranged approximately between 450 and 20 K. The scattered light was analyzed by a T800 Coderg triple monochromator ended by a cooled 56 TPV multiplier with magnetic defocusing and dc detection. The spectra were recorded with a spectral resolution between 1 and 4 cm⁻¹. A spectrometer scan speed of $1 \text{ cm}^{-1}/\text{min}$ in conjunction with an integration time of 10 s was used for particularly low scattering intensities.

A. First-order Raman lines

As the $Ga_{1-x}Al_xAs$ layers were (001) oriented, only the LO modes were allowed, but rather weak lines corresponding to the forbidden TO modes were also observed since they result from deviation from the strict backscattering geometry. Although in general it was possible to measure the peak position of the TO modes, the intensity was usually insufficient for a precise determination of their profile.

1. Frequency variations versus composition

The composition and homogeneity of the $Ga_{1-x}Al_xAs$ epitaxial layers were determined by electron microprobe analysis. The values of x were hence obtained with an uncertainty Δx of the order of 0.02. We have plotted (Fig. 1) the frequency ω of the LO and TO modes of both GaAs type and AlAs type as a function of x at room temperature. Our experimental points are represented by triangles (MBE samples), squares (LPE), and circles



FIG. 1. Frequency variations versus composition of the first-order Raman lines in $Ga_{1-x}Al_xAs$ mixed crystals. Our experimental points are represented by triangles (MBE), squares (LPE), and circles (VPE). Theoretical curves obtained from Bonneville's model¹² are also reported (----), as well as experimental curves obtained by Tsu¹¹ (broken lines).

(VPE). The result of Tsu et al.¹¹ is also reported (broken lines) as well as theoretical curves calculated by Bonneville.¹² Upon comparison of our results with those of Ref. 11 we find discrepancies which, for certain compositions, can reach 6 cm^{-1} a disagreement too big to be attributed to the experimental errors on Raman frequency measurements. A possible origin could be the difference between the experimental conditions. In Ref. 11 the samples were bulk materials which were excited by a He-Ne laser (6328 Å). The emitting zone was therefore much larger than in our experimental setup where the penetration depth is typically 2000 Å. The results of Ref. 11 are consequently more sensitive to the compositional inhomogeneity which could occur in the bulk. Besides, no indication is given concerning the determination of the alloy composition. The model of Ref. 12 treats the mass disorder in the coherent potential approximation (CPA), though the electronic properties and the force constants are handled by the virtual crystal approximation (VCA). The frequencies of the first-order LO and TO modes of GaAs and AlAs type calculated from this model are in good agreement with our experimental measurements.

2. Line profile dependence on composition

Investigations of linewidth and profile have been performed only on a few pure semiconductors such as GaAs¹³ and GaP.¹⁴ Concerning mixed crystals, one finds only information in the case of $In_{1-x}Ga_xP$ (Ref. 15), where the dominant feature is the variation of anharmonicity versus composition.

The instrumental profile of our monochromator being Gaussian, phonon lines which display a Lorentz profile, give registered lines with a Voigt profile. Such is the case of the LO and TO modes in the pure compounds GaAs and AlAs. In the case of the alloys, the profile of the GaAs-type as well as the AlAs-type LO modes become asymmetric, as can be noticed in Fig. 2. This feature has been already reported elsewhere¹⁶ for x = 0.45. We have observed a low-energy tail, which can be described in terms of two different half-widths at half maximum Γ_l and Γ_h , which are plotted at room temperature and at liquid nitrogen temperature versus composition x (Fig. 3). Two interpretations can be given for the asymmetric broadening of a Raman line: either an anharmonic decay into



FIG. 2. Profile of the LO lines in $Ga_xAl_{1-x}As$, reported for several compositions.

a nearly degenerate continuum of two-phonon combinations of acoustical phonons around a Brillouinzone boundary, as in GaP,¹⁴ or a disorder-induced effect with large wave-vector dependence of the Raman line.¹⁶ As the observed asymmetry in $Ga_{1-x}Al_xAs$ does not vary substantially with the temperature, the second interpretation seems to prevail over the first one.

3. Temperature dependence of the peaks frequency

The variations of the frequency versus temperature have been determined for GaAs, AlAs, and



FIG. 3. Variations versus x of the two half-bandwidths Γ_l and Γ_h corresponding to the GaAs-type LO lines. Γ_l is associated with the low-frequency side (LFS), as can be seen in the upper inset. The results are uncorrected from the instrumental resolution: (full width: 1.3 cm⁻¹); the symbols \triangle , \Box , \bigcirc have the same meaning as in Fig. 1.



FIG. 4. Temperature dependence of the frequencies, approximated by straight lines with the same slope $d\omega/dT = 1.35 \times 10^{-2} \text{ cm}^{-1} \text{ K}^{-1}$: • TO in GaAs; \odot LO in GaAs; I TO in AlAs; \Box LO in AlAs; and \times GaAs-type LO in Ga_{0.73}Al_{0.27}As. The temperature is determined from the Stokes-anti-Stokes ratio.

two intermediate compositions corresponding to x = 0.27 and 0.75. The temperature was measured in the close vicinity of the sample, but a better estimate of the temperature of the emitting zone of the crystal can be made when the ratio of the Stokes and anti-Stokes lines is taken into account. This procedure could not be used for $Ga_{1-r}Al_rAs$ with x = 0.75, because the resonance effects which occur for the Ar^+ laser lines make the ratio difficult to interpret. The results with the corrected temperatures are shown in Fig. 4. It appears that between 100 and 450 K the slope $d\omega/dT$ is a constant, independent of the mode polarization (LO and TO) and of the sample composition. We found $d\omega/dT$ $=(-1.35+0.1)\times 10^{-2}$ cm⁻¹ K⁻¹ in good agreement with the experimental results of Chang et al. on GaAs.¹³ This determined value refers to the variation $(\partial \omega / \partial T)_P$ at constant pressure and can be decomposed into two terms: the variation $(\partial \omega / \partial T)_V$ at constant volume and the contribution due to the thermal expansion (see Sec. III).

4. Temperature effects on the linewidth

The knowledge of the instrumental profile corresponding to a given slit aperture of the monochromator is obtained by recording the laser exciting line. One can then determine the actual linewidth in the case of the pure compounds GaAs and AlAs by convolving Lorentzian lines with the instrumental profile and fitting to the experimentally observed spectra. Although in Ga_{0.73}Al_{0.27}As the GaAs-type LO mode does not have a Lorentzian shape, the same kind of deconvolution has been applied to Γ_l and Γ_h , the experimental half-widths at half-maximum. As in the case of GaAs and AlAs, we obtain a total linewidth where the instrumental resolution is taken into account. The corrected values 2Γ of the linewidth corresponding to x = 0 and x = 1 and $\Gamma_l + \Gamma_h$ for x = 0.27 are reported in the same diagram versus temperature (Fig. 5). As in Sec. IIA 3, the temperature of the



FIG. 5. Temperature dependence of the width 2Γ corrected from the instrumental resolution. The experimental points are represented by the same symbols as in Fig. 4. For the GaAs-type LO line (\times): $2\Gamma = \Gamma_h + \Gamma_l$ (see Fig. 3). The full lines are the theoretical curves: • $2\Gamma(cm^{-1})=0.48[2n(136)+1]; \circ 2\Gamma(cm^{-1})=0.57 + 0.52[2n(148)+1]; \times 2\Gamma(cm^{-1})=2.22 + 0.57 \times [2n(143)+1];$ here *n* is the thermal population factor. The interrupted line merely joins the experimental points (\Box) in AlAs.

phonons is determined through the Stokes-anti-Stokes-lines intensity ratio.

B. Short-wavelength Raman investigations

In a second-order Raman spectrum, phonons throughout the Brillouin zone are accessible. The pairs of phonons concerned are those for which the sum of the wave vectors is nearly equal to zero. The Raman tensor for zinc-blende-type semiconductors contains three components, Γ_1 , Γ_{12} , and Γ_{15} . The observed components depend on the scattering configurations and are given for our experimental conditions in Table I. The Γ_1 component consists almost exclusively of phonon overtones (the two phonons belong to the same branch) and mirrors rather well the one-phonon density of states, the Γ_{15} component contains combinations of two phonons of different branches and the Γ_{12} component is negligible. We report (Fig. 6) the low-frequency Γ_1 spectra of GaAs and AlAs between 100 and 250 cm⁻¹ (below 100 cm⁻¹ nothing has been observed). This is the range of the 2TA maxima of the two-phonon density of states. The assignments of the second-order scattering peaks are indicated in Fig. 6, but one must consider that there is a contribution to the spectra which comes from other points of the Brillouin zone, which broadens the peaks 2TA(X) and 2TA(L) and lowers the contrast. Our results on the frequency of the second-order lines of GaAs and AlAs are in correct agreement with the data of the literature.4-6,17

As one approaches the middle-range concentration, one can observe a sharp change in the lowfrequency part of the spectra. New modes appear which are usually weak and are clearly resolved only under resonance conditions. These conditions were realized for a $Ga_{0.25}Al_{0.75}As$ layer which had been grown by VPE. The extrema at k = 0 of the conduction band and valence band are, for this

composition, separated by an amount of energy which lies in the range of the argon-ion laseremitting lines. The sample has been studied using the 6 Ar⁺ laser lines at several temperatures ranging between 80 and 300 K. These temperature variations actually give rise to small modifications of the energy gap at k = 0. The spectra obtained with the scattered light polarization parallel to the incident one are reproduced in Fig. 7 for the 4880 and 5145 Å laser lines at different temperatures. When the polarizations are perpendicular the scattered signal is very weak. One can notice two sets of lines: one around 200 cm^{-1} which compares well to one already reported (dotted line in Fig. 7), generally attributed to the disorder-activated longitudinal-acoustical mode (DALA) and the other, never reported before in $Ga_{1-x}Al_xAs$, which is situated between 70 and 150 cm^{-1} . This is the short-wavelength transverse-acoustical frequency range and we will show that it corresponds to a disorder-activated transverse-acoustical band (DATA).

III. DISCUSSION

A. First-order lines

Our Raman study on $Ga_{1-x}Al_xAs$ alloys has been undertaken on a series of epitaxial layers of different compositions within the concentration range $0 \le x \le 1$ and prepared by the three usual epitaxy techniques. It appeared that the frequencies of the first-order Raman modes were independent of the crystal quality (i.e., samples of same composition display the same peak frequencies). On the contrary, the linewidth and profile of the LO mode differed from one sample to another, probably owing to various crystalline defects or the occurrence of residual stress. We selected the best samples on the criterion of narrow linewidth in the whole investigated temperature range. This criterion is a

TABLE I. Correspondence between the three independent components of the second-order Raman tensor and the experimental scattering configuration in zinc-blende-type semiconductors with (001) scattering faces.

Polarization of incident light	Polarization of scattered light	Associated representation
[100]	[100]	$\Gamma_1 + 4\Gamma_{12}$
[100]	[010]	Γ_{15}
[110]	[110]	$\Gamma_1 + \Gamma_{12} + \Gamma_{15}$
[110]	[1]0]	$3\Gamma_{12}$



FIG. 6. Low-frequency second-order spectra of GaAs and AlAs belonging to the Γ_1 representation. Full line \rightarrow GaAs; interrupted line \rightarrow AlAs. The value of TA(L) in GaAs is taken from Ref. 17.

priori obvious and seems to have given consistent results. As a consequence of the selection, we think that the profile data presented are crystal-intrinsic and chiefly characteristic of the random substitution in the GaAs(AlAs) lattice of Ga(Al) atoms by miscible isoelectric Al(Ga) atoms.

1. The asymmetry of the LO mode

The asymmetry of the LO line is most probably due to contributions of other modes of the LO branch whose wave vector is situated in the proximity of k = 0, and which are activated by the sub-



FIG. 7. Disorder-activated longitudinal-acoustic structure (DALA) and disorder-activated transverseacoustic structure (DATA) in the Γ_1 spectra of Ga_{0.75}Al_{0.25}As at several temperatures and for the two main laser lines: 5145 Å (full lines) and 4880 Å (dotted lines). The results of Ref. 11 obtained at room temperature (6328 Å) for a sample corresponding to the same composition are indicated by interrupted lines (lowest curve). The symbols I, II, III, IV, and V are used in the discussion.

stitutional disorder. As these modes have a frequency ω lower than the frequency ω_0 of the chief mode at k = 0, one can understand qualitatively the tail observed in the low-frequency side of the LO line. We have tried to explain in a rather quantitative way the data obtained (Fig. 3) at low temperature where the effects of anharmonicity are considerably reduced. For an exact calculation of the Raman line shape, the zone-center density of states as well as the Raman tensor in the allov are needed. They are not currently available in the literature and the calculation is beyond the purpose of this paper. We propose an elementary phenomenological model which is questionable but has the credit of simplicity and accounts for the asymmetric broadening of the GaAs-type LO line with increasing x. Let us consider a one-dimensional model where the Raman-scattered light by the different contributing modes has a Lorentzian distribution around the frequency $\omega(q)$ with the halfwidth $\gamma(q)$. Here q is equal to k/Q, Q being the wave-vector magnitude corresponding to the extremity of the Brillouin zone. The Raman intensity $R(\omega)$ is thus a weighted sum of these lines:

$$R(\omega) = \int_0^1 P(q) \frac{\gamma(q)/\pi}{[\omega - \omega(q)]^2 + \gamma(q)^2} dq \quad . \tag{1}$$

Let us assume that (i) the optical branch is parabolic:

$$\omega(q) = \omega_0 - \beta q^2$$

This is a good approximation in the vicinity of the Brillouin-zone center. (ii) γ is independent of q. This is probably a good approximation since the energy of the LO phonon varies only slowly in the vicinity of zone center. The decay process remains therefore approximately unchanged. (iii) The distribution of probability P(q) is a Lorentzian centered around q = 0, with a half-width α :

$$P(q) = \frac{2\alpha/\pi}{q^2 + \alpha^2}$$

This choice was made for analytical facility.

One obtains an expression for the Raman signal which depends on the two parameters γ and α :

$$R_{\alpha,\gamma}(\omega) = \frac{2A\gamma}{\pi^2} \int_0^1 \frac{dq}{(q^2 + \alpha^2)[(\omega - \omega_0 + \beta q^2)^2 + \gamma^2]}$$
(2)

In the case of $\alpha^2 << 1$ (weak disorder), $R_{\alpha,\gamma}(\omega)$ can be approximated by taking the integral between the limits 0 and $+\infty$; by setting $\beta q^2 = X^2$, $\beta \alpha^2 = A^2$, and $\omega - \omega_0 = W$:

$$R_{\alpha,\gamma}(\omega) \simeq \frac{2A\gamma}{\pi^2} \int_0^\infty \frac{dX}{(X^2 + A^2)[(W + X^2)^2 + \gamma^2]}$$

The solution of the integral gives

$$R_{\alpha,\gamma}(\omega) \simeq \frac{\gamma(W^2 + \gamma^2)^{1/2} + A(W + A^2)H^+(W) - \gamma AH^-(W)}{\pi(W^2 + \gamma^2)^{1/2}[(W + A^2)^2 + \gamma^2]}$$

Here

$$H^{\pm}(W) = \left(\frac{(W^2 + \gamma^2)^{1/2} \pm W}{2}\right)^{1/2}.$$
 (5)

To obtain the shape of the experimental lines one must take into account the instrumental profile under the experimental conditions of Sec. II A 2. The calculated half-widths are then compared with the results at 80 K plotted in Fig. 3. The fitted values of A and γ are reported in Table II. One can see from Table II that these parameters increase with increasing values of x. This pictures rather well the effect of the disorder: as alloying increases, a greater number of modes of different k belonging to the Brillouin zone contribute to the process. In the case of $x \simeq 0$, let us estimate the magnitude of α . We obtain β from the shape of the optic branch which is given by¹⁹

$$\omega(q) = \omega_0 \left[1 - \frac{1}{8} \frac{M_1 M_2}{(M_1 + M_2)^2} \pi^2 q^2 \right].$$
 (6)

Here M_1 and M_2 are the atomic mass of Ga and As. One thus obtains $\beta \simeq 90 \text{ cm}^{-1}$. For $A \simeq 1$, one finds $\alpha \simeq 0.1$ leading to a linewidth in the \vec{k} space extending to one-tenth of the Brillouin zone.

TABLE II. Parameters of the model which accounts for the asymmetry of the LO Raman line, fitted with the experimental results of Fig. 3 (T = 80 K). γ is the halfwidth of the contributing modes whose distribution is a Lorentzian with a half-bandwidth α . β is a parameter relative to the curvature of the LO dispersion curve.

x	$\gamma(\mathrm{cm}^{-1})$	$A = \alpha \sqrt{\beta} (\mathrm{cm}^{-1/2})$
0.0	0.55	0.0
0.07	0.58	0.6
0.12	0.55	0.8
0.165	0.55	0.8
0.27	0.9	1.1
0.325	0.95	1.43
0.4	1.15	1.67
0.5	1.3	1.83

One can notice that α increases faster than A for increasing values of x, as β is expected to decrease with respect to x (the normal modes being partially localized). It is clear that the introduction of the composition-dependent γ parameter has been necessary to obtain a good fit with the experimental curves and expresses the decrease of the lifetime of the modes which contribute to the Raman signal as x increases.

2. Anharmonic effects

Consider a pure compound such as GaAs or AlAs, where the normalized Raman spectral distribution associated with an optical phonon is $(\Gamma/\pi)/[(\omega_S - \omega_I + \Omega + \Delta)^2 + \Gamma^2]$ in the case of the Stokes line. Here, ω_S and ω_I refer to the scattered and incident light and Ω is the frequency of the phonon in a perfectly harmonic lattice. The anharmonicity produces a shift Δ in the peak and a finite half-width Γ related to the vibration damping; $\omega = \Omega + \Delta$ is the frequency of the phonon in the anharmonic lattice. The effective half-width Γ can be decomposed into two contributions, a damping Γ_3 due to cubic anharmonicity and a damping Γ_1 independent of T due to other attenuation processes (such as phonon scattering by electrons and defects):

$$\Gamma = \Gamma_1 + \Gamma_3 \ . \tag{7}$$

Quartic anharmonicity is neglected in (7) as it gives rise to higher-order contribution²⁰ to the linewidth. The cubic process consists of the decay of the optical phonon into two acoustic phonons of one-half the optical frequency ω and of equal and opposite wave vector. Pine and Tannenwald²¹ have calculated Γ_3 and found

$$\Gamma_3 = \Gamma_3^0 [2n(\omega/2) + 1] . \tag{8}$$

Here, n is the thermal population factor:

$$n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$$

 Γ_3^0 is the anharmonic contribution to the residual low-temperature damping. Equation (8) is valid

24

(3)

(4)

7200

for acoustic phonons of frequency $\omega/2$ whose wave vector is far from the Brillouin-zone edge, where elastic isotropy and frequency-independent density of states can be reasonably assumed. Such is the case of GaAs where the decay of the LO and TO phonons into two acoustic phonons occur in the LA branch, respectively, at 148 and 136 cm⁻¹.

Let us now consider Δ the peak shift due to anharmonicity. One can write

$$\Delta = BT + \Delta_3 + \Delta_4 . \tag{9}$$

 Δ_3 and Δ_4 are the shifts due to cubic and quartic anharmonicity, respectively. *BT* is a contribution of the thermal expansion which can be easily obtained from partial derivatives in a cubic crystal:

$$\left(\frac{\partial\omega}{\partial T}\right)_{P} = \left(\frac{\partial\omega}{\partial T}\right)_{V} + B .$$
 (10)

Here $B = -(1/\chi_T)(1/V)(\partial V/\partial T)_P(\partial \omega/\partial P)_T$ is taken to be temperature independent; $\chi_T = -(\partial V/\partial P)_T/V$ is the isothermal compressibility which is equal to $3(s_{11}+2s_{12})$; the thermal expansion is $(\partial V/\partial T)_P/V = 3(\partial a/\partial T)_P/a$, a being the lattice parameter; $(\partial \omega/\partial P)_T$ can be obtained by Raman experiments under hydrostatic pressure. The same assumptions as used in Ref. 21 for Γ_3 allow us to determine the temperature variations Δ_3 . One finds (see the Appendix)

$$\Delta_3 = -\Gamma_3 \mathcal{A}(q) \ . \tag{11}$$

In Eq. (11), q is the reduced wave vector of the acoustic phonons involved in the process and

$$A(q) = \left[\frac{1}{4q^4} + \frac{1}{3q^3} + \frac{1}{2q^2} + \frac{1}{q} + \ln\left[\frac{1}{q} - 1\right]\right] / \pi .$$

Thus Δ_3/Γ_3 is a constant which depends only on the phonon dispersion curves. Let us consider the case of GaAs. One finds Γ_1 and Γ_3^0 from the experimental curves of Fig. 5:

$$2\Gamma_3^0 = 0.52 \text{ cm}^{-1}$$
,
 $2\Gamma_1 = 0.57 \text{ cm}^{-1}$

for the LO and

$$2\Gamma_3^0 = 0.48 \text{ cm}^{-1}$$

$$\Gamma_1 = 0 \text{ cm}^{-1}$$

for the TO.

Concerning the frequency shift given by (9), we have calculated *B* from the data of the literature. Taking $s_{11} = 11.75 \times 10^{-12} \text{ Pa}^{-1}$, $s_{12} = -3.66 \times 10^{-12} \text{ Pa}^{-1}$ (Ref. 22), $(1/a)(\partial a/\partial T) =$ 6.8×10⁻⁶ K⁻¹ (Ref. 23), and $(\partial \omega / \partial P)_T = \frac{3}{8}$ cm⁻¹ Pa⁻¹ (Ref. 24) for both LO and TO, one finds $B = -0.58 \times 10^{-2}$ cm⁻¹K⁻¹. Starting from the experimental value $(\partial \omega / \partial T)_P = -1.35 \times 10^{-2}$ cm⁻¹K⁻¹, one obtains $(\partial \omega / \partial T)_V = -0.77 \times 10^{-2}$ cm⁻¹K⁻¹.

The cubic contribution Δ_3 is obtained from the experimental determination of Γ_3^0 through (11). For the decay of the LO mode $1/q = 1.9 \pm 0.05$, whatever the chosen direction in the k space.¹⁷ Similarly, one obtains $1/q = 2\pm 0.05$ for the TOmode decay. In the range 100-450 K the Δ_3 variations versus temperature are quasilinear with a slope -0.76×10^{-1} cm⁻¹K⁻¹ and -0.81×10^{-2} cm⁻¹K⁻¹, respectively, for LO and TO modes. These values are close to the value of $(\partial \omega / \partial T)_V$ calculated above. The quartic anharmonicity is therefore weak compared to the cubic anharmonicity and can be neglected in GaAs. Neglecting Δ_4 , we have reported (Fig. 8) the calculated values of



FIG. 8. Temperature dependence of the anharmonic shift $\Delta = \omega - \Omega$. The curve is obtained from the theoretical expression $\Delta(\text{cm}^{-1}) = -0.55 \times 10^{-2} \text{ T}$ -0.8[2n (140)+1]. 0.8 and 140 correspond, respectively, to $A(q)\Gamma_3^0$ and $\omega/2$, the values of which are very close for the TO and LO modes in GaAs. The experimental points, represented by the same symbols as in Fig. 4, are obtained by subtracting a fitted harmonic frequency Ω to the measured peak frequency ω . $\Omega(\text{LO})=297\pm0.5 \text{ cm}^{-1}$, $\Omega(\text{TO})=273\pm0.5 \text{ cm}^{-1}$ for GaAs. $\Omega(\text{LO})=287.25\pm0.5 \text{ cm}^{-1}$ for Ga $_{0.73}$ Al $_{0.27}$ As.

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 $\Delta = BT + \Delta_3$ in the case of GaAs (full line). To compare this curve to the experimental results ω , one has to fit the harmonic frequency Ω . In Fig. 8 we have indicated the values $\omega - \Omega$ for both TO and LO of GaAs.

The same study can be applied to the GaAs-type mode of $Ga_{1-x}Al_xAs$. In the case of the sample corresponding to x = 0.27, which has been the most investigated, one can see in Figs. 4 and 5 that the variation of frequency and total linewidth versus temperature are parallel to those of GaAs. The anharmonicity is therefore only weakly affected by the disorder. One can observe between GaAs and Ga_{0.73}Al_{0.27}As a linewidth increase due to the disorder, which is constant versus temperature and of the order of 2 cm⁻¹. Concerning the anharmonic shift $\omega - \Omega$, it can be well accounted for by the same Δ values as in GaAs (see Fig. 8).

On the other hand, this model is not suitable for AlAs where the value $\omega/2$ of one-half the optical frequency falls at k vectors near the critical point X and L on the LA branches. The same conclusion is valid for AlAs-type modes in Ga_{1-x}Al_xAs.

B. Identification of the disorder-induced Raman structure and determination of critical-point phonon energy

Since neutron scattering data are not available in AlAs, one has to obtain information on criticalpoint phonon energy by other methods. With the consideration of the set of already published data on III-V compounds, some general laws appear. For instance, the frequency of the LO and LA modes at the X and L points of the Brillouin zone can be obtained from the set of the independent elastic constants C_{11} , C_{12} , and C_{44} of the point group $\overline{4}3m$ of zinc-blende and diamond-type structures. The results derive from a simple onedimensional model with one and two force constants, respectively, for the X and L points.²⁵ This model, as it respects the symmetry of the vibrations at X and L, is in good agreement with the experimental results in practically all the investigated materials of this structure. One obtains²⁵

$$\omega_{\text{LO}(X)} = (8C_{11}a/M_2)^{1/2}, \qquad (13)$$

$$\omega_{\text{LA}(X)} = (8C_{11}a / M_1)^{1/2} , \qquad (14)$$

$$(\omega_{\text{LO}(L)}^2 + \omega_{\text{LA}(L)}^2)^{1/2} = (8C_{11}a/\mu)^{1/2},$$
 (15)

$$\omega_{\text{LO}(L)}\omega_{\text{LA}(L)}^{1/2} = [16C_{11}(C_{11} + 2C_{12} + 4C_{44})a^2/M_1M_2]^{1/4}$$

a is the lattice parameter, M_2 is the light-atom mass, M_1 the heavy-atom mass, and μ is the reduced mass. Actually if one plots the first members of Eqs. (13)—(16) versus the second member for most of the diamond- and zincblende-type semiconductors, one finds linear variations²⁵ with a slope which varies slightly from the theoretical value 1 [0.93 for Eqs. (13) and (14) and 0.91 for Eqs. (15) and (16)].

Taking for the C_{ij} of AlAs the same set of values as in GaAs and considering the abovementioned corrections, one obtains for AlAs the values reported in Table III. It is clear that $\omega_{LA(X)}$ takes the same value for GaAs and AlAs because it depends only on the As mass, but this conclusion seems to be good also for $\omega_{LA(L)}$ (the calculation gives no significant difference between the corresponding values in GaAs and AlAs).

This simple model of a one-dimensional chain with a single force constant is not valid for the transverse modes. Fortunately, $\omega_{TA(L)}$ and $\omega_{TA(X)}$ can be obtained from second-order Raman measurements. We measure $\omega_{2TA(L)} = 160 \text{ cm}^{-1}$ and $\omega_{2TA(X)} = 206.5 \text{ cm}^{-1}$ in AlAs. One can compare these values with the corresponding ones in GaAs (Ref. 17) ($\omega_{2TA(L)} = 124 \text{ cm}^{-1}$ and $\omega_{2TA(X)}$ = 158 cm⁻¹). As the As mass is greater than the Ga and Al masses, one can predict an acoustical one-mode behavior at X and L points in Ga_{1-x}Al_xAs mixed crystals.²⁶ Taking for TA(L) and TA(X) linear interpolated values, one obtains for x = 0.75

$$\omega_{TA(L)} = 75 \text{ cm}^{-1} \text{ and } \omega_{TA(X)} = 97 \text{ cm}^{-1}$$

Concerning $\omega_{LA(X)}$ and $\omega_{LA(L)}$, one can predict very weak variations in the whole range of concentration.

TABLE III. Calculated frequencies (cm^{-1}) of the phonons at X and L points of the Brillouin zone for AlAs compared to the experimental values for GaAs (Ref. 17).

	AlAs	GaAs
$\omega_{\rm LO}(X)$	387	241
$\omega_{\rm LO}(L)$	390	238.5
$\omega_{\rm LA}(X)$	227	227
$\omega_{\rm LA}(L)$	208.5	209

(16)

Let us return to Fig. 7. One can notice that the variation of intensity of the peaks I, II, IV, and V are chiefly related to the difference between the energy of the incident photon and the value of the gap at k = 0 corresponding to temperature of the sample. More precisely, the spectrum obtained at 350 K for 5145 Å is very similar to the spectrum obtained at 80 K for 4880 Å. This is due to the fact that the temperature shift of the gap between 80 and 350 K is of the same order of magnitude $(\sim 100 \text{ meV})$ as the energy difference between the two laser lines. Actually these peaks exhibit the same resonant behavior as the LO and TO modes, according to our measurements. This kind of behavior is not compatible with the strong lowering of intensity of the second-order Raman lines with decreasing temperature. The peaks of Fig. 7 are therefore first-order intrinsic Raman lines and cannot be attributed to impurities²⁷ such as crystalline or amorphous arsenic.28,29

The frequencies 73 and 96 cm^{-1} of the peaks I and II (Fig. 7) are very close to the values $\omega_{TA(L)}$ and $\omega_{TA(X)}$ calculated above. These peaks can thus be identified as the TA(L) and TA(X) modes of Ga_{0.25}Al_{0.75}As. Concerning the DALA structure, one can notice the existence of two peaks IV and V situated at 200 ± 5 cm⁻¹ and 210 ± 5 cm⁻¹, which can be assigned as the LA(L) and LA(X) modes although these values seem to be a little inferior to those of GaAs and AlAs (see Table III). One can notice on Fig. 7 the difference between the results of Tsu et al. and ours. The DALA mode of Ref. 7 is a single mode, though in our experiments it is resolved into two distinct chief components IV and V. Peak IV is the same as the peak reported in Ref. 7. Peak V is an additional one and it undergoes a resonance clearly stronger than all others.

We report in Fig. 9 the intensity of the Raman lines obtained at 80 K for five Ar^+ laser lines. These intensities are uncorrected and the experimental errors can reach 20% for the low-intensity lines, but it is clear that the resonance behavior of lines I, II, III, and IV is quite similar to that observed for the GaAs-type and AlAs-type LO modes in the allowed configurations while the line V has a "forbidden resonant behavior"⁵ (Fröhlich interaction). No clear interpretation of this behavior has been yet found.

Moreover, the polarized Raman study shows that the DALA structure is of the Γ_1 symmetry as predicted theoretically.³⁰ Concerning the DATA structure, we have observed that it is preferentially Γ_1 polarized although the theory predicts strong



FIG. 9. Incident wavelength dependence of the intensity of the Raman lines for the sample Ga_{0.25}Al_{0.75}As at 80 K. These results are uncorrected for the response function of the experimental set-up and the wavelengthdependent absorption of the sample: \times AlAs-type LO (forbidden configuration); + AlAs-type LO (allowed configuration); \circ GaAs-type LO (forbidden configuration); \bullet GaAs-type LO (allowed configuration); \triangle lowenergy line V (\times 10); and \blacktriangle low-energy lines I, II, IV (\times 10), and III (\times 50). It can be seen that line V has the same resonant behavior as the GaAs-type LO and AlAs-type LO in the forbidden configuration.

components belonging to Γ_{12} and Γ_{15} irreducible representations.

CONCLUSION

In this study, chiefly experimental, the detailed Raman spectra of $Ga_{1-x}Al_xAs$ between 20 and 450 cm⁻¹ have been reported versus temperature and composition. Long-wavelength modes have been investigated as well as several short-wavelength lattice vibrations. This technique gives useful information on dispersion curves in thin films where neutron experiments are practically impossible to perform. We have made a new determination of the frequency dependence on composition of the first-order Raman lines for the range $0 \le x \le 1$. These results can help for material characterization³¹ and lead to a more severe test for theoretical prediction and a better knowledge of

model parameters. The profile of the LO mode with its noticeable asymmetric feature is analyzed as a function of the Al concentration x. The study of the anharmonicity has been completely carried out in the case of GaAs, and the experiments performed on $Ga_{1-x}Al_xAs$ indicate that, concerning the GaAs-type mode, the anharmonicity is not affected by the substitutional disorder. DALA and DATA structures have been assigned as arising from the high-density phonon states of the Brillouin zone.

It is clear that the two topics discussed in this paper, the anharmonicity and the disorder effects in $Ga_{1-x}Al_xAs$ mixed crystals, can each occupy a study in its own right. More detailed studies of each aspect are planned. Experiments on (111) oriented layers are to be carried out to investigate the profile of the TO mode. It is anticipated that the use of a dye laser will provide greater flexibility for the resonance studies of the disorder-induced Raman lines.

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APPENDIX

Following Pine and Tannenwald,²¹ one can write for the damping and frequency shift of a phonon due to cubic anharmonicity:

$$\Gamma_{3} = \Gamma_{3}^{0} [2n(\omega/2) + 1] \frac{\eta}{\pi q^{4}} \int_{0}^{1} \frac{x^{4} dx}{(q-x)^{2} + \eta^{2}} ,$$
(A1)
$$\Delta_{3} = \Gamma_{3}^{0} [2n(\omega/2) + 1] \frac{1}{\pi q^{4}} \int_{0}^{1} \frac{x^{4}(q-x) dx}{(q-x)^{2} + \eta^{2}} .$$
(A2)

Here ω is the phonon frequency and $\eta = 2\gamma_1/\omega$, γ_1 being the attenuation due to the own collision of the optical phonons. Both Γ_3 and Δ_3 are therefore obtained through an elementary integration and are proportional:

$$\Gamma_3 = \Gamma_3^0 [2n(\omega/2) + 1] F(\eta, q) , \qquad (A3)$$

$$\Delta_3 = \Gamma_3^0 [2n(\omega/2) + 1] G(\eta, q) , \qquad (A4)$$

with

$$F(\eta,q) = \left\{ (1-6\eta^2 + \eta^4) \left[\tan^{-1} \left[\frac{(1/q) - 1}{\eta} \right] + \tan^{-1} \left[\frac{1}{\eta} \right] \right] + \eta \left[\frac{1}{3q^3} + \frac{1}{q^2} + (3-\eta^2) \frac{1}{q} \right] + 2\eta (1-\eta^2) \ln \left| \frac{\left[(1/q) - 1 \right]^2 + \eta^2}{1+\eta^2} \right| \right\} / \pi \right].$$
(A5)

$$G(\eta,q) = \left\{ 4\eta(1-\eta^2) \left[\tan^{-1} \left[\frac{(1/q)-1}{\eta} \right] + \tan^{-1} \left[\frac{1}{\eta} \right] \right] - \frac{1}{4q^4} - \frac{1}{3q^3} - \frac{1}{2q^2} (1-\eta^2) - \frac{1}{q} (1-3\eta^2) - (\frac{1}{2} - 7\eta^2 + \frac{1}{2}\eta^4) \ln \left| \frac{\left[(1/q)-1 \right]^2 + \eta^2}{1+\eta^2} \right| \right\} / \pi \right\}.$$
(A6)

In the case of a GaAs optical phonon, $\eta << 1$ (weakly-damped modes) and $\eta << 1/q - 1$ (the acoustical phonons involved in the decay are far from the Brillouin-zone edge). Taking $\eta = 0$ in (A3) and (A4), one obtains

 $\Gamma_3 = \Gamma_3^0 [2n(\omega/2) + 1], \qquad (A7)$

$$\Delta_3 = -\Gamma_3^0 [2n(\omega/2) + 1] A(q) . \tag{A8}$$

 Γ_3 and Δ_3 differ only by a constant factor:

$$A(q) = \left[\frac{1}{4q^4} + \frac{1}{3q^3} + \frac{1}{2q^2} + \frac{1}{q} + \ln\left[\frac{1}{q} - 1\right]\right] / \pi ,$$
(A9)

which solely depends on the phonon dispersion curves.

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