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Characterization of Raman scattering spectra in ternary compound semiconductors

D. N. Talwar and T. D. Fang
Department of Physics, Indiana University of Pennsylvania, Indiana, Pennsylvania 15705-1087

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Impurity-induced first-order Raman scattering spectra are reported, in the optical- and acoustical-phonon-frequency region for a ternary compound $Al_xGa_{1-x}P$, using an "average-Green's-function" theory. Numerical calculations for the pure GaP and AlP are based on a rigid-ion model, with a perturbation scheme that includes mass change at the metallic-ion site and nearest-neighbor impurity-host interactions. A modified random element isodisplacement (MREI) model is employed to treat the compositional dependence of optical phonons. The observed strong (weak) dependence of phonons in ternary compounds is suggested to be related to the interference between sets of oscillators caused by small (large) lattice relaxation. Results of the Green's-function method are compared and discussed with the MREI model calculations and with the experimental data.

I. INTRODUCTION

Remarkable progress in the growth processes of artificial layered structures has put III-V materials and their technology in a special category that promises to be revolutionary in nature. Many physical properties of the mixed ternary alloys can be tailored to satisfy the special needs of modern devices.[1-5] In optical information processing systems, there have been recent demands to replace the commonly used $Al_xGa_{1-x}As$/GaAs diode by the true visible-light semiconductor laser. The material suitable for realizing such a laser is $Al_xGa_{1-x}P$ with $In_xGa_{1-x}P$ strained-quantum-well (SQW) structure.[6]

Despite a great deal of success in the growth front, data on the basic physical properties (viz., band structure, lattice dynamics, elastic-stiffness constants, etc.) of the above ternary compounds are rather meager. For investigating details of structural disorder in ternary alloys, the study of lattice vibrations plays a significant role. The complete knowledge of phonon dispersions in perfect binary compounds can be obtained from inelastic neutron scattering experiments. In the absence of such data for Al pnictides (AlP, AlAs, and AlSb), partial information of lattice dynamics may be gathered from infrared reflectance (IR) (Ref. 7) and/or Raman scattering[8-10] techniques. Several Raman measurements for $Al_xGa_{1-x}P$ ($x < 0.8$) ternary alloys have been performed in recent years,[8-10] and these measurements display some interesting contrasts in the high (optical-phonon) frequency region. However, no impurity-induced first-order Raman spectra (IFORS) have been reported for the low-frequency (acoustical) region. The experimental determination of polarization-dependent IFORS for the acoustical region is considerably more demanding than for the optical region. This information, although sensitive to the local environment, is needed in material characterization for device structures. The theoretical study of IFORS in various Raman-active representations can play an equally important role both in probing the nature of impurity-host bonding in semiconductors and in searching for the physical *realism* of lattice dynamical and perturbation models, which are also at a primitive stage.

In this paper a theory of IFORS in mixed crystals, based on an average-Green's-function $\langle \mathcal{G} \rangle$ formalism,[11] is reported and applied to $Al_xGa_{1-x}P$. Recently in a different system $Hg_xCd_{1-x}Te$, similar types of calculations have also been reported by Fu and Dow.[12] However, the authors of Ref. 12 have obtained the phonon density of states for random substitutional alloys by using a recursion method and by adopting a simplified short-range force model for the lattice dynamics of CdTe and HgTe. In partially ionic compounds, the neglect of long-range Coulomb forces[13] would cause the longitudinal- and transverse-optical phonons to be degenerate at $\mathbf{q}=0$. Since finite splitting has been observed in inelastic neutron scattering experiments of CdTe and HgTe compounds,[13] the inclusion of long-range Coulomb forces is essential to improve the overall phonon-dispersion relations especially in the region where the "cluster mode" in $Hg_{0.8}Cd_{0.2}Te$ is detected. In the present study the host-lattice Green's functions ($\mathcal{G}^0$) of GaP and AlP are obtained by incorporating phonons from an eleven-parameter rigid-ion model,[14] which includes both short- and long-range forces. The self-energy functions, required for the explicit expression in the Raman scattering intensity, are evaluated to first order in the composition x. Numerical calculations in the *low-concentration limit* are performed for the impurity-induced Raman intensities in $Al_xGa_{1-x}P$. To treat the observed compositional dependence of optical phonons in $Al_xGa_{1-x}P$, a relatively less-rigorous method based on a *modified random element isodisplacement* (MREI) scheme[15] is considered. The results obtained from the MREI method are compared and discussed with the existing Raman scattering experiments[8-10] and with the sophisticated Green's-function technique. Since very little is known about IFORS in the low-frequency region, the Green's-function predictions in different irreducible representations represent a relevant contribution which may encourage experimentalists to check our theoretical conjectures. Finally, the observed strong (weak) dependence of optical phonons on the Al content x in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{P}$ (Refs. 8-10) ($\mathrm{Al}_x\mathrm{In}_{1-x}\mathrm{As}$) (Ref. 16) is suggested to be related to the interference between two sets of oscillators, caused primarily by the lattice relaxation.[17]

II. THEORY OF RAMAN SCATTERING: A CLASSICAL APPROACH

Raman scattering, the inelastic scattering of light from matter, is a process associated with the excitation or deexcitation of various degrees of freedom in the scattering medium. Raman scattering in solids is associated with the creation or annihilation of phonons. An electromagnetic wave of frequency ω_i with electric field $E(t)$ $(=E_0 e^{i\omega_i t})$ incident on a crystal induces an electric dipole moment $\{\mathcal{m}\}$ which corresponds to the modification of the polarizability tensor $\{P\}$:

$$\mathcal{m}_\alpha(t)=\sum_\beta P_{\alpha\beta}E_\beta(t)\ . \tag{1}$$

The Raman-active lattice vibrations are determined by selection rules established by standard group-theoretical methods.[11] It is shown that a phonon can participate in a first-order Raman transition if and only if its irreducible representation is the same as one of the irreducible representations which occurs in the reduction of the representation of the polarizability tensor.

In a perfect AlP (or GaP) crystal (i.e., a crystal with long-range order), the selection rules for the photon-phonon Raman process confine the transitions to the vicinity of the center ($\mathbf{q}\sim\mathbf{0}$) of the Brillouin zone. The presence of defects destroys the long-range order and the momentum-conservation rule is no longer maintained. Because of the *two* important changes, this induces IFORS by phonons which were otherwise Raman inactive. These changes are: (i) The vibrations of the impurity and its neighboring ions will have different values both in phase and in amplitude from corresponding ions elsewhere in the crystal, and (ii) the change in polarizability caused by the displacement of the impurity or its neighbors will be different from the changes induced by the displacement of ions elsewhere in the lattice.

The description of IFORS in crystals has been very elegantly represented in the Green's-function formalism. In this formalism the intensity of linearly polarized Raman scattering for unit solid angle Ω and for unit frequency shift ω_S $(=\omega_i+\omega)$ is explicitly given by[11]

$$I(\omega_i,\omega_s;\Omega)\sim\frac{\hbar\omega_i^4}{2\pi^2c^3}\sum_{\alpha,\beta,\gamma}\sum_{\alpha',\beta',\gamma'}\sum_{l,k,l',k'}n_\alpha n_{\alpha'}E_\beta E^*_{\beta'}\eta(\omega_i-\omega_s)\mathsf{P}_{\alpha\beta,\gamma}(l,k)\cdot\mathsf{P}_{\alpha'\beta',\gamma'}(l',k')\lim_{\zeta\to 0}[\mathrm{Im}\langle lk\gamma|\mathcal{G}(z)|l'k'\gamma'\rangle]\ , \tag{2}$$

where ω_i and ω_s are the frequencies of the incident and scattered light, n_α is the α component of a unit polarization vector parallel to the scattered light, E_β is the β component of the incident field, $\mathcal{G}$ is the Green's-function matrix of the imperfect crystal, η is the thermal occupation number, and c is the speed of light. The term z stands for $\omega^2-i\zeta$ with the limit $\zeta\to 0$ being understood. In Eq. (2) the polarizability tensor due to lattice vibrations is expanded as a function of ionic displacements $\mathbf{u}$ and the only terms $\mathsf{P}_{\alpha\beta,\gamma}(l,k)$ describing the first-order Raman scattering[11] have been retained.

III. NUMERICAL CALCULATIONS, RESULTS AND DISCUSSIONS

A. IFORS in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{P}$: Green's-function calculation

In actual calculations of IFORS for $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{P}$ using Eq. (2), assumptions must be made on the force constant changes induced by defects in order to keep the impurity subspace as small as possible. In the present perturbation $\{L\}$ model, we assume that the long-range Coulomb forces are not affected by the presence of a defect. Only the mass change at the metal-ion site $\{\varepsilon\}$ along with the changes in the nearest-neighbor (NN) short-range interactions $\{t\}$ between the impurity and the host-lattice atoms are considered to be significant. These requirements retain the tetrahedral (T_d) point-group symmetry. In the defect space, there are only five atoms (e.g., the GaP_4 molecule in AlP) involved. These will expand the size of the perturbation matrix to 15×15. By intuition, it is possible to construct 15-dimensional column vectors that can be used as basis functions to reduce the $\mathcal{G}$ and $\mathcal{L}$ matrices into block form, corresponding to the A_1, E, F_2 (Raman-active; see Fig. 1), and F_1 representations of the point-group T_d.

Calculation of the $\langle\underline{\mathcal{G}}\rangle$ matrix requires the evaluation of $\underline{L}[\underline{I}+\underline{\mathcal{G}}^0\underline{L}],^{-1}$ where $\underline{\mathcal{G}}^0$ is the Green's function for the host lattice imbedded in the impurity subspace. In the present study, the elements of the Green's-function matrix $\{\underline{\mathcal{G}}^0\}$ are obtained by incorporating phonons from an eleven-parameter rigid-ion model[14] fitted to the inelastic neutron scattering data of GaP and to the optical data of AlP. The influence of impurity-induced changes on the vibrational properties of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{P}$ is considered in terms of the NN force-constant variation parameter t. In the low-composition limit x, the observed impurity modes are fitted and the values of t are retained to obtain the $\underline{L},\underline{\mathcal{G}}$ matrices and, consequently, the impurity-induced first-order Raman scattering intensities using Eq. (2). The results of our calculations in different Raman-active representations for *Ga*P:Al and *Al*P:Ga are displayed in Figs. 2 and 3.

B. Phonon-mode behavior: MREI model calculation

By properly including the influence of the effective electric field on the motion of the ions in a random isodisplacement model,[15] we have studied the compositional dependence of optical phonons in $Al_xGa_{1-x}P$. Before we analyze the trends of force variations and compare the results with the sophisticated Green's-function method, it would be useful to point out the approximations adopted in the MREI scheme. First, the $A_xB_{1-x}C$ ternary alloy is assumed to be a single unit cell comprising one ion of C, x ions of A, and $1-x$ ions of B interacting with each other by binding forces which depend on x through an adjustable parameter θ. The involved force constants (cf. Table I) are considered to have the same compositional dependence; i.e.,

$$\frac{f_{AC}}{F_{AC}}=\frac{f_{BC}}{F_{BC}}=\frac{f_{AB}}{F_{AB}}=(1-\theta x)\ , \tag{3}$$

where F_{AC}, F_{BC}, and F_{AB} are, respectively, the force-constant parameters between AC, BC, and AB in the limit $x=0$. The second assumption is that all the atoms in a given species vibrate in phase with identical amplitudes, and that the impurity-mode frequencies,

$$\omega_{\rm loc}^2(\underline{B}C:A)=(F_{BC}+F_{AC})/M_A \tag{4a}$$

and

$$\omega_{\rm gap}^2(\underline{A}C:B)=(F_{AC}+F_{BC})/M_B\ , \tag{4b}$$

involve only the masses of the vibrating defect, while the host-lattice atoms are assumed to be at rest. Based on the results obtained for the end member compounds ($x=0$, $x=1$), the MREI model provides the following criteria for the crossover from one- to two-phonon mode behavior:

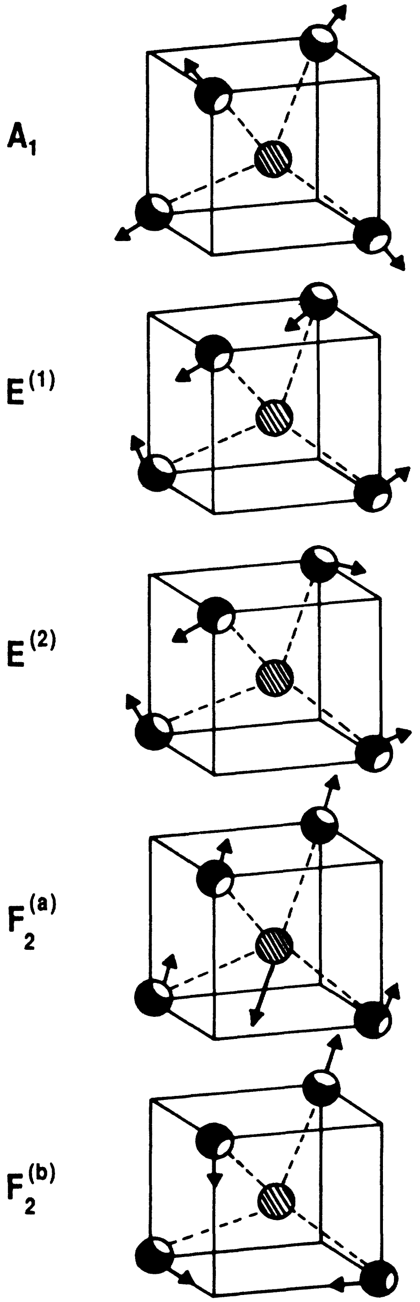

FIG. 1. The substitutional defect Al (Ga) in tetrahedral site of GaP (AlP) crystal and Raman-active symmetry coordinates in a nearest-neighbor defect space.

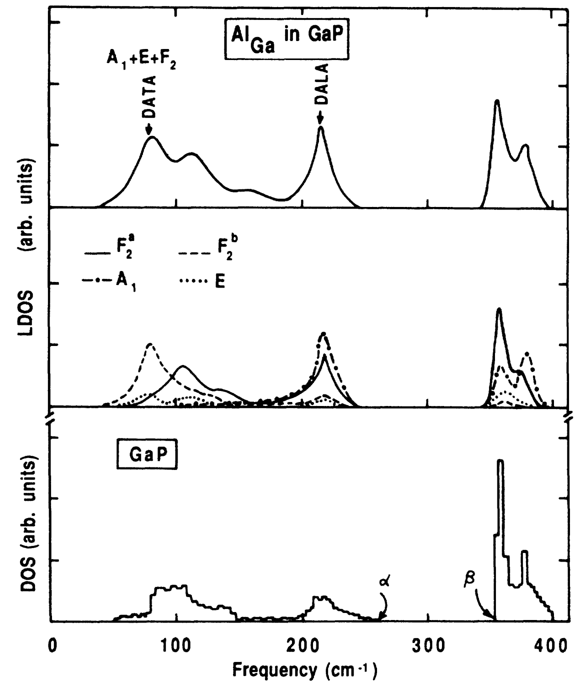

FIG. 2. Calculated local density of states due to Al_{Ga} in GaP with the perturbation-parameter value as given in Table I. The upper panel represent the sum of A_1+E+F_2, whereas in the middle panel we have plotted the individual contributions of A_1-, E-, and F_2-type representations to the scattering intensity. In the lowest panel we have shown the calculated density of states for GaP on the basis of RIM11. The terms α and β represent, respectively, the start and end points of the gap in the phonon density of states.

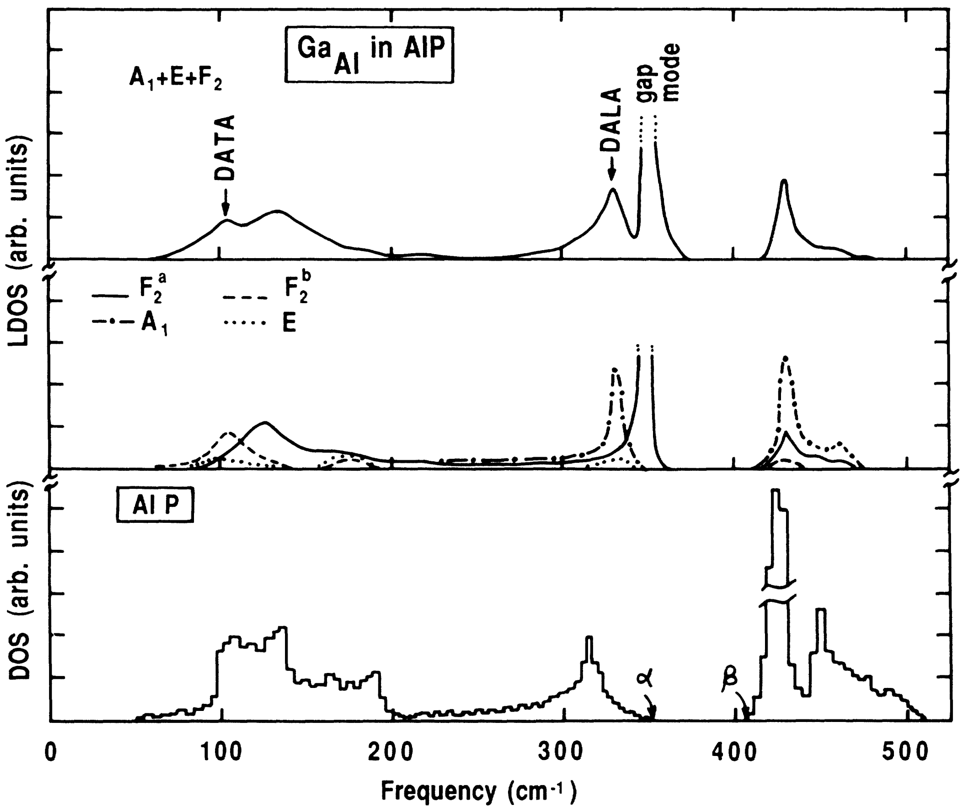

FIG. 3. Same key as Fig. 2 and for Ga$_{\mathrm{Al}}$ in AlP.

$$(F_{AB}+F_{BC})/F_{AC} < M_B/\mu_{AC} \ , \tag{5a}$$

$$(F_{AB}+F_{AC})/F_{BC} > M_C/\mu_{BC} \ . \tag{5b}$$

Here M_A, M_B are the atomic masses, and μ_{BC}, μ_{AC} are the reduced masses. For Al$_x$Ga$_{1-x}$P, the criterion Eq. (5b) is also satisfied which concludes the two-mode behavior.

While calculating the involved *six* MREI model parameters, we have noticed a considerable experimental[7–10] disagreement between results for the dependence of optical phonons on x. There was a general consensus for the localized vibrational mode of Al in GaP (Refs. 7-10) ($\underline{Ga}$P:Al ~ 445 cm^{-1}). However, the value reported by different authors for the gap mode due to Ga in AlP ($\underline{Al}$P:Ga) has a large scatter. In this situation, we have opted to use our Green's-function results of impurity modes to evaluate the MREI model parameters (see Table I). The compositional dependence of optical phonons in Al$_x$Ga$_{1-x}$P were calculated and the results compared against the existing Raman scattering data.[8–10] A perusal of Fig. 4 reveals that although our MREI results are at variance with the Raman values reported earlier by Tsu[8] from the melt-grown Al$_x$Ga$_{1-x}$P, they agree reasonably well with the recent measurements of Bour *et al.*[10] and of Armelles *et al.*[9] At this point it is worth pointing out that the good agreement achieved by the MREI model in Al$_x$Ga$_{1-x}$P is mainly confined to optical

TABLE I. Calculated values of the *six* model parameters used in the modified random isodisplacement model of Ref. 13 to explain the concentration dependence of optical phonons in Al$_x$Ga$_{1-x}$P (see Fig. 4). The force constants are in the unit of 10^5 dyn/cm. The input parameters used are $\varepsilon_{\infty AC}=7.65$ ($\varepsilon_{\infty BC}=8.467$), $\omega_{\mathrm{LO}(\Gamma)AC}=500$ cm^{-1} ($\omega_{\mathrm{LO}(\Gamma)BC}=402$ cm^{-1}), $\omega_{\mathrm{TO}(\Gamma)AC}=440$ cm^{-1} ($\omega_{\mathrm{TO}(\Gamma)BC}=367$ cm^{-1}), $\omega_{\underline{A}C:B}=348$ cm^{-1}, and $\omega_{\underline{B}C.A}=448$ cm^{-1}. The experimental data are taken from the work of Bour *et al.* (Ref. 10).

			Parameters			
F_{BC}	F_{AC}	F_{AB}	Z_{BC}	Z_{AC}	θ	$\Delta f/f^{a}=t$
1.98	1.50	1.70	0.575e	0.710e	−0.35	0.23 (local mode) 0.32 (gap mode)

[a] Force-constant-change parameter derived from the Green's-function theory (see text).

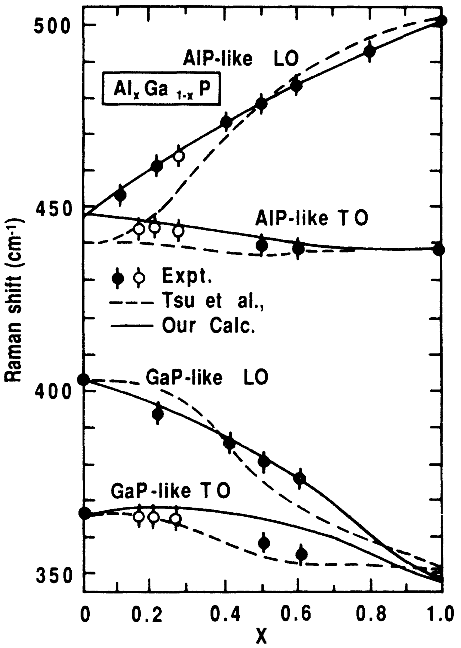

FIG. 4. Calculated fit of the composition dependence of the optical phonons in mixed $Al_xGa_{1-x}P$ using the MREI model with parameters given in Table I. The results are compared with the existing experimental data of Tsu (— — —) (Ref. 8) and Bour *et al.* (◊,◆) (Ref. 10).

phonons in the long-wavelength limit. The reason for this is that it is in that limit that the basic assumptions of the model are most valid. Again, the calculated force variations in the MREI method are found to be very much different from the results derived from the sophisticated Green's-function technique (see Table I). In the calculation of impurity modes, only the masses of vibrating defects are involved [cf. Eqs. (5a) and (5b)] while the host-lattice atoms are assumed to be frozen. On the other hand, in an actual case of a gap mode (e.g., in $\underline{Al}$P:Ga), the *two* (Al and Ga) atoms vibrate in opposite phase and the neglect of the vibrations of host-lattice atoms reflects the basic shortcoming of the MREI model. While the mobile masses involved in the real movements are not well estimated, they are compensated for by adjusting the second-nearest-neighbor force constant $F_{\text{Al-Ga}}$ which is always found to be of the same order of magnitude as the nearest-neighbor force constants (cf. Table I). the discrepancy in the force constant changes with respect to a full lattice-dynamical (Green's-function) treatment is, therefore, not surprising. Again, our Green's-function method has clearly established the observed two-phonon mode behavior in $Al_xGa_{1-x}P$. In the low-frequency region, it predicts (see Figs. 2 and 3) new impurity-induced features [especially the defect-activated longitudinal- and transverse-acoustical (DALA, DATA) modes] that can be observed by the polarization-dependent Raman scattering experiments. Here, it is worth pointing out that our recent calculations on $Al_xGa_{1-x}As$ (Ref. 18) have provided reasonably good agreement with most of the impurity-activated Raman features observed by Xiao-jun and Xin-yi.[19]

To predict the *one*- or *two*-phonon-mode behavior in ternary compounds, Eqs. (5a) and (5b) are frequently used in the literature. Since the effects of force-constant changes in MREI are neglected, the above criterion has been disobeyed in some cases. In ternary compounds $A_xB_{1-x}C$, we feel that the change in optical phonons with x is caused by the interference between the *two* (AC and BC) sets of oscillators. With the presence of A (or B) in BC (or AC) such an interference may be affected by the lattice relaxation. The larger the lattice distortion, the greater the possibility of interference, and this may also cause charge transfer from a weaker to the stronger bond. In the $Al_xIn_{1-x}As$ ternary compound, for example, when the larger-size impurity In occupies a smaller-size Al atom in *Al*As, our total-energy calculation in the bond-orbital model predicts an outward ($\sim 5.32\%$) relaxation.[15] A charge transfer from InAs$\rightarrow$AlAs is expected and the transfer can provide strength to the polar character of the LO mode of AlAs at the expense of weakening the same for InAs. The observed weak dependence of optical modes of InAs in $Al_xIn_{1-x}As$ (Ref. 16) lend support to the above arguments. On the other hand, for those mixed crystals (e.g., $Al_xGa_{1-x}P$, $Al_xGa_{1-x}As$,[19] $Cd_xHg_{1-x}Te$,[20] etc.) where the effects of lattice relaxation are much smaller, one would expect the possibility of weak interference between the sets of oscillators that could result in either no or minimum charge transfers. This means that in the above compounds, the LO-TO splitting over a large range of composition will remain much larger, which supports the experimental observations.

IV. CONCLUSION

We have calculated the polarization-dependent IFORS intensities for a ternary compound $Al_xGa_{1-x}P$ (in the low-concentration limit) by using an average Green's-function theory. Despite the choice of a simplified perturbation model, it is demonstrated that the Green's-function formalism does predict the qualitative features in the optical-phonon frequency region (two-phonon-mode behavior) observed in recent Raman[7-10] measurements. Due to the small lattice distortion involved in $Al_xGa_{1-x}P$, the effect of impurities has provided the localized vibrational states and the defect-activated features in the low-frequency region, whose specific Raman effect may allow us the precise description of its environment. Extensive measurements in the low-frequency region are necessary not only to test our theoretical conjectures, but also for improvements, if needed, in the present theoretical formalism. Although the simple MREI model does explain the compositional dependence of optical phonons, the values of force constants used to evaluate the impurity modes (especially the gap modes) are physically unrealistic. Additional theoretical work is needed to make the MREI model more realistic.

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