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Local-mode frequencies due to substitutional impurities in zinc-blende-type crystals. II. Effect of force-constant changes

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A model which has earlier been seen to be successful in explaining the main features of the infrared absorption due to Be impurities in CdTe has been employed to understand the local-mode frequencies in different III-V and II-VI semiconducting compounds. The effects of force-constant changes due to various impurities in a large class of the compound semiconductors have been studied. The local-mode frequencies have been calculated and discussed with the existing experimental and theoretical data. It has been observed that in the case of isoelectronic impurities the force-constant changes are well within ±20%, whereas in the case of other impurities, e.g., Li isotopes in III-V and II-VI compounds and Al impurities in II-VI compounds, the force-constant changes are as large as ±58%. The force-constant changes are similar for the different isotopes of an impurity atom. The differences in the ionic radii of the impurity and the host ions are not suggestive of the probable force-constant changes in these compound semiconductors.

I. INTRODUCTION

It is quite well known that the vibrational spectrum of a crystal containing a small concentration of impurities often exhibits the occurrence of modes whose frequencies lie within the band or in the gap, or lie outside the vibrational-frequency spectrum of the perfect crystal. These exceptional modes, in fact, depend on the nature of the impurity-lattice interaction. Quasilocalized or resonance modes may occur if the impurity is too heavy or weakly bound to the host lattice. The frequencies of the resonance modes lie within the band-mode region and they characterize themselves by large vibrational amplitudes of the impurity or its immediate neighbors. Localized or bound states may also appear due to very light impurities or impurity ions strongly bound to the host lattice. The frequencies of these modes lie outside the range of allowed phonon frequencies of the host crystal. These are nonpropagating modes and their amplitudes fall faster than exponentially as one moves away from the defect. When the frequencies of these modes are greater than the maximum phonon frequency they are called localized modes, and if they lie within the forbidden gaps of the phonon spectrum they are named gap modes. There is, in fact, no fundamental distinction between a localized mode and a gap mode.

In order to observe these impurity modes directly, a wide variety of experimental techniques, viz., impurity-induced infrared absorption, Raman spectroscopy, specific-heat measurements, tunneling between superconductors, Mössbauer effect and neutron scattering, etc., have been extensively used.[1] Experimental studies of local modes have been made for a large number of systems. At first the experimental investigations were confined to the vibrations of H^- and D^- ions (U centers) in the alkali halides[2,3] and the alkaline-earth fluorides.[4] In the case of elemental semiconductors particular attention was given to boron[5] and carbon[6] impurities in silicon. More recently, the list has grown to include the study of various impurities both in the elemental and the group semiconductors.[7]

In the earlier theoretical studies[8,9] the Einstein model or the Born–von-Kármán model were used in the case of diatomic cubic lattices with nearest-neighbor interactions to study the influence of a single defect on the lattice dynamics of ionic crystals. A phenomenological linear diatomic chain model[10] has been utilized to predict the local-mode frequencies in a large class of systems. A molecular model[11] has also been applied to calculate the local-mode frequencies due to U and F centers in alkali halides.[12] However, its application to impurity modes in zinc-blende-type crystals[13,14] did not provide very convincing results. Considerable recent refinements in the theory and the use of more realistic models for the lattice dynamics of host lattices and defects have led to a mutual stimulation between theory and experiment resulting in a good understanding of the phenomena.

From the theoretical point of view, the most natural way to analyze the experimental results on impurity modes is the use of the Green's-function technique. In the case of strongly localized states one may assume that the perturbation extends over a few neighbors only and one can, thus, perform simple calculations. Actual calculations[15] in zinc-blende-type crystals have, however, been hampered due to the lack of knowledge of the real phonon spectrum (through neutron spectroscopy).

Most of the previous work[16,17] based on a Green's-function method used the isotopic-defect approximation (IDA). Although the method does provide a qualitative explanation of experimental results, nevertheless for a quantitative agreement it is necessary to consider the effects of the force-constant changes caused by the impurity ion in the host lattice. The inclusion of force-constant changes would make, no doubt, the computational job more difficult, but they are worth pursuing since they might allow more information to be extracted from infrared, Raman, or other optical measurements. Recent work on impurity-doped metals,[18,19] alkali halides,[19] and cesium halides[20] has shown that alterations in short-range interactions sometimes contribute predominantly to the physical properties of the impure crystals. Since, through neutron spectroscopy, extensive data on the phonon spectrum of various[21–25] III-V and[26–28] II-VI compound semiconductors crystallizing in the ZnS (*c*) structure have been accumulated in the literature within the last few years, it is worthwhile to study the behavior of impurities in these group semiconductors with a realistic theoretical approach.

In an earlier paper[17] (hereafter called I), a second-neighbor-ionic (SNI) model was employed for describing the phonons of the perfect lattice and a mass-defect model was assumed for determining the local-mode frequencies. In a later paper[29] we have included also the changes in the nearest-neighbor force constants and noted that the model was moderately successful in explaining the observed infrared absorption due to a low concentration of Be impurities in CdTe. In the present paper, we perform a theoretical analysis of the impurity modes by considering the changes in the nearest-neighbor central force constant due to various impurities in a number of III-V and II-VI compound semiconductors.

The paper is organized into four sections. In Sec. II we briefly describe the basic theoretical considerations relating the lattice dynamics of perfect and imperfect zinc-blende-type crystals. Section III deals with the numerical computation of the local-mode frequencies due to various force-constant changes and the comparison of the results with those of experimental and other theoretical findings. The conclusions are contained in Sec. IV.

II. THEORETICAL CONSIDERATIONS

In order to study the dynamics of an imperfect crystal by the Green's-function method, a detailed knowledge of the frequencies and polarization vectors of the phonons in the perfect crystal is very much needed. Here we would like to remark that for a meaningful picture of the physical situation around the defect in a perturbation model, the choice of the lattice-dynamical model should be such that it should not produce any conceptual difficulty.

A. Lattice dynamics of perfect crystals

The phenomenological force-constant model,[15] rigid-ion model,[30–38] shell model,[21–23,25,26] and valence shell model[28] have been extensively used to study the lattice dynamics of crystals with the zinc-blende structure. In a most simple lattice-dynamical model one may consider only the short-range interactions and may neglect the Coulomb forces as well as the polarization forces of the ions. But the difficulty with this model is that it does not reproduce the real phonon-dispersion curves. This, in turn, affects the calculation of the involved Green's functions and thereby the impurity modes. The conventional dipolar shell model is also inadequate in several respects. A large number of disposable parameters are required to fit the neutron data and the known physical constants. Some of these parameters are not always realistic. Also, the shell model loses its significance when one studies the band effects of narrow-gap semiconductors. Ferriera[39] has pointed out the shortcomings of the shell model and has proposed a new definition of the shell. Furthermore, the difficulties encountered in describing the impurity in a deformation-dipole model or a shell model in alkali halides are well known.[40] On the other hand, no conceptual difficulty exists if we chose a nearest-neighbor perturbation model in the case of Kellermann's rigid-ion lattice.[41]

Keeping in view the aforementioned points, we have selected a seven-parameter SNI model[33] to study the lattice vibrations of perfect zinc-blende-type crystals. It is, in fact, an extension of the four-parameter rigid-ion model proposed earlier by Rajagopal and Srinivasan.[30] The SNI model incorporates a combination of the classical treatment by Kellarmann[41] for the electrostatic interactions and the treatment of the diamond lattice by Smith[42] for the nonelectrostatic part. The electrostatic part includes long-range Coulomb interactions, whereas the nonelectrostatic part of the model includes force constants up to second neighbors.

In the framework of the adiabatic and harmonic approximations the equation for the vibrational amplitudes ϕ in the perfect lattice reads[36]

$$(\overleftrightarrow{L}^0 - \omega^2\overleftrightarrow{I})\vec{\phi} = \vec{0} , \tag{1}$$

where $\overleftrightarrow{L}^0$ is the dynamical matrix of the perfect rigid-ion lattice (in $\vec{q}$ space) and is given by

$$L^0_{xy}(\vec{q};\,\kappa\kappa') = \{1/[m(\kappa)m(\kappa')]^{1/2}\} \times [D^s_{xy}(\vec{q};\,\kappa\kappa') - D^C_{xy}(\vec{q};\,\kappa\kappa')] , \tag{2}$$

with $D^s_{xy}(\vec{q};\,\kappa\kappa')$ and $D^C_{xy}(\vec{q};\,\kappa\kappa')$ as the short-range part and the long-range Coulomb part of the dynamical matrix, respectively; $m(\kappa)$ $(\kappa = 1, 2)$ denote the masses of the two atoms in a unit cell. The matrix elements for the short-range interaction depend on the two first-neighbor (α, β) and eight second-neighbor (μ_κ, ν_κ, λ_κ, and δ_κ) force constants. However, the number of parameters have been reduced to six by taking $\mu = \nu$ in concurrence with the central-force model of Smith. The elements of the long-range Coulomb interaction matrix depend on the effective charge and the lattice parameters of the systems.

The elements of the short-range part of the dynamical matrix are given by[31]

$$\begin{aligned} D^s_{xx}(\vec{q}\,;\,\kappa\kappa) &= 4[\alpha + \lambda_\kappa(1 - \cos\pi q_y \cos\pi q_z) \\ &\qquad + \mu_\kappa(2 - \cos\pi q_x \cos\pi q_y - \cos\pi q_x \cos\pi q_z)] \;, \\ D^s_{xy}(\vec{q}\,;\,\kappa\kappa) &= 4\mu_\kappa \sin\pi q_x \sin\pi q_y = D^s_{yx}(\vec{q}\,;\,\kappa\kappa) \;, \\ D^s_{xx}(\vec{q}\,;\,\kappa\kappa') &= -\,\alpha(a+b+c+d) \\ &= D^s_{yy}(\vec{q}\,;\,\kappa\kappa') = D^s_{zz}(\vec{q}\,;\,\kappa\kappa') \;, \\ D^s_{xy}(\vec{q}\,;\,\kappa\kappa') &= -\,\beta(a+b+c-d) = D^s_{yx}(\vec{q}\,;\,\kappa\kappa') \;, \end{aligned}$$

where

$$\begin{aligned} a &= \exp[\tfrac{1}{2}i\pi(q_x + q_y + q_z)] \;, \\ b &= \exp[\tfrac{1}{2}i\pi(q_z - q_x - q_y)] \;, \\ c &= \exp[\tfrac{1}{2}i\pi(q_y - q_x - q_z)] \;, \\ d &= \exp[\tfrac{1}{2}i\pi(q_x - q_y - q_z)] \;. \end{aligned} \qquad (3)$$

The remaining elements can be obtained by cyclic permutations of the indices and by using the fact that

$$D^s_{xy}(\vec{q}\,;\,21) = D^{s*}_{xy}(\vec{q}\,;\,12) \;, \qquad (4)$$

where $D^{s*}_{xy}(\vec{q}\,;\,12)$ is the Hermitian conjugate of $D^s_{xy}(\vec{q}\,;\,12)$.

The expressions for the Coulomb coupling coefficients obtained by Kellermann for the rocksalt structure have been modified by Cochran[43] for the diamond structure and by Merten[44] for the zinc-blende lattice. The elements of the long-range part of the dynamical matrix have already been given in an earlier paper.[36]

The solutions of Eq. (1) give the characteristic frequencies ω as a function of the wave vector $\vec{q}$, i.e., the dispersion curves of the host lattice. For each value of ω, there exists a set of polarization vectors that satisfy the familiar orthogonality and closure relations.

In the computer calculations for the lattice vibrations of perfect crystals, the translational vector of the reciprocal space was divided into 16 equal parts to give rise to a grid of 4096 equally spaced points inside the first Brillouin zone. The calculated dispersion curves in the various III-V and II-VI compound semiconductors have been reported elsewhere.[35–38]

B. Lattice dynamics of imperfect crystals

Let $\overleftrightarrow{P}(\omega^2)$ be the perturbation on the dynamical matrix $\overleftrightarrow{L}^0$ of the perfect crystal that accounts for the change of ionic mass and the changes of coupling coefficients due to the substitutional impurity ions. The equation for the vibrational amplitudes $\vec{\psi}$ in the imperfect lattice reads

$$[\overleftrightarrow{I} + \overleftrightarrow{G}^0(z)\, \overleftrightarrow{P}(\omega^2)]\vec{\psi} = 0 \;, \qquad (5)$$

where $\overleftrightarrow{G}^0(z) = (\overleftrightarrow{L}^0 - z\overleftrightarrow{I})^{-1}$ is the Green's-function matrix for the perfect lattice, and $z = \omega^2 + i\zeta$ is the complex squared frequency in the limit $\zeta \to 0^+$.

For a low concentration of impurities it can safely be assumed that the atomic interactions in the imperfect lattice do not differ basically from those of the host lattice. It is, therefore, sufficient to describe the defects by considering the changes in atomic masses and nearest-neighbor interactions only. For the case of a single substitutional impurity in the lattice, the non-zero elements of the perturbation matrix lie only in the impurity space (the space occupied by the impurity and its immediate neighbors).

The condition for the occurence of nontrivial solutions for the frequencies of the impurity modes (localized, gap, or resonance) is that the real part of the secular determinant vanish, i.e.,

$$\mathrm{Re}\det|\overleftrightarrow{I} + \overleftrightarrow{g}(z)\overleftrightarrow{p}(\omega^2)| = \mathrm{Re}D(z) = 0 \;, \qquad (6)$$

where $\overleftrightarrow{g}(z)$ and $\overleftrightarrow{p}(\omega^2)$ are the Green's function $[\overleftrightarrow{G}(z)]$ and the perturbation $[\overleftrightarrow{P}(\omega^2)]$ matrices in the impurity-space, respectively.

Perturbation matrix and Green's functions

The isolated impurity in a zinc-blende-type crystal has been described in the deLaunay's lattice-dynamical model[45] for the diamond lattice. In this model, let f be the force constant associated with the radial (central) part of the nearest-neighbor interaction and f' the force constant associated with the angular part. The nearest-neighbor force constants (α, β) defined in the SNI lattice-dynamical model are related with the deLaunay's model parameters (f, f') by the relations

$$\alpha = \tfrac{1}{3}(f + 2f') \text{ and } \beta = \tfrac{1}{3}(f - f') \;.$$

With the substitution of an impurity in the host-crystal, both the atomic mass and the nearest-neighbor interactions (f, f') are assumed to be changed. The changes are described by the parameters

$$\epsilon(\pm) = [m'(\pm) - m(\pm)]/m(\pm) \;;$$

$$\lambda = \Delta f/m(\pm) \quad\text{and}\quad \lambda' = \Delta f'/m(\pm) \;.$$

The elements of the perturbation matrix of dimension 15×15 are

$$
\begin{aligned}
&p_{ii}(\vec{0}, \vec{0}) = -\epsilon\omega^2 + \tfrac{4}{3}(\lambda + 2\lambda') , \\
&p_{ij}(\vec{0}, \vec{0}) = 0 , \\
&p_{ii}(\vec{0}, \vec{R}_n) = -\tfrac{1}{3}\chi^{1/2}(\lambda + 2\lambda') , \\
&p_{ij}(\vec{0}, \vec{R}_n) = -\tfrac{1}{3}\chi^{1/2}(\lambda - \lambda')n_i n_j , \\
&p_{ii}(\vec{R}_n, \vec{R}_n) = \tfrac{1}{3}\chi(\lambda + 2\lambda') , \\
&p_{ij}(\vec{R}_n, \vec{R}_n) = \tfrac{1}{3}\chi(\lambda - \lambda') n_i n_j , \quad i, j = 1, 2, 3 .
\end{aligned}
\tag{7}
$$

Here $\chi = m(\pm)/m(\mp)$ is the ratio of the masses of the ions of the two sublattices; $\vec{R}_n = \frac{1}{2}a(n_1, n_2, n_3)$ is the lattice vector of the nearest-neighbor of the impurity site; and the upper signs in ϵ, λ, λ', and χ are taken when the impurity occupies a positive ion site and the lower signs when it occupies a negative-ion site.

In order to solve Eq. (6) it is not necessary to work with the full 15×15 matrix. The decomposition of the total representation into the various irreducible representations for an impurity site with T_d symmetry is[46, 47]

$$\Gamma(T_d) = E + A_1 + F_1 + 3F_2 . \tag{8}$$

The impurity modes in the far-infrared absorption involve only those linear combinations of defect-space displacements which transform according to the F_2 irreducible representation. The perturbation matrix in the F_2 irreducible representation is

$$
P_{F_2}(\omega^2) = \frac{1}{3}\begin{pmatrix}
-3\epsilon\omega^2 + 4(\lambda + 2\lambda') & -2\chi^{1/2}(\lambda + 2\lambda') & -2\sqrt{2}\chi^{1/2}(\lambda - \lambda') \\
-2\chi^{1/2}(\lambda + 2\lambda') & \chi(\lambda + 2\lambda') & \sqrt{2}\chi(\lambda - \lambda') \\
-2\sqrt{2}\chi^{1/2}(\lambda - \lambda') & \sqrt{2}\chi(\lambda - \lambda') & \chi(2\lambda + \lambda')
\end{pmatrix} . \tag{9}
$$

Similarly, the Green's-function matrix in the impurity space in the F_2 irreducible representation is

$$
g_{F_2}(\omega^2) = \begin{pmatrix}
g_1(\pm) & 2g_3(\pm) & 2\sqrt{2}g_4(\pm) \\
2g_3(\pm) & g_2(\pm) + 2g_5(\pm) + g_6(\pm) & 2g_7(\pm) \\
2\sqrt{2}g_4(\pm) & 2g_7(\pm) & g_2(\pm) - g_6(\pm) - g_7(\pm) - 2g_8(\pm)
\end{pmatrix} , \tag{10}
$$

where

$$
\begin{aligned}
&g_1(\pm) = g_{xx}(000; 000) , \\
&g_2(\pm) = g_{xx}(111; 111) , \\
&g_3(\pm) = g_{xx}(000; 111) , \\
&g_4(\pm) = g_{xy}(000; 111) , \\
&g_5(\pm) = g_{xx}(111; -1-11) , \\
&g_6(\pm) = g_{zz}(111; -1-11) , \\
&g_7(\pm) = g_{xy}(111; -1-11) , \\
&g_8(\pm) = g_{xz}(111; -1-11) .
\end{aligned}
$$

In most of the impurity-host systems[18–20] the angular force-constant changes have been seen to be an order of magnitude smaller than the central ones; we therefore assume that $\lambda' = 0$. In earlier studies this model has been found to be successful in understanding the observed infrared absorption due to a low concentration of Be substitutional impurities in CdTe.[29]

The frequency of an impurity mode (resonant, gap, or localized) in the infrared-active F_2 irreducible representation in a zinc-blende-type crystal is given by

$$\mathrm{Re}\, D_{F_2}(z) = 0 ,$$

where

$$
\begin{aligned}
D_{F_2}(z) = {}& [1 - \epsilon\omega^2 g_1(\pm)]\{1 + \tfrac{1}{3}\chi\lambda[3g_2(\pm) + 2g_5(\pm) - g_6(\pm) + 2g_7(\pm) - 4g_8(\pm)]\} \\
& + \tfrac{4}{3}\lambda\{g_1(\pm) - 2\chi^{1/2}[g_3(\pm) + 2g_4(\pm)] + \chi\epsilon\omega^2[g_3(\pm) + 2g_4(\pm)]^2\} .
\end{aligned}
\tag{11}
$$

III. NUMERICAL COMPUTATIONS

A. Computation of lattice Green's functions

In order to analyze the experimental results on impurity modes in zinc-blende-type crystals we have incorporated the eigenvalues and the eigenvectors of the phonon states as determined by the SNI model using IBM7044/1401 computers. A staggered-bin averaging procedure suggested by Sievers *et al.*[48] has been followed for the numerical

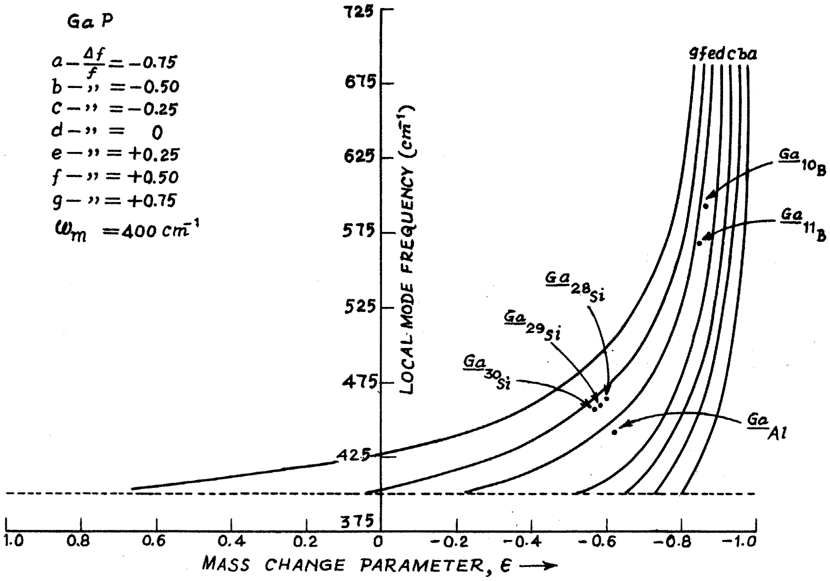

FIG. 1. Plot of the local-mode frequencies vs mass-change parameter with an appreciable change of force constants for positive impurities in GaP. Dots show the experimentally observed frequencies.

integration of the real part of the Green's functions. In actual practice, the frequency increment used is of vital importance, especially when a finite number of $\vec{q}$ points in the Brillouin zone has been used. A too small value of the frequency increment will cause spurious fluctuations in the Green's function, while with a too large value the frequency-dependent nature of the Green's function will be lost. With the present choice of 4096 uniformly distributed $\vec{q}$ points inside the Brillouin zone, a value (ranging from 0.32 to 0.35) of the frequency increment in units of bin was found to be appropriate for all the III-V and II-VI semiconductor compounds under study. For details we refer to an earlier paper.[29]

B. Local-mode frequencies

We now consider Eq. (11) to determine the impurity modes in zinc-blende-type crystal lattices. For $\lambda = 0$, Eq. (11) reduces to the isotopic-defect-approximation (IDA) and we may have a rough idea

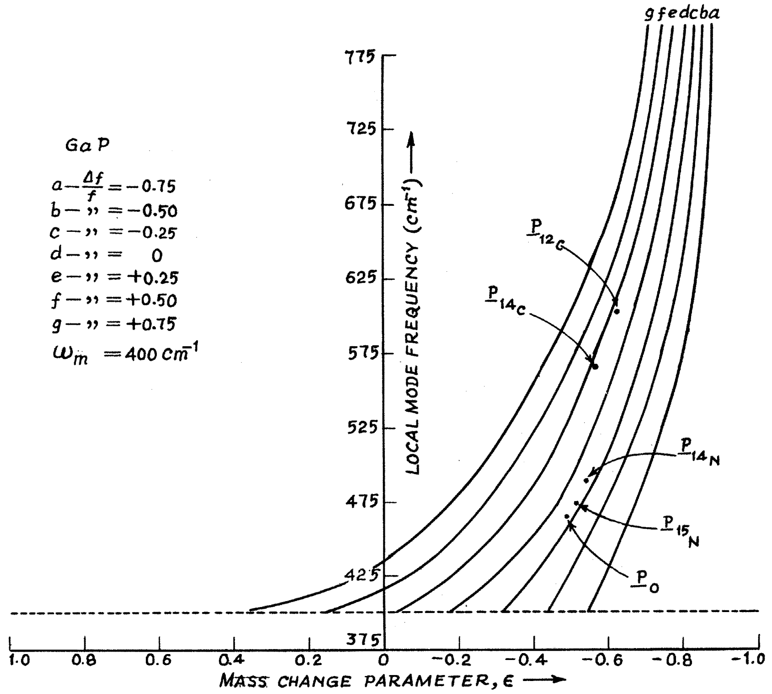

FIG. 2. Plot for the local-mode frequencies vs mass-change parameter with an appreciable change of force constants for negative impurities in GaP. Dots show the experimentally observed frequencies.

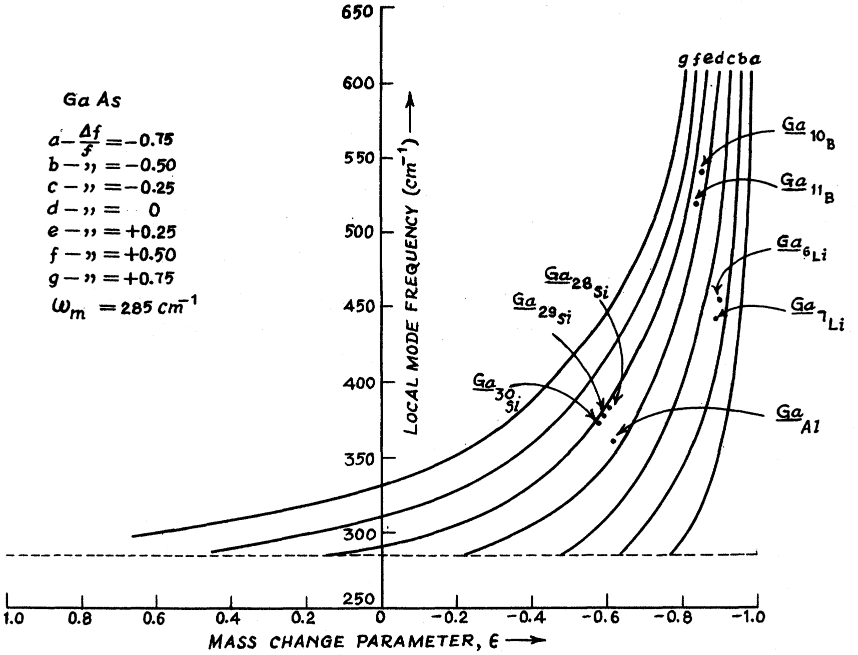

FIG. 3. Plot for the local-mode frequencies vs mass-change parameter with an appreciable change of force constants for positive impurities in GaAs. Dots show the experimentally observed frequencies.

regarding the trends of force-constant changes in impurity-host systems. The effect of force-constant softening is to push the local-mode frequency towards the band edge, whereas the opposite is the case with force-constant hardening. For appreciable force-constant changes the variations of the local-mode frequencies as a function of mass-defect parameter have been studied in detail.

Some of the representative curves for the replacement of anions or cations have been displayed in Figs. 1–8. Explicit calculations have been performed for GaP, GaAs, GaSb, InSb, InAs, ZnSe, ZnTe, ZnS, and CdTe. A list of local-mode frequencies due to various impurities detected so far in III-V and II-VI semiconductor compounds has been given in Table I. In this table we have also listed our earlier results obtained in the IDA and the necessary force-constant changes required to reproduce the experimental data in various impurity-host systems.

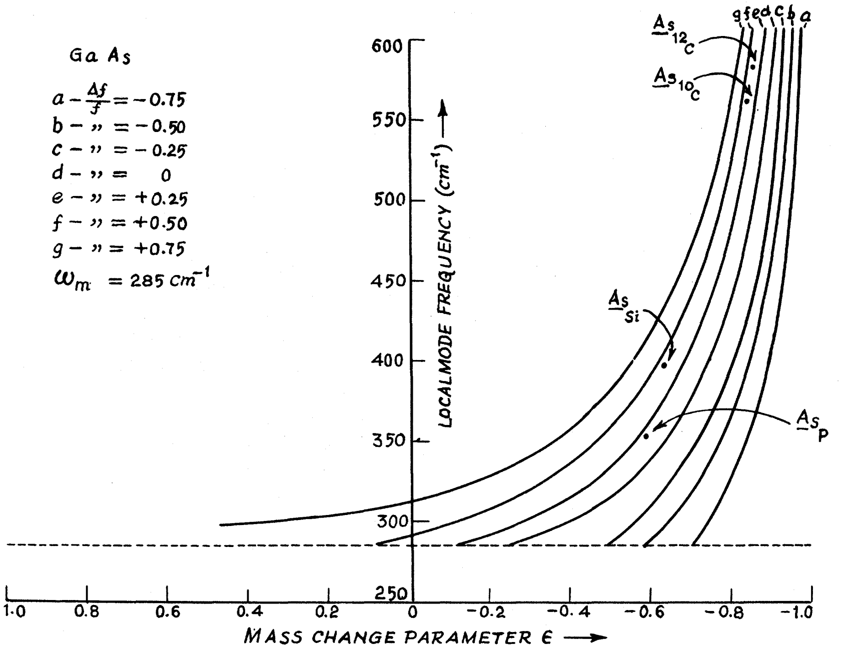

FIG. 4. Plot for the local-mode frequencies vs mass-change parameter with an appreciable change of force constants for negative impurities in GaAs. Dots show the experimentally observed frequencies.

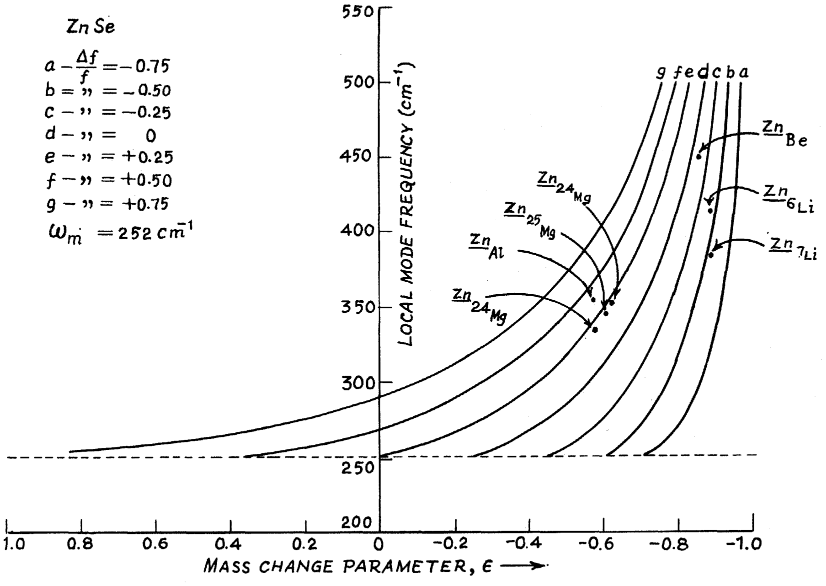

FIG. 5. Plot for the local-mode frequencies vs mass-change parameter with an appreciable change of force constants for positive impurities in ZnSe. Dots show the experimentally observed frequencies.

C. Comparison with experimental and other theoretical works

1. III-V compound semiconductors

a. GaP. A large amount of infrared data on localized modes due to various impurities in GaP exist in the literature.[49–53] Unfortunately, the interpretations of the observed infrared peaks due to impurities are not unique. Very recently, Thompson and Newman[54] have resolved the uncertainties in the previous experimental results by performing extensive experimental observations on a large number of samples. Our results of lattice-dynamical calculations confirm their assignment. The observed separations between adjacent peaks due to boron, silicon, nitrogen, and carbon isotopes are in very good agreement with the calculated values. For Al, B, and Si impurities that occupy the Ga site in GaP, the IDA values are smaller than the observed ones and we find a stiffening of force constants of about (18–40)% (Table I). For impurities replacing the P site we find a hardening in the coupling coefficient of about 21% due to C and a softening of about 15% due to O and N impurities. Recent calculations by Gaur *et al.*[55] in the IDA using a four-parameter rigid-ion model give results similar to ours except in the case of boron isotopes. In order to understand their experimental results of the local-mode frequencies due to nitrogen isotopes, Thompson and Nicklin[56] have obtained very approximate results which are

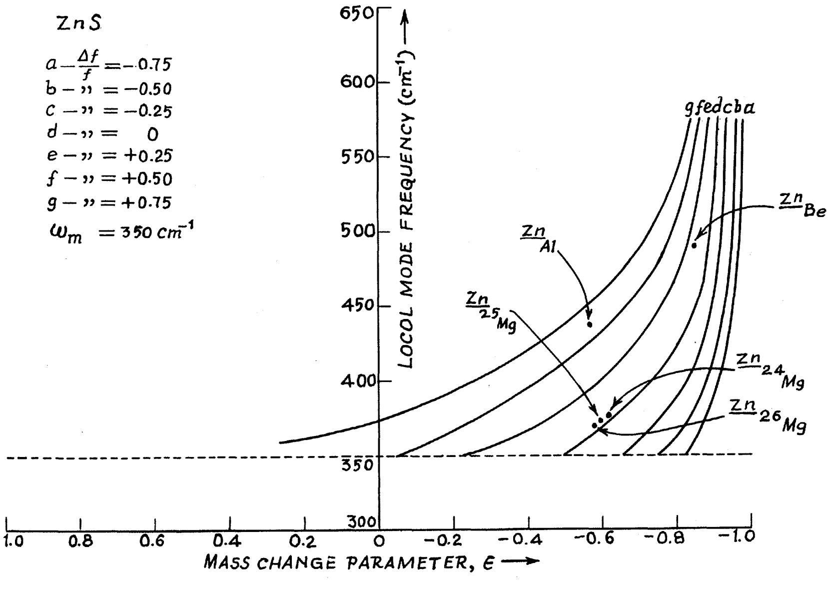

FIG. 6. Plot for the local-mode frequencies vs mass-change parameter with an appreciable change of force constants for positive impurities in ZnS. Dots show the experimentally observed frequencies.

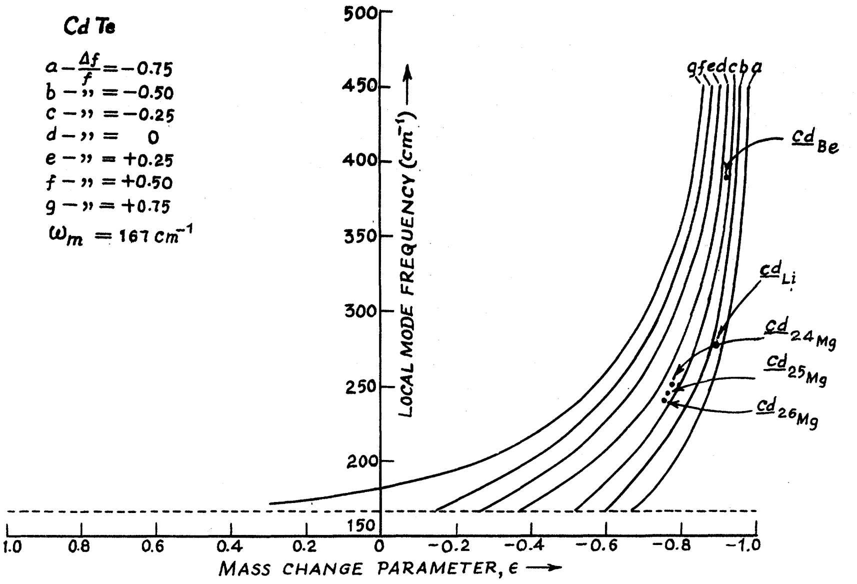

FIG. 7. Plot for the local-mode frequencies vs mass-change parameter with an appreciable change of force constants for positive impurities in CdTe. Dots show the experimentally observed frequencies.

in disagreement with ours and those of other workers.[55]

b. GaAs. A perusal of Table I gives an idea of the trends of force-constant changes due to various impurities in GaAs. In order to achieve the observed local-mode frequencies due to Al, B, and Si isotopes that occupy the Ga site, our results suggest a hardening of force constants of about (5–23)%. Again, for C, Si, and P impurities that replace the As site, we find a hardening of force constants of about (18–40)%. The local-mode frequencies due to Li isotopes differ significantly from the experimental data. A softening of the force constant of about 43% is found for the substitutional Li isotopes. For impurities that replace the Ga atom our results are corroborated by Grimm *et al.*[15] who have performed calculations using a Green's-function theory but employing a very simple lattice-dynamical model. However, in some cases our results do not tally with those of Gaur *et al.*[55] For example, we predict a hardening in the force constant for Al impurities whereas the results of Gaur *et al.* show a softening in the force constant. Also our result for P impurities replacing the As site is in agreement with that of Grimm[15] and of Govindarajan and Haridasan[16] but is in disagreement with that of Gaur *et al.*, who have predicted no force-constant change in this impurity-host

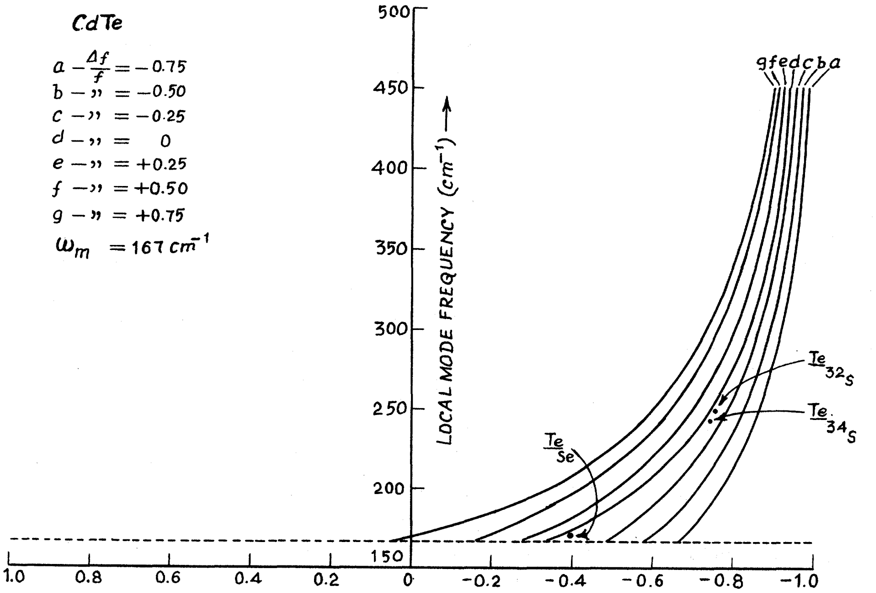

FIG. 8. Plot for the local-mode frequencies vs mass-change parameter with an appreciable change of force constants for negative impurities in CdTe. Dots show the experimentally observed frequencies.

TABLE I. Local-mode frequencies due to substitutional impurities in zinc-blende-type crystals. The local-mode frequencies in the IDA and the relative changes of central-force constant for impurities in various III-V and II-VI semiconductor compounds are given in columns 3 and 4, respectively. Substituted atoms have been underlined.

System	Local-mode frequency (cm^{-1}) Expt.	Calc. in IDA	$\Delta f/f$	Source of experimental data
		(i) III-V compounds		
GaP : ^{10}B	593.6 (592)	534	0.18	a(b)[c]
GaP : ^{11}B	571 (569)	515	0.18	a(b)[c]
GaP : Al	444.7	415	0.19	a
GaP : ^{28}Si	464.9	410	0.39	d
GaP : ^{29}Si	461.1	407		d
GaP : ^{30}Si	456.6 (495)	404		d(a)[c]
GaP : ^{12}C	606.2 (527)	560	0.21	a(b)[c]
GaP : ^{14}C	564	530		a
GaP : ^{14}N	488	517	−0.15	a
GaP : ^{15}N	472	502	−0.15	a
GaP : O	464	488	−0.13	a
GaAs : ^{6}Li	451	650	−0.43	a
GaAs : ^{7}Li	442	607		a
GaAs : ^{10}B	540	527.5	0.09	a
GaAs : ^{11}B	517	507.5		a
GaAs : Al	362	355	0.05	a
GaAs : ^{28}Si	384	345	0.23	e(a)
GaAs : ^{29}Si	378.5	339		e
GaAs : ^{30}Si	373.5	334		e
GaAs : Si	399	348	0.39	a
GaAs : P	355	335	0.18	a
GaAs : ^{12}C	582.4	485	0.40	f
GaAs : ^{13}C	561.2	465		f
GaSb : Al	316.7	315	0.012	a
GaSb : P	324	303	0.18	a
GaSb : As	240	242	−0.017	a
InSb : Al	296	302	−0.04	a
InSb : Ga	196	206	−0.08	a
InSb : P	293	270	0.19	a
InSb : As	200	199	0.008	a
InAs : Ga	240	243	−0.02	a
InAs : P	295	302	−0.05	g
		(ii) II-VI compounds		
ZnSe : Be	450	487	−0.13	a
ZnSe : ^{24}Mg	352	323	0.20	a
ZnSe : ^{25}Mg	345	318	0.19	a
ZnSe : ^{26}Mg	334	313	0.19	a
ZnSe : Al	359	305	0.38	a
ZnSe : S	297	290	0.05	a
ZnTe : Be	415	438	−0.08	a
ZnTe : Al	313	260	0.52	a
ZnTe : S	269	279	−0.09	a
ZnS : Be	490	455	0.16	a
ZnS : ^{24}Mg	380	372	0.07	a
ZnS : ^{25}Mg	377.5	369		a
ZnS : ^{26}Mg	374	366		a
ZnS : Al	438	363	0.58	a
CdTe : Be	391	397	−0.05	a
CdTe : ^{24}Mg	249	261	−0.12	a
CdTe : ^{25}Mg	245	259		a
CdTe : ^{26}Mg	241	256		a
CdTe : ^{32}S	249	253	−0.04	a
CdTe : ^{34}S	244	248		a
CdTe : Se	170	173	−0.02	a

[a] Reference 7.

[b] Reference 51.

[c] The values given in parentheses are not used in calculations.

[d] Reference 54.

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system. Molecular-model calculations are found to be at variance with lattice-dynamical calculations.[14]

c. GaSb *and indium compounds* (InAs *and* InSb). Al, P, and As impurities in GaSb; Ga and P in InAs; and Al, Ga, P, and As impurities in InSb are isoelectronic impurities. One may expect the IDA to give good results. From Table I we observe that there is a hardening in force constants of about 19% due to P impurities in GaSb and InSb, but a softening in the force constant of about 5% in InAs. For As impurities in GaSb, however, the calculations by Gaur *et al.*[55] yield results similar to ours, whereas their results for P and Al impurities are at variance not only with ours but also with those of others.[16] The results for Ga and P impurities in InAs are in line with those of earlier workers.[55,57]

2. *II-VI compound semiconductors*

Infrared studies of several light impurities in various Zn-Cd chalcogenides have been performed by Mitsushi[7] and his collaborators.[58–61] Except for Be impurities replacing the Zn site in ZnS, the results of our calculations for different impurities in the IDA are similar to those of others.[55] Beryllium seems to be an interseting impurity in ZnS. Experimental observations of Be impurities in ZnS show the localized as well as the gap mode.[62] Our lattice-dynamical calculations in the IDA for the localized and gap modes yield the values 455 and 237 cm^{-1}, respectively. These values are smaller than the observed ones. We, therefore, find a hardening in the force constant of about 16% in this impurity-lattice system. The results of Gaur *et al.*[55] are in agreement with ours for the gap mode but are in contradiction for the local mode. The Al impurities in these group semiconductors do not possess the same valence structure as that of the replaced host ion and, thus, require a maximum hardening of 58% in force constant.

IV. CONCLUSIONS

By employing a simple perturbation model for the impurity that includes the change in mass at the impurity site along with the changes in the nearest-neighbor force constants, we have studied the dynamics of imperfect zinc-blende-type crystals on the basis of a Green's-function technique. The changes in nearest-neighbor central force constant due to various impurities in the different classes of III-V and II-VI compound semiconductors have been calculated by fitting the local-mode frequencies with experimental ones. For impurities that possess the same valence structure as that of the replaced host ions (isoelectronic impurities) the calculated results for local-mode frequencies in the IDA are in good accord with existing experimental data. The force-constant changes required to reproduce the experimental values for the local-mode frequencies due to isoelectronic impurities in these semiconductor compounds lie within ±20%. Carbon, silicon, and lithium isotopes in III-V semiconductors and Al impurities in group II-VI semiconductors presumably cause complications in the host lattices because of a charge-compensation mechanism. Furthermore, since infrared measurements alone do not indicate that group-IV impurities in III-V semiconductor compounds act as acceptor or donor centers, there remains some doubt as to whether the observed local mode is due to the replacement of anion or cation atoms. These impurities incur force-constant changes as large as ±58%. It is observed that except for the case of Li isotopes in ZnSe, the force-constant changes incurred by the different isotopes of an impurity atom in the semiconductor compounds are similar. From this study one can observe that the ionic radii of the impurities provide a rough and not the definite clue to the possible changes of force constants in these compound semiconductors. It seems that more important criteria would be the consistency of the electronic configurations and their polarizability.

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