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-principd nOsthe phonon freqk=0ies 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 $\phi=$! *LO→TO→TO→LO. However, there is no theoretical support for this sequence of modes at either*

ϕ $=0$ or $\phi=$ /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 lar vector $\hat{k}$ and ordering direction $[111]$ ($\phi=0$ for $\hat{k}\|[111]$ and $\phi=$ /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 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 charac-

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

where $\epsilon^{\infty}_{\alpha,\beta}$ is high-frequency electronic dielectric tensor, n labels optical modes at $\mathbf{k}=0$, $\;_n$ are optical dispersion frequencies, $\mathbf{u}_j(n$

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 .

iii) The 360 cm^{-1} mode of disordered $GaInP_2$, may either disappear with increasing 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

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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 $\epsilon_{\perp}(\ )$], while both A_1 and E modes [i.e., both $\epsilon_{\perp}(\ )$ and $\epsilon_{\parallel}(\ )$] 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 $\ =1$ 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 $\ =0.5$ 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 $GaInP_2$