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

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(Received 5 December 1997)

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 ⟨111⟩ 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

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

$$N_s(\omega)\,5\sum_i \delta(\omega\,2\,\omega_i)|\hat{p}\ \mathbf{e}_{si}|^2, \qquad (1)$$

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 $W\,5\,5$ cm^{21}, and $\hat{p}$ is a unit vector $\hat{p}\,\mathrm{i}\,(111)$ for LO and $\hat{p}$ ' (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 cm^{21}) shoulder containing Ga and P vibrations with the longitudinal GaP-like peak observed[2–4] at $\approx$380 cm^{21} in Raman measurements. The frequency of this mode is lower than that of the LO-phonon mode in pure GaP (403 cm^{21}, 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 ν_{LO} 5 373 cm^{21}, while in pure AlAs $\nu_{\mathrm{LO}}\,5$ 401 cm^{21}), and a relaxation part. We estimate the latter using the calculated Grüneisen parameter $\gamma_{\mathrm{LO}}\,5\,1$, and obtain $\Delta\nu_{\mathrm{LO}}/\nu\,5\,2\,3\gamma\Delta a/a\,5\,6\%$, which is consistent with the $\approx 7\%$ decrease in ν_{LO} from 403 cm^{21} to 375 cm^{21}.

(b) There is a broad structure between 350 cm^{21} and 365 cm^{21}, corresponding to *mixed* longitudinal-optical vibrations involving both Ga and In atoms. Raman measurements[4] have detected longitudinal modes at 360 cm^{21}, 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 cm^{21} involves almost equal participation of Ga and In atoms. This peak can be identified with the transversal phonon peak at 330 cm^{21} seen in Raman experiments.[2–4] In addition, we find some GaP-like TO character at 355 cm^{21} 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 cm^{21}, and the LO-phonon modes of InP and GaP have merged into an alloy mode 350 cm^{21} and 365 cm^{21}. 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 $(Ga_{1\,1\,\eta}In_{1\,2\,\eta}P_2)$/ $(Ga_{1\,2\,\eta}In_{1\,1\,\eta}$

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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_3In 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

(c) A new peak, corresponding to the InP-like LO-phonon mode, is predicted to appear in highly ordered samples around 340 cm$^{2 1}$. It has not been resolved with certainty experimentally, although it might be the experimentally observed new peak at 354 cm$^{2 1}$.

(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$^{2 1}$ and 380 cm$^{2 1}$. Hassine *et al.*[8] have suggested the existence of a TO-phonon mode of ordered $GaInP_2$ between 360 cm$^{2 1}$ and 380 cm$^{2 1}$, 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$^{2 1}$ in the ''ordered'' samples originates from the amalgamated LO-phonon modes (350-365 cm$^{2 1}$) of the random alloy domains present in the sample.

(f) The frequency of the highest LO mode (Fig. 2) shifts from 375 cm$^{2 1}$ in the random alloy to 385 cm$^{2 1}$ in the ordered $GaInP_2$. Experimental observations show that the GaP-like LO peak blueshifts from 380 cm$^{2 1}$ at $\eta 5 0$ to 381 cm$^{2 1}$ at $\eta \approx 0.5$. Following the theory of Ref. 20, which showed that with increasing long-range order parameter η alloy properties scale as $\Delta\omega_{\mathrm{LO}} 5\, \omega_{\mathrm{LO}}^{\mathrm{ord}} 2\, \omega_{\mathrm{LO}}^{\mathrm{disord}} \propto \eta^2$, we obtain an estimated 384 cm$^{2 1}$ for the measured frequency of this mode in perfectly ordered $GaInP_2$. This 4 cm$^{2 1}$ blueshift should be compared to the predicted 10 cm$^{2 1}$ 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$^{2 1}$ and GaP-like LO-phonon mode at 385 cm$^{2 1}$ in the ordered compound form upon disordering a single broadband of LO phonons of mixed character extending from 355 cm$^{2 1}$ to 375 cm$^{2 1}$.

This work has been supported by the Office of Energy Research, Basic Energy Sciences, Materials Science Division, U.S. Department of Energy, under Contract No. DE-AC36-83CH10093. We gratefully acknowledge Dr. F. Alsina and Dr. A. M. Mintairov for their valuable comments on the manuscript.

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