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First-principles theory of the evolution of vibrational properties with long-range order in $GaInP_2$

V. Ozoliņš and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

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We predict the phonon spectra of zinc-blende GaP and InP, of CuPt-type ordered $GaInP_2$, and of the random $Ga_{0.5}In_{0.5}P$ alloy using first-principles density-functional linear-reponse theory. We find that (i) ordered $GaInP_2$ exhibits two GaP-like and two InP-like phonon modes (a ‘‘two-mode’’ behavior), (ii) ordering reverses the order of frequencies of the TO-phonon modes of zinc-blende GaP and InP due to a frustrated bond geometry in the ordered phase, and (iii) each of the LO-phonon modes of the ternary $GaInP_2$ phase represents a mixture of Γ and L phonons of the corresponding binary compound (LO_1 is GaP-like, LO_2 is InP-like), yet the TO (LO) modes of the random alloy represent an amalgamation of the TO (LO) modes of GaP+InP. Consequently, the ordered phase is predicted to exhibit a two-mode behavior, while the random alloy is a pseudo-one-mode system. [S0163-1829(98)50112-9]

III-V semiconductor alloys exist both as random substitutional solid solutions and as long-range ordered compounds.[1] For instance, $Ga_{1-x}In_xP$ can be grown epitaxially in the random phase and in the long-range ordered $(GaP)_1/(InP)_1$ CuPt-type structure, formed by alternate stacking of GaP and InP monolayers along the $\langle 111 \rangle$ direction.[1] The vibrational properties of these two phases exhibit the following unusual features.

(a) *Disordered* $Ga_{1-x}In_xP$. Most $A_{1-x}B_xC$ III-V alloys are two-mode systems, i.e., four separate Raman peaks are observed, corresponding to longitudinal-optical (LO) and transverse-optical (TO) phonons of each of the binary constituents AC and BC. Disordered $Ga_{1-x}In_xP$ is the only exception exhibiting a modified two-mode behavior,[2–4] with *one* TO-phonon and *two* LO-phonon peaks at all compositions.

(b) *Ordered* $GaInP_2$. Ordering is seen to induce interesting changes in the phonon spectrum:[5–9] (i) emergence of new peaks at 60 cm^{-1} and 205 cm^{-1} in the acoustic region, (ii) appearance of a new peak at 354 cm^{-1} in the optical region, (iii) blueshift of the highest LO-phonon peak at 380 cm^{-1}, and (iv) decrease of the peak-to-valley ratio between LO peaks at 360 cm^{-1} and 380 cm^{-1}. These observations provide a unique opportunity to study theoretically phonon evolution with long-range order in a semiconductor system.

We separately calculate the phonon spectra of the random $Ga_{0.5}In_{0.5}P$ alloy and the CuPt-type ordered $GaInP_2$ structure using the density-functional perturbation theory.[10] We employ first-principles pseudopotentials[11] in conjuction with the plane-wave basis set. The nonlinear core correction[12] is used in Ga and In pseudopotentials. Born effective charges, dielectric matrices, and LO/TO splittings at $\mathbf{k} \rightarrow 0$ are calculated using the method of Giannozzi *et al.*[10] Since calculation of these quantities require a highly accurate Brillouin-zone sampling,[10] the effective charges and the dielectric matrices were calculated on a $16 \times 16 \times 16$ equivalent $\mathbf{k}$-point mesh,[13] while the dynamical matrices were found to be well converged using a $8 \times 8 \times 8$ equivalent $\mathbf{k}$-point mesh.

(i) *Pure binary compounds.* The calculated and measured[14–17] phonon dispersion curves of zinc-blende GaP and InP are shown in Fig. 1. The middle column of Fig. 2 summarizes the calculated phonon frequencies of the binary compounds at Γ and L points. Our calculations, using no adjustable parameters, are in excellent agreement with the experimental results.[14–17] No other first-principles calculations for GaP or InP are available.

(ii) *Random* $Ga_{0.5}In_{0.5}P$ alloy. Configurationally disordered $Ga_{0.5}In_{0.5}P$ is modeled by two 16-atom special quasirandom structures[18] (SQS). These supercells are designed to closely reproduce the spatial correlation functions of the perfectly random alloy. The equilibrium geometry of each SQS is obtained by minimizing the total local-density approximation energy with respect to the atomic positions and cell volume. Table I shows that the calculated sample-averaged Ga-P and In-P bond lengths in the random alloy are close to their equilibrium values for the binaries. Phonon frequencies were calculated for $\mathbf{k} \rightarrow 0$ as $\mathbf{k} \| (111)$. The partial TO- and

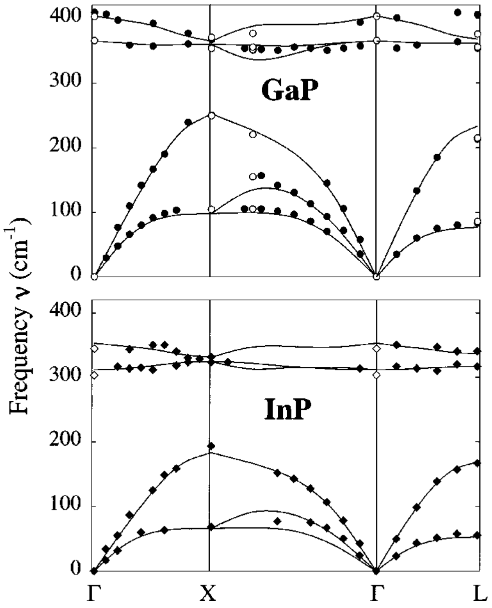

FIG. 1. Phonon dispersion curves of binary GaP and InP. Experimental data are from Refs. 14 (filled circles), 15 (empty circles), 16 (filled diamonds), and 17 (empty diamonds).

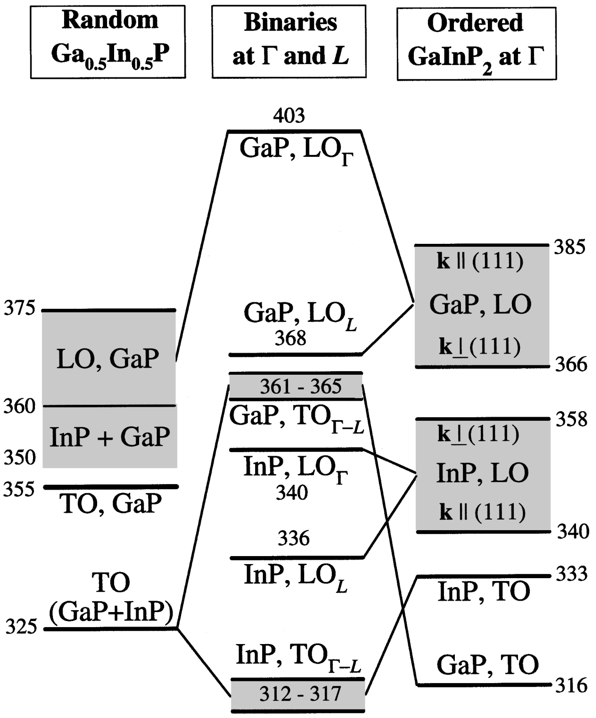

FIG. 2. Calculated zone-center optical frequencies of zinc-blende GaP, zinc-blende InP, ordered $GaInP_2$, and random $Ga_{0.5}In_{0.5}P$ alloys.

LO-decomposed phonon densities of states (DOS) were obtained from

$$N_s(\omega)=\sum_i \delta(\omega-\omega_i)|\hat{p}\cdot\mathbf{e}_{si}|^2, \tag{1}$$

where s labels the atom type, i is a mode index, $\mathbf{e}_{si}$ is a normalized eigenvector of mode $i,\delta(\omega)$ is a broadened δ function of width $W=5\ \mathrm{cm}^{-1}$, and $\hat{p}$ is a unit vector $\hat{p}\|(111)$ for LO and $\hat{p}\perp(111)$ for TO mode character. Figure 3 shows the calculated optical-phonon DOS of random $Ga_{0.5}In_{0.5}P$, and the left column of Fig. 2 summarizes the mode frequencies. From Figs. 2 and 3 we conclude the following.

(a) We identify the high-frequency ($\approx 375\ \mathrm{cm}^{-1}$) shoulder containing Ga and P vibrations with the longitudinal GaP-like peak observed[2–4] at $\approx 380\ \mathrm{cm}^{-1}$ in Raman measurements. The frequency of this mode is lower than that of the LO-phonon mode in pure GaP ($403\ \mathrm{cm}^{-1}$, Fig. 2). In general, the reduction in alloy ν_{LO} has a chemical contribution due to a decrease in the polarization field and thus the LO/TO splitting (e.g., in $Al_{0.5}Ga_{0.5}As$ the AlAs-like $\nu_{\mathrm{LO}}=373\ \mathrm{cm}^{-1}$, while in pure AlAs $\nu_{\mathrm{LO}}=401\ \mathrm{cm}^{-1}$), and a relaxation part. We estimate the latter using the calculated Grüneisen parameter $\gamma_{\mathrm{LO}}=1$, and obtain $\Delta\nu_{\mathrm{LO}}/\nu=-3\gamma\Delta a/a=6\%$, which is consistent with the $\approx 7\%$ decrease in ν_{LO} from $403\ \mathrm{cm}^{-1}$ to $375\ \mathrm{cm}^{-1}$.

TABLE I. The calculated bond lengths and lattice constants (in Å) of ordered CuPt-type $GaInP_2$ and random $Ga_{0.5}In_{0.5}P$. For the ordered $GaInP_2$ we give cation-anion bond lengths parallel (∥) to the ordering direction [111] and parallel to $[\bar{1}11]$ (⊥). The range given for the random alloy represents the standard deviation of the bond-length distribution.

Bond	Pure GaP $a=5.42$	Pure InP $a=5.85$	Random $Ga_{1-x}In_xP$ $a=5.66$	Ordered $GaInP_2$ $a=5.66$ $c/a=1$
$(Ga\text{-}P)_\parallel$	2.34		2.38 ± 0.02	2.36
$(Ga\text{-}P)_\perp$	2.34		2.38 ± 0.02	2.43
$(In\text{-}P)_\parallel$		2.52	2.53 ± 0.01	2.53
$(In\text{-}P)_\perp$		2.52	2.53 ± 0.01	2.48

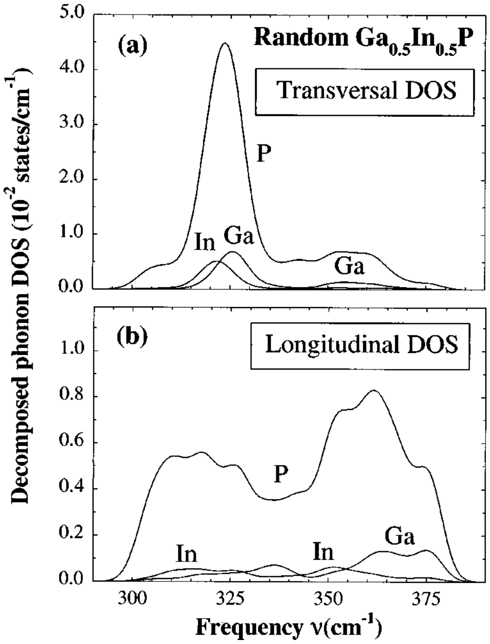

FIG. 3. Partial LO- and TO-decomposed phonon densities of states of random $Ga_{0.5}In_{0.5}P$.

(b) There is a broad structure between $350\ \mathrm{cm}^{-1}$ and $365\ \mathrm{cm}^{-1}$, corresponding to *mixed* longitudinal-optical vibrations involving both Ga and In atoms. Raman measurements[4] have detected longitudinal modes at $360\ \mathrm{cm}^{-1}$, which have been assigned as InP-like modes. Our calculations [Fig. 3(b)] show a stronger Ga component at this frequency.

(c) The strong TO-phonon mode at $325\ \mathrm{cm}^{-1}$ involves almost equal participation of Ga and In atoms. This peak can be identified with the transversal phonon peak at $330\ \mathrm{cm}^{-1}$ seen in Raman experiments.[2–4] In addition, we find some GaP-like TO character at $355\ \mathrm{cm}^{-1}$ that has not been seen experimentally.

We conclude that disordered $Ga_{0.5}In_{0.5}P$ has a pseudo-one-mode behavior: while the GaP LO-phonon mode is isolated and distinct, the individual TO modes of GaP and InP have merged into an alloy TO mode $325\ \mathrm{cm}^{-1}$, and the LO-phonon modes of InP and GaP have merged into an alloy mode $350\ \mathrm{cm}^{-1}$ and $365\ \mathrm{cm}^{-1}$. These mode amalgamation effects are made possible by the strong coupling between the Ga-P and In-P vibrations.

(iii) *CuPt-ordered* $GaInP_2$. Imperfectly ordered samples are characterized by long-range order parameter η, related to the composition of (111) layers in $(Ga_{1+\eta}In_{1-\eta}P_2)/(Ga_{1-\eta}In_{1+\eta}P_2)$ $\langle 111\rangle$ superlattice. $\eta=0$ corresponds to the perfectly random $Ga_{0.5}In_{0.5}P$, while $\eta=1$ corresponds to the

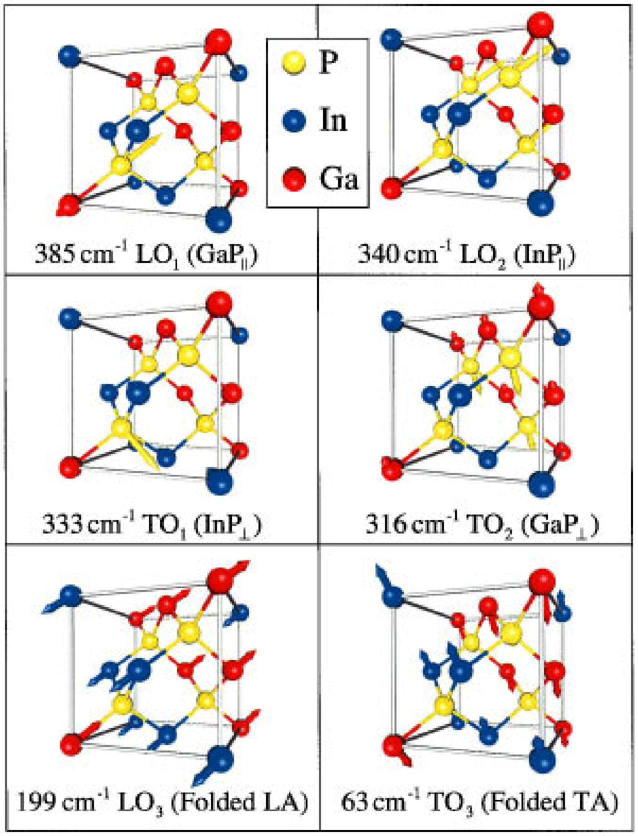

FIG. 4. (Color) Phonon normal modes of CuPt-type ordered GaInP$_2$ at the Γ point of the Brillouin zone. Vector length is proportional to the spectral weight of each atom, given by $|\mathbf{e}_{si}|^2$.

perfectly ordered CuPt-type GaInP$_2$. Currently, the most ordered samples attain $\eta \approx 0.5$. One may conceptualize the ordering process as starting from a virtual $\langle$GaIn$\rangle$P crystal and then splitting the average $\langle$GaIn$\rangle$ cation into Ga and In, creating a $\langle 111 \rangle$ periodicity. This reduces the Brillouin zone (BZ) by half and folds L into Γ, doubling the number of phonon modes in the zone center of the halved BZ. The perfectly ordered CuPt-type structure has four atoms per unit cell: Ga, In, and two symmetry inequivalent P atoms, surrounded by GaIn$_3$ and Ga$_3$In tetrahedra, respectively. The atoms are free to relax along the $\langle 111 \rangle$ ordering direction, leading to four different cation-anion bond lengths. Table I shows that the (Ga-P)$_\parallel$ and (In-P)$_\parallel$ bond lengths that are parallel ($\parallel$) to the ordering direction [111] are practically equal to their equilibrium zero-pressure values in binary GaP and InP, respectively. However, in the ''perpendicular'' ($\perp$) direction [111] the (Ga-P)$_\perp$ bond is much longer and the (In-P)$_\perp$ bond is much shorter than in the respective binaries. The relaxation of the c/a ratio along [111] is found to be negligible (less than 1%).[19] The existence of a special ordering direction ([111]) leads to directional dependence of zone-center optical-mode frequencies. The zone-center frequencies are shown in the right column of Fig. 2, where the shaded regions represent the width of the angular dispersion for LO-phonon modes. In what follows, we show the results for $\mathbf{k} \rightarrow 0$ along Λ ($\mathbf{k} \parallel [111]$). Eigenvectors of zone-center phonon modes of ordered GaInP$_2$ are given in Fig. 4. We see the following properties of the phonons of ordered GaInP$_2$.

(a) The two modes appearing at 63 cm^{-1} and 199 cm^{-1} are folded TA (transverse acoustic) (L) and LA (longitudinal acoustic) (L) phonons, respectively. Figure 4 shows that these modes involve displacements of the Ga and In cations with little participation of the P anions.

(b) In the optical region, we identify two transversal modes at 316 cm^{-1} (TO$_2$) and 333 cm^{-1} (TO$_1$) with eigenvectors that are GaP-like and InP-like, respectively. The GaP-like TO$_2$ mode involves movement of Ga and P$_2$ ions in the $\langle 111 \rangle$ direction, deforming the stretched (Ga-P)$_\perp$ bonds (see Fig. 4). Since the (Ga-P)$_\perp$ bond in the ordered compound is much longer than the same bond in pure GaP (Table I), its frequency (316 cm^{-1}) is much *lower* (Fig. 2) than the TO-phonon frequency in zinc-blende GaP (365 cm^{-1}). Similarly, the frequency of the InP-like TO mode at 333 cm^{-1} is *higher* than the TO-phonon frequency in pure InP. We thus see that the inability of the perpendicular (Ga-P)$_\perp$ and (In-P)$_\perp$ bonds to attain the ideal (binary) values in the ordered phase (''bond-length frustration'') reverses the order of the GaP- and InP-like TO-phonon frequencies relative to the pure binary compounds (Fig. 2). Naive assignment of the peak character based on the order of TO-phonon frequencies in the pure binaries (rather than on inspection of the eigenvectors) would be incorrect.

(c) We predict two LO-phonon modes at 340 cm^{-1} (InP-like) and 385 cm^{-1} (GaP-like), which involve deformation of (Ga-P)$_\parallel$ and (In-P)$_\parallel$ bonds along the ordering direction [111] (see Fig. 4). Since (Ga-P)$_\parallel$ and (In-P)$_\parallel$ bonds are close to their values in pure GaP and InP, respectively (Table I), bond deformation does not affect the frequencies of these modes. As Fig. 2 shows, each of these LO modes in GaInP$_2$ can be thought of as resulting from a hybridization of LO(Γ) and LO(L) phonons of the respective pure binary compound (see Fig. 2). Both LO modes of GaInP$_2$ are very sensitive to the direction of the approach of the wave vector $\mathbf{k}$ to the origin. For instance, if $\mathbf{k} \parallel [111]$ changes to $\mathbf{k} \parallel [110]$ as $\mathbf{k} \rightarrow 0$, LO-phonon frequencies change from 340 cm^{-1} to 358 cm^{-1} and from 385 cm^{-1} to 366 cm^{-1} (Fig. 2). We thus predict that Raman measurements on highly ordered samples will show strong dependence of LO-phonon frequencies on the direction of incident light.

We see that the phonon spectrum of CuPt-type ordered GaInP$_2$ exhibits a two-mode behavior: it consists of two GaP-like and two InP-like modes. Upon CuPt-type ordering of Ga$_{1-x}$In$_x$P, the following changes occur in the phonon spectrum (Fig. 2).

(a) Our calculations reproduce the emergence of a folded L-point TA mode at 63 cm^{-1} (experimentally 60 cm^{-1}) and a folded L-point LA mode at 199 cm^{-1} (experimentally 205 cm^{-1}).

(b) The amalgamated TO-phonon peak of the random alloy at 325 cm^{-1} is predicted to split into a GaP-like TO$_2$ mode at 316 cm^{-1} and InP-like TO$_1$ mode at 333 cm^{-1}. These TO modes are not observed experimentally, presumably because the magnitude of the shift in the currently most highly ordered samples ($\eta \approx 0.5$) is estimated to be only ≈ 2 cm^{-1}, which can be easily masked by the TO-phonon peak of the random alloy. The predicted *inverted order* of these GaP- and InP-like TO$_2$ and TO$_1$ peaks relative to the pure binaries (Fig. 2) awaits experimental testing when better ordered samples are available.

(c) A new peak, corresponding to the InP-like LO-phonon mode, is predicted to appear in highly ordered samples around 340 cm^{-1}. It has not been resolved with certainty experimentally, although it might be the experimentally observed new peak at 354 cm^{-1}.

(d) There is some disagreement in the literature about what causes the decrease of the peak-to-valley ratio between LO peaks at 360 cm^{-1} and 380 cm^{-1}. Hassine *et al.*[8] have suggested the existence of a TO-phonon mode of ordered GaInP_2 between 360 cm^{-1} and 380 cm^{-1}, attributing the decrease in the peak-to-valley ratio to increasing intensity of this new TO peak upon ordering. Our calculations do not support this hypothesis as no modes of ordered GaInP_2 are predicted in this spectral range (Fig. 2).

(e) Currently available ‘‘ordered’’ GaInP_2 samples exhibit domains of different degrees of ordering.[1] Optical interband transitions, used to characterize the degree of long-range order, have a long coherence length and therefore produce domain-averaged results. However, due to the shorter coherence length of Raman scattering the experimentally measured spectra can exhibit Raman peaks from both disordered and ordered domains (rather than one set of averaged peaks). We thus suggest that the observed LO peak at 360 cm^{-1} in the ‘‘ordered’’ samples originates from the amalgamated LO-phonon modes (350-365 cm^{-1}) of the random alloy domains present in the sample.

(f) The frequency of the highest LO mode (Fig. 2) shifts from 375 cm^{-1} in the random alloy to 385 cm^{-1} in the ordered GaInP_2. Experimental observations show that the GaP-like LO peak blueshifts from 380 cm^{-1} at $\eta=0$ to 381 cm^{-1} at $\eta\approx0.5$. Following the theory of Ref. 20, which showed that with increasing long-range order parameter η alloy properties scale as $\Delta\omega_{\text{LO}}=\omega_{\text{LO}}^{\text{ord}}-\omega_{\text{LO}}^{\text{disord}}\propto\eta^2$, we obtain an estimated 384 cm^{-1} for the measured frequency of this mode in perfectly ordered GaInP_2. This 4 cm^{-1} blueshift should be compared to the predicted 10 cm^{-1} blueshift.

There is a *qualitative* change in the phonon spectrum with disordering. In particular, two distinct GaP-like TO_2 and InP-like TO_1 modes in the ordered compound produce upon disordering a single TO-phonon peak of mixed character. Furthermore, the distinct InP-like LO-phonon mode at 340 cm^{-1} and GaP-like LO-phonon mode at 385 cm^{-1} in the ordered compound form upon disordering a single broadband of LO phonons of mixed character extending from 355 cm^{-1} to 375 cm^{-1}.

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