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Long-Wavelength Optical Phonons in $Ga_{1-x}In_xP$

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We report the results of a study, by infrared and Raman spectroscopy, of the long-wavelength ($\vec{q} \simeq 0$) optical phonons in the alloy system $Ga_{1-x}In_xP$. We find one-mode behavior in this diatomic alloy system. Fine structure is also observed and is attributed to disorder-induced one-phonon processes involving shorter-wavelength phonons.

I. INTRODUCTION

In this paper, we report the results of a study of the long-wavelength ($\vec{q} \simeq 0$) optical phonons in III-V alloy system $Ga_{1-x}In_xP$. The emphasis here is on the number of observable optical-phonon modes in the alloy samples and on the variation of the mode frequencies with composition. The frequencies of the TO and LO phonons were obtained from far-infrared reflectance and Raman-scattering spectra. In each of the alloy samples, the spectra indicate one dominant band with weaker structure occurring at frequencies intermediate between the TO and LO components of the "main" resonance. The TO-phonon frequency of the dominant mode varies linearly with composition, while its oscillator strength is approximately constant. We believe that the results presented here represent the first example of one-mode[1] behavior in a III-V alloy system. For the other III-V alloys studied to date, workers have reported either two-mode behavior over the entire composition range, as in $GaP_{1-x}As_x$,[2,3] $InP_{1-x}As_x$,[4] and $Al_{1-x}Ga_xAs$,[5] or two-mode behavior over a part of the alloy range, as in $Ga_{1-x}In_xSb$,[6] $Ga_{1-x}In_xAs$,[7,8] $GaAs_{1-x}Sb_x$,[8,9] and $InAs_{1-x}Sb_x$.[8]

In Sec. II we discuss crystal growth, compositional determination, sample preparation, and the infrared and Raman spectra measurements. Section III contains the experimental results: the infrared and Raman spectra, and the results of a Kramers-Kronig (KK) dispersion analysis of the infrared data. Section IV contains a discussion of the results, emphasizing the behavior of optical phonons in this alloy system as it is related to the physics which governs the observability of impurity modes near $x = 0$ and $x = 1$. The principal features are illustrated by a comparison of $Ga_{1-x}In_xP$, $Ga_{1-x}In_xAs$, and $Ga_{1-x}In_xSb$.

II. EXPERIMENTAL AND ANALYTICAL PROCEDURES

A. Crystal Growth and Sample Characterization

The samples of $Ga_{1-x}In_xP$ used in these experiments were grown by a solid-liquid-solid technique,[1] a regenerative solution growth process. The pure compounds GaP and InP were the starting materials and were arranged in a vertical sandwich structure (GaP: InP: GaP) within a BN crucible. The crucible together with sufficient phosphorous to provide a 20-atm overpressure was sealed within a quartz ampoule *in vacuo*. The ampoule was heated and allowed to equilibrate at a preselected temperature. Crystal growth was obtained either by applying a small temperature gradient to the otherwise isothermal ampoule or by slowly lowering the ampoule into a cooler zone of the furnace. The composition of the resulting crystals was determined by the temperature of equilibration of the ampoule and the shape of the pseudobinary diagram for the Ga-In-P ternary system.

$Ga_{1-x}In_xP$ layers grown by this technique were

approximately 1 cm^2 in area and several millimeters long, and had both radial and longitudinal composition gradients. The radial composition gradient was not as severe as the longitudinal composition gradient. For the $Ga_{1-x}In_xP$ sample with $x = 0.18$ the growth was single crystalline and oriented wafers could be cut from the crystal; other crystals, however, were polycrystalline.

Wafers for this study were cut from crystals of different composition ($x = 0.18$, 0.35, 0.58, 0.80), were lapped using 8-μm boron carbide grit and 3-μm aluminum grit, and were then mechanically polished with 0.05-μm alumina. The compositions of the specific $Ga_{1-x}In_xP$ samples used here were measured by electron-microprobe analysis. Specimens were cut from adjacent wafers, and electrical measurements using the Hall technique were made for the various compositions. Typically the samples displayed n-type conductivity with carrier concentrations in the $10^{17}/cm^3$ range. For these carrier concentrations the plasma modes are well removed from the reststrahlen.

B. Infrared Studies

Reflectance measurements were made with the samples at ambient temperature ($\simeq 300$ °K), at nearly normal incidence ($\simeq 9°$), using a conventional grating monochromator. The reflectance of each sample was compared to that of Al. At both the long- and short-wavelength limits of our experiments ($\simeq 250$ and $\simeq 500$ cm^{-1}, respectively), the reflectance of the alloy samples approached a value which was wavelength independent. A KK dispersion analysis was applied to these truncated spectra to obtain the frequencies of the optical phonons. Previous experience[6] with spectra of this sort, where the reststrahlen bands are well separated from both the interband electronic transitions and the free-carrier plasmon modes, has demonstrated that the phonon frequencies so obtained agree (to within about ± 1 cm^{-1}) with the frequencies as obtained from the preferred method of analysis: that of fitting the observed reflectance spectra with spectra synthesized from damped Lorentzian oscillators.

C. Raman Scattering

Raman spectra for GaP and three of the alloy samples ($x = 0.18$, 0.35, and 0.58) were obtained using a He-Ne laser as an exciting source in a 90° scattering geometry. Attempts to obtain a spectrum from the $x = 0.80$ sample were unsuccessful due to sample luminescence. The spectrum for InP was obtained using a Nd^{3+} : YAG (yttrium-aluminum-garnet) laser.

III. EXPERIMENTAL RESULTS

Figure 1 contains the reflectance spectra for the alloy samples, $x = 0.18$, 0.35, 0.58, and 0.80,

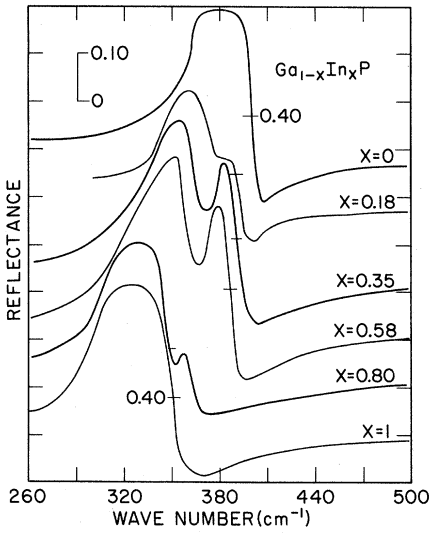

FIG. 1. Reflectance as a function of wave number for the alloy system $Ga_{1-x}In_xP$. The fiducial marks indicate a reflectance of 0.40.

and for the end-member compounds GaP ($x = 0.0$) and InP ($x = 1.0$). There are several features to note. Whereas the spectra of GaP and InP exhibit no fine structure, those of the alloy samples do: a shoulder in the $x = 0.18$ sample and a dip in each of the other samples. The KK dispersion analysis was used to obtain the complex dielectric constant $\epsilon = \epsilon_1 + i\epsilon_2$. Figure 2 contains plots of ϵ_2 and $-\mathrm{Im}\,(1/\epsilon)$ vs wave number for one of the alloy samples ($x = 0.35$). The results for the other alloy samples differ from those shown in Fig. 2 only to the extent that the frequencies of the relative maxima shift with composition. TO-phonon frequencies were obtained from the positions of the peaks in ϵ_2; LO-phonon frequencies were obtained from the positions of the peaks in $-\mathrm{Im}(1/\epsilon)$. The relative oscillator strengths of modes 1 and 2 are estimated from the areas under the ϵ_2 curves. In all of the alloy samples, the mode strength of the lower-frequency TO phonon (TO_1) is at least an order of magnitude greater than that of the higher-frequency TO mode (TO_2). The second feature to note is that the reststrahlen band as defined by the TO- and LO-phonon frequencies of the dominant mode (TO_1, LO_1 in Fig. 4) shifts continuously between the bands associated with the end-member compounds. This type of behavior is designated as one-mode behavior.[6]

In Fig. 3(a) we show the room-temperature Raman spectra of the $x = 0.0$, 0.18, 0.35, 0.58, and 1.0 samples. In Fig. 3(b) the spectra of the $x = 0.18$ samples are shown at room ($\simeq 300$ °K) and liquid-nitrogen ($\simeq 77$ °K) temperatures. The strong features of the scattering occur at frequencies which are very nearly equal to the TO- and

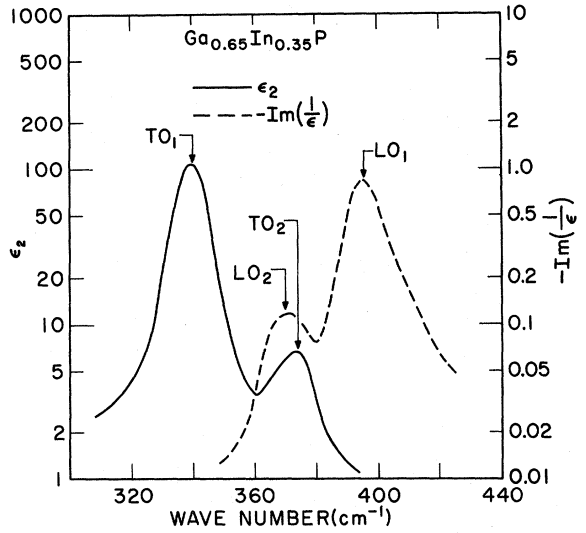

FIG. 2. Dielectric dispersion properties of $Ga_{0.65}In_{0.35}P$; ϵ_2 is the imaginary part of the dielectric constant ϵ, and $-\mathrm{Im}(1/\epsilon)$ is the energy-loss function.

LO-phonon frequencies as they are obtained from the KK analysis of the infrared reflectance. At 300 °K weaker structure is present as a mode occurring at a frequency intermediate between ω_{LO_1} and ω_{TO_1}, and in the $x = 0.18$ and 0.35 samples as a low-frequency asymmetry in the shape of the TO_1 line. The midband lines occur at almost the same frequencies as those obtained from the dispersion analysis of the infrared data; however, there is no structure in the infrared that corresponds to the low-frequency TO_1-line asymmetries. On cooling to 77 °K, the shoulder on the TO_1 line in the $x = 0.18$ sample is clearly resolvable and the weak singlet becomes a resolvable doublet.

Figure 4 indicates the ir and Raman phonon frequencies as a function of composition. TO_1 varies almost linearly between the TO-phonon frequencies of GaP and InP, whereas the variation in LO_1 is clearly nonlinear with composition.

IV. DISCUSSION

There are two aspects of this work which warrant discussion. The first concerns the one-mode behavior. Lucovsky, Brodsky, and Burstein[1] argued that the behavior of optical phonons, with particular regard to the number of modes, in mixed crystals could be predicted from the impurity-mode behavior of the particular system at the low composition limits near $x = 0$ and $x = 1$. The arguments were subsequently extended[6] to include three classes of behavior for diatomic crystals: (a) local and gap (local mode in the gap) modes *both* allowed, two-mode behavior is observed for all x; (b) *either*, but *not both*, types of impurity modes allowed, two-mode behavior is observed for some range of x near either 0.0 or 1.0 depending on which impurity mode is allowed; and (c) *neither* impurity mode allowed, one-mode behavior should be observed for all x. The definitions as used above refer to the dominant phonon modes and not to the weaker structure which is sometimes also present. $Ga_{1-x}In_xP$ provides an example of the type-c behavior.

First consider the situation near $x \simeq 0$. Here we are concerned with the possible occurrence of a gap mode associated with the substitution of In for Ga in GaP. The existence of a gap between

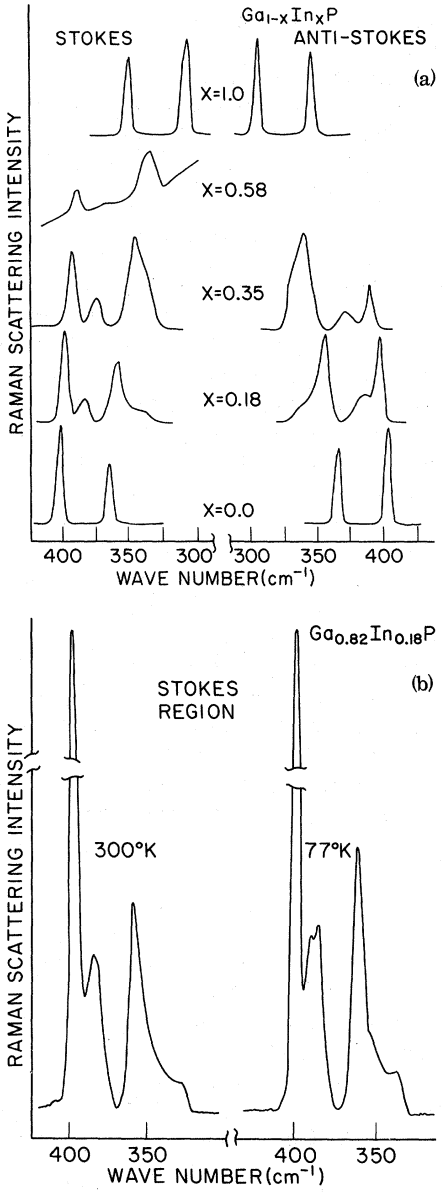

FIG. 3. (a) Room-temperature Raman spectra for the alloy system $Ga_{1-x}In_xP$. (b) Raman spectra $Ga_{0.82}In_{0.18}$ at 300 and 77 °K.

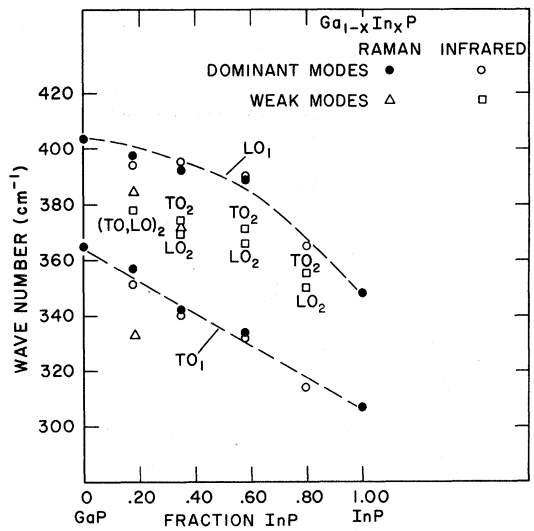

FIG. 4. Compositional dependence of long-wavelength optical phonons in the alloy system $Ga_{1-x}In_xP$.

the optical and acoustical branches of GaP has been confirmed by neutron scattering.[11] Within the theoretical framework of models based on mass-defect formulations and nearest-neighbor forces, a gap mode does not occur in a diatomic crystal when a heavier mass is substituted for the heavier component of the host crystal. This result has been derived for both linear diatomic chains[12] and three-dimensional lattices.[13] Since the reduced elastic constants[14] and effective charges[15] of GaP and InP are almost equal, one would not expect this conclusion to break down due to differences in effective force constants.

For the other end of the system $x \simeq 1.0$, Lucovsky, Brodsky, and Burstein[16] have developed a model for estimating local-mode frequencies in real crystals. Their calculation predicts that the impurity mode of Ga in InP falls at 330 cm^{-1} or at the center of the reststrahlen band, and as such is not observable as a distinctly separate impurity mode. Thus, the one-mode behavior reported here is in accord with the predictions of the criterion based on the observability of impurity modes near $x = 0.0$ and $x = 1.0$.

The behavior of the impurity modes near $x = 1.0$ in the systems $Ga_{1-x}In_xSb$, $Ga_{1-x}In_xAs$, and $Ga_{1-x}In_xP$ illustrates the role of reststrahlen bandwidth in determining local-mode behavior. The mass defect ($\simeq 0.39$) associated with the Ga impurity mode is the same for all three systems. The reststrahlen bandwidth ($\omega_{LO} - \omega_{TO}$) increases from 12 cm^{-1} in InSb to 23 cm^{-1} in InAs, and to 44 cm^{-1} in InP. Local modes, above the optical-phonon branches, occur for the Ga for In substitution at 199 or 8 cm^{-1} above ω_{LO} in InSb, and at 240 or 2 cm^{-1} above ω_{LO} in InAs. These values are in good agreement with the predictions of local-mode theory.[16] For each of the three systems (Ga: InSb, Ga: InAs, and Ga: InP) the impurity-mode frequency is calculated to be 20–25 cm^{-1} above ω_{TO}. Since the reststrahlen bandwidth in InP is substantially greater than 25 cm^{-1}, no local mode occurs in that host. On the other hand, the reststrahlen bandwidths of InSb and InAs are, respectively, smaller than and approximately equal to the critical value of 20–25 cm^{-1}, so that local modes are produced in these two systems.

The results of this study on $Ga_{1-x}In_xP$ have been interpreted in the manner proposed by Lucovsky, Brodsky, and Burstein[1] which had previously been used to interpret the optical-phonon behavior in $Ga_{1-x}In_xSb$[6] and $Ga_{1-x}In_xAs$.[7,8] Other authors have interpreted results on similar alloy systems in terms of the modified random-element isodisplacement model (MREI).[17] The MREI model predicts one-mode behavior for $Ga_{1-x}In_xP$ in accord with the results presented here. However, it fails to predict the behavior in $Ga_{1-x}In_xAs$ and $Ga_{1-x}In_xSb$ as well as some other III-V alloy systems.[8]

The second point concerns fine structure in the reststrahlen bands of alloy crystals. This occurs in some but not all mixed III-V systems, as well as in other systems. Specifically, considerable fine structure has been reported in both the high- and low-frequency bands of $GaP_{1-x}As_x$,[2,3] whereas there is a complete lack of fine structure in other systems, e. g., $Ga_{1-x}In_xSb$.[6] Still other systems, $Al_{1-x}Ga_xAs$[5] and $Ga_{1-x}In_xAs$,[7,8] show some weak structure. Verleur and Barker[2] have used a harmonic model in discussing the reflectance spectra of $GaAs_{1-x}P_x$. In this model the significant features of the spectra—the two-mode behavior with considerable fine structure—are a result of the existence of five distinct molecular complexes with significant clustering of like anions. An alternative explanation for the fine structure in $GaAs_{1-x}P_x$, which is more easily reconciled with other two-mode III-V systems in which no fine structure is reported, e.g., $Ga_{1-x}In_xSb$, has been put forth by Strahm and McWhorter.[18] They attributed the weak structure in $GaP_{1-x}As_x$ to disorder-induced one-phonon transitions, specifically to zone-boundary optical phonons. This is in accord with the observation that the strength of disorder-induced transitions depends on the phonon density of states, and that these are usually highest in the vicinity of the zone-boundary phonon frequencies. The situation which enhances the observability of disorder-induced transitions via ir reflectance spectra is one in which the zone-boundary phonons, in particular the zone-boundary LO phonons, have frequencies in excess of ω_{TO} ($\vec{q} \simeq 0$). This situation is likely in crystals with wide reststrahlen bandwidth, and occurs in GaP.[11] The structure in

the high-frequency branch in $GaP_{1-x}As_x$ is accounted for in this way by Strahm and McWhorter.[18] The "in-band" frequencies we observe in the $x = 0.18$ and $x = 0.35$ samples are very close to the frequencies reported in alloys of $GaP_{1-x}As_x$ with similar values of x, i.e., As concentration, and suggest that the structure reported here in $Ga_{1-x}In_xP$ can also be attributed to disorder-induced one-phonon transitions involving zone-boundary LO modes. The absence of any structure in the $Ga_{1-x}In_xSb$ system is then explained by the fact that the zone-boundary optical phonons (both TO and LO) lie below ω_{TO} at $\vec{q} \simeq 0$. This is true for InSb[19] and inferred for GaSb.[20] The behavior for the two arsenide systems is intermediate, suggesting that the zone-boundary optical phonons lie just below ω_{TO} at $\vec{q} \simeq 0$; this is indeed the case for GaAs where the phonon-dispersion curves have been obtained by neutron scattering.[21] The structure, which is present as an asymmetry on the low-energy side of the TO_1 modes in the $x = 0.18$ and $x = 0.35$ samples, is also attributed to disorder-induced one-phonon transitions. Here the temperature dependence supports a one-phonon mechanism. Asymmetries noted in line shapes in simple diatomic crystals, e.g., GaP[22] and AlAs,[23] are attributed to multiphonon processes and diminish in intensity as the temperature is decreased.

V. SUMMARY

We have measured the infrared and Raman spectra of the $Ga_{1-x}In_xP$ system and found that the dominant behavior of the optical phonons is that of a one-mode system. One-mode behavior has not been previously reported for any other simple alloy system in which the end-member components have nonoverlapping reststrahlen bands, nor for any other III-V alloy system. Fine structure is also observed which we here attribute to disorder-induced processes involving zone-boundary (or, more generally, shorter-wavelength) phonons.

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[1]G. Lucovsky, M. H. Brodsky, and E. Burstein, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 592.

[2]H. W. Verleur and A. S. Barker, Jr., Phys. Rev. 149, 715 (1966).

[3]Y. S. Chen, W. Shockley, and G. L. Pearson, Phys. Rev. 151, 648 (1966).

[4]F. Oswald, Z. Naturforsch. 14a, 347 (1959).

[5]M. Ilegems and G. L. Pearson, Phys. Rev. B 1, 1576 (1970).

[6]M. H. Brodsky, G. Lucovsky, M. F. Chen, and T. S. Plaskett, Phys. Rev. B 2, 3303 (1970).

[7]M. H. Brodsky and G. Lucovsky, Phys. Rev. Letters 21, 990 (1968).

[8]G. Lucovsky and M. F. Chen, Solid State Commun. 8, 1397 (1970); one-mode behavior had been reported for $GaAs_{1-x}Sb_x$ (Ref. 9); however, this report has been shown to be incorrect.

[9]R. F. Potter and D. L. Stierwalt, in *Proceedings of the Seventh International Congress Physics of Semiconductors* (Dunod, Paris, 1964), p. 1111.

[10]S. E. Blum and R. J. Chicotka, in Proceedings of the 137th Conference of the Electrochemical Society, Los Angeles, 1970 (unpublished).

[11]J. L. Yarnell, J. L. Warren, R. G. Wenzel, and P. J. Dean, in *Neutron Inelastic Scattering* (International Atomic Energy Agency, Vienna, 1968), p. 301.

[12]P. Mazur, E. W. Montroll, and R. B. Potts, J. Wash. Acad. Sci. 46, 2 (1956).

[13]S. S. Jaswal, Phys. Rev. 137, 320 (1965).

[14]R. M. Martin, Phys. Rev. B 1, 4005 (1970).

[15]G. Lucovsky, R. M. Martin, and E. Burstein, Bull. Am. Phys. Soc. 16, 427 (1971).

[16]G. Lucovsky, M. H. Brodsky, and E. Burstein, Phys. Rev. B 1, 3295 (1970).

[17]I. F. Chang and S. S. Mitra, Phys. Rev. 172, 924 (1968).

[18]N. D. Strahm and A. L. McWhorter, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer, New York, 1969), p. 455.

[19]W. G. Spitzer and H. Y. Fan, Phys. Rev. 99, 1891 (1955).

[20]S. S. Mitra, Phys. Rev. 132, 986 (1963).

[21]G. Dolling and J. L. T. Waugh, in *Proceedings of the International Conference on Lattice Dynamics*, edited by R. F. Wallis (Pergamon, New York, 1965).

[22]A. S. Barker, Jr., Phys. Rev. 165, 917 (1968).

[23]A. Onton, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors*, edited by S. P. Keller, J. C. Hensel, and F. Stern (U. S. Atomic Energy Commission, Washington, D. C., 1970), p. 107.