

Comparative study of phonon modes in $\text{Ga}_{1-x}\text{In}_x\text{P}$ and $\text{GaAs}_x\text{P}_{1-x}$ alloys

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The "one-mode" and "two-mode" behaviors of $\text{Ga}_{1-x}\text{In}_x\text{P}$ and $\text{GaAs}_x\text{P}_{1-x}$ alloys have been studied as a function of the concentration x and the hydrostatic pressure by means of Raman spectroscopy. A detailed comparative study of the experimental results shows that the concept of a one-mode system is not appropriate to describe the physics of this kind of alloy. A more realistic picture should involve a selective activation of the alloy phonon density of states for each observed structure.

I. INTRODUCTION

The study of the vibrational properties of mixed ternary alloys, combining in a continuous way two binary compounds, has been extensively studied on the experimental as well as the theoretical points of view. The alloys obtained by mixing III-V and II-VI zinc-blende compound semiconductors have especially been the object of many investigations and some review papers.¹⁻³ The main problem which has yet to be satisfactorily solved is the explanation of the two types of behavior which these compounds exhibit. Each compound shows either "one-mode" behavior, with the dominant peaks in their Raman or infrared spectrum varying continuously between the end members of the family, or "two-mode" behavior, with the Raman or infrared spectrum being the juxtaposition of two distinct spectra which evolve independently at each end of the series toward the normal spectrum of the pure binary compound and the localized phonon of the third element. Many criteria have been proposed to explain these two types of systems,^{4,5} and the one which seems to be ultimately more reliable is the degeneracy of the localized mode with the density of states of the host crystal, which would induce the one-mode behavior. However, the more refined model⁶ still fails in reproducing all of the experimental facts.

In III-V compounds the only one-mode system is $\text{Ga}_{1-x}\text{In}_x\text{P}$, at least for low x values. In this range of x , we have resumed careful measurements comparing its Raman spectrum with that of the $\text{GaP}_{1-x}\text{As}_x$ system. We have also noticed some important differences in the variation of dominant modes between the two alloys, and have applied hydrostatic stresses to eventually differentiate these variations. All of the experimental findings are described in Sec. II of this paper.

The discussion of these results is given in Sec. III. We are led to reject the assumption that the dominant peaks in a one-mode system still have a LO or TO character, since this was a supposition in all theories. It is shown that a more physical picture would involve a selective activation of modes inside the Brillouin zone which progressively span the dispersion curves of phonons as the disorder increases. Therefore, in the one-mode system the concept of coupled oscillators no longer seems appropriate.

II. EXPERIMENTAL RESULTS

A. Samples and experimental techniques

The results presented here have been obtained on polycrystalline $\text{Ga}_{1-x}\text{In}_x\text{P}$ samples for $x \geq 0.02$, and on samples grown by epitaxy on bulk GaP for $\text{Ga}_{1-x}\text{In}_x\text{P}$ ($x \leq 0.02$) and $\text{GaP}_{1-x}\text{As}_x$. In the latter case, the GaP substrate has been eliminated by mechanical polishing in order to reduce the thickness of the samples to 20–25 μm . This is necessary to perform experiments under high pressure in a diamond-anvil cell, and allows the relaxation of most of the spurious strains eventually induced by the epitaxy process. In polycrystalline samples, the typical size of the grains is larger than 100 μm , which prevents the observation of surface Raman modes.⁷ The x value of each sample has been checked by microprobe analysis. Since these samples are n type, all data are reported at 80 K, where carriers are all trapped and plasmon-LO-phonon coupling is negligible.

Raman scattering experiments have been performed, in a backward geometry, using the standard krypton- or argon-laser lines. The features reported here are not qualitatively dependent on the excitation energy. The analysis of the scattered light was performed through a double-

additive Coderg spectrometer with a resolution of 2 cm^{-1} ; light detection was facilitated by using a cooled RCA photomultiplier and a photon-counting unit. The high pressure was applied with a diamond-anvil-cell technique. This cell was specially designed, with sapphire windows supporting the diamonds in order to increase the optical aperture of the cell. It was filled with xenon gas, which preserves the hydrostaticity of the pressure at 300 and 80 K (at least in the range of explored pressures—170 kbar). Pressure was controlled by recording the ruby emission line of different tiny ruby samples introduced in the cell. Low-temperature measurements were performed in the vacuum by cooling the cell embedded in a cold finger of a liquid-nitrogen cryostat.

B. Experimental results at atmospheric pressure

In the range of x that we investigated, both alloys are known to behave differently.⁸⁻¹⁰ Ga-In-P (Fig. 1) exhibits its one-mode behavior. This means that its spectrum is made of only two groups of bands issued from the TO and LO peaks of GaP without InP localized modes. Each band has a dominant peak (L_1 or T_1) with a low-energy-side shoulder or bump that we call BL_1 and BT_1 for convenience. Another structure seen in the BT_1 band of Ga-In-P is called BI. From polarization measurements, each band behaves as a whole for a given sample, but the relative importance of peaks existing inside each band varies from sample to sample with x .

Ga-As-P (Fig. 2) exhibits two-modes behavior, meaning that, in addition to the bands originating from GaP (with almost the same breakdown in L_1, BL_1 and T_1, BT_1), localized modes induced by GaAs appear around 270 cm^{-1} , as a split broadband (L_2 and T_2).

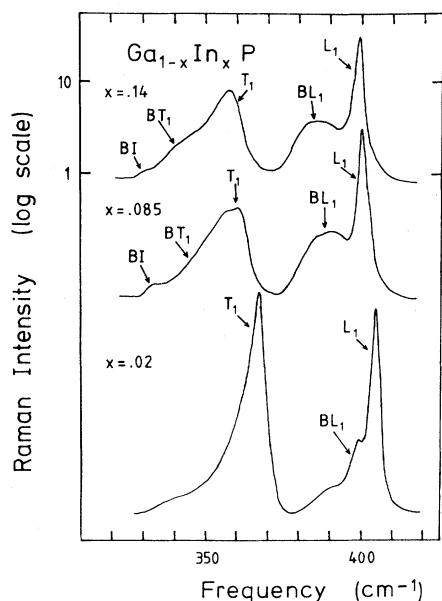


FIG. 1. Raman spectra of $\text{Ga}_{1-x}\text{In}_x\text{P}$ alloys for $x=0.02$, 0.085 , and 0.14 . These spectra have been recorded at atmospheric pressure and 85 K, with an incident wavelength of 514.5 nm.

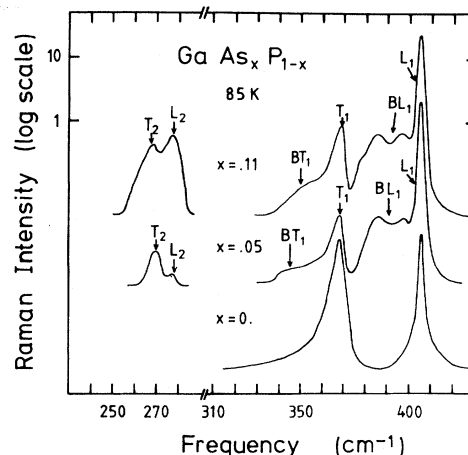


FIG. 2. Raman spectra of $\text{GaP}_{1-x}\text{As}_x$ alloys for $x=0$, 0.05 , and 0.11 . These spectra have been recorded at atmospheric pressure and 85 K, with an incident wavelength of 514.5 nm.

The frequencies of the T_1 and L_1 peaks for both alloys are given in Fig. 3 and correspond quite well to those already reported in the literature.⁸⁻¹⁰ Note that the variation is different for the two alloys. A more instructive plot is the one presented in Fig. 4, where the splitting of these peaks is given as a function of the concentration x . This splitting for $x=0$ is the well-known LO-TO splitting of the polar modes of zinc-blende compounds. It is due to the long-range forces and it characterizes the dynamic ionicity of the compound. For two-modes alloys, the splitting varies smoothly and linearly, whereas its variation for $x \geq 0.03$ is nonlinear and important for the one-mode compound. This is the main quantitative difference observed between these two alloys in this range of frequencies.

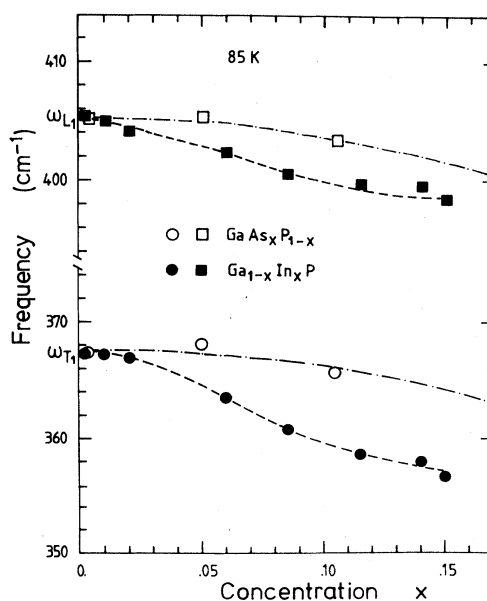


FIG. 3. Variation of the frequencies of dominant peaks for $\text{Ga}_{1-x}\text{In}_x\text{P}$ and $\text{GaP}_{1-x}\text{As}_x$ as a function of x .

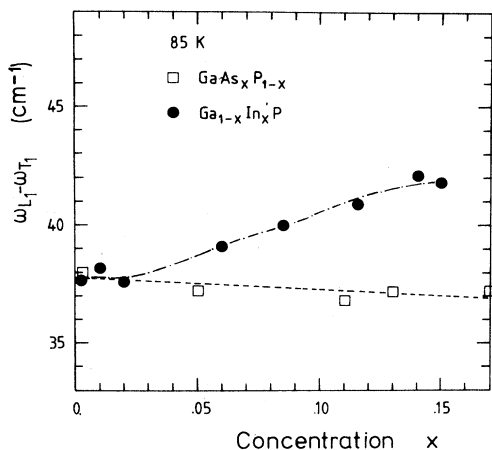


FIG. 4. Variation of the splitting $\omega_{L_1} - \omega_{T_1}$ as a function of x for $\text{Ga}_{1-x}\text{In}_x\text{P}$ and $\text{GaP}_{1-x}\text{As}_x$ alloys.

C. Experimental results as a function of pressure

The spectra for different pressures are given in Fig. 5 for $\text{GaAs}_x\text{P}_{1-x}$ ($x=0.05$ and 0.11) and in Fig. 6 for $\text{Ga}_{1-x}\text{In}_x\text{P}$ ($x=0.02$ and 0.14). The localized modes of GaAs in Ga-As-P are not presented in Fig. 5 and will be discussed later. As one can see, the variation of the spectra is qualitatively different for the two compounds: in Ga-As-P the dominant features L_1 and T_1 behave independently of their relative subbands for all values of x , a behavior also encountered for the Ga-In-P alloy with $x \leq 0.03$. However, for larger values of x , in this latter compound, each band moves as a whole with pressure, and the relative intensity of the features inside each band also varies significantly. These qualitative behaviors have been observed for all the samples we investigated. We now try to quantify some of these differences.

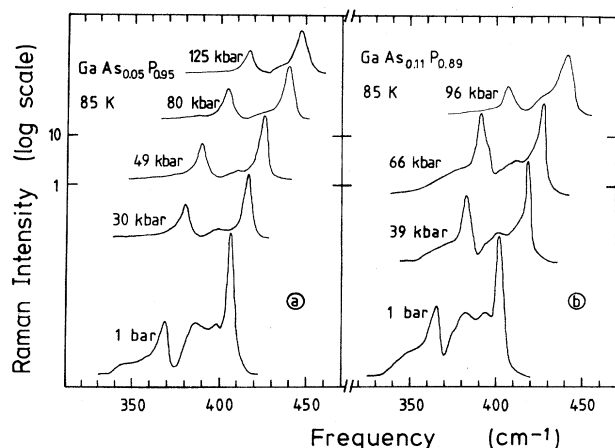


FIG. 5. Raman spectra for different pressures of $\text{GaAs}_x\text{P}_{1-x}$ alloys for (a) $x=0.05$ and (b) $x=0.11$. The excitation line is 514.5 nm.

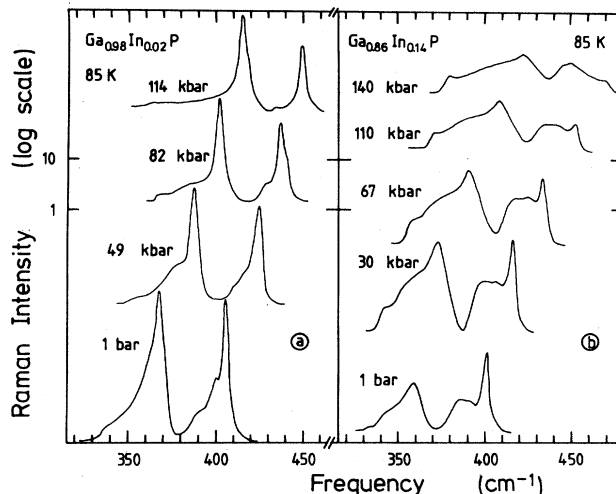


FIG. 6. Raman spectra for different pressures of $\text{Ga}_{1-x}\text{In}_x\text{P}$ alloys for (a) $x=0.02$ and (b) $x=0.14$. The excitation line is 514.5 nm.

1. Variation of the dominant peaks L_1 and T_1

The frequencies of these peaks are reported in Figs. 7 and 8 together with the TO and LO frequencies of GaP. For the Ga-As-P alloys and $\text{Ga}_{0.98}\text{In}_{0.02}\text{P}$, the variation is very similar to that of pure GaP including the nonlinear part of this variation, due to the variation of the compressibility with pressure. This similarity is also observed when plotting the difference $(\omega_{L_1} - \omega_{T_1})$ for these com-

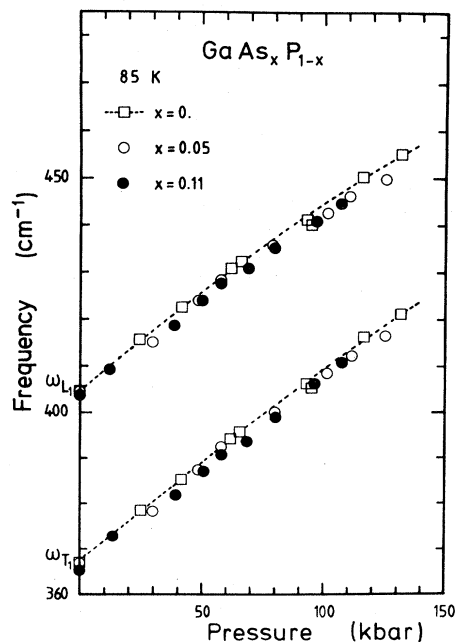


FIG. 7. Variation of the frequencies of dominant peaks of $\text{GaAs}_x\text{P}_{1-x}$ alloys as a function of the pressure.

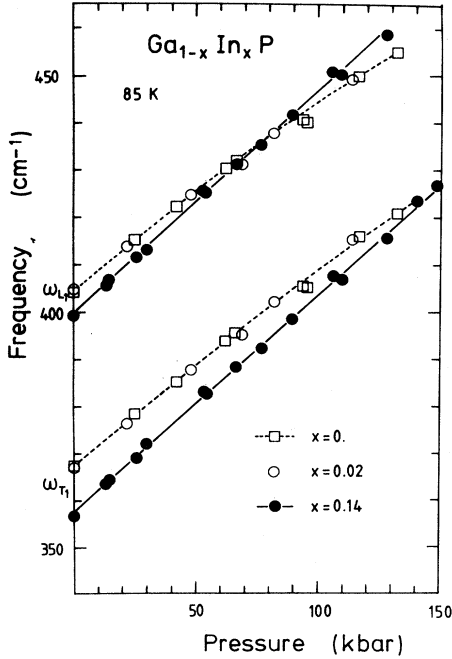


FIG. 8. Variation of the frequencies of dominant peaks of $\text{Ga}_{1-x}\text{In}_x\text{P}$ alloys as a function of the pressure.

pounds (Figs. 9 and 10). We find, in fact, within the experimental errors, the same pressure coefficients for all these compounds,

$$\omega_{L_1}(P) = \omega_{L_1}(0) + (0.45 \pm 0.01)P - (5.00 \pm 1.00) \times 10^{-4}P^2,$$

$$\omega_{T_1}(P) = \omega_{T_1}(0) + (0.45 \pm 0.01)P - (3.00 \pm 1.00) \times 10^{-4}P^2,$$

$$(\omega_{L_1} - \omega_{T_1})(P) = (\omega_{L_1} - \omega_{T_1})(0) - (3.00 \pm 0.02) \times 10^{-4}P^2,$$

where all of the frequencies are expressed in cm^{-1} and the

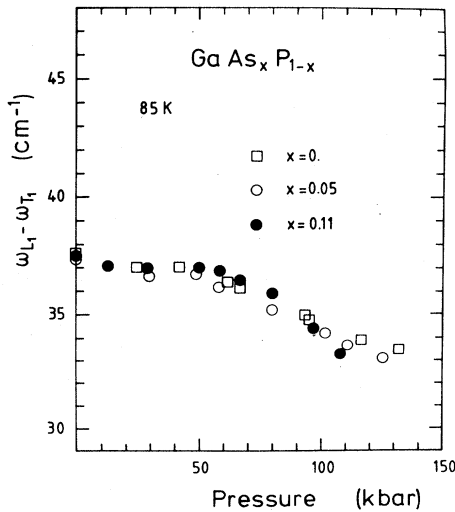


FIG. 9. Variation of the splitting $\omega_{L_1} - \omega_{T_1}$ of $\text{GaAs}_x\text{P}_{1-x}$ alloys as a function of the pressure.

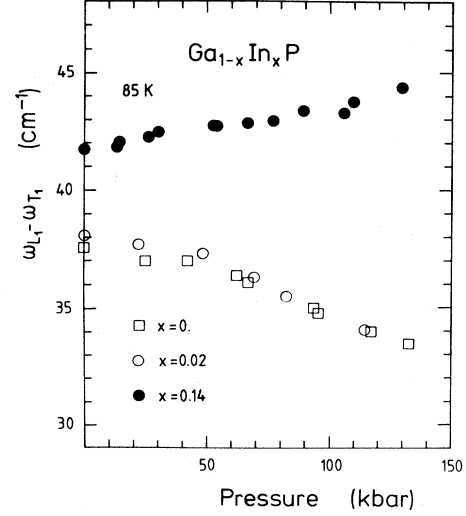


FIG. 10. Variation of the splitting $\omega_{L_1} - \omega_{T_1}$ of $\text{Ga}_{1-x}\text{In}_x\text{P}$ alloys as a function of the pressure.

pressure in kbar. It is worth noting that the variation of $\omega_{L_1} - \omega_{T_1}$ can be fitted without a significant linear term. The decrease of this last quantity has been observed in all the zinc-blende-type II-VI (Ref. 11) and III-V (Ref. 12) compounds at 300 K. This decrease has been interpreted as a decrease of the dynamic ionicity (or the Born effective charge) as a function of the pressure.^{12,13} This difference in energy is indeed that between the zone-center TO and LO modes split by the Coulombic interaction. The absence or weakness of the linear term in the $\omega_{LO} - \omega_{TO}$ variation with pressure can, therefore, be well understood by considering that, without the Coulombic interaction, the LO and TO modes are degenerate at the zone center, and then have a unique deformation potential. The decrease of $\omega_{LO} - \omega_{TO}$ with pressure can then be attributed to the effect of pressure on the long-range forces, and appears to be characteristic of the zone-center LO and TO modes exclusively. This effect is also confirmed by calculations performed on II-VI (Ref. 14) as well as III-V (Ref. 15) compounds, where the pressure coefficient of the difference between the LO- and TO-mode frequencies is always found to be negative around the Γ point of the Brillouin zone. In this respect, the T_1 and L_1 modes, in Ga-As-P and $\text{Ga}_{0.98}\text{In}_{0.02}\text{P}$ alloys, still behave as the zone-center TO and LO modes, respectively.

The behavior is quite different for $\text{Ga}_{1-x}\text{In}_x\text{P}$ with $x \geq 0.03$. The variations with pressure are now linear within experimental error (Fig. 8). We find, for $x = 0.14$,

$$\omega_{L_1} = 400 + (0.47 \pm 0.015)P,$$

$$\omega_{T_1} = 358 + (0.46 \pm 0.015)P,$$

$$\omega_{L_1} - \omega_{T_1} = 41.8 + (1.7 \pm 0.2) \times 10^{-2}P,$$

with the frequencies expressed in cm^{-1} and the pressure in kbar. A similar positive pressure coefficient $+(1.6 \pm 1.2) \times 10^{-2} \text{ cm}^{-1}/\text{kbar}$ is found for $\omega_{L_1} - \omega_{T_1}$ in

$\text{Ga}_{0.85}\text{In}_{0.15}\text{P}$. Since the experiments are performed at a sufficiently low temperature to trap the free carriers in these compounds, we cannot argue for an eventual LO-plasmon coupling to explain the singular behavior of $\omega_{L_1} - \omega_{T_1}$. Logically, it is derived from the preceding discussion that these T_1 and L_1 modes can no longer correspond to the zone-center LO and TO phonons.

2. Variation of the subbands with pressure

The existence of these subbands can be related to the activation of some phonon density of states by the disorder, as has already been suggested.¹⁶ However, they could also be assigned to the strong asymmetric line shape of the TO mode observed in pure GaP. This asymmetry was first studied by Barker¹⁷ and attributed to an anharmonic coupling between the zone-center (Γ -point) TO and the zone-edge (X -point) phonons. More detailed analyses were performed later by Weinstein¹⁸ and Galtier *et al.*¹⁹ using high-pressure experiments. They *all* show that the intensity of the low-energy side of the TO line decreases sharply with pressure, the remaining intensity being at least 2 orders of magnitude smaller than that of the TO mode. This result is just the opposite of what is observed here in both alloys for the behavior of the subbands under pressure (see Figs. 5, 6, and 12). Therefore, the anharmonicity process cannot be responsible for the existence of the subbands, and their assignment to disorder-activated modes,¹⁶ confirmed experimentally on Ga-Al-As by Carles *et al.*,²⁰ is currently very likely. This activation is expected to similarly affect the two types of compounds. We shall analyze the BT_1 subbands in both alloys, the behavior of the BL_1 subband being more difficult to follow due to the overlap of this band with the L_1 peak in Ga-As-P alloys.

a. Ga-As-P alloys. In Ga-As-P alloys, BT_1 originates necessarily from the GaP density of states (the one due to GaAs being much lower in energy). By inspecting the known dispersion curves of GaP (Ref. 21) in the optical branches, the nature of the activated density of states at the lower frequency below T_1 is necessarily of the M_0 type. We have tried to fit the lower part of BT_1 in a logarithmic scale by a density $\rho \sim (\omega - \omega_{\text{BT}_1})^{1/2}$ [Fig. 11(a)].

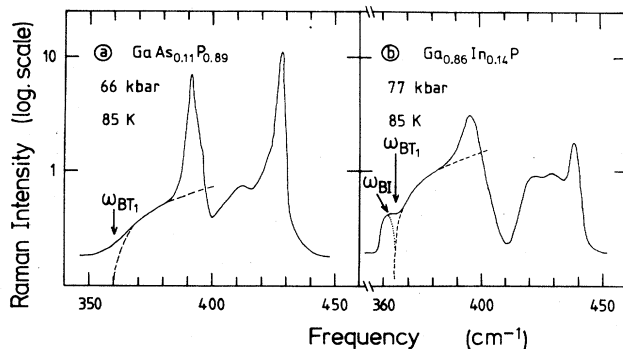


FIG. 11. Procedure of deconvolution of (a) and (b) BT_1 subbands and (b) Bi subband as described in the text.

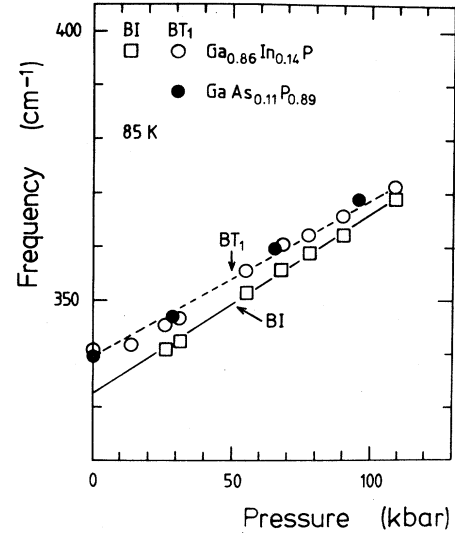


FIG. 12. Variation of the frequencies of BT_1 and BI subbands as a function of the pressure.

We then deduce the variation of ω_{BT_1} (Fig. 12),

$$\omega_{\text{BT}_1} = (338 \pm 2) + (0.27 \pm 0.02)P(\text{kbar}) \text{ cm}^{-1}.$$

b. Ga-In-P alloys. For $x \geq 0.03$, the subband related to T_1 is composed of at least two bands. It is possible to fit the high-frequency subband in the same way that BT_1 was fitted for Ga-As-P. Clearly, in both alloys, the variations of the BT_1 bands are identical. This implies the same origin for these bands. Then one contribution remains, namely BI [Fig. 11(b)], which must be attributed to InP since it does not exist in Ga-As-P alloys. BI varies at a rate

$$\omega_{\text{BI}} = 333 + (0.34 \pm 0.02)P(\text{kbar}) \text{ cm}^{-1},$$

with a coefficient significantly higher than that of BT_1 .

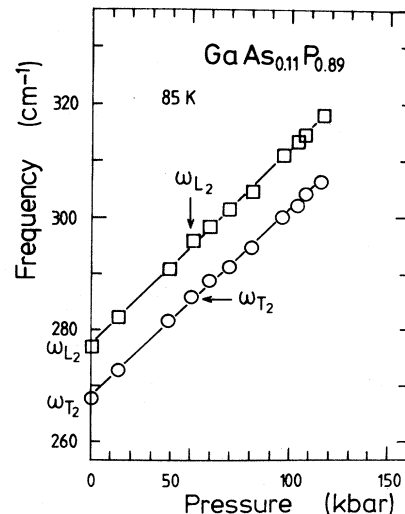


FIG. 13. Variation of the localized frequencies of GaAs in $\text{GaAs}_{1-x}\text{P}_x$ alloys as a function of the pressure.

3. Variation of the localized frequencies of GaAs

As shown in Fig. 13, the localized-frequency of GaAs variations are linear as a function of pressure. The splitting δ of these bands increases with x to finally give the TO and LO bands of GaAs for $x=1$. These bands are split by the cubic crystal field surrounding the GaAs molecule in the host, GaP. The pressure acts to increase this local field, and then the splitting δ should increase with it. This is indeed observed: With $x=0.11$, for instance, we obtain

$$\delta = 9 + (1.2 \pm 0.3) \times 10^{-2} P (\text{kbar}) \text{ cm}^{-1}.$$

III. DISCUSSION OF THE RESULTS

From the experimental information, we can deduce the following.

(i) For both alloys, the activation of a one-phonon density of states, induced by the disorder, is observed.

(ii) For the relatively large concentration of the ternary element, the main peaks behave quite differently in the

$$\frac{1}{\tau} \propto \sum_{\vec{q}, \vec{k}_f} \sum_{a,b} \left| \frac{\langle f | H_{er} | b \rangle \langle b | H_{e-ph} | a \rangle \langle a | H_{er} | i \rangle}{(\omega_a - \omega_i)(\omega_b - \omega_i)} + \dots \right|^2 \delta(\Omega - \omega(\vec{q})). \quad (2)$$

where i and f stand for initial and final states, a and b denote intermediate states, \vec{q} is the phonon wave vector, $\Omega = \omega_i - \omega_f$ is the Stokes shift, H_{er} and H_{e-ph} the perturbative Hamiltonians for the electron-radiation and electron-phonon interactions, respectively, and the ellipsis represent some unspecified equivalent terms. Setting the perturbed wave function (1) in (2) leads to the following expression for the Raman cross section:

$$\begin{aligned} \frac{d\sigma}{d\omega} &\propto \int \frac{|C(\vec{q})|^2}{\omega(\vec{q})} \delta(\Omega - \omega(\vec{q})) d^3q \\ &= \int \frac{|C(\omega)|^2}{\omega} \rho(\omega) \delta(\Omega - \omega) d\omega \\ &\propto \frac{|C(\Omega)|^2}{\Omega} \rho(\Omega), \end{aligned} \quad (3)$$

where $C(\vec{q})$ is the Fourier transform of the perturbed part of the charge density for the conduction band, and $\rho(\Omega)$ is the one-phonon density of states. This theory satisfactorily predicts the common features observed for both alloys. The BT_1 bands are likely to be due to this effect and, if we inspect the dispersion curves of GaP, we can assign this band to an extremum either in the Δ direction or the Σ direction near the zone boundary. The neutron measurements on GaP (Ref. 22) give a value of the frequency for this region of $(346 \pm 13) \text{ cm}^{-1}$, which fits our results quite well.

The observation of the localized frequencies of GaAs and InP (band BI) are also probably due to the same effect. We note that the splitting of the GaAs localized

two compounds. For the two-mode alloy, they appear to keep their character of longitudinal- and transverse-optical phonons of the zone center, whereas this is no longer true for the one-mode alloy where zone-center phonons do not seem to exist any longer.

A. Activation of the disorder-induced density of states

One way to introduce the concept of the disorder-induced density of states was proposed by Kawamura *et al.*¹⁶ in the case of $\text{Ga}_x\text{Al}_{1-x}\text{As}$ alloys, where the disorder generates fluctuations of charge densities. The perturbed electronic wave functions are written as

$$\psi_{\vec{k}}(\vec{x}) = \phi_{\vec{k}}(\vec{x}) + R_{\vec{k}}(\vec{x}), \quad (1)$$

$\phi_{\vec{k}}$ being a Bloch function of the perfect crystal, and

$$R_{\vec{k}}(\vec{x}) = \int d\vec{k}' g(\vec{k} - \vec{k}') e^{i\vec{k}' \cdot \vec{x}}$$

describing a mean fluctuation with a weight function g , the extension of which depends on disorder.

The Raman scattering probability is written conventionally as

modes increases with pressure. These two bands give, by continuity, the TO and LO bands on GaAs. On the other hand, we know that the activation of impurity states begins with those modes which have a high density (around the X and K points). The positive pressure coefficient for the splitting of these modes is in accordance with their origin since, model calculations of Grüneisen coefficients in zinc-blende compounds^{14,15} show that this is the only region of the Brillouin zone where the Grüneisen coefficient of the LO branch is larger than that of the TO branch. This results, as pointed out in Sec. IIC3, from the increase with pressure of the cubic crystal field around the GaAs molecule.

B. One-mode versus two-mode alloys

Whatever the merit of the theory proposed by Kawamura *et al.*, it does not explain the differences observed in the two alloys. Indeed, this theory predicts the observation of extra features, but not the disappearance of already existing structures such as those due to zone-center LO and TO phonons. Thus, this theory satisfactorily fits the behavior of two-mode alloys, such as GaAs-P, but not that of Ga-In-P: Experimentally the increase of the splitting ($\omega_{L_1} - \omega_{T_1}$) with pressure for this alloy (Fig. 10) cannot be explained assuming that these modes originated from the zone center of the Brillouin zone. Physically, the one-mode character appears when the localized density of states overlaps that of the host lattice.⁵ In this situation the modes of the host lattice are significantly affected even quite far away from the impur-

ity site, since the localized modes of the impurity can propagate inside the unperturbed lattice.²³ In other words, it is now possible, in a first approximation, and for dilute alloys, to break down the phonon part of the wave function in a way similar to that proposed by Kawamura *et al.* for the electronic part: We write

$$|\phi_{\vec{q}}\rangle = \sum_{\vec{q}'} f(\vec{q} - \vec{q}') b_{\vec{q}'}^\dagger |0\rangle, \quad (4)$$

where $f(\vec{q})$ is a weighting function, the extension of which increases with disorder as $g(\vec{k})$ does in the term $R_{\vec{k}}(\vec{x})$ of (1). If we neglect, for simplicity, the disorder in the electronic wave functions and proceed as earlier, the Raman cross section appears to now be proportional to

$$\begin{aligned} \frac{d\sigma}{d\omega} &\propto \sum_{\vec{q}} \frac{|f(\vec{q})|^2}{\omega(\vec{q}=\vec{0})} \delta(\Omega - \omega(\vec{q})) \\ &\simeq \frac{1}{\omega(\vec{q}=\vec{0})} \int |f(q(\omega))|^2 \delta(\Omega - \omega) \rho(\omega) d\omega \\ &= \frac{|f(\Omega)|^2}{\omega(\vec{q}=\vec{0})} \rho(\Omega). \end{aligned} \quad (5)$$

We now obtain the phonon density of states convoluted with a \vec{q} -dependent weighting function. This simple formalism can only be reliable for small x , where f has a rather small extension in \vec{q} . We therefore expect to observe, in this small- x range, a phonon spectrum given by (5). When the width of $f(\vec{q})$ increases, we probe the dispersion curves of phonons from the Brillouin-zone center to inside the zone. This should be true for T_1 as well as L_1 peaks. Therefore, it should be possible, at least

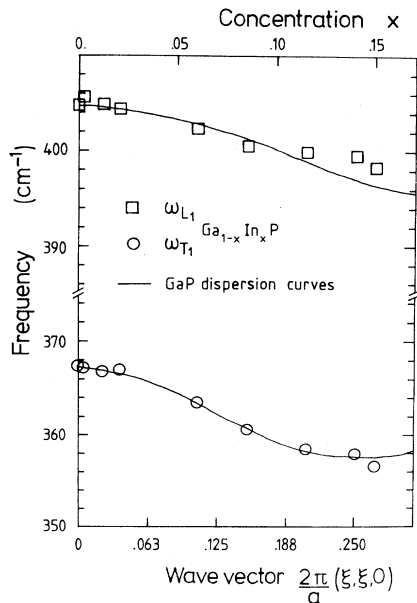


FIG. 14. Comparison of the dispersion curves of GaP for ω_{TO} and ω_{LO} along the (110) direction (Ref. 13) (solid lines), with an appropriate scaling of the ω_{T_1} and ω_{L_1} frequencies in $\text{Ga}_{1-x}\text{In}_x\text{P}$ alloys.

for small values of x , to fit the frequencies of L_1 and T_1 peaks with the dispersion of the LO and TO branches of GaP. This is shown on Fig. 14, where the x and \vec{q} (along [110]) scales have been adjusted. It is interesting to note that, up to values of $x \simeq 0.1$, the dispersion is well reproduced by both L_1 and T_1 frequencies, and this was not obvious *a priori*, since the LO dispersion is twice as weak as that of TO in GaP. This is in accordance with our preceding discussion (Sec. II C 1), in which we have already argued that the phonons observed in a one-mode alloy no longer have LO or TO zone-center character.

On the other hand, an expression such as (4) cannot be written in alloys where the density of impurity modes is completely localized. This is the reason why it was neglected by Kawamura *et al.*, who were dealing with Ga-Al-As alloys. In that case, the phonon disorder does not significantly influence the unperturbed lattice.

Another way to discuss the specific behavior of the one-mode alloy is to examine the lifetime of zone-center phonons. For a concentration x larger than 0.03, this lifetime decreases drastically. Kuhl and Bron²⁴ have measured it in pure GaP, and found a value for optical phonons of about 10 psec. The velocity of the optical phonons is not known, but can be estimated to be 1 order of magnitude smaller than the sound velocity ($4.10^5 \text{ cm sec}^{-1}$). If we take this velocity to be of the order of 10^4 cm sec^{-1} , the mean free path Δl of the optical phonons is about 10 Å. A rough estimate of the mean separation between two impurity sites gives about 13 Å for $x \simeq 0.02$ and 7 Å for $x = 0.14$. Thus the threshold concentration of 0.03, beyond which the TO mode is no longer observed, corresponds to a mean separation between the impurity sites of the order of the mean free path Δl . For higher impurity concentrations, one can assume that an emitted TO phonon is trapped quickly by an impurity site, and reemitted nonelastically with an energy corresponding to a high density of states. This could explain the flattening of the variation of L_1 and T_1 modes for $x > 0.13$. This trapping is only possible for overlapping densities of states, which do not occur in the case of two-mode alloys. Although this discussion has some speculative character, the point, clearly shown by the experiment, is that the dominant peaks L_1 and T_1 , in the one-mode alloy, have lost their long-wavelength character.

All of the models that have been used to explain the different behaviors of ternary compounds are based on the concept of coupled oscillators: they involve use of a virtual-crystal approximation²⁵ or a random element isodisplacement model,²⁶ eventually including the Coulombic interaction⁴ and the dispersion in the optical branches.⁶ Calculations based on the coherent-potential approximation,²⁷⁻²⁹ the application of the renormalization-group method,³⁰ or the recursion method³¹ have also been proposed. Whatever the result of these models, they always give two sets of solutions (simply because the starting point is two coupled oscillators). Even when such a model reveals something resembling a one-mode behavior for one solution, it always predicts a second one, which for Ga-In-P,¹⁰ is localized and has never been observed experimentally. We believe that this second solution does not exist physically and is just an ar-

tifact of the concept of coupled oscillators, which turns out to be inappropriate to describe the actual physics. The designation of one mode alloy itself is not appropriate and should be replaced by a "fully-activated-mode" alloy.

IV. CONCLUSIONS

The Raman spectra of $\text{GaP}_{1-x}\text{As}_x$ and $\text{Ga}_{1-x}\text{In}_x\text{P}$ alloys have been studied as functions of x and of the pressure. We have observed some differences which lead to

conclude that alloys, known as one-mode compounds, do not exhibit long-wavelength optical phonons. All of the structures, in terms of their phonon spectrum, appear to originate from the activation of the density of states. This behavior rules out the basic concept of coupled oscillators used by all theories which have tried, up until now, to describe them. A more pertinent theory should include the disorder in the electronic part as well as in the phonon part of the total wave function of these compounds.

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