Long wavelength lattice dynamics for quaternary alloys: GaInPSb and AlGaAsSb

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Long wavelength lattice dynamics of the quaternary alloys $Ga_{1-x}In_xP_{1-y}Sb_y$ and $Al_xGa_{1-x}As_ySb_{1-y}$ have been investigated. The optical phonons show a four mode behavior in $Ga_{1-x}In_xP_{1-y}Sb_y$ and a three mode behavior in $Al_xGa_{1-x}As_ySb_{1-y}$ over the composition ranges investigated. An average random cell model is used to describe the behavior of the optical phonons of both systems. The calculations of the dependence of the long wavelength optical phonon frequencies on solid composition are in good agreement with the experimental results.

I. INTRODUCTION

The behavior of optical phonons in disordered systems is of special interest in view of the many fundamental aspects of lattice vibrations involved. Until now, most well-studied disordered systems were ternary alloys of the type AB_xC_{1-x}.[1] Investigation of the phonon modes for quaternary alloy systems leads to a better understanding of phonon behavior in general. In this article, we describe for the first time the phonon behavior in the quaternary alloys $Ga_{1-x}In_xP_{1-y}Sb_y$ and $Al_xGa_{1-x}As_ySb_{1-y}$.

The III-V quaternary alloys $Ga_{1-x}In_xP_{1-y}Sb_y$ and $Al_xGa_{1-x}As_ySb_{1-y}$ have been grown by organometallic vapor phase epitaxy.[2,3] The lattice dynamics of these two quaternary alloys have been investigated using Raman scattering measurements.[4,5] The Raman spectra for $Ga_{1-x}In_xP_{1-y}Sb_y$ show a four mode behavior. Table I summarizes the experimental result of the phonon frequencies for the $Ga_{1-x}In_xP_{1-y}Sb_y$ system extracted from the measured Raman spectra in Ref. 4. The Raman spectra for $Al_xGa_{1-x}As_ySb_{1-y}$ show a three mode behavior over the composition range investigated. The phonon frequencies extracted from the measured Raman spectra in Ref. 5 for $Al_xGa_{1-x}As_ySb_{1-y}$ alloys are shown in Table II.

Several models have been proposed in an attempt to explain the observed phonon behavior of mixed alloys. The theoretical calculations are based on phenomenological models such as the virtual crystal,[6] linear chain,[7] cluster,[8] coherent potential approximation,[9] and random element isodisplacement models.[10] Most of these models have been proposed for ternary alloys. The generalization to quaternary systems is limited by the increase of complexity and the lack of experimental data. Thus, only a few models have been generalized to quaternary systems. The cluster calculation has been done for GaInAsSb by Redfield and Dow.[11] However, no comparison to experimental data was given. The linear chain calculation was done for AlGaAsP by O'Hara *et al.*[12] Again, no comparison to experimental data was given. Self-consistent coherent-potential approximation calculations have been done by Kleinert for $Al_xGa_{1-x}As_yP_{1-y}$, $Ga_xIn_{1-x}P_yAs_{1-y}$,[13] and $Al_xGa_{1-x}As_ySb_{1-y}$.[14] No comparison between calculated results and experimental data was given. The average t-matrix approximation has been applied to the $Al_x(Ga_{1-y}In_y)_{1-x}P$ system by Sen and Hartmann.[15] The agreement between the calculated results and the data from infrared reflection measurements is not very consistent. The random element isodisplacement (REI) model calculation for $Ga_{1-x}In_xAs_ySb_{1-y}$ was done by the present authors.[16] Good agreement with the experimental results was demonstrated. However, the direct generalization of the REI model to four mode systems is difficult. A modification of the REI model, the random cell isodisplacement (RCI) theory, has been proposed by Zinger *et al.*[17] and Inoshita[18] to treat the lattice dynamics of $Ga_{1-x}In_xP_yAs_{1-y}$ alloys. The results are in good agreement with the experimental data. In this article, a modification of the random cell isodisplacement model is used to treat the phonon behavior of the $Ga_{1-x}In_xP_ySb_{1-y}$ and $Al_xGa_{1-x}As_ySb_{1-y}$ quaternary alloys.

II. THEORY

The random cell isodisplacement model begins by randomly dividing the crystals into different cells similar to the crystal bonds. Each cell has one group III atom and one group V atom. For the $A_xB_{1-x}C_yD_{1-y}$ type quaternary alloys, there are four different types of cells corresponding to the four different binary bonds. The model assumes that the displacements of the same types of cells are the same, independent of the position of the cell in the crystal. The displacement of the group III atom in cell i is denoted $U_{i,\mathrm{III}}$ and the displacement of the group V atom is denoted $U_{i,\mathrm{V}}$. We now consider the equation of motion for a group III atom in cell i. It can be written

$$M_{i,\mathrm{III}}\ddot{U}_{i,\mathrm{III}}=F_i(U_{i,\mathrm{V}}-U_{i,\mathrm{III}})+\sum_{j=1}^{4}P_jF_{ij,\mathrm{III}}(U_{j,\mathrm{III}}-U_{i,\mathrm{III}})+\sum_{j=1}^{4}P_jF_{ij,\mathrm{V}}(U_{j,\mathrm{V}}-U_{i,\mathrm{III}}),$$

where the first term is due to the force of the group V atom in the same cell. The second term is due to the average results from group III atoms in cell type j. The coefficient P_j is the probability of cell j occurring in the crystal. The

TABLE I. Measured phonon frequencies for $Ga_{1-x}In_xP_{1-y}Sb_y$ alloys (units: cm^{-1}).

x	y	GaP-LO	InP-LO	GaInP-TO	GaSb-LO	InSb-LO	InSb-TO
0.19	0.17	385	347	---	236	222	---
0.24	0.16	383	362	340	235	---	184
0.32	0.14	382	364	339	234	196	181
0.42	0.17	379	359	333	229	199	---
0.61	0.05	375	353	320	223	201	---
0.66	0.08	370	353	319	221	199	---
0.65	0.24	354	344	322	222	196	---
0.69	0.26	353	339	310	220	193	187
0.70	0.27	354	344	313	---	---	---
0.93	0.42	---	330	313	---	194	181
0.39	0.02	388	368	333	---	---	---
0.43	0.07	385	365	332	232	201	---
0.81	0.12	---	342	314	217	194	---
0.84	0.18	---	344	313	---	195	---
0.80	0.21	---	341	308	---	196	---
0.75	0.22	382	366	328	233	---	---
0.22	0.88	---	322	---	230	---	---
0.92	0.93	---	297	---	204	---	188

third term is due to group V atoms in cell j. To simplify the equation, we introduce the center of mass coordinates D_i and d_i,

$$U_{i,\text{III}} = D_i + \frac{(M_{i,\text{V}})}{(M_{i,\text{III}} + M_{i,\text{V}})} d_i,$$

$$U_{i,\text{V}} = D_i - \frac{(M_{i,\text{III}})}{(M_{i,\text{III}} + M_{i,\text{V}})} d_i,$$

where $M_{i,\text{V}}$ is the mass of the group V atom in cell i. D_i is the center of mass for cell i and d_i is the relative displacement of atoms from this center of mass. After substitution into the equation of motion, we have

$$M_{i,\text{III}} \ddot{D}_i + \mu_i \ddot{d}_i = -F_i^0 d_i - \sum_{j=1}^{4} P_j F_{ij}^1 d_j - \sum_{j=1}^{4} P_j F_{ij}^2 D_j - \sum_{j=1}^{4} P_j F_{ij}^3 d_i - \sum_{j=1}^{4} P_j F_{ij}^4 D_i,$$

where the F^i's are the renormalized force constants. Now, we assume the motion of D_i, which describes the acoustic mode, can be decoupled from d_i, which describes the optical mode. We rewrite the equation of motion for d_i as

$$\mu_i \ddot{d}_i = -F_i^0 d_i - \sum_{j=1}^{4} P_j F_{ij}^1 d_j - \sum_{j=1}^{4} P_j F_{ij}^3 d_i + e_i E_{\text{eff}},$$

TABLE II. Measured phonon frequencies for $Al_xGa_{1-x}As_ySb_{1-y}$ alloys (units: cm^{-1}).

x	y	AlAsSb-LO	AlAsSb-TO	GaAs-LO	GaSb-LO
0.74	0.98	391	359	260	---
0.66	0.92	386	358	258	240
0.63	0.76	374	347	252	234
0.46	0.53	---	338	245	229
0.37	0.32	347	330	244	230
0.2	0	323	---	233	---

where the last term is included to represent the long range Coulomb force due to an effective field induced by the lattice vibration, which gives rise to the LO-TO splitting. e_i is the effective charge of the atoms in cell i and E_{eff} is the effective local field, which can be expressed by the atom displacements as[18]

$$E_{\text{eff}} = k \sum_i P_i e_i d_i.$$

k is a constant given by

$$k = \frac{4\pi N}{3} \left(\frac{\epsilon_\infty + 2}{3} \right) \quad \text{for TO modes,}$$

$$= -\frac{8\pi N}{3} \left(\frac{\epsilon_\infty + 2}{3\epsilon_\infty} \right) \quad \text{for LO modes.}$$

By substituting these expressions into the equation of motion for d_i, we obtain the secular equation:

$$-\omega^2 \mu_i d_i = -F_i^0 d_i - \sum_{j=1}^{4} P_j F_{ij}^1 d_j - \sum_{j=1}^{4} P_j F_{ij}^3 d_i + \sum_{j=1}^{4} k P_j e_i e_j d_j.$$

A similar expression has been obtained by Inoshita[18] by spatially averaging over the harmonic Hamiltonian for mixed alloys.

The force constants needed in the calculation can be obtained from the boundary conditions. Assuming $P_i = 1$

TABLE III. Parameters used in the random cell isodisplacement calculation.

Compound	Lattice constant (Å)	LO (cm^{-1})	TO (cm^{-1})	ϵ_∞
GaP	5.451	403	367	8.5
GaSb	6.09	237	227	14.4
InP	5.869	347	306	9.79
InSb	6.479	197	165	15.7
AlAs	5.66	402	364	8.5
GaAs	5.653	292	268	10.9
AlSb	6.136	340	319	9.88

Impurity mode phonon frequency (units: cm^{-1})*

GaP@InP:390	InP@GaP:330	GaSb@InSb:199	InSb@GaSb:185
GaP@GaSb:324	GaSb@GaP:240	InP@InSb:294	InSb@InP:196
GaSb@InP:220	GaP@InSb:317	InP@GaSb:322	InSb@GaP:184
AlSb@GaSb:317	GaSb@AlSb:215	AlAs@GaAs:356	GaAs@AlAs:252
GaAs@GaSb:240	GaSb@GaAs:242	GaAs@AlSb:215	AlSb@GaAs:364
GaAs@AlAs:242	AlAs@GaSb:317		

*(GaP@InP means the GaP impurity mode in the InP host crystal.)

and $P_j=0$ for other cells $j\neq i$, the equations can be solved, yielding four solutions. The first one has the form

$$\omega_{ii}^2=\frac{F_i^0+F_{ii}^1+F_{ii}^3+ke_i^2}{\mu_i},$$

which represents the optical phonon frequency for the binary compound i. The other three solutions have the form

$$\omega_{ji}^2=\frac{F_j^0+F_{ji}^3}{\mu_i},$$

which represents the impurity mode induced by adding impurity cell j into the binary compound i.

With the knowledge of the phonon frequencies discussed above, the diagonal part of the secular equation can be rewritten as the combination of the phonon frequencies. The secular equation becomes

$$\mathrm{Det}\left|\left(\sum_{k=1}^{4} P_k\omega_{ik}^2-\omega^2\right)\delta_{ii}+P_j\left(\frac{F_{ij}^1-ke_i\,e_j}{\mu_i}\right)\right|=0.$$

This is the equation used in this article. The force constants F_{ij}^1 are obtained by fitting the calculated results to the experimental data for the boundary ternary alloys. All parameters needed in the calculation are listed in Table III.

III. RESULTS

A. $Ga_{1-x}In_xP_{1-y}Sb_y$

Due to the two degrees of freedom in composition for quaternary alloys, it is not possible to represent the phonon frequencies over all compositions of the alloys in a single two dimensional figure. To simplify the task, samples were selected having a linear relationship between the compositions x and y, i.e., the samples lie near a straight line in the square composition figure. For $Ga_{1-x}In_xP_{1-y}Sb_y$ alloys, the samples are collected into two groups. The first group is grown nearly lattice matched to GaAs substrates. Thus, the compositions follow the linear relationship $y=0.22-x/3.4$. The frequencies of the optical phonon modes as functions of the composition, x, are shown in Fig. 1. The curves generated from the RCI model follow the experimental results quite well. The second group of samples has compositions following the equation $y=0.627x-0.157$. The curves of phonon frequencies versus alloy composition for these samples are shown in Fig. 2. Again, the agreement between the calculated results and the experimental data is excellent. The random cell isodisplacement model is demonstrated to be a useful model for interpretation of the phonon behavior of the $Ga_{1-x}In_xP_{1-y}Sb_y$ quaternary alloy system.

B. $Al_xGa_{1-x}As_ySb_{1-y}$

The $Al_xGa_{1-x}As_ySb_{1-y}$ samples were chosen so that the compositions x and y satisfy the relationship $x=0.55y+0.2$. The relation between Raman peak frequency and sample composition is plotted in Fig. 3. Because the phonon behavior of AlAsSb ternary alloys has not been re-

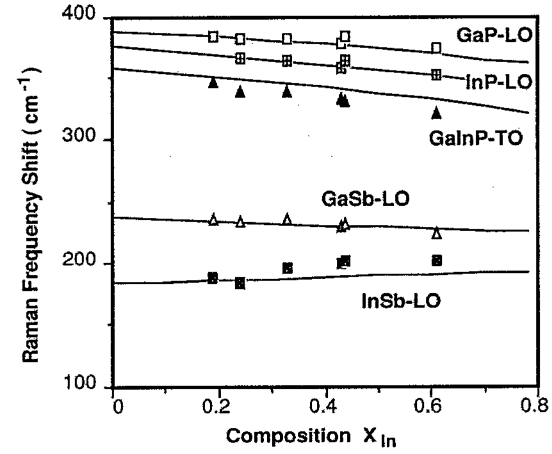

FIG. 1. Optical phonon frequencies vs composition for $Ga_{1-x}In_xP_{1-y}Sb_y$ with the compositions x and y related by $y=0.22-x/3.4$. Solid curves are calculated by the random cell isodisplacement model. Discrete notations denote the experimental results extracted from the Raman spectra in Ref. 4.

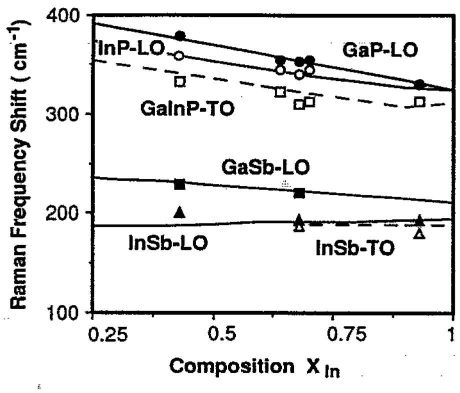

FIG. 2. Optical phonon frequencies vs composition for $Ga_{1-x}In_xP_{1-y}Sb_y$ with the compositions x and y related by the $y=0.627x-0.157$. Solid curves are calculated by the random cell isodisplacement model. Discrete notations denote the experimental results extracted from the Raman spectra in Ref. 4.

ported, a few assumptions are needed to calculate the phonon behavior of the AlAs and AlSb modes. Raman spectra over all available samples show only one LO peak in the wave number region between the AlAs and AlSb modes. Thus, we assume that AlAsSb is a one mode system; or at least has only one mode over the observed area. We treat the RCI model for a one mode system in the following way: First, the impurity modes are assigned as the lowest LO and highest TO modes between the two boundary binary compounds. The phonon frequencies for the one mode system are chosen as the highest LO and the lowest TO modes calculated by the random cell model. A similar method in the random element model is discussed by Chang and Mitra.[19] The results calculated by this method are found to agree well with the experimental data.

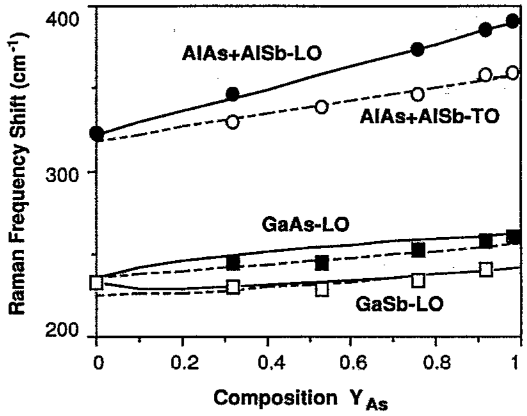

FIG. 3. Optical phonon frequencies vs composition for $Al_xGa_{1-x}As_ySb_{1-y}$ with the compositions x and y related by $x=0.55y+0.2$. Solid curves are calculated by the random cell isodisplacement model. Discrete notations denote the experimental results extracted from the Raman spectra in Ref. 5.

IV. SUMMARY

The random cell isodisplacement model has been used to calculate the behavior of the optical phonons in the quaternary alloys $Ga_{1-x}In_xP_{1-y}Sb_y$ and $Al_xGa_{1-x}As_ySb_{1-y}$. The model is applicable for both four mode systems, such as $Ga_{1-x}In_xP_{1-y}Sb_y$, and three mode systems, such as $Al_xGa_{1-x}As_ySb_{1-y}$. The predicted frequency dependencies of the long wavelength LO and TO phonons on solid composition agree well with the experimental data for both systems.

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