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Effect of nonrandomness on the phonons in mixed $InP_{1-x}As_x$

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A concentration dependent model using the effect of nonrandomness has been investigated to demonstrate the two-mode behavior of mixed crystals of the type $AB_{1-x}C_x$ having zinc-blend structure. The mixed crystal shows two-mode behavior for all the composition range and the pure crystal behavior at exact $x = 0$ and at $x = 1.0$. The model has been applied to $InP_{1-x}As_x$ to investigate the phonon dispersion curves in the symmetry directions. The results for $x = 0$, $x = 0.22$, $x = 0.78$, and $x = 1.0$ are found to be in agreement with experiment.

I. INTRODUCTION

There has been great interest in the last few years, in studying the vibrational spectra of mixed crystals of the type $AB_{1-x}C_x$ and it is known that there are three types of compositional variations of the phonon frequencies. One-mode behavior for which one set of phonon frequency varies with the concentration of the components. In some systems, two sets of phonon frequencies are observed to occur at frequencies close to those of the end members for all compositions. This behavior is defined as a two-mode type. In addition, there are few mixed crystals in which two sets of phonon frequencies are observed only over certain composition ranges and one set of phonon frequencies over the remaining composition. This intermediate type of behavior is referred to as a partly two-mode type. Several models have been in the literature to describe the observed variation of frequency with composition[1-8] of mixed crystals having two atoms per unit cell. A problem in all these attempts is apparent that at exact $x = 0$ and $x = 1.0$, i.e., the case of pure crystals, the theoretical results on mixed crystal systems do not reduce to provide only one set of optical phonon frequency as observed experimentally. The existence of the local, the reasonance and the gap vibrational modes result only from small concentration of substitutional impurities in crystalline lattice.

In the present paper we propose a concentration dependent model which explains all the physical features of the mixed and pure crystals. We describe $InP_{1-x}As_x$ as a typical example exhibiting two-mode behavior for all the concentration and reducing to the case of pure crystals at exact $x = 0$ and $x = 1.0$.

II. THEORY

Consider the mixed crystal lattice of the type $AB_{1-x}C_x$ having zinc-blend structure constituted by two interpenetrating sublattices numbered 1 and 2. The sublattice 1 is occupied by atoms of type A and sublattice 2 is occupied by atoms of types B and C. If the occupancy of sublattice 2 is randomly distributed in such a way that the concentration of B is $(1-x)$ and that of C is x, than the situation is of a homogeneous mixed crystal. In this case, the dynamical matrix will be given by, on the similar lines as derived by Kutty[9]

$$\begin{vmatrix} P - m_A w^2 & (1-x)\,Q & xQ \\ (1-x)\,Q^* & (1-x)^2 P - m_B w^2 & x(1-x)P \\ xQ^* & x(1-x)P & x^2 P - m_C w^2 \end{vmatrix} = 0 \quad , \tag{1}$$

where for the pure crystal AB, the dynamical matrix at $x = 0$, is

$$\begin{vmatrix} P - m_A w^2 & Q \\ Q^* & P - m_B w^2 \end{vmatrix} = 0 \quad , \tag{2}$$

and for the pure crystal AC at $x = 1.0$, the dynamical matrix is

$$\begin{vmatrix} P - m_A w^2 & Q \\ Q^* & P - m_C w^2 \end{vmatrix} = 0 \quad . \tag{3}$$

The elements of the dynamical matrix are given as follows:

$$P_{11} = \tfrac{4}{3}\alpha_1 + 4\alpha_2\left[2S_1^2 + (1-2S_1^2)(S_2^2+S_3^2)\right] + \tfrac{8}{3}\alpha_1^1 + 4\alpha_2^1\left[2S_1^2 + 3S_2^2 + 3S_3^2 - 2S_1^2\ S_2^2 - 2S_1^2\ S_3^2 - 4S_2^2\ S_3^2\right] + \frac{Z_{\text{eff}}^2 e^2}{V_a \epsilon_\infty}\,[P_{11}]^C \quad ,$$

$$P_{12} = 8(\alpha_2 - \alpha_2^1)\,S_1\ S_2\ C_1\ C_2 + \frac{Z_{\text{eff}}^2 e^2}{V_a \epsilon_\infty}\,[P_{12}]^C \quad ,$$

$$Q_{11} = -\left(\tfrac{4}{3}\alpha_1 + \tfrac{8}{3}\alpha_1^1\right)(C_1\ C_2\ C_3 + iS_1\ S_2\ S_3) + \frac{Z_{\text{eff}}^2 e^2}{V_a \epsilon_\infty}\,[Q_{11}]^C \quad .$$

TABLE I. Numerical values of the parameters used (M in gm, a in Å, C_{11}, C_{12}, and C_{44} in 10^{11} dyn/cm^2).

	$InP_{1-x}As_x$
M_{In}, M_P, M_{As}	114.8, 31, 74.9
ϵ_∞(InP), ϵ_∞(InAs)	9.6, 12.3
a(InP), a(InAs)	2.935, 3.020
Z_{eff}(InP), Z_{eff}(InAs)	2.64, 2.53
InP InAs	
C_{11} C_{11}	10.20, 8.329
C_{12} C_{12}	5.76, 4.526
C_{44} C_{44}	4.60, 3.959
$\lambda(0.22)$, $\lambda(0.78)$	3.6605, 6.6743

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$$Q_{12}=(\tfrac{4}{3}\alpha_1-\tfrac{8}{3}\alpha_1^1)(S_1\quad S_2\quad C_3+iC_1\quad C_2\quad S_3)+\frac{Z_{eff}^2e^2}{V_a\epsilon_\infty}[Q_{12}]^C$$

$$S_i=\sin\frac{aq_i}{2}\,,\qquad C_i=\cos\frac{aq_i}{2}\,. \tag{4}$$

Superscript C stands for Coulombian contribution on the lines of Kellermann.[10]

If we analyze Eq. (1), we find that it exhibits one-mode behavior for all values of x. This in general is not necessarily the case. So, we have the occupancy of sublattice 2 as nonrandomly distributed in such a way that the $(1-x)B$ atom will interact with the $(1-x)B$ atom as well as the $x\lambda C$ atom, where λ is a parameter varying with the concentration called the mixing parameter. Similarly, the xC atom will interact with the xC atom and the $(1-x)\lambda B$ atom. Hence, the dynamical matrix will be given by

$$\begin{vmatrix} P-m_Aw^2 & (1-x)Q & xQ \\ (1-x)Q^* & (1-x)[1-x+x\lambda]-m_Bw^2 & x(1-x)(1-\lambda)P \\ xQ^* & x(1-x)(1-\lambda)P & x[x+(1-x)\lambda]P-m_Cw^2 \end{vmatrix}=0\,. \tag{5}$$

If we analyze this determinant, we observe a two-mode behavior which reduces to one-mode behavior [Eq. (1)] if $\lambda=0$. It is important to mention that at exact $x=0$ and $x=1$, Eq. (5) again reduces to Eqs. (2) and (3), respectively, giving only two optical phonon frequencies at the zone center for the pure AB and AC crystals. Equation (5) will give local and gap modes only for $x\simeq 0$ and $x\simeq 1.0$, respectively.

III. RESULTS AND DISCUSSION

The $InP_{1-x}As_x$ system displays a two-mode type behavior over the whole composition range as shown by Carles *et al.*[11] This also confirms the infrared reflectivity measurements of Kekelidge *et al.*[12] The four force constants α_1, α_1^1, α_2, α_2^1 for the end members InP and InAs are determined from three elastic constants and the experimental frequency at the Brillouin zone center from Kunc.[13] The value of the mixing parameter λ for a particular concentration is determined by fitting one of the long wavelength transverse optical phonon frequency of the experimental two-mode spectra for the $InP_{1-x}As_x$ system given by Carles *et al.*[11] The lattice constant a, the effective ionic charge parameter Z_{eff}, and the dielectric constant ϵ_∞ are also taken for the pure crystal from the work of Carles *et al.*[11] These values are listed in Table I. A linear variation of x from Vegards *et al.*[14] has then been considered for evaluating the lattice constant, the effective ionic charge parameter, the dielectric constant, and the force constants of the mixed crystal. Figures 1–4 show the dispersion curves of $InP_{1-x}As_x$ at $x=0$, $x=0.22$, $x=0.78$, and $x=1.0$ in the symmetry direction [100] and [111], respectively. Figure 2 for $x=0.22$ and Fig. 3 for $x=0.78$ show the two-mode behavior for the $InP_{1-x}As_x$ system. The experimental results at the zone center and at the zone boundaries obtained from Raman scattering in $InP_{1-x}As_x$ by Carles *et al.*[11] are also shown in

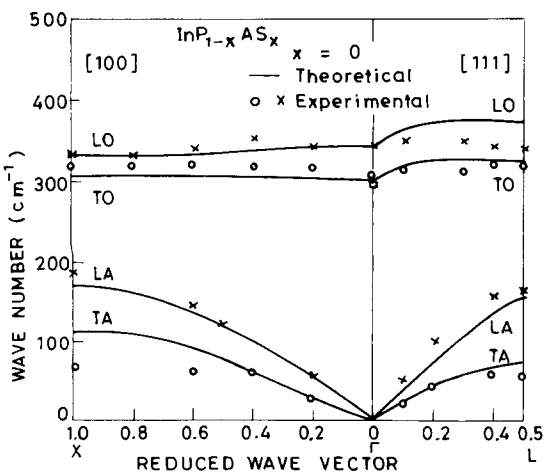

FIG. 1. Phonon dispersion curves in $InP_{1-x}As_x$ at $x=0$. Experimental points are of Borchards *et al.* (Ref. 15).

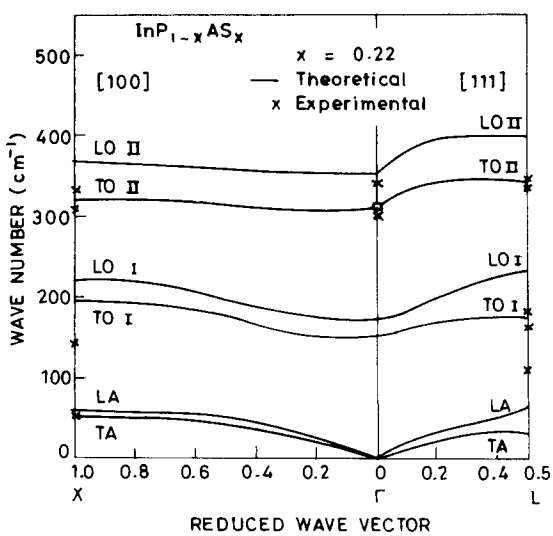

FIG. 2. Phonon dispersion curves in $InP_{1-x}As_x$ at $x=0.22$. Experimental points are of Carles *et al.* (Ref. 11).

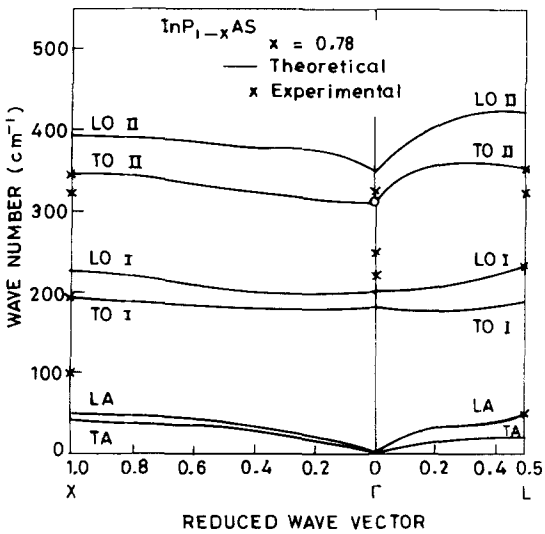

FIG. 3. Phonon dispersion curves in $InP_{1-x}As_x$ at $x=0.78$. Experimental points are of Carles *et al.* (Ref. 11).

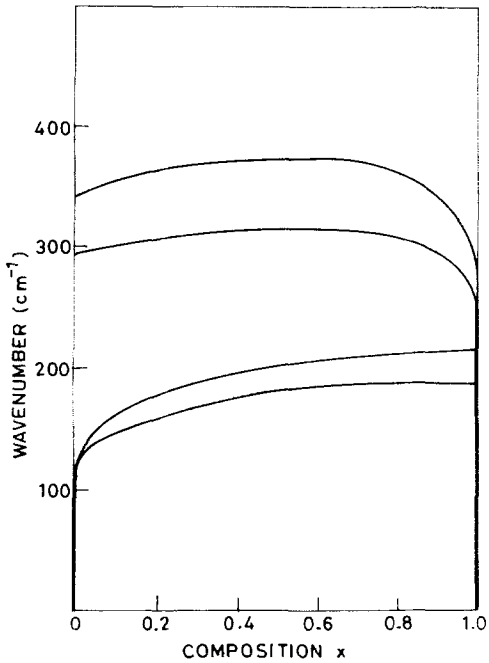

FIG. 5. Two-mode behavior as a function of x.

the figures. The two-mode behavior for the whole composition range can be shown by drawing similar curves for different values of x. Figure 1 for $x=0$ and Fig. 4 for $x=1$ show the pure crystal behavior for InP and InAs crystals, respectively. The experimental results from the neutron scattering in InP by Borchards *et al.*[15] are shown in Fig. 1 and the experimental results from second order Raman spectra in InAs by Carles *et al.*[16] are shown in Fig. 4. As is obvious from all these figures, a satisfactory agreement has been obtained with the experiment. Figure 5 exhibits the two-mode behavior as a function of x at the zone center, which confirms the infrared-reflectivity measurements by Kekelidze *et al.*[12]

IV. CONCLUSION

The present proposed concentration dependent model shows the two-mode behavior for the whole composition range and pure crystal behavior at exact $x=0$ and $x=1.0$, which has not yet been explained by any other model. Also, the condition suspected by Chang and Mitra[17] for local and gap modes for two-mode behavior of three-dimensional crystals is not necessary as the present model exhibits two-mode behavior for the entire composition range $0<x<1$ and for $x=0$, and $x=1.0$ it reduces to one-mode behavior as expected physically. It is interesting to mention that local or gap modes can also be exhibited from the present model at $x\simeq 0$ and $x\simeq 1.0$, respectively.

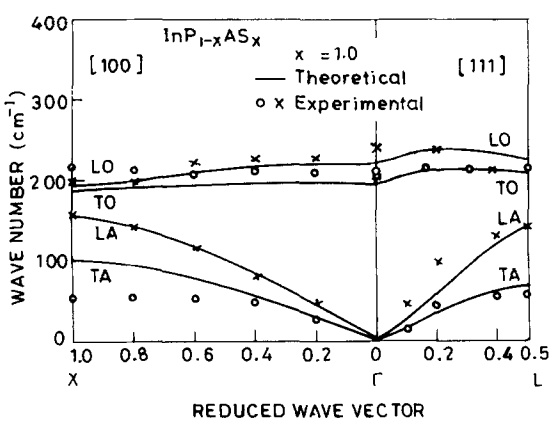

FIG. 4. Phonon dispersion curve in $InP_{1-x}AS_x$ at $x=1.0$. Experimental points are of Carles *et al.* (Ref. 16).

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