Reply to ''Comment on 'First-principles theory of the evolution of vibrational properties with long-range order in $GaInP_2$' ''

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We show that, contrary to the assertion of Alsina *et al.* in the preceding Comment, the theoretically calculated phonon sequence in ordered $GaInP_2$ does not violate the ''alternation rule.'' Analysis of the first-principles calculated phonon dispersion shows that CuPt-ordered $GaInP_2$ is a system where anisotropy of short-range forces is of the same magnitude as the electrostatic Coulomb interactions and the associated LO/TO splittings. We show how the phonon modes change with the degree of order, and demonstrate that our results, without revision, successfully account for the experimental infrared data.

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I. INTRODUCTION

In the $R3m$ space group symmetry of CuPt-type ordered $GaInP_2$ the phonon frequencies for $\mathbf{k}\rightarrow 0$ depend on the angle ϕ between the phonon wave vector $\hat{k}$ and the ordering direction [111]. In our paper,[1] we have used first-principles density-functional linear-response theory, mostly concentrating on the phonon frequencies at $\phi=0$, i.e., with the wave vector parallel to the ordering direction. The comment of Alsina *et al.*[2] concerns phonons along the $\phi=\pi/2$ direction, i.e., with wave vector perpendicular to the ordering direction. Since these phonons were not the subject of our paper, in their comment Alsina *et al.* attempt to guess the order and LO/TO character of these frequencies from the limited data presented in Fig. 2 of Ref. 1. They then proceed to criticize this order of modes as violating the ''alternation rule,'' which in their interpretation states that a TO mode must be followed by an LO mode (neglecting degeneracies). Finally, they point out that their recent experiments were interpreted in terms of what they call ''model $1c$'' with a phonon mode order TO→TO→LO→TO→TO→LO. However, there is no theoretical support for this sequence of modes at either $\phi=0$ or $\phi=\pi/2$.

We regret that in our original paper we did not provide more detail on the character of the phonon modes perpendicular to the ordering direction other than to give the change in frequency with direction. In what follows, we

(i) Extend our previous calculations[1] to $\phi=\pi/2$ and analyze the character of these modes, thus supplying the missing information in the preceding Comment. We find that our first-principles calculation does not produce the mode order termed ''model $1c$'' by Alsina *et al.*,[2,4] but rather a different order: TO→LO→TO→TO→TO→LO.

(ii) Show that our results are fully consistent with the ''alternation rule.'' In its correct formulation, this rule allows for the appearance of two doubly degenerate TO-phonon modes followed by two LO-phonon modes for a wave vector along the ordering direction ($\phi=0$). Thus, the results of our first-principles calculations do not violate this rule.

(iii) Compare our first-principles calculated dielectric functions with recent experimental data,[3,4] finding that our calculations without revision account very well for the infrared measurements of Refs. 3 and 4.

II. PHONON DISPERSION AS A FUNCTION OF ANGLE ϕ

Figure 1 shows the calculated Γ-point optical frequencies $\nu(\phi)$ as functions of angle ϕ between the phonon wave

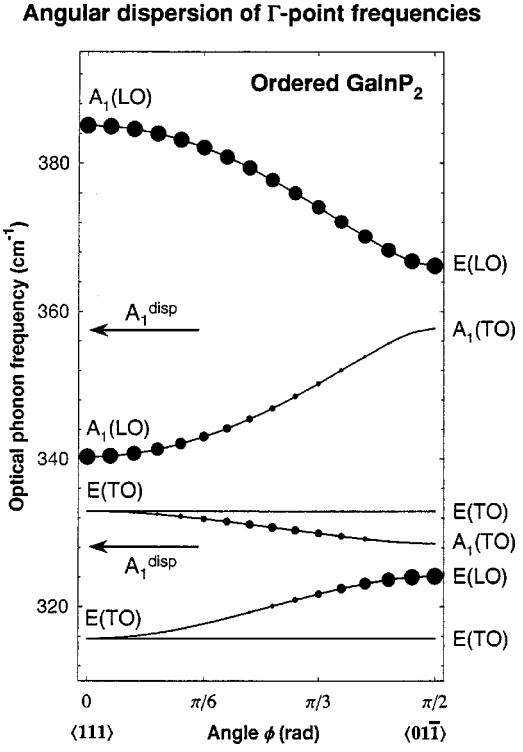

FIG. 1. Calculated angular dispersion of zone-center optical frequencies in ordered $GaInP_2$. Dot size indicates the degree of LO character for each mode. Dispersion frequencies of A_1-symmetric modes (A_1^{disp}) are denoted by horizontal arrows at 329 and 358 cm^{-1}.

vector $\hat{k}$ and ordering direction [111] ($\phi=0$ for $\hat{k}\|[111]$ and $\phi=\pi/2$ for $\hat{k}\|[01\bar{1}]$). We omit from Fig. 1 a TO/LO pair of practically dispersionless modes with calculated frequencies at 63 and 199 cm^{-1} (experimentally measured[5] at 65 and 205 cm^{-1}) corresponding to folded transverse-acoustic and longitudinal-acoustic phonons, respectively. The zone-center optical phonons in ordered $GaInP_2$ decompose into three one-dimensional irreps of A_1 symmetry (polarized parallel to [111]) and three two-dimensional irreps of E symmetry (polarized perpendicular to [111]). When $\phi=0$, the A_1 symmetric modes are LO, while the doubly degenerate E-symmetric modes are TO. When $\phi=\pi/2$, the A_1 symmetric modes convert to TO, and for each E state, one of the modes stays TO while the other converts to LO. From Fig. 1 we find the following mode sequence at $\phi=0$:

$$E(\mathrm{TO})\rightarrow E(\mathrm{TO})\rightarrow A_1(\mathrm{LO})\rightarrow A_1(\mathrm{LO}) \quad (\phi=0), \quad (1)$$

while at $\phi=\pi/2$ we find

$$E(\mathrm{TO})\rightarrow E(\mathrm{LO})\rightarrow A_1(\mathrm{TO})\rightarrow E(\mathrm{TO})\rightarrow A_1(\mathrm{TO}) \rightarrow E(\mathrm{LO}) \quad (\phi=\pi/2). \quad (2)$$

Thus, our first-principles results in Eqs. (1) and (2) correspond to ''model 1*b*,'' rather than ''model 1*c*'' used by Alsina *et al.* to interpret the experimental data. We will show in Sec. IV D that ''model 1*b*'' accounts for the observed infrared and Raman data.

When the phonon wave vector $\hat{k}$ is neither parallel nor perpendicular to the ordering axis [111] (i.e., *between* $\phi=0$ and $\phi=\pi/2$), the so-called *ordinary* TO-phonon modes (at 316 and 333 cm^{-1} in Fig. 1) remain completely dispersionless, corresponding to phonon polarizations that are orthogonal to both the phonon wave vector $\hat{k}$ and the ordering direction [111]. The long-range Coulomb field mixes the remaining A_1- and E-symmetric modes, leading to phonons that are neither strictly LO or TO. To calculate the LO character of mode n we define

$$\xi_n^{\mathrm{LO}}(\hat{k})=\sum_{j=1}^{N_{\mathrm{at}}} |\hat{k}\cdot\mathbf{e}_j(\hat{k}n)|^2, \quad (3)$$

where $\mathbf{e}_i(\hat{k}n)$ is the phonon eigenvector of mode n and wave vector $\hat{k}$. The sum in Eq. (3) extends over all atoms in the unit cell ($N_{\mathrm{at}}=4$). The variation of $\xi_n^{\mathrm{LO}}(\hat{k})$ with the angle ϕ is shown in Fig. 1 as the size of the filled circles, i.e., circles are largest for pure longitudinal modes ($\xi^{\mathrm{LO}}=1$) and absent for transversal modes ($\xi^{\mathrm{LO}}=0$). It is seen from Fig. 1 that the highest LO-phonon mode (at 385 cm^{-1} for $\phi=0$) retains its LO character, accordingly changing its symmetry from A_1 to E. In contrast, the lower A_1(LO) mode (at 340 cm^{-1} for $\phi=0$) gradually changes to a TO-phonon mode for $\hat{k}\perp[111]$, retaining its A_1 symmetry. The *extraordinary* TO mode at 333 cm^{-1} for $\phi=0$ remains transversal, changing its symmetry from A_1 to E, as $\hat{k}$ changes from [111] to $[01\bar{1}]$. The other extraordinary TO mode changes to a LO-phonon mode for $\hat{k}\|[01\bar{1}]$, retaining E symmetry and polarization along $[01\bar{1}]$. We will return to these changes in phonon symmetry and LO/TO character when interpreting the experimental data in Sec. IV.

III. AGREEMENT WITH THE ''ALTERNATION RULE''

We disagree with the statement of the alternation rule by Alsina *et al.* The dielectric function indeed has zeros at the LO-phonon frequencies, but its poles are located at the so-called *dispersion frequencies*, determined by eigenvalues of the nonsingular (i.e., nonelectrostatic) part of the dynamical matrix [see Eqs. (6.5.19)–(6.5.29) in Ref. 6]. In cubic crystals, dispersion frequencies indeed coincide with TO-phonon frequencies, but in uniaxial crystals (such as ordered $GaInP_2$) the dispersion frequencies polarized along the ordering direction [111] do not correspond to any TO frequencies when $\hat{k}\|[111]$. Instead, the dispersion frequencies correspond to TO phonons of A_1 symmetry when $\hat{k}$ is perpendicular to the ordering axis [111], indicated by arrows in Fig. 1. As seen from Fig. 1, the latter indeed alternate with the A_1(LO)-phonon frequencies for $\hat{k}\|[111]$. Thus, a sequence of two consecutive TO modes followed by two LO-phonon modes for $\hat{k}\|[111]$ *does not violate the alternation rule*. Similarly, when phonon wave vector $\hat{k}$ is perpendicular to the ordering direction ($\phi=\pi/2$), dispersion frequencies are given by the frequencies of ordinary E(TO) phonons, which again alternate with the E(LO) frequencies, see Fig. 1. We conclude that the order of modes in Eqs. (1) and (2) does not contradict any rule, in contrast with the statement of Alsina *et al.*[2]

IV. ANALYSIS AND COMPARISON WITH EXPERIMENT

To refute the claim of Alsina *et al.* that ''model 1c'' (which differs from our results) is needed to interpret the experimental data of Refs. 3 and 4, we demonstrate that the phonon dispersion in Fig. 1 agrees with experiment. First, in Sec. IV A we examine the anisotropy of short-range force constants relative to the magnitude of long-range Coulomb interactions in CuPt-ordered $GaInP_2$, finding that these effects are of the same magnitude, in contrast with the interpretation given in Ref. 3. The dielectric functions of disordered and ordered $GaInP_2$, required for the comparison with the experimental infrared data,[3,4] are analyzed in Sec. IV B. Phonon frequencies of *partially ordered* samples (such as the ones used in Refs. 3–5) are deduced in Sec. IV C. Finally, in Sec. IV D we show that the experimental data agrees with our first-principles calculations.

A. Mode mixing and anisotropy

Disordered $Ga_{1-x}In_xP$ is usually considered to be a ''two-mode system'' (exhibiting an InP-like TO+LO mode complex followed by a GaP-like TO+LO pair), or a ''modified two-mode system''[7] (mixed TO, InP-like LO, and GaP-like TO+LO modes). Experimentally, in a system like $Ga_{1-x}In_xP$, this assignment can only be done by studying phonon spectrum as a function of composition,[7] since it is

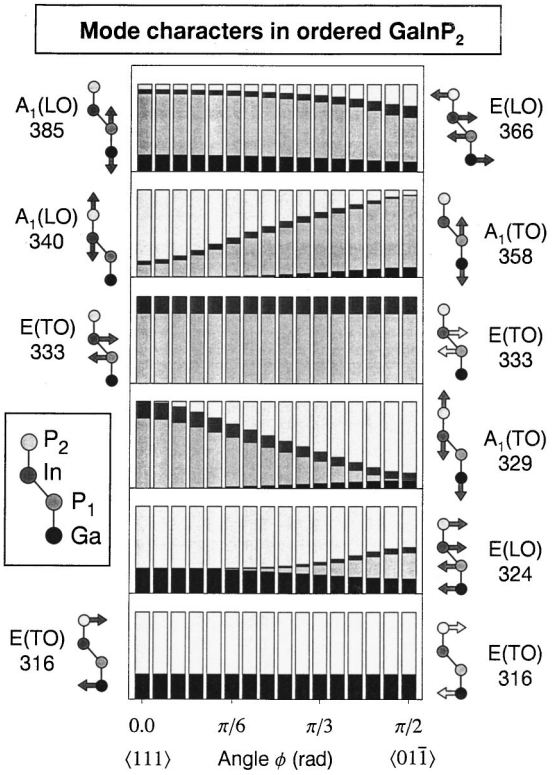

FIG. 2. Decomposition of Γ-point phonon eigenmodes into contributions from Ga, In, and P atoms as functions of the angle between phonon wave vector $\hat{k}$ and the ordering direction [111] in perfectly ordered $GaInP_2$. Schematic displacement patterns for atom chains along [111] are shown for $\hat{k}\|[111]$ and $\hat{k}\perp[111]$. Frequencies are given in cm^{-1}. White arrows denote displacements perpendicular to the plane defined by the ordering direction [111] and phonon wave vector $\hat{k}$ (i.e., along $[\bar{2}11]$).

rarely possible to directly determine the ionic character of a particular mode at a fixed composition. In contrast, theoretical calculations allow a detailed study of the ionic character of each mode based on its eigenvectors, and thus an unambiguous assignment of mixed GaP-like or InP-like characters. In Ref. 1 we confirmed the modified two-mode behavior of disordered $GaInP_2$. We also showed that ordered $GaInP_2$ closely resembles a two-mode system when the phonon wave vector is parallel to the ordering direction, $\hat{k}\|[111]$, with an unusual mode sequence:

$$\mathrm{TO(GaP)}\rightarrow\mathrm{TO(InP)}\rightarrow\mathrm{LO(InP)}\rightarrow\mathrm{LO(GaP)}. \qquad (4)$$

The reversal GaP-like and InP-like TO-phonon modes with respect to their ''natural'' sequence TO(InP)$\rightarrow$TO(GaP) was attributed to Ga-P and In-P bond-length frustration perpendicular to the ordering direction, as imposed by the uniaxial symmetry of the ordered compound (see Table I in Ref. 1). Here we extend our analysis to all angles ϕ and explain some of the peculiarities of the phonon dispersion in Fig. 1. Figure 2 shows the Ga-, In-, and P-like ionic characters (defined by mode eigenvectors as $w_j=|\mathbf{e}_j(\hat{k}n)|^2$) and schematic displacement patterns of Γ-point optical phonon modes in perfectly ordered $GaInP_2$. We see that change in phonon wave vector $\hat{k}$ causes dramatic changes and intermixing between the GaP-like and InP-like modes, as well as between different symmetry representations:

(i) Two ordinary E(TO) modes at 316 and 333 cm^{-1} remain dispersionless.

(ii) The lower extraordinary GaP-like TO-phonon mode (at 316 cm^{-1} for $\phi=0$) hybridizes with the InP-like mode of E symmetry and becomes a longitudinal mode of mixed GaP +InP character (at 324 cm^{-1} for $\phi=\pi/2$). The displacement pattern of this mode suggests a very small dipole moment, since pairs of oppositely charged ions move in phase along $\hat{k}$, leading to a weak LO/TO splitting of only 8 cm^{-1}. We expect that both Raman and infrared signatures of this mode will be very weak, and difficult to observe in partially ordered samples.

(iii) The InP-like extraordinary TO phonon (at 333 cm^{-1} for $\phi=0$) retains its TO character by hybridizing with modes of A_1 symmetry and mixing both GaP-like and InP-like character. Its frequency changes very little (to 329 cm^{-1} at $\phi=\pi/2$), which we attribute to competing effects: decreasing In-like character and increasing Ga-like character lead to frequency increase, while the change of polarization from $[01\bar{1}]$ ($\phi=0$) to [111] ($\phi=\pi/2$) leads to frequency decrease, since the latter does not involve the frustrated In-P bond perpendicular to [111].

(iv) The LO phonon of A_1 symmetry at 340 cm^{-1} retains its A_1 symmetry, but gradually changes into a GaP-like TO mode, which leads to an increase in frequency by a remarkable 18 cm^{-1}, despite losing the longitudinal character and the associated frequency increase due to LO/TO splitting. From the displacement pattern we conclude that this mode is likely to have strong infrared and Raman signatures.

(v) Finally, the uppermost GaP-like LO-phonon mode (at 340 cm^{-1} for $\phi=0$) changes its symmetry from A_1 to E, and becomes a mixed GaP+InP LO-phonon mode. Admixture of InP-like character leads to a decrease in frequency from 385 to 366 cm^{-1}.

In conclusion, as the phonon wave vector $\hat{k}$ varies from [111] to $[01\bar{1}]$, modes of different symmetry representations and different ionic character mix strongly, leading to a change in ionic character, LO and TO character, and symmetry properties. This mixing indicates that ordered $GaInP_2$ is a system where anisotropy of short-range force constants (measured by $\nu_{A_1}^{\mathrm{TO,LO}}-\nu_{E}^{\mathrm{TO,LO}}$) is of the same magnitude as the LO/TO splitting (given by $\nu_{A_1,E}^{\mathrm{LO}}-\nu_{A_1,E}^{\mathrm{TO}}$). Thus, our findings disagree with the interpretation of experimental data given by Alsina *et al.* in Ref. 3, where it was concluded that LO/TO-splitting dominates over the anisotropy in force constants.

B. Dielectric functions

We next proceed to discuss the optical properties of ordered and disordered $GaInP_2$, which will establish a link with the infrared reflectivity (Ref. 3) and infrared transmission (Ref. 4) experiments.

The optical properties in the infrared range are determined by the complex dielectric tensor:[6]

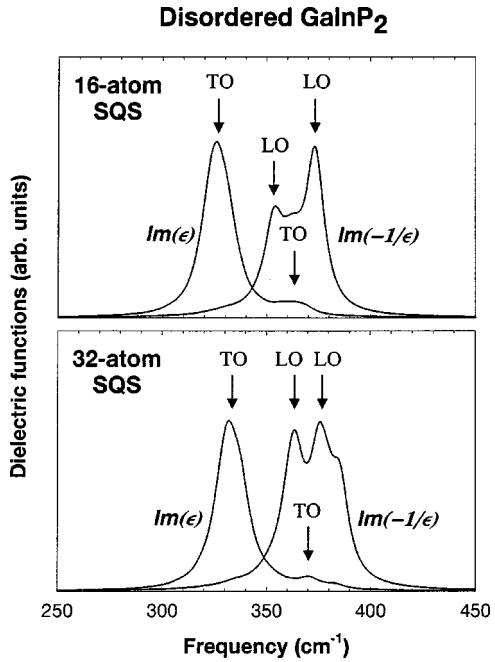

FIG. 3. Calculated dielectric functions of disordered $GaInP_2$. The top panel shows results obtained from two 16-atom SQS's in Ref. 1, and the bottom panel shows results for a 32-atom SQS.

$$\epsilon_{\alpha,\beta}(\nu)=\epsilon^{\infty}_{\alpha,\beta}+\frac{4\pi}{V}\sum_{n=4}^{3N_{\rm at}}\frac{\sum_{j=1}^{N_{\rm at}}[\mathbf{Z}_j\mathbf{u}_j(n)]_\alpha\sum_{l=1}^{N_{\rm at}}[\mathbf{Z}_l\mathbf{u}_l(n)]^*_\beta}{\nu^2-\nu_n^2-i\gamma_n\nu_n}, \tag{5}$$

where $\epsilon^{\infty}_{\alpha,\beta}$ is high-frequency electronic dielectric tensor, n labels optical modes at $\mathbf{k}=0$, ν_n are optical dispersion frequencies, $\mathbf{u}_j(n)$ is the displacement of ion j corresponding to ν_n, γ_n are damping constants determined by optical phonon lifetimes, and $\mathbf{Z}_j$ is a 3×3 effective charge tensor for atom j. All quantities entering Eq. (5) are obtained directly from density-functional linear-response calculations, except the phonon lifetimes which are difficult to calculate theoretically, and in the present work have been (somewhat arbitrary) chosen as $\gamma_n=10\ \mathrm{cm}^{-1}$. The imaginary part of the dielectric tensor, $\mathrm{Im}(\epsilon)$, determines energy dissipation and has Lorentzian peaks at dispersion frequencies ν_n, which show up as minima in transmission spectra. Another useful function is $\mathrm{Im}(-1/\epsilon)$, which has peaks at LO-phonon frequencies. The widths of absorption peaks in $\mathrm{Im}(\epsilon)$ are determined by phonon lifetimes $1/\gamma_n$.

In Fig. 3 we show the calculated dielectric functions for *disordered* $GaInP_2$, which are obtained from direct supercell calculations for special quasirandom structures.[1] It is seen from Fig. 3 that both random structures have TO-phonon peaks in $\mathrm{Im}(\epsilon)$ around 330 and 370 cm^{-1}, while the corresponding LO-phonon peaks in $\mathrm{Im}(-1/\epsilon)$ are located around 360 and 380 cm^{-1}, in good agreement with the values extracted from infrared experiments in Refs. 3 and 4. Furthermore, note that the maxima in the dielectric functions in Fig. 3 do not always coincide with the maxima in the phonon density of states (DOS) shown in Fig. 3 of Ref. 1. For instance, the GaP-like TO-phonon DOS peak is found around 355 cm^{-1} (Figs. 2 and 3 in Ref. 1), while $\mathrm{Im}(\epsilon)$ in Fig. 3 gives somewhat higher values around 370 cm^{-1}. These differences are caused by the fact that $\mathrm{Im}(\epsilon)$ is weighted by phonon mode dipole moments [see Eq. (5)].

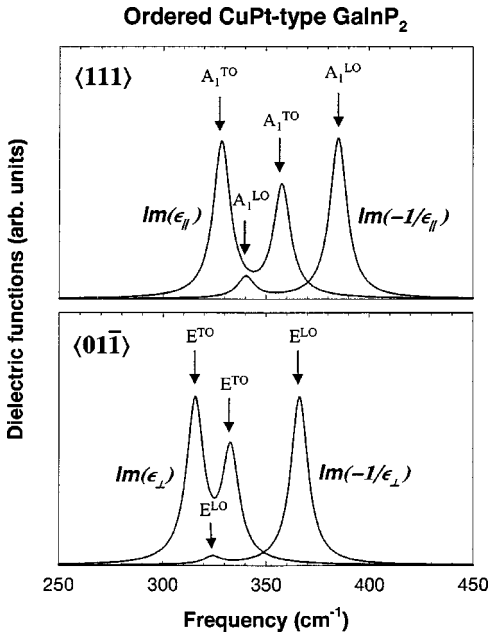

FIG. 4. Calculated dielectric functions $\epsilon_\parallel$ (top panel) and $\epsilon_\perp$ (bottom panel) for perfectly ordered $GaInP_2$.

The dielectric function of *ordered* $GaInP_2$ has two components: parallel to the ordering direction $[\epsilon_\parallel(\nu)]$ and perpendicular to the ordering direction $[\epsilon_\perp(\nu)]$. These components are shown in Fig. 4. In accordance with the discussions in Sec. III and Fig. 1, $\mathrm{Im}(\epsilon_\parallel)$ has peaks at $A_1(\mathrm{TO})$ phonon frequencies for $\hat{k}\perp[111]$, while $\mathrm{Im}(\epsilon_\perp)$ displays structure at $E(\mathrm{TO})$ phonon frequencies for $\hat{k}\parallel[111]$. It is also seen from Fig. 4 that peaks in $\mathrm{Im}(\epsilon)$ alternate with peaks in $\mathrm{Im}(-1/\epsilon)$, in accordance with the ''alternation rule.''

C. Evolution of modes with the order parameter η

For the comparison of experimental measurements on *partially ordered* $GaInP_2$ (the samples used in Refs. 3 and 4 had $\eta\approx0.5$) with the theoretical predictions for *perfectly ordered* $GaInP_2$ ($\eta=1$) we need a theory that describes the dependence of phonon frequencies on the order parameter η. While a complete theory is beyond the scope of this paper, useful insights can be gained by using the ''η^2 rule'' proposed in Ref. 8, which states that a physical property P varies with the order parameter η as $P(\eta)=(1-\eta^2)P_{\eta=0}+\eta^2P_{\eta=1}+o(\eta^2)$. We propose the following scenario of phonon-mode evolution with the order parameter η, shown in Fig. 5:

(i) The 380 cm^{-1} LO-phonon mode of the disordered alloy evolves into the 385 cm^{-1} $A_1(\mathrm{LO})$ mode of the ordered compound. This mode shows correspondingly increasing angular ϕ dependence of the frequency (showed by vertical arrows in the direction of increasing ϕ in Fig. 5). At $\eta=0.5$ (the dashed vertical line in Fig. 5), this ϕ dependence is expected to be only 5 cm^{-1}.

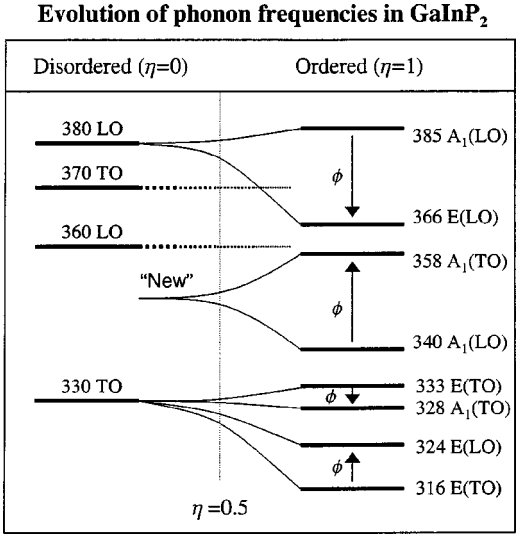

FIG. 5. Proposed phonon mode evolution with the long-range order parameter η in partially ordered $GaInP_2$. Arrows denote angular dispersion in the direction of increasing angle ϕ between the phonon wave vector $\hat{k}$ and ordering direction. Dotted lines denote phonon modes due to disorder in (111) planes, which are absent in perfectly ordered $GaInP_2$ and become weaker with increasing η.

(ii) The 370 cm^{-1} TO-phonon mode of the disordered alloy has no ordered analog, and we expect that its intensity will decrease with increasing η.

(iii) The 360 cm^{-1} mode of disordered $GaInP_2$, may either disappear with increasing η (as indicated by a dashed line in Fig. 5) or hybridize and merge with the LO-phonon modes of ordered $GaInP_2$.

(iv) A new phonon mode intrinsic to *ordered* $GaInP_2$ appears between 340 and 358 cm^{-1}. This mode has no analog in the disordered phase. It is observed experimentally at 354 cm^{-1} in the Raman spectra of partially ordered samples.[5]

(v) The 330 cm^{-1} TO-phonon mode of disordered $GaInP_2$ splits into two pairs of ordinary + extraordinary TO-phonon modes, as shown in Fig. 5. At $\eta=0.5$, this splitting is only approximately 4 cm^{-1}. Thus, experimentally one may hope to see a slight broadening of the 330 cm^{-1} peak for $\eta=0.5$.

D. Comparison with experiments

Table I summarizes the comparison between our first-principles calculations, experimental infrared,[3,4] and Raman[5] results on disordered ($\eta=0$) and partially ordered ($\eta\approx0.5$) samples. The theoretical phonon frequencies for $\eta=0$ were obtained directly from the calculated maxima in $\mathrm{Im}(\epsilon)$ and $\mathrm{Im}(-1/\epsilon)$ (see Fig. 3), while for $\eta\approx0.5$, they were obtained from the phonon-mode evolution scheme shown in Fig. 5 (see also discussion in Sec. IV C). Table I also shows a comparison with the results of recent adiabatic-bond-charge model calculations for CuPt-ordered ($\eta=1$) $GaInP_2$ by Alsina *et al.*[9]

For *disordered* $GaInP_2$, theoretical predictions are in excellent agreement with the measurements of Refs. 3 and 4. In particular, the criticism[4] that the theory is inaccurate for the 372 cm^{-1} minimum seen in the infrared spectra of the disordered sample and assigned to TO phonons is unfounded, since the theory places this minimum at 370 cm^{-1}.

For *partially ordered* $GaInP_2$, our results for the LO-phonon modes are in good agreement with the Raman spectra of partially ($\eta\approx0.5$) ordered samples:[5] the latter find a blue shift of the highest 380 cm^{-1} LO-phonon peak by 1 cm^{-1}, and show that the mode at 354 cm^{-1} behaves as LO phonon when $\hat{k}\|[111]$. These Raman spectra[5] also exhibit TO-phonon peaks at 330 and 372 cm^{-1}, in agreement with our results in Table I.

Infrared experiments of Refs. 3 and 4 were performed in two different polarizations of the incident light: perpendicu-

TABLE I. Comparison of the first-principles calculated local-density approximation (LDA-LR) zone-center phonon frequencies (in cm^{-1}) for disordered and CuPt-ordered $GaInP_2$ with the experimental measurements (Ref. 3–5) and bond-charge model calculations of Alsina *et al.*[9] Theoretical results for $\eta=0.5$ (LDA+η^2) are obtained from Fig. 5. (T) and (L) denote transverse and longitudinal polarizations, respectively. Numerical uncertainties in the theoretical values for $\eta=0$ and $\eta=0.5$ are ≈5 cm^{-1}.

Disordered ($\eta=0$)		Partially ordered ($\eta\approx0.5$)				Ordered ($\eta=1$)			
		$\hat{k}\|[111]$		$\hat{k}\perp[111]$		$\hat{k}\|[111]$		$\hat{k}\perp[111]$	
Expt.	LDA-LR	Expt.	LDA+η^2	Expt.	LDA+η^2	Ref. 9	LDA-LR	Ref. 9	LDA-LR
380(L)	380(L)	381(L)	381(L)	381(L)	376(L)	379(L)	385(L)	378(L)	366(L)
372(T)	370(T)	372(T)	370(T)	372(T)	370(T)				
364(L)	360(L)	364(L)	360(L)	364(L)	360(L)				
		354(L)	≈350(L)	354(T)	≈350(T)	358(L)	340(L)	359(T)	358(T)
332(T)	330(T)	332(T)	331(T)	332(T)	330(T)	340(T)	333(T)	340(T)	333(T)
								339(T)	328(T)
			327(T)		329(T)	333(T)	316(T)	335(L)	324(L)
								333(T)	316(T)
		205(L)	199(L)	205(T)	199(T)	179(L)	199(L)	179(T)	199(T)
		60(T)	63(T)	60(T)	63(L)	64(T)	63(T)	65(L)	63(L)
				60(T)	63(T)			64(T)	63(T)

lar to the plane defined by the surface normal and ordering direction (s polarization) and parallel to it (p polarization). Only modes of E symmetry are allowed in s polarization [i.e., transmission is determined by $\epsilon_{\perp}(\nu)$], while both A_1 and E modes [i.e., both $\epsilon_{\perp}(\nu)$ and $\epsilon_{\parallel}(\nu)$] contribute in p polarization. The total spectrum depends strongly on the angle of incidence.

(i) *The 320–330 cm^{-1} region:* For the completely ordered $\eta=1$ case, theory predicts (Fig. 5) splitting in s polarization for the lowest TO-phonon peak of disordered $GaInP_2$ (330 cm^{-1}) into two E(TO) modes at 333 and 316 cm^{-1}. However, for $\eta=0.5$ this splitting will be only ≈ 4 cm^{-1} (Table I), and therefore it will be extremely difficult to detect in infrared spectra due to overlap with TO modes from disorder *within* the (111) planes. Indeed, infrared spectra in Fig. 2(a), Ref. 4, shows very little change with increasing order in the shape of the broad minimum around 330 cm^{-1}. It is hard to say whether the appearance of a slight shoulder in the infrared transmission spectra at 325 cm^{-1}, not present in the disordered sample (Fig. 1 in Ref. 4), is a reflection of ordering-induced TO-mode splitting. We predict that when samples of higher degree of order become available, the 330 cm^{-1} peak will split into two E-mode peaks at ≈ 316 and ≈ 333 cm^{-1}.

(ii) *The 370 cm^{-1} mode:* Regarding the TO-phonon mode of partially ordered $GaInP_2$ seen[4] in both s and p polarizations at 372 cm^{-1}, we note that the minimum in transmittance is much shallower than that in disordered $GaInP_2$ (Fig. 1 in Ref. 4) suggesting that its intensity decreases with increasing order. We propose that *this mode is intrinsic to the disorder within the (111) planes*, and therefore it should be assigned to the highest TO-phonon peak of the random alloy (our calculations give 370 cm^{-1} for the frequency of this mode). This interpretation is further supported by the poor agreement between Alsina's *et al.*[4] calculated and measured transmittivity, who assumed that the 372 cm^{-1} TO phonon is intrinsic to both ordered and disordered $GaInP_2$.

(iii) For p polarization, our calculations predict that a new structure will appear around 350 cm^{-1}, corresponding to the 358 cm^{-1} maximum Im($\epsilon_{\parallel}$) of *perfectly ordered* $GaInP_2$. Experimental data in Fig. 2(b) of Ref. 4 indeed show a definite transmittance minimum at 354 cm^{-1}. However, it is classified by Alsina *et al.* as a ''quasilongitudinal mode'' on the basis of the assumption that the LO/TO splitting dominates over the A_1/E splitting. As shown in Sec. IV A, this assumption is unwarranted.

For *ordered* ($\eta=1$) $GaInP_2$, the empirical force-field calculation of Alsina *et al.*[9] shows differences of the order of up to 20 cm^{-1} relative to the first-principles calculations. The former also severely underestimate the width of the angular dispersion as ϕ varies from 0 to $\pi/2$.

In conclusion, it seems that theory can account for experimental data very well and provide no support for ''model $1c$'' proposed by Alsina *et al.*[2], since there is no theoretical evidence for the existence of an ordinary TO-phonon peak between the LO-phonon peaks in perfectly ordered $GaInP_2$.

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