Resonant Raman scattering in mixed $GaAs_{1-x}P_x$ crystals

K. P. Jain, R. K. Soni, and S. C. Abbi
Laser Technology Research Programme, Indian Institute of Technology, New Delhi 110 016, India
(Received 19 October 1984)

Dual aspects of resonant Raman scattering in mixed $GaAs_{1-x}P_x$ crystals due to band-to-band transitions at the direct energy gap as well as the effect of electron localization due to alloying and disorder are presented. Also described are resonance effects of the zone-edge phonons due to scattering at the indirect gap in the mixed crystals.

INTRODUCTION

The vibrational properties of ternary mixed III-V crystals have been studied at length both theoretically and experimentally for many years. One of the earliest works[1] was the study of infrared lattice vibration spectra of $GaAs_{1-x}P_x$ in which two distinct reststrahlen bands were discovered, the strengths and frequencies of which depend upon x. This was followed[2] by a Raman study of lattice vibrations of $GaAs_{1-x}P_x$, which confirmed the two-mode behavior of the mixed crystals, i.e., structures between 250 and 295 cm^{-1} associated with GaAs and between 345 and 405 cm^{-1} associated with GaP-like behavior. Raman scattering was also used to study the resonant properties of $Al_xGa_{1-x}As$ in detail.[3] In this the resonance behavior of the GaAs-like and AlAs-like LO phonons enabled the energy of the direct band gap to be determined accurately.

This study was extended[4–6] to cover $Al_xGa_{1-x}As$ and other ternary alloys like $Ga_xIn_{1-x}P$ and $GaAs_{1-x}P_x$, where it was found that in addition to the usual one-phonon scattering anomalously large second-order amplitudes were seen under resonant condition with the direct gap. This replica effect was attributed to a localized exciton-phonon complex as an intermediate state in light scattering,[4] the localization being due to alloying and disorder. Configuration model calculations indicated that large oscillator strengths for the second-order scattering were possible when localized exciton interacts strongly with the LO-phonon system. Further theoretical work[7] involved an ensemble of two-level systems modulated by the optic phonon field coupled to the radiation field to explain phonon replica in mixed crystals.

A recent paper[8] describes how two-phonon processes can be used to study the effect of disorder in mixed crystal systems. In this the line shape and linewidth of the zone-edge phonons were studied for various alloying concentrations. Off-resonance configurations were chosen to preclude the phonon replicas, which would otherwise mask the weak second-order scattering.

Resonant Raman scattering has also been studied at indirect gaps of silicon and GaAs (Refs. 9–11) and in this system, selective resonance enhancement of two-phonon amplitudes corresponding to phonons of particular symmetry takes place. It should be mentioned that the phonon density of states is high for zone-edge phonons and usually the two-phonon process consists of contributions from several zone-edge regions. However, selective enhancement takes phonons of particular symmetry and enables one to differentiate between iterative electron–one-phonon and electron–two-phonon vertices in the two-phonon processes.[11]

It is the purpose of the present paper to study dual aspects of resonant Raman scattering in mixed $GaAs_{1-x}P_x$ crystals, i.e., resonance effects due to band-to-band transitions at the direct and indirect energy gaps, as well as the effect of electron localization due to alloying and disorder. We present resonant Raman scattering data of $GaAs_{0.11}P_{0.89}$ crystal and show that the GaP-like LO-phonon and 2LO-phonon peaks exhibit different resonant behavior. This difference is explained quantitatively if one assumes that the scattering amplitudes consist of two channels—one due to band-to-band transition and other due to transition to a localized exciton. Resonance behavior of the $2TA(X)$ combination modes is also presented and described in terms of selective enhancement at the indirect gap of the mixed crystal.

EXPERIMENTAL RESULTS

Resonant Raman scattering experiments from mixed $GaAs_{0.11}P_{0.89}$ were performed in the back-scattering geometry at room temperature using various lines of the argon-ion laser, Ramanor double monochromator, and photon-counting electronics. The $GaAs_{0.11}P_{0.89}$ crystal was grown on a GaP substrate by liquid-phase epitaxy with a layer thickness $\sim 30\ \mu m$.

Figure 1 shows the resonant Raman spectra of $GaAs_{0.11}P_{0.89}$ excited by the 4765-Å laser line. Two-mode behavior of the zone-center phonons, one corresponding to GaAs-like modes (labeled by subscript 1) around 280 cm^{-1} and other corresponding to GaP-like modes between 360 and 400 cm^{-1} (labeled by subscript 2) is observed as expected. The structure around 400 cm^{-1} shows the usual GaP-like TO and LO modes, in addition to the X mode, which is seen only in the alloy. This mode, whose origin is still uncertain, has been reported in the literature previously.[12] Combinations of optical zone-edge phonons give Raman peaks in the high-frequency range of the spectrum. The most important aspect of this end of the spectrum is the appearance of the Raman replica of the GaP-like modes between 760 and 800 cm^{-1}. Combinations of zone-edge acoustic phonons are seen at the low-frequency end of the spectrum, while the structure at 125 cm^{-1} is attributed to the difference mode $(LO_2 - LO_1)$.

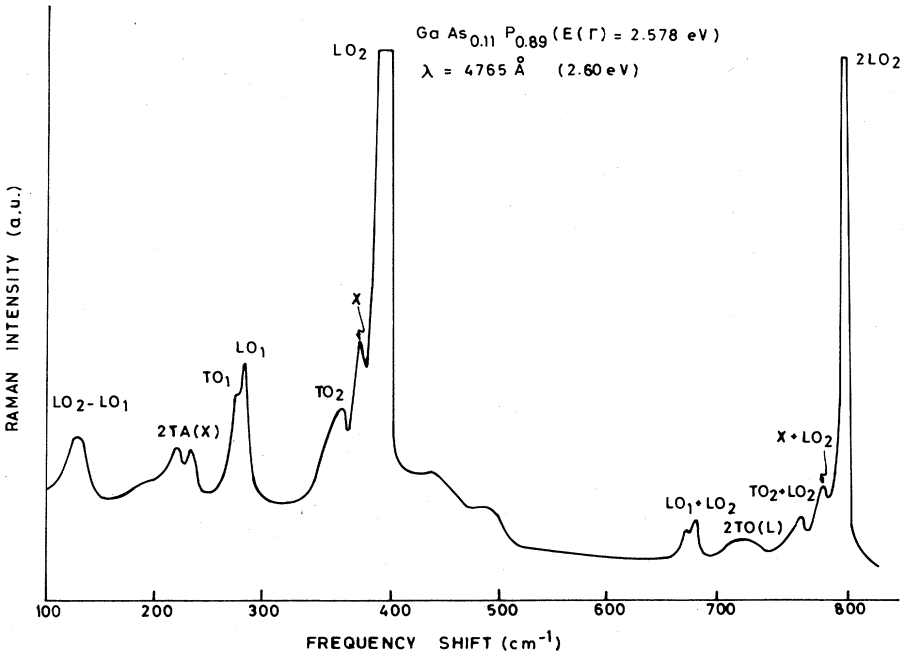

FIG. 1. Room-temperature backscattering Raman spectrum of $GaAs_{0.11}P_{0.89}$. The scattered light is not analyzed. The crystal plane is perpendicular to the [100] axis.

Figure 2 shows the resonant aspect of the replica spectrum of Fig. 1. Far from resonance, the strong feature at 800 cm^{-1} disappears leaving behind only the usual second-order combination band, reminiscent of pure GaP.

The resonance Raman behavior of $2LO_2$ and LO_2 modes are given in Figs. 3 and 4, respectively. All experimental points were corrected for absorption. Finally, the resonance behavior of $2TA(X)$ combination modes is given in Fig. 5.

DISCUSSION

The spectra given in Fig. 1 differ drastically and qualitatively from the spectrum of pure GaP (Ref. 13) due to the appearance of the LO_2-phonon replica at resonance. It has already been conjectured[4] that the sharpness and the resonant character is due to a dispersionless localized exciton as an intermediate state in the Raman process. With this assumption, the Raman intensities for the one-LO_2 and two-LO_2 processes become[4]

$$I(\mathrm{LO}_2)=A\frac{Z^2(1-Z^2)}{[\hbar\omega_1-\hbar\omega(\mathrm{LO}_2)-\epsilon]^2+\gamma^2}\ , \tag{1}$$

$$I(2\mathrm{LO}_2)=\frac{A}{2}\frac{Z^4(1-2Z^2+Z^4/2)^2}{[\hbar\omega_1-\hbar\omega(2\mathrm{LO}_2)-\epsilon]^2+\gamma^2}\ , \tag{2}$$

where A is a normalization constant including the matrix element of the electromagnetic interaction between ground and bare-exciton states, ω_1 the angular frequency of the incoming photon, ϵ the effective exciton energy, $\hbar\omega(\mathrm{LO}_2)$ the phonon energy, γ the linewidth of the localized exciton, and $Z\equiv|V|/\hbar\omega(\mathrm{LO}_2)$, where V is the exciton-phonon coupling constant.

It will be seen from Eqs. (1) and (2) that the two intensities should have identical resonance behavior, which is not

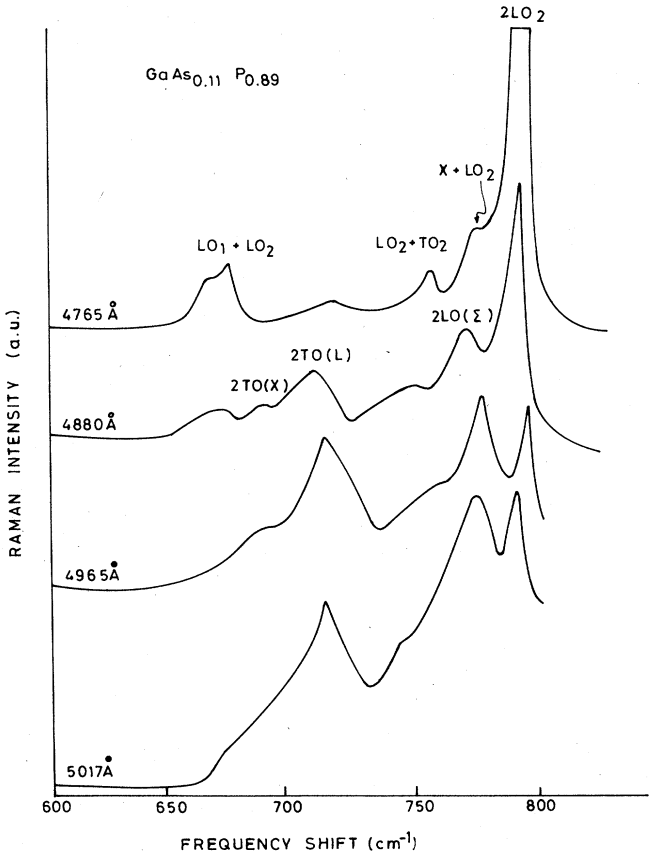

FIG. 2. Resonant Raman behavior of $GaAs_{0.11}P_{0.89}$ for different laser wavelengths.

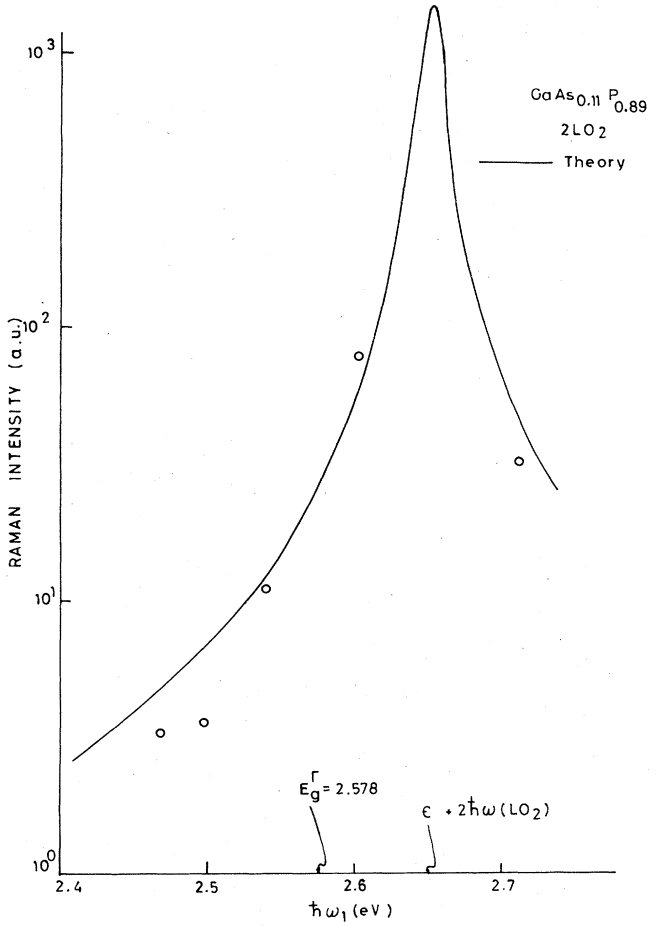

FIG. 3. Resonance behavior of GaP-like $2LO_2$ phonon. The solid theory curve is Eq. (2) with $\hbar\omega(LO_2)=0.049$ eV, $\epsilon=2.566$ eV, $\gamma=0.01$ eV, and $Z=0.78$.

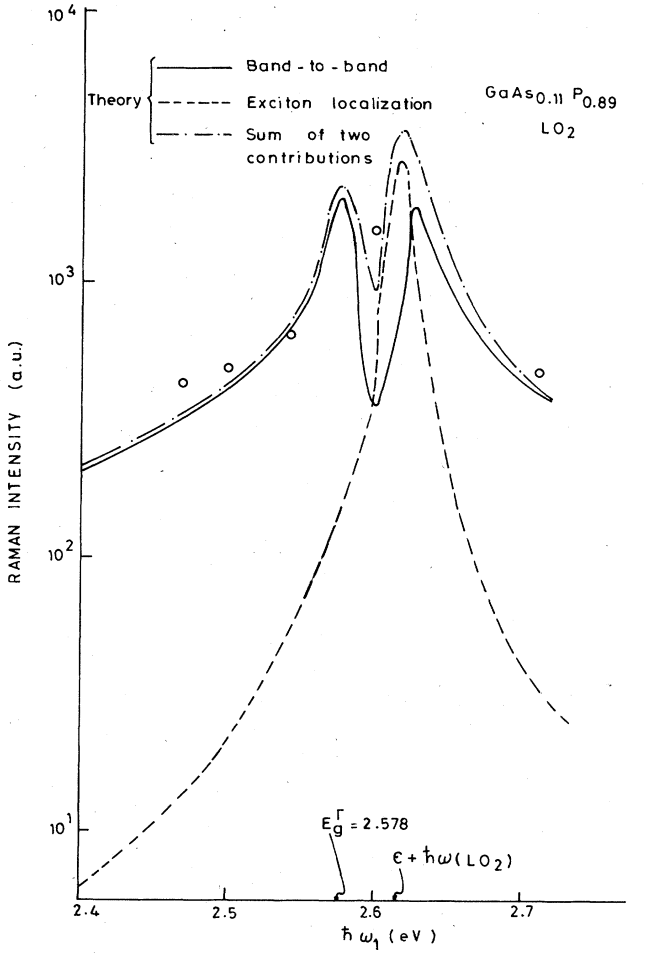

FIG. 4. Resonance behavior of GaP-like LO_2 phonon. The dashed curve gives the theory [Eq. (1)] with the same parameters as in Fig. 3. The points represent the resonant behavior of the LO_1 phonon.

what is found experimentally (see Figs. 3 and 4). In fact, the $2LO_2$ resonance is much sharper than the LO_2 resonance. Equation (2) has been fitted to the experiment with Z, ϵ, and γ as disposable parameters, and this is shown in Fig. 3. The same parameters are then used in Eq. (1) for the one-LO_2-phonon resonant behavior, and this is shown by the dotted curve in Fig. 4. It is evident that there is a large mismatch between the theory and experiment, so that there must be another contribution to the one-LO_2-phonon scattering. The obvious candidate is the resonance due to excitation across the direct band gap ($E_g^\Gamma=2.578$ eV), for which the Raman amplitude may be calculated from the simple Loudon theory:[14]

$$R(\omega_1)\sim B\{[\omega_g^\Gamma+\omega(LO_2)-\omega_1]^{1/2}-(\omega_g^\Gamma-\omega_1)^{1/2}\}\ , \qquad (3)$$

where B is another normalization constant including all the matrix elements. The formula is fitted to the experimental values, and the results are given in Fig. 4. It is evident that the optimum fit is obtained when contribution from both scattering channels is included. It should be mentioned that the ordinary Loudon-theory contribution to the second-order scattering is some two orders of magnitude smaller than the first-order scattering, and therefore this has been neglected in Fig. 3.

Turning now to Fig. 5, resonance Raman scattering at the indirect gap has been considered theoretically by one of the present authors.[11] Selective enhancement of the acoustic phonons with X symmetry yields a weak singularity of the threshold type in the Raman amplitude

$$R(\omega_1)\sim C-\sqrt{\hbar\omega_1-(E_g^I+\hbar\Omega)}\ , \qquad \hbar\omega_1>E_g^I+h\Omega\ . \qquad (4)$$

Here E_g^I is the energy of the indirect gap and $\hbar\Omega$ is the energy of the TA(X) phonon. It is evident from Fig. 5 that this simple theory describes the experimental results rather well.

The mode labeled X in Figs. 1 and 2 has been discussed in the literature previously[12,15] in terms of anharmonic coupling between a single-phonon state and a continuum of interacting combinations of phonons. More recent studies of localized states in GaAs-P crystals[16] attribute the X mode to oscillation of phosphorus at the edge of the Brillouin zone made Raman active by the disorder. We conclude this part by noting that more experiments are needed to elucidate the character of this mode.

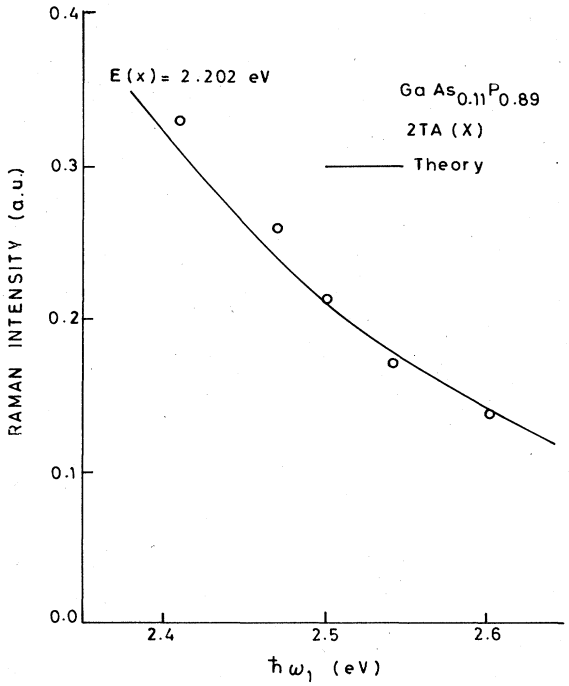

FIG. 5. Resonant behavior of the 2TA(X) combination modes at the indirect gap $E(X) = 2.202$ eV.

SUMMARY AND CONCLUSIONS

In this paper we have examined resonance effects due to band-to-band transitions at the direct and indirect gaps, as well as the effect of electron localization due to alloying and disorder. The GaP-like LO_2 and $2LO_2$ modes show different resonance behavior, and this is described quantitatively by simple atomistic and band theories. Replica of the first-order spectrum occurs at frequencies displaced from the original by $\omega(LO_2)$ in phosphorus-rich samples. It is natural to assume that a similar effect would occur at the GaAs-like LO_1 mode in arsenic-rich samples. Unfortunately, this has not yet been seen due to large fluorescence in these samples which masks the Raman spectrum. Selective enhancement of the 2TA(X) phonons at the indirect gap has also been studied, and again a simple theory is used to treat this effect.

The effect of clustering and disorder in III–V ternary alloys has been discussed recently[8] by Teicher, Beserman, Klein, and Morkoc who studied the effect of structural disorder on zone-edge Raman phonons far away from resonance. Near resonance, on the other hand, the structure of the intermediate electronic state becomes important and preliminary calculations[17] indicate an exciton localization energy ~ 30 meV due to the formation of clusters. A complete theory of resonant Raman scattering from disordered system would have to consider the effect of this localization due to potential fluctuations and clustering.

[1]H. W. Verleur and A. S. Barkar, Jr., Phys. Rev. B **149**, 715 (1966).
[2]N. D. Strohm and A. L. McWhorter, in *Proceedings of the International Conference on Light Scattering Spectra in Solids,* edited by G. B. Wright (Springer-Verlag, New York, 1969), p. 455.
[3]Jagdeep Shah, A. E. DiGovanni, T. C. Damen, and B. I. Miller, Phys. Rev. B **7**, 3481 (1973).
[4]M. Balkanski, L. M. Falicov, C. Hirlimann, and K. P. Jain, Solid State Commun. **25**, 261 (1978).
[5]M. Balkanski, C. Hirlimann, and J. F. Morhange, in *Proceedings of the International Conference on Lattice Dynamics,* Paris, edited by M. Balkanski (Flammarion, Paris, 1978), p. 174.
[6]C. Hirlimann, Ph.D. thesis, University of Paris, 1981.
[7]D. Schmeltzer and R. Beserman, J. Phys. C **14**, 273 (1981).
[8]M. Teicher, R. Beserman, W. V. Klein, and H. Morkoc, Phys. Rev. B **29**, 4652 (1984).
[9]P. B. Klein, M. Masui, Jin-Joo Song, and R. K. Chang, Solid State Commun. **14**, 1163 (1974).
[10]R. Trommer and M. Cardona, Solid State Commun. **21**, 153 (1977).
[11]K. P. Jain and C. S. Jayanthi, Phys. Rev. B **19**, 4198 (1979).
[12]C. Hirlimann, R. Beserman, M. Balkanski, and J. Chevallier, in *Proceedings of the International Conference on Light Scattering in Solids,* Campinas, edited by M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flammarion, Paris, 1976), p. 129.
[13]B. A. Weinstein and M. Cardona, Phys. Rev. B **8**, 2795 (1973).
[14]R. Loudon, Proc. R. Soc. London, Ser. A **275**, 218 (1963).
[15]K. P. Jain and M. Balkanski, Ref. 12, p. 106.
[16]D. Schmeltzer and R. Beserman, Phys. Rev. B **22**, 6330 (1980).
[17]K. P. Jain and R. Gupta (unpublished).