PHYSICAL REVIEW B VOLUME 36, NUMBER 3 15 JULY 1987-II

Theory of impurity vibrations due to isolated interstitials and interstitial-substitutional pair defects in semiconductors

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(Received 7 November 1986; revised manuscript received 8 April 1987)

Dynamical properties of isolated interstitials and "interstitial substitutional" pair defects in semiconductors are reported with use of the well-known Green's-function technique. To make the problem amenable to calculations, we exploit the symmetry properties of the defect environment and assume the interstitial site to be tetrahedral. For the isolated-impurity case, the perturbation is restricted to the impurity interacting with the host lattice atoms up to and including second-nearest neighbors. Similar to the substitutional-impurity vibrations, the contribution of the nearest-neighbor interactions to the dynamical properties of interstitials in semiconductors is found to be appreciable. For light defects (e.g., $\mathrm{Li_{int}}$ in Si and CdTe), a single dimensionless nearest-neighbor perturbation parameter τ has provided the isotopic frequency shifts of localized vibrational modes, in excellent agreement with the observed optical data. To explain the observed isotopic shifts of inband resonance modes due to heavier impurities (e.g., ^{63}Cu, ^{65}Cu in Si, etc.) the effect of second-nearest-neighbor impurity-host interaction is found to be important. Finally, the calculated force-constant changes due to isolated substitutional and interstitial impurities are used to understand the "interstitial-substitutional" pair defect vibrations in Si and CdTe.

I. INTRODUCTION

The dynamical properties of imperfect solids, including impurity-induced ir absorption, Raman scattering, phonon sidebands on optical transitions, etc., have been solved in recent years with use of the Green's-function method. Despite numerous cases of substitutional defects, the study of self-interstitial and foreign-interstitial vibrations in solids has not received much attention. Even at very low temperature ($\sim$4.2 K), although there exists indirect evidence for the mobility of Si *self-interstitials*[3] (expected to be formed in radiation damage experiments), so far it has, however, eluded direct experimental detection. The study of *foreign interstitials* including transition-metal (TM) impurities in semiconductors has been and still is particularly interesting as they form deep levels and can drastically influence the electrical conductivity and, consequently, the lifetime of electronic devices.[7–10]

Over the last several years, electron-paramagnetic-resonance (EPR) studies suggested that under normal preparation conditions most of the TM impurities in Si occupy the tetrahedral interstitial sites, preserving the cubic symmetry and causing no symmetry-breaking static Jahn-Teller distortions.[11,12] From the unusually large diffusion coefficients and solubility at high temperatures, copper in Si is also speculated to exist in an interstitial position.[11] New photoluminescence studies have emerged in recent years to add to the knowledge of the deep levels caused by TM defects in semiconductors.[13–15] In Fe-doped Si, for example, a number of luminescence features are tentatively ascribed as being due to (Fe,In), (Fe,Tl), and (Fe,B) pairs, while some are related to the isolated Fe-complex alone.[13–15] Similar studies with a variety of emission lines in the wavelength range $\sim 1.2-1.7\ \mu$m are also observed in Cr-doped and Cu-doped Si.[13] In each case the observed luminescence spectra exhibit general characteristics usually consisting of *one* or *two* sharp lines identified as a no-phonon (NP) peak followed at lower energies by transitions describable as local "phonon replicas" of the NP line. The low-lying vibrational modes observed in Si:Cr (~ 108 cm^{-1}), Si:Fe (~ 76 cm^{-1}), and Si:Cu (~ 56 cm^{-1}) are typical in spite of their slight variation in energy due to the perturbation caused by the different impurity atoms involved. Isotopic shifts, (^{54}Fe,^{56}Fe) and (^{63}Cu,^{65}Cu), of the phonon satellites have also been observed.

The importance of II-VI compounds as infrared window materials for high-power-laser applications has prompted the need for more detailed studies of the microstructural features of the defects and their relationships to infrared and Raman spectroscopy. The presence of Li in semiconductors exhibits many interesting features.[16–28] In II-VI compounds Li diffuses rapidly at relatively low temperatures, mainly through interstitial mechanisms, and dissolves in large concentrations.[26] Recent ir, photoluminescence, and electrical measurements in Li-doped CdTe and ZnSe samples have suggested that Li occupies both substitutional and interstitial positions. Not only has Li the tendency to form defect complexes with other types of Li and native (e.g., vacancies and antisite) defects, but it can also form impurity centers with the chemical defects present in the lattices.[16–28] The ir measurements[25] due to localized vibrational modes (LVM's) in Li-doped CdTe and ZnSe crystals have shown the formation of nearest-neighbor (NN) "Li_{Cd}-Li_{int}" pairs; however, the nature of the defect centers occurring in ZnSe has not been well established. Zielinska *et al.*[28] have also performed independent ir experiments due to Li-diffused and/or simultaneously doped with group-III*A* (Al, Ga, or In) impurities in CdTe. The main emphasis of their study was to propose models of Li-related defects responsible for the observed LVM's in the ir spectra. Despite the earlier assertion of strongly coupled second-nearest-neighbor (2NN) "Li_{Cd}-X_{Cd}" pairs,[24] the authors of Ref. 28 have speculated on the formation of "X_{Cd}-V_{Cd}-Li_{int}" complexes in CdTe depending on the conditions of Li diffusion. In all cases X_{Cd} (X = Al, Ga, or In) means an X atom on the Cd site, Li_{int} indicates an interstitial species, and V_{Cd} means a vacancy at the Cd site. Defects similar to some of these proposed by Zielinska *et al.*[28] have been suggested in luminescence studies[13–15] also.

When B-doped Si is diffused with lithium, the resulting material is highly compensated and Li acts as a donor. The Coulomb attraction and the mobility of Li are believed to favor the formation of "B_{Si}-Li_{int}" pairs.[16] The analyses of ir measurements performed in ^{7}Li (^{6}Li) -diffused ^{11}B (^{10}B) -doped Si crystals suggest that the 620- (644-) cm^{-1} band for ^{11}B (^{10}B) is replaced by peaks at 655, 564, and 522 cm^{-1} (683, 584, and 534 cm^{-1}). The assignment of the bands is carried out by changing $^{10}\text{B}\rightarrow{}^{11}\text{B}$ and by compensating with ^{6}Li in place of ^{7}Li. Despite all the experimental analyses supporting the formation of the defect complexes, the exact nature of the impurity-center involvement in Si- and CdTe-based materials has not been fully established. In the technology of solid-state devices,[7–10] it is essential that we identify the defects (especially their site selectivity) which cause deep traps before measures can be suggested to control their concentration. Viewing the existing experimental situation, it is believed that reliable theoretical calculations are equally important.

Two *theoretical* schemes have emerged in recent years with which to understand the microstructural features of the defect centers responsible for the patterns observed in various optical experiments: (i) studying the electronic structure of the deep defect states,[9,10] and (ii) understanding the physical aspects of the phonons and impurity vibrations.[1,2] The former approach is rooted in a formalism exploiting our knowledge of the electronic bands of the perfect material in **k** space. Despite numerous efforts made in recent years to solve the Hamiltonian representing an impurity potential using various approximations, the electronic structure of deep defect states in semiconductors is still an unsolved problem.[9] However, a great deal of progress has been made to treat the vibrational properties of impurity centers[1,2] using a sophisticated Green's-function technique. In the *phenomenological approach*[29] one considers a *phonon* to be a small perturbation to be handled by the dielectric-response theory, whereas in the self-consistent methods[30] one views a crystal with periodic distortions as a structure to be dealt with as a completely new system independent of the undistorted one. Except for the earlier work of Brice[31] on weakly bound and, more recently, on the split interstitials in Si,[32] the dynamics of *self*-interstitials and *foreign* interstitials in elemental and compound semiconductors has not been studied in such great detail.

In the present paper we have developed the Green's-function theory to understand the impurity modes associated with an isolated interstitial defect in zinc-blende- or diamond-type crystals to address the following questions: (a) Whether or not the observed resonant lines due to Fe, Cr, and Cu defects in Si exhibit the same structural (interstitial) behavior proposed in EPR studies; (b) whether the calculated isotopic shifts due to ^{54}Fe, ^{56}Fe, and ^{63}Cu, ^{65}Cu interstitials can be comparable with the magnitudes of the shifts actually observed in the photoluminescence experiments; (c) whether the theory can be extended to treat the pair-defect vibrations due to Li_{Cd}-Li_{int} (B_{Si}-Li_{int}) centers in CdTe (Si). Starting with the basic introduction of the Green's function in Sec. II, we will examine the problem of the vibration of isolated interstitial and defects paired with NN substitutional impurities in elemental and compound semiconductors. Details of the group-theoretical arguments are given in Sec. III, which simplify the problem by block-diagonalizing both the Green's function and perturbation matrices to sizes amenable to calculations. The results of the numerical calculations are reported in Sec. IV and compared with the existing optical data followed by a discussion and concluding remarks in Sec. V.

II. THEORY OF INTERSTITIAL DEFECT VIBRATIONS IN ZINC-BLENDE-TYPE CRYSTALS

The Green's-function treatment described here to understand the vibrational spectrum of the perturbed systems is general and has been discussed and frequently applied in the literature.[29] Maradudin *et al.*[6] have nicely explained the case of a substitutional impurity vibration and mentioned without detailed exposition its applicability to interstitials. We summarize here the relevant part of the theory in abbreviated form, which will be important for discussion of the impurity vibrations due to interstitials in real solids and here in application to zinc-blende- or diamond-type crystals.

A. Green's functions and impurity modes

In a perfect-crystal lattice with N unit cells ($l=1,2,\ldots,N$) containing r ($\kappa=1,2,\ldots,r$) atoms per unit cell, we define the Green's function of the vibrating system as

$$\left[\underline{M}\frac{d^2}{dt^2}+\underline{\Phi}\right]\underline{G}(t)=-\delta(t)\underline{I}\ , \tag{1}$$

where $\underline{M}$, $\underline{\Phi}$, and $\underline{G}$ are, respectively, the mass, potential energy, and the Green's-function matrices, and $\underline{I}$ is a unit matrix.

In the Hilbert space, the matrix elements $\langle l,\kappa,\alpha \mid \underline{G}(t) \mid l',\kappa',\beta\rangle$ represent the displacement $u_\alpha(l,\kappa)$ $(\equiv\langle l,\kappa,\alpha \mid u\rangle)$ of atom (l,κ) along the α direction due to the force-$\delta(t)$ on the atom (l',κ') in the β direction. The Fourier transform of $\mathbf{G}(t)$ may be easily seen to satisfy the relation

$$\underline{G}^{-1}(\omega)\underline{u}=(\underline{M}\omega^2-\underline{\Phi})\underline{u}=\underline{L}\ \underline{u}\ , \tag{2a}$$

or, equivalently,

$$\underline{L}\ \underline{G}(\omega)=\underline{I}\ , \tag{2b}$$

where $\underline{L}$ is usually called the $3rN\times 3rN$ dynamical matrix and $\underline{u}$ is a column vector of dimensional space $3rN$.

If $\delta\underline{L}$ is the perturbation caused by a substitutional defect on the dynamical matrix of the host lattice, the Green's-function matrix for the imperfect solid, $\underline{U}$, can be defined [in a way similar to Eqs. (2)] as

$$(\underline{M}\omega^2-\Phi-\delta\underline{L})\underline{U}(\omega)=(\underline{L}-\delta\underline{L})\underline{U}(\omega)=\underline{I}\ , \tag{3a}$$

or, equivalently,

$$\underline{U}(\omega)=\underline{G}(\underline{I}-\delta\underline{L}\ \underline{G})^{-1}=(\underline{I}-\underline{G}\ \delta\underline{L})^{-1}\underline{G}\ , \tag{3b}$$

with the perturbation matrix

$$\delta\underline{L}=-\Delta\underline{M}\ \omega^2+\Delta\underline{\Phi}\ . \tag{3c}$$

Here, $\Delta\underline{M}$ and $\Delta\underline{\Phi}$ are the mass change and force-constant change matrices, respectively. The resonance denominator contained in the inverse of the matrix $(\underline{I}-\underline{G}\delta\underline{L})^{-1}$ is of central importance for investigating the impurity modes [cf. Eq. 3(b)]. Again, to make the problem easily tractable, $\delta\underline{L}$ is usually considered to be very localized around the defect. Following Maradudin *et al.*,[6] one can write $\underline{G}$ and $\delta\underline{L}$ matrices in a partitioned form as

$$\underline{G}=\begin{bmatrix} \underline{g} & \underline{G}_{12} \\ \underline{G}_{21} & \underline{G}_{22} \end{bmatrix} \quad \text{and}\ \delta\underline{L}=\begin{bmatrix} \delta\underline{l} & \underline{0} \\ \underline{0} & \underline{0} \end{bmatrix}\ , \tag{4}$$

where the index 1 refers to the impurity space and the index 2 stands for the rest of the lattice. We therefore need to solve a small subblock of Eqs. (3) which gives the condition for the occurrence of impurity modes as

$$\mathrm{Re}\,|\underline{I}-\underline{g}\ \delta\underline{l}\,|=0\ . \tag{5}$$

The complexity of Eq. (5) in evaluating $\underline{g}$ requires a transformation of $\langle l,\kappa,\alpha \mid u\rangle$ to a representation that diagonalizes Eqs. (2). From the elementary theory of lattice dynamics, the required transformation for periodic lattices is

$$\langle l,\kappa,\alpha \mid \mathbf{q},j\rangle=N^{-1/2}e_\alpha(\kappa \mid \mathbf{q},j)\exp[-i\mathbf{q}\cdot\mathbf{x}(l,\kappa)]\ , \tag{6}$$

where $\mathbf{q}$ forms a set of N wave vectors in the first Brillouin zone, j is the polarization index, $\mathbf{x}(l,\kappa)$ is the equilibrium position vector of atom (l,κ), and e_α $(\kappa \mid \mathbf{q},j)$ forms the components of the polarization vector for the mode $\omega(\mathbf{q},j)$ which are orthonormal and complete. Using Eq. (6) the component form of the perfect-lattice Green's function in the site representation can be obtained as

$$g^{\text{lat}}_{\alpha\beta}(l,\kappa;l',\kappa';\omega^2)=\frac{1}{N(M_\kappa M_{\kappa'})^{1/2}}\sum_{\mathbf{q}j}\frac{e_\alpha(\kappa \mid \mathbf{q},j)e^*_\beta(\kappa' \mid \mathbf{q},j)}{\omega^2-\omega^2(\mathbf{q},j)}\exp\{i\mathbf{q}\cdot[\mathbf{x}(l,\kappa)-\mathbf{x}(l',\kappa')]\}\ . \tag{7}$$

With the presence of an *interstitial* defect in the host lattice, the number of degrees of freedom will be increased by three. If the impurity interacts with p host atoms, the $\underline{g}$ and $\delta\underline{l}$ matrices of Eq. (5) would be of dimension $3(p+1)\times 3(p+1)$. To bring the situation of an *interstitial* defect vibration into harmony with the dynamics of *substitutional* defects, one can write $\underline{g}$ (following Brice[31]) as

$$\underline{g}=\underline{g}^{\text{int}}\oplus\underline{g}^{\text{lat}}\ , \tag{8}$$

where $\underline{g}^{\text{int}}$ is a 3×3 matrix for the interstitial vibrating in a fixed "frozen" lattice with elements defined as $\underline{g}^{\text{int}}$ $[\equiv(1/M_i\omega^2)\delta_{\alpha\beta}]$, and $\underline{g}^{\text{lat}}$ is the Green's-function matrix $(3p\times 3p)$ of the host lattice with elements defined in the usual way [cf. Eq. (7)]. This choice is different from the existing calculations[33] as the mass-dependent part placed here in defining the $\underline{g}$ matrix rather than the $\delta\underline{l}$ matrix. The inclusion of mass dependence in the perturbation actually gives a trivial redefinition of the $\delta\underline{l}$ matrix and does not affect the numerical results.

B. Perturbation models

1. Isolated interstitial defect

In elemental and compound semiconductors, unlike substitutional defects, the isolated interstitials do not necessarily occupy the tetrahedral site (T_d) and might find themselves to be more stable in a less symmetric position.[3] However, in the present Green's-function calculations we assume the interstitial site to be tetrahedral, which will help us exploit the symmetry properties of the defect environment to make the vibrational problem tractable. The present choice of interstitial site (preserving the cubic symmetry) is supported, at least, for the case of an unionized Li atom in Si (Ref. 34) and also from the recent optical experiments of the TM impurities in Si,[11,12] and of Li defects[16–28] in CdTe.

To treat the vibrational properties of an interstitial $\{I_{\text{int}}\}$ impurity in a zinc-blende-type lattice, we assume the center of the fcc conventional unit cell to be the defect site. The vacancy or any other charge-compensating impurity associated with the defect is assumed to be sufficiently far away to prevent any distortion of the tetrahedral symmetry. The perturbation is limited to the interstitial interacting with *four* nearest-neighbor (NN) Zn (or S) and *six* second-nearest-neighbor (2NN) S (or Zn) atoms (see Fig. 1). The atoms at the corners of the large cube in Fig. 1 are the third or more distant neighbors to the interstitial.

To describe the lattice dynamics of perfect zinc-blende-type crystals with an eleven parameter rigid-ion model

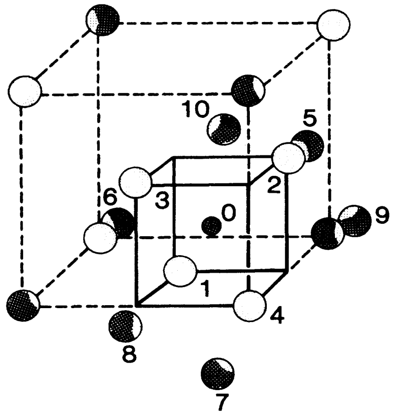

FIG. 1. Location of atoms considered in a perturbation model with interstitial I_{int} defect (●) interacting with nearest-neighbor Zn (○) and next-nearest-neighbor S (◐) atoms in a zinc-blende-type (ZnS) crystal with the following notations.

Atom No.	Location	Type of atom
0	(000)	I_{int}
1	$(a/4)(\bar{1}11)$	Zn
2	$(a/4)(1\bar{1}1)$	Zn
3	$(a/4)(11\bar{1})$	Zn
4	$(a/4)(\bar{1}\bar{1}\bar{1})$	Zn
5	$(a/2)(\bar{1}00)$	S
6	$(a/2)(0\bar{1}0)$	S
7	$(a/2)(00\bar{1})$	S
8	$(a/2)(100)$	S
9	$(a/2)(010)$	S
10	$(a/2)(001)$	S

(RIM11) (see Sec. IV), we require *two* NN parameters (A,B) plus *eight* 2NN parameters $(C_\kappa, D_\kappa, E_\kappa, F_\kappa$, with $\kappa = 1,2)$ plus *one* parameter (Z) connected with the long-range Coulomb interactions (see Ref. 35 for detailed description). For diamond-type crystals the number of parameters reduces to *five* as $C_1 = C_2 = D_1 = D_2$, $E_1 = E_2$, $F_1 = F_2$, and $Z = 0$. In defining the perturbation matrix, the impurity-host coupling is modeled by connecting the interstitial defect to each of its four Zn (S) NN's with parameters (α, β) and to each of its *six* S (Zn) 2NN's with parameters $(\gamma, \delta$ radial interactions only) in the ZnS lattice. Although the changes in NN host-lattice interactions $(\Delta A, \Delta B)$ caused by the presence of interstitial defects are small, they are, however, included in defining the full $\delta \underline{l}$ matrix.[36] Similar to the substitutional impurity vibrations, it is shown in Sec. IV that the NN interactions alone provide the major contribution for understanding the dynamical properties of isolated interstitials in elemental or compound semiconductors. Again, in defining the impurity by a single dimensionless parameter τ (η) (similar to the substitutional case[37,38] with NN interactions only), it is assumed that α and β are proportional to A and B,

$$\tau \text{ (or } \eta) = \alpha / A = \beta / B \ , \tag{9}$$

as if the interstitial has the Zn (or S) NN in the ZnS lattice.

2. *Interstitial-substitional pair defects*

Elliott and Pfeuty[39] were the first to initiate the theoretical calculations of impurity modes due to "interstitial-substitutional" pair defects in silicon. To treat the actual numerical calculations with only six Green's-function matrix elements,[40] these authors were forced to undertake several approximations in defining the perturbation matrices. Recently, we have developed a complete Green's-function theory by introducing more precise perturbation models for studying the vibrations of impurity complexes (with a maximum of three defect centers) in diamond- or zinc-blende-type crystals.[41,42] A rigorous check of the theory is made by comparing the calculated results with the existing ir and Raman data of impurity modes. The trends of force variation due to charged defects have clearly supported the fact that in covalent and partially ionic compounds the bonding stability results from the equilibrium between repulsion of the cores and attraction due to the valence electrons and is associated with the charge overlap.

In the present case, where no conclusive identifications of "interstitial-substitutional" pair defects in elemental and compound semiconductors are made experimentally, we feel that the simplified perturbation models based on the results of isolated defect vibrations will be adequate. Similar to the case described in subsection 1, the interstitial impurity is regarded to be on the tetrahedral site (say, site 0) and is paired with a substitutional defect on one of the NN sites to I_{int} (say, site 4 in Fig. 2). In the perturbation matrix we include (i) the relative force variation τ (or η) between the interstitial and NN host atoms, (ii) the mass change at the impurity site 4 $[\varepsilon_4 \equiv (M_4 - M_4'/M_4)]$, (iii) the interaction F_{45} between the substitutional impurity and host atom (at site 5) along the line of the interstitial defect, and (iv) the interaction F_{40} between the impurity pair. The complete descriptions of the Green's-function and perturbation matrices for an "interstitial-substitutional" pair defect involving *six* atoms are obtained.

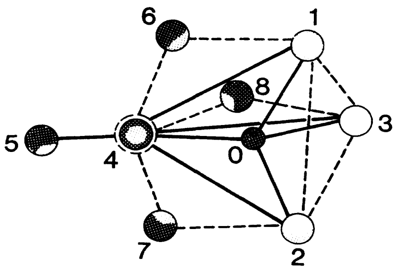

FIG. 2. Location of atoms considered in a perturbation model for an "interstitial-substitutional" pair defect in zinc-blende-type crystals. Atoms 0–4 have the same coordinates as Fig. 1, while atoms 5–8 are the nearest neighbors to the substitutional impurity at site 4 (see text for details).

III. GROUP-THEORETICAL ANALYSES

To examine the effect of an isolated interstitial (case 1 in Sec. II B) or the "interstitial-substitutional" pair defect (case 2 in Sec. II B) on the vibrational properties of elemental or compound semiconductors, it is not necessary to work with the full size $\underline{g}$ and $\delta \underline{l}$ matrices. Introducing the symmetry adapted displacements $\underline{x}$ for the subspace of the perturbation, one can write the squared matrix $\underline{s}$ representing the unitary transformations from the subspace of the Cartesian coordinates $\underline{u}$ to the symmetry coordinates as

$$\underline{x}(\Gamma_i)=\underline{s}\,\underline{u} \ , \tag{10}$$

where Γ denotes any irreducible representation of the point group pertaining to the perturbation and i is an index which runs from one to the number of times, $n(\Gamma)$, the irreducible representations are contained in the perturbation. In case 1 of Sec. II B, the 33-dimensional defect space can be expressed in terms of the various irreducible representations of T_d as[36]

$$\Gamma_{T_d}=2A_1 \oplus 2E \oplus 3F_1 \oplus 6F_2 \ . \tag{11}$$

For the pair defect (cf. case 1 in Sec. II B) restricted to *six* atoms, the 18-dimensional impurity space can also be reduced to its irreducible parts of C_{3v} symmetry as[36]

$$\Gamma_{C_{3v}}=5A_1 \oplus A_2 \oplus 6E \ . \tag{12}$$

Here, A denotes one-dimensional, E two-dimensional, and F three-dimensional representations. The transformation matrix $\underline{s}$ for each case can be obtained by the standard projection-operator method to block-diagonalize both $\underline{g}$ and $\delta \underline{l}$ matrices.

IV. NUMERICAL COMPUTATIONS AND RESULTS

A. Lattice dynamics and Green's functions

To study the lattice dynamics of imperfect diamond- and zinc-blende-type crystals, one needs an adequate model to describe the phonon dispersions and the density of phonon states of the parent compounds. Although various theoretical techniques are known,[35] it is not simple to assess their internal coherence, which sometimes claims a good fit to the neutron data (of phonon dispersions) but suffers from several internal inconsistencies. For a meaningful picture of the physical situation around the defect in a perturbation model, the choice of the lattice-dynamical model is very important. In zinc-blende- or diamond-type crystals, almost all the existing calculations of defect properties use the rigid-ion model (RIM),[37,38,41–44] although shell-model- and valence-shell-model fitted lattice phonons in several perfect systems are available.[45,46] We understand this reason primarily because of its relative simplicity, that, with fewer parameters, it provides practically identical phonon dispersions when compared to those obtained from more complicated models. However, in the zinc-blende-type crystals, when the long-range Coulomb forces are neglected, the RIM does not reproduce the splitting in the LO-TO branches in the long-wavelength limit and also fails to give the characteristic flattening of the TA branches. Except for the above shortcomings, the overall agreement of the phonon dispersions for Si, Ge, α-Sn, and C is found to be reasonable[47] and we believe that these shortcomings are unlikely to prove serious in our study of defect vibrations. To find some consistency in the force variation due to substitu-

TABLE I. Calculated RIM parameters (10^5 dyn/cm) for the lattice dynamics of Si and CdTe. The lattice parameter is in Å.

Model parameter	Si[a]	CdTe
a	2.670 35	3.24
A	−0.5558	−0.1997
B	−0.3850	−0.1940
C_1	−0.040	−0.0180
C_2	−0.040	−0.0170
D_1	−0.040	−0.0139
D_2	−0.040	−0.0230
E_1	0.016	0.0300
E_2	0.016	0.0400
F_1	0.078 10	−0.0520
F_2	0.078 10	0.0720
Z	0	0.8670

[a]The parameters for Si are evaluated by assuming the condition $C_1=C_2=D_1=D_2$ in concurrence with the central-force model of Smith (Ref. 57) and the angular force model of Braunstein *et al.* (Ref. 58).

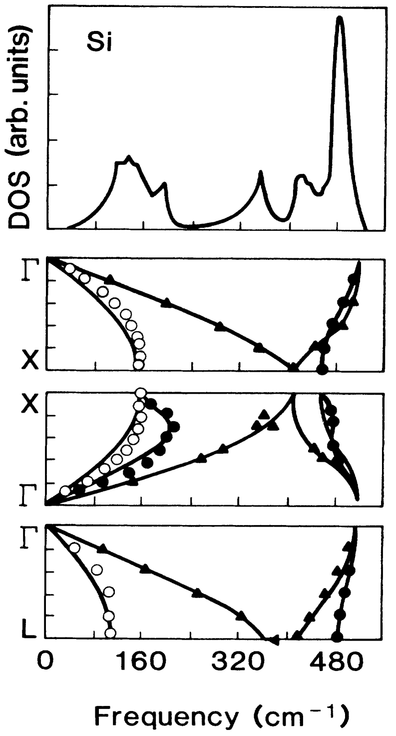

FIG. 3. Calculated lattice dynamics and the density of states of Si using the parameters of Table I.

TABLE II. Critical-point phonon frequencies (in cm^{-1}) calculated by the RIM (with parameters of Table I) are compared with the existing neutron data.

Critical point	Mode	Frequency (cm^{-1}) Si[a] Expt.	CdTe[b] Expt.	Si Calc.	CdTe Calc.
Γ	LO	520	169	518.37	169.6
	TO	520	140	518.37	140.2
X	LO	417		415.97	134.46
	TO	463	148	457.16	149.89
	LA	417		415.97	125.35
	TA	150.3	35	151.22	35.43
L	LO	420	144	424.31	147.82
	TO	489	144	488.73	142.77
	LA	378	108	358.14	116.16
	TA	114.3	29	106.93	30.29

[a] Reference 48.
[b] Reference 49.

tional defects (already estimated[37,38,41,42] in several semiconductors) and the interstitial impurities, we feel that the choice of RIM is worthwhile.

In Table I we list the parameter values for Si and CdTe used to calculate their lattice dynamics and compare the calculated values of phonon energies at critical points with the existing neutron data[48,49] (see Table II and Fig. 3). The perfect-lattice Green's-function matrix elements are calculated from the phonons generated by the lattice-dynamical model at a sample of wave vectors using fairly standard techniques.[6] In actual calculations we use the eigenvalues and eigenvectors at 6280 regularly spaced **q** points in the reduced $\frac{1}{48}$th wedge of the Brillouin zone, which corresponds to 64 000 points uniformly distributed in the full Brillouin zone. For computational details, we refer to an earlier paper.[41]

B. Impurity modes

1. Isolated defects

The theoretical method developed in Sec. II for isolated interstitial defect vibrations in zinc-blende-type crystals is equally suitable for diamond-type crystals. In ZnS, if the impurity atom is light compared to the NN Zn (or S) host-lattice atoms, the vibrational mode of interest will be triply degenerated (with F_2 character) and will appear as a single band in optical experiments. For heavier interstitial defects, however, there occurs the possibility of in-band resonance modes (of A_1 and F_2 character) to be detected by the ir Raman experiments. By setting $\gamma=\delta=\Delta A=\Delta B=0$, one can solve the determinantal equation (5) to get the results for the simplest case of interstitial defect vibrations with interaction confined to NN's alone.

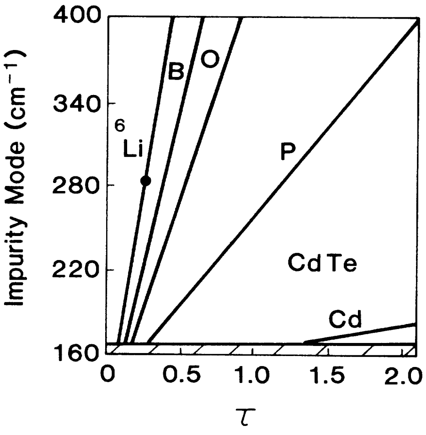

FIG. 4. Calculated impurity modes (localized) due to interstitial defects in CdTe vs the force-constant–variation parameter τ (see text).

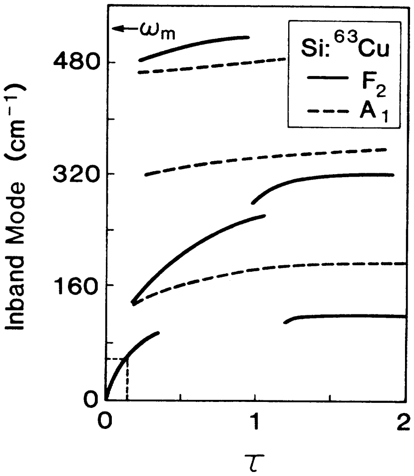

FIG. 5. Calculated in-band resonance modes due to an interstitial ^{63}Cu in Si vs the force-constant–variation parameter τ (see text).

Again, for simplicity, we have considered defects of the form $\alpha/A=\beta/B=\tau$ (or η).

The results of local in-band mode calculations in CdTe and Si are summarized in Figs. 4 and 5 for a different choice of τ (or η). Here, we have plotted the impurity-mode frequencies for those values of ω which satisfy Eq. (5) as a function of impurity-host interaction parameter. The calculated results, when compared with the optical data, will help us in estimating the impurity-induced force-constant changes (see Table III). The effects of 2NN impurity-host interaction on the defect modes will be discussed in Sec. V.

2. Pair defects

The trends of force variations obtained for isolated (substitutional and/or interstitial) defects (cf. Table III) are important in understanding the vibrations of pair defects in elemental and compound semiconductors. The presence of substitutional (interstitial) defects in the neighborhood of an interstitial (substitutional) impurity in the [111] direction lowers the symmetry from $T_d \rightarrow C_{3v}$, which will cause partial or total splitting of the triply degenerate F_2 mode into a nondegenerate A_1 mode and doubly degenerate E-type modes. For very light pair defects (e.g., $\mathrm{Li_{Cd}}$-$\mathrm{Li_{int}}$ in CdTe),[25] four LVM's are expected—*two* because of its movement parallel to the line and *two* because of its movement perpendicular to it. In earlier ir studies[14] due to boron associated with lithium interstitials in silicon, however, only *three* LVM's were observed. For each Li isotope, a single line [534 $\mathrm{cm^{-1}}$ (^{6}Li), 522 $\mathrm{cm^{-1}}$ (^{7}Li)] was detected near the maximum ($\omega_m \simeq 520$ $\mathrm{cm^{-1}}$) phonon frequency, while the B lines [644 $\mathrm{cm^{-1}}$ (^{10}B), 620 $\mathrm{cm^{-1}}$ (^{11}B)] were each found to be split into doublets (681 and 584 $\mathrm{cm^{-1}}$, 653 and 564 $\mathrm{cm^{-1}}$) (see Table III). The modes at higher frequencies were seen to be twice as intense as those observed at lower frequencies. This suggests that the 681-$\mathrm{cm^{-1}}$ (653-$\mathrm{cm^{-1}}$) line is *double degenerate* and the mode at 584 $\mathrm{cm^{-1}}$ (564 $\mathrm{cm^{-1}}$) is *nondegenerate.* Although Ko and Spitzer[25] have established the formation of "$\mathrm{Li_{Cd}}$-$\mathrm{Li_{int}}$" pairs in CdTe, the nature of Li complexes, however, in ZnSe:Li has not been completely resolved. The effects of Al impurities in Li-diffused CdTe (ZnSe) crystals have also been investigated by two different groups.[24,28] The spectra obtained by Ko and Spitzer[24] are interpreted in terms of 2NN "$\mathrm{Li_{Cd(Zn)}}$-$\mathrm{Al_{Cd(Zn)}}$" pairs with C_s point-group symmetry. Depending on the conditions of Li diffusion in Al-doped CdTe, Zielinska *et al.*[28] do believe in the formation of 2NN pairs; they have, however, speculated on the possibilities of "$\mathrm{Li_{int}}$-V_{Cd}-$\mathrm{Al_{Cd}}$" centers also.

TABLE III. Localized vibrational modes due to isolated substitutional and/or interstitial defects in Si and CdTe.

System	Mode	LVMs ($\mathrm{cm^{-1}}$) Expt.[a]	Relative change in NN force constant[d] t or τ
Si:^{10}B	F_2	644	0.205
Si:^{11}B	F_2	620	0.205
Si:^{12}C	F_2	605	0.18
Si:^{13}C	F_2	586	0.18
Si:^{14}C	F_2	570	0.18
Si:$^6\mathrm{Li_{int}}$	F_2	534	0.16
Si:$^7\mathrm{Li_{int}}$	F_2	522	0.16
CdTe:^{6}Li	F_2		0.91[e]
CdTe:^{7}Li	F_2		0.91[e]
CdTe:Be	F_2	391	0.50
CdTe:^{24}Mg	F_2	249	0.36
CdTe:^{25}Mg	F_2	245	0.36
CdTe:^{26}Mg	F_2	241	0.36
CdTe:Al	F_2	299	-0.23
CdTe:^{32}S	F_2	248.5	-0.38
CdTe:P(?)	F_2	322[c]	-1.15
CdTe:$^6\mathrm{Li_{int}}$	F_2	283.5[b]	0.22
CdTe:$^7\mathrm{Li_{int}}$	F_2	265.5[b]	0.22

[a] Reference 1.

[b] References 24 and 28.

[c] Reference 25.

[d] This work.

[e] See text.

We start with an attempt to fit the "$\mathrm{Li_{int}}$-$\mathrm{B_{Si}}$" pair modes in silicon and use the results of our earlier calculations for isolated-Li ($^6\mathrm{Li_{int}}$, $^7\mathrm{Li_{int}}$) and B ($^{10}\mathrm{B_{Si}}$, $^{11}\mathrm{B_{Si}}$) defect vibrations (cf. Table IV). For the "$^6\mathrm{Li_{int}}$-$^{10}\mathrm{B_{Si}}$" pair vibrations, with $\tau \simeq 0.16$, our Green's-function calculations provide a frequency which matches exactly the $^6\mathrm{Li_{int}}$ mode, while the other two corresponding to $^{10}\mathrm{B_{Si}}$ modes are found at much higher values. This requires the inclusion of force-constant softening in between the "B—Si" bonds. Choosing $F_{45}=0.205$ in our perturbation model lowers the B modes close to the experimental energy range; however, it causes only a small splitting in the E and A_1 frequencies. The inclusion of force variation in F_{40} further splits the E, A_1 energies and, for stiffening in the F_{40} force constant, put the A_1-mode frequency $\omega(A_1)$ at a higher value than the E-mode frequency $\omega(E)$, and considering softening in F_{40} gives $\omega(A_1)<\omega(E)$. The set of parameters $\{\tau, F_{45}, F_{40}\}$ required to obtain the best fit between theoretical and experimental data for the "$\mathrm{B_{Si}}$-$\mathrm{Li_{int}}$" pair mode in Si is reported in Table IV. Similar calculations for "$\mathrm{Li_{Cd}}$-$\mathrm{Li_{int}}$" vibrations in CdTe are also included (cf. Table IV).

V. DISCUSSION AND CONCLUSIONS

The Green's-function theory of isolated interstitial defect vibrations has been used to extract the nature of force constants between impurity and neighboring host-lattice atoms in Si and CdTe. Our calculations in the F_2 representation to fit the observed LVM's in CdTe:$^7\mathrm{Li_{int}}$ (Si:$^7\mathrm{Li_{int}}$) systems provide $\tau=0.22$ (0.16)—the softening in the interstitial–host-atom bondings (cf. Table III). With the same force-constant–change parameters, the isotopic shifts of LVM's replacing $^7\mathrm{Li_{int}} \rightarrow {}^6\mathrm{Li_{int}}$ provide results in very good agreement with the observed values. To fit the observed in-band resonance mode due to the heavier impurity $^{63}\mathrm{Cu_{int}}$ in Si, our Green's-function calculation in the F_2 representation has provided a softening in the NN parameter [e.g., of $\tau=0.14$ (cf. Fig. 5)]. The fre-

TABLE IV. Localized vibrational modes due to "interstitial-substitutional" pair defects in Si and CdTe.

System	LVM's (cm^{-1}) Expt.[a]	Calc.[b]	Mode	Parameters[c] (τ,F_{40},F_{45})
$^{10}\mathrm{B}_{\mathrm{Si}}$-$^{6}\mathrm{Li}_{\mathrm{int}}$	683	679.2	E	0.167
	584	585.7	A_1	0.193
	534	538.2	E	0.22
		519.0	A_1	
$^{11}\mathrm{B}_{\mathrm{Si}}$-$^{7}\mathrm{Li}_{\mathrm{int}}$	655	651.4	E	0.167
	564	565.3	A_1	0.193
	522	525.1	E	0.22
		518.7	A_1	
$^{6}\mathrm{Li}_{\mathrm{Cd}}$-$^{6}\mathrm{Li}_{\mathrm{int}}$	370	367.1	E	0.23
	326.5	328.2	A_1	0.272
	282	284.6	E	0.91
	271	274.2	A_1	
$^{7}\mathrm{Li}_{\mathrm{Cd}}$-$^{7}\mathrm{Li}_{\mathrm{int}}$	344	341.4	E	0.23
	304	307.1	A_1	0.272
	262	265.1	E	0.91
	252	255.3	A_1	

[a] References 1, 24, 25, and 28.

[b] This work.

[c] See text for the description of the parameters.

quency shift of the impurity mode due to $^{65}\mathrm{Cu}_{\mathrm{int}}$ for $\tau=0.14$ corresponds to a slightly higher value, of ~ 1.05 cm^{-1}, than actually observed (~ 0.6 cm^{-1}). Similar results, with a slightly different choice of force-constant variation, are found for the frequency shifts of the in-band resonance modes due to $^{54}\mathrm{Fe}_{\mathrm{int}}$ and $^{56}\mathrm{Fe}_{\mathrm{int}}$ isotopes in Si.

To understand the cause for this discrepancy in the isotopic frequency shifts due to heavier impurities, let us consider the vibrations of the atoms involved in the F_2 mode. It is obvious that, in addition to the motion of the impurity, the NN and 2NN host-lattice atoms also participate in the triply degenerate F_2 mode. Perusal of Fig. 5 reveals that for $\tau \to 0$ (i.e., in the limit of vanishing impurity-host interaction in the NN model) the motion in the lowest-frequency F_2 mode becomes increasingly that of the defect alone. We therefore suspect that for heavier impurities a model with interactions up to and including 2NN ones will provide better understanding of the dependence on the impurity mass and the energy of the F_2 mode. The choice of the parameter values for the NN [$\tau=0.12$ (and 0.133)] and 2NN [$\theta=\gamma/A=\delta/A=0.035$ (and 0.041)] interactions fit reasonably well the frequency-shift values due to $^{63}\mathrm{Cu}$ and $^{65}\mathrm{Cu}$ (and $^{54}\mathrm{Fe}$ and $^{56}\mathrm{Fe}$) impurity vibrations in Si.

After analyzing nearly 80 cases of substitutional impurity vibrations in 15 elemental and compound semiconductors, we have strongly argued the existence of a close relationship between the *force perturbation* and the variation of the *covalency of the bond*.[38] Based on simple physical arguments, empirical relationships are proposed which provide correction to the force constants for closest-mass isoelectronic, donor and acceptor impurities carrying static charges. If sufficient experimental data on interstitial impurity vibrations come to light, we hope to find similar trends of force-vibration correlation with bond ionicity. It is worth mentioning, however, that the relative change of force constants obtained for isolated defects have helped us in explaining the impurity vibrations due to "interstitial-substitutional" pairs in elemental and compound semiconductors. In the calculations of "$\mathrm{Li}_{\mathrm{Cd}}$-$\mathrm{Li}_{\mathrm{int}}$" pair modes in CdTe, the effective force constant between "$\mathrm{Li}_{\mathrm{Cd}}$-$\mathrm{Li}_{\mathrm{int}}$" has caused the triply degenerate F_2 vibrations of substitutional and/or interstitial defects to split each into *two* modes, thereby causing a total of four LVM's—*two* nondegenerate axial modes and *two* doubly degenerate transverse modes. In the fitting procedure, we find the force constant between pair defects (cf. Table IV) which put the doubly degenerate vibration of $\mathrm{Li}_{\mathrm{Cd}}$ ($\mathrm{Li}_{\mathrm{int}}$) at a higher frequency than the nondegenerate axial mode. To further check the assignments of the calculated mode behavior, we use a simple perturbation relationship which connects the split LVM of a defect in a complex C_{3v} (ω_i, $i=1,2,3$, where ω_1 is the mode axial and $\omega_2=\omega_3$ is the transverse mode) with the isolated case $T_d(\omega)$as

$$\omega^2=\tfrac{1}{3}\sum_{i=1}^{3}\omega_i^2 \, . \tag{13}$$

If the two higher- (lower-) energy values in our calculations of pair-defect vibrations are considered as the split modes of $\mathrm{Li}_{\mathrm{Cd}}$($\mathrm{Li}_{\mathrm{int}}$), then Eq. (13) can be used to give the LVM for the isolated case $^{6}\mathrm{Li}_{\mathrm{Cd}}$ ($^{6}\mathrm{Li}_{\mathrm{int}}$) in CdTe near 354.6 cm^{-1} (281.2 cm^{-1}). Despite recent studies of Li-induced LVM's in CdTe,[24,25,28] the results for the isolated $^{6}\mathrm{Li}_{\mathrm{Cd}}$ or $^{7}\mathrm{Li}_{\mathrm{Cd}}$ impurities are rather sparse; however, our calculated value for the impurity mode due to $^{6}\mathrm{Li}_{\mathrm{int}}$ is seen to be in good agreement with the recent ir measurements of Zielinska *et al.*[28]

For NN "B_{Si}-Li_{int}" pair vibrations in Si, the lack of isotopic shift for Li with respect to B suggests that the lithium vibration in the pair is almost independent of the amplitude of the vibration of the boron and the interaction is almost entirely electrostatic in nature. This argument is further supported by the fact that lines in almost identical positions have also been observed for Al-Li and Ga-Li pairs.[1,3] With considerable softening in between the defects, our Green's-function calculations suggest that the triply degenerate $^{10}B_{Si}$ mode splits into a nondegenerate A_1 mode and a doubly degenerate E mode at a higher frequency. Although a similar split is expected in the Li mode, with the choice of the parameter (cf. Table IV) our calculation, however, shows the axial lithium mode to lie in the band-mode region. This mode has not been observed experimentally, perhaps because of its occurrence in the region of a high density of phonon states.

It has been well accepted that B and C are the commonly occurring impurities in the undoped GaAs and GaP crystals grown by the liquid-encapsulation Czochralski (LEC) pulling method.[50,51] These impurities are usually derived from the boron nitride crucible and encapsulant (boric oxide) and graphite heating elements inside the apparatus. Irradiation and annealing treatments lead to the formation of complexes with the native defects. As compared to C, B is particularly sensitive, and some ten different centers [B(1)–B(10)] have now been classified.[51] One set of defects which has been debated in recent years[50–53] is the B(2) center and its complexes with shallow donors.[54] The B(2) LVM's at 601 and 628 cm^{-1} are observed in electron-irradiated LEC GaAs and have been attributed both to boron (^{10}B and ^{11}B) on the arsenic site, B_{As}, and to interstitial boron, B_{int}, with gallium nearest neighbors in the tetrahedral symmetry. Our recent calculations[38] for the LVM's due to Ga isotopic masses (^{69}Ga, ^{71}Ga) in $GaAs{:}^{11}B$ have provided strong evidence that the B(2) center is an antisite defect in its single negative charge state. The interstitial site would have *four* Ga nearest neighbors and *six* As second-nearest neighbors. Preliminary calculations[55] in the nearest-neighbor approximation with a single perturbation parameter has provided fine structure similar to the antisite case, but the widths of the lines are much broader. Moreover, systematic analyses[55] of the observed impurity modes due to "B(2)-donor" pairs in GaAs and GaP have provided convincing support in favor of antisite structure for the B(2) center.

Finally, we are also planning to implement the present theory to treat the vibrational aspects of the "Cu-Li" complexes in GaP recently studied with the use of photoluminescence experiments.[56] This approach is believed to have important implications concerning our basic knowledge of defects, especially their site selectivity, and it may be of significance in relation to the specification of materials for fabrication of optical devices.

ACKNOWLEDGMENTS

One of us (D.N.T.) wishes to thank the Chairman of the Département de Physico-Chimie, Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Saclay, for providing him with an opportunity of acting as a collaborator in the Service Chimie Moléculaire. This work was also partly supported by a grant from the Texas Advanced Technological Research Program through the University of Houston–University Park, Houston, Texas.

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