

Green's-function theory of impurity vibrations due to defect complexes in elemental and compound semiconductors

Michel Vandevyver and Devki N. Talwar*

Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Saclay, Services d'Electronique de Saclay, Laboratoire d'Etudes et de Recherches Avancées, B.P. N°2 91190, Gif-sur-Yvette, France

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Green's-function theory has been reported for studying the vibrations of impurity complexes with a maximum of three defect centers in zinc-blende-type crystals. By incorporating appropriate perturbation models and lattice phonons from an eleven-parameter rigid-ion model we have made numerical calculations for the localized vibrational modes of almost all the existing cases of pair defects with C_2 and C_3 , point-group symmetries. The results of force perturbation for isolated charged defects have assisted us to reasonably fit the various optical experiments and tentatively assign the movements of "donor-acceptor," "acceptor-donor," "donor-host-acceptor," and "donor-host-vacancy" complexes. The force perturbation correlation with bond ionicity noticed for isolated donor or acceptor impurities has also proved to be an important factor for studying the pair vibrations in elemental and compound semiconductors.

I. INTRODUCTION

Localized vibrational modes (LVM's) due to light isoelectronic substitutional impurities in diamond or zinc-blende-type crystals have been studied in recent years both by experimental¹⁻⁴ (mainly by ir absorption and also through the Raman-scattering technique) and theoretical methods.⁵⁻¹⁰ For nonisoelectronic substituents, however, the resulting free-carrier concentration poses serious problems for measuring the vibrational spectrum. In the infrared experiments^{11,12} for example, the free-carrier absorption coefficient (α_{FC}) in *p*-type silicon (with the hole concentration $\approx 10^{18}$ cm⁻³) lies in the range $500 \text{ cm}^{-1} \leq \alpha_{FC} \leq 1000 \text{ cm}^{-1}$ for the spectral region $500 \text{ cm}^{-1} \leq \omega \leq 700 \text{ cm}^{-1}$. The absorption coefficient α for the local mode of boron acceptors ($\approx 10^{18}$ cm⁻³) in an Si lattice is $\approx 1 \text{ cm}^{-1}$. As the local mode frequencies of the boron isotopes [Si: ¹⁰B(644 cm⁻¹), Si: ¹¹B(620 cm⁻¹)] lie within the α_{FC} spectral region, it is therefore essential to reduce the concentration of the free carriers without reducing the impurity concentration. The reduction of free-carrier concentration is generally accomplished¹⁻⁴ by (a) double doping during crystal growth, (b) using electron or proton irradiation, (c) introducing intrinsic defects (e.g., vacancies at Cd sites in CdTe: Al-doped samples), and/or (d) by diffusion under conditions where the solubility of the diffusant is controlled by the impurity to be compensated. In all the above methods of compensation there results the possibility of ion pairing, and such pair centers are expected to give rise to impurity vibrations which are detectable by optical experi-

ments.

In addition to the extensive data of pair defects in diamond-type crystal,¹¹⁻¹⁷ there have also been many results accumulated for LVM's due to impurity complexes in zinc-blende-type crystals.¹⁸⁻³² For comprehensive reviews of experimental results on impurity modes due to several defect centers (isolated and pair impurities) in ionic, partially ionic, and homopolar crystals, we refer to the articles by Spitzer,¹ Mitsuishi and Manabe,² Newman,³ and more recently by Barker and Sievers.⁴ Again, the success for observing LVM's has initiated experimentalists to detect resonance modes; consequently, some experimental speculations are known for the occurrence of resonance modes due to copper and zinc complexes in GaAs crystals.^{33,34}

Despite the detailed experimental information concerning the vibrations of impurity complexes of known symmetry, reasonable defect model calculations are rather sparse. Most of the existing theoretical results based on the Green's-function technique are related to the vibrations of isolated point defects.⁵⁻¹⁰ The use of the Green's-function theory for studying the effect of impurities on the properties of crystals is contained in several review articles by Maradudin,³⁵⁻³⁸ who confines his attention to the phonon aspects of the problem. A unified view of electronic, magnetic, and vibrational impurity states on the basis of the Green's-function approach can be found in the articles by Izyumov³⁹ and more recently by Elliott *et al.*⁴⁰ Also noteworthy are the monographs by Klein⁴¹ and by Barker and Sievers⁴ on local and resonant modes in ionic and partially ionic crystals.

Elliott and Pfeuty⁷ (EP) were the first to initiate theoretical calculations of impurity modes due to various pair defects of different configurations in an Si lattice. To treat the actual numerical calculations with only six Green's-function matrix elements, EP were bound to undertake several approximations in defining the perturbation matrices. In the case of two adjacent impurities, for example, EP assumed change of coupling only between the impurities, neglecting all other impurity-host lattice interactions which were certainly nonzero. Grimm, Maradudin, Ipatova, and Subashiev⁸ (GMIS) have recently extended the EP theory for application to the low-lying resonance lines due to copper complexes in GaAs crystals. Again, to cope with the complicated mathematics in defining the perturbation for impurity complex of C_s point-group symmetry, GMIS have also neglected the interaction of impurity at site 6 with the host lattice atoms at 9, 10, and 11 [cf. Fig. 1(c) of the present article]. Furthermore, GMIS have used the simplest possible two-parameter force model for generating the lattice phonons and thereby evaluating the involved lattice Green's-function matrix elements. Since a two-parameter force model fails to explain the neutron experiment of phonon dispersions along high-symmetry directions for zinc-blende-type crystals, the calculated values of lattice Green's functions and consequently their defect properties may not be very reliable.

Recently, in the framework of the Green's-function technique and using a more elaborate rigid-ion model for the lattice dynamics, we have studied the vibrations of several isolated substitutional impurities in I-VII,⁴² II-VI, and III-V compounds of zinc-blende-type crystals.^{9,10} We found that the calculated values of force variation between the impurity and its nearest neighbors are nonzero even for the isoelectronic case.^{9,10} Again, the force variation is clearly correlated both with the nature of the impurity (donor or acceptor) and with the substituted site.

In the present paper, 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. This study is also intended to find whether or not the simple empirical law of force variation related with bond ionicity for isolated charged impurities can be generalized for pair-defect vibrations in elemental and compound semiconductors. Starting from the simplest structure of a single point defect [cf. Fig. 1(a)] we present in Figs. 1(b) and 1(c) the modeling for two and three point defects occupying

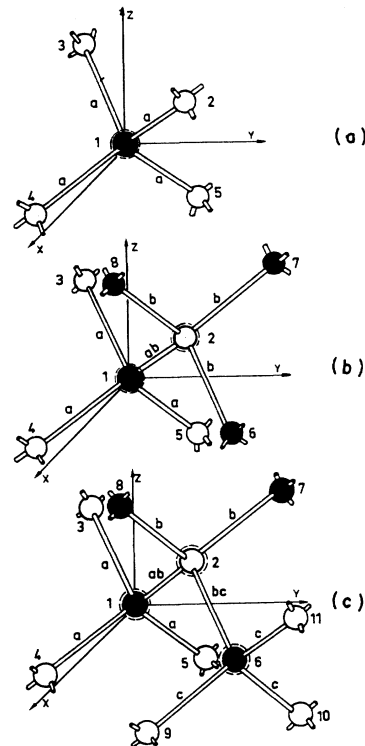


FIG. 1. Impurity models for the vibrations of one-, two-, and three-defect centers in zinc-blende-type crystals. The number of atoms 1, 2, 3, . . . 11 and their respective coordinates have been considered with the following notations: 1 cation $\frac{1}{2}a_0$ (0, 0, 0), 2 anion $\frac{1}{2}a_0$ (1, 1, 1), 3 anion $\frac{1}{2}a_0$ ($\bar{1}$, $\bar{1}$, 1), 4 anion $\frac{1}{2}a_0$ (1, $\bar{1}$, $\bar{1}$), 5 anion $\frac{1}{2}a_0$ ($\bar{1}$, 1, $\bar{1}$), 6 cation $\frac{1}{2}a_0$ (2, 2, 0), 7 cation $\frac{1}{2}a_0$ (0, 2, 2), 8 cation $\frac{1}{2}a_0$ (2, 0, 2), 9 anion $\frac{1}{2}a_0$ (3, 1, $\bar{1}$), 10 anion $\frac{1}{2}a_0$ (1, 3, $\bar{1}$), and 11 anion $\frac{1}{2}a_0$ (3, 3, 1). Dotted circles represent the impurity centers occupying 1, 2, or 6 sites in (a), (b), and (c), respectively.

nearest-neighbor lattice sites. We assume that the force variations about the defects (at sites 1, 2, and 6) are significant only up to the first nearest neighbors. Additional interactions in between the impurity atoms (viz., 1-2 and 2-6) have also been considered whenever necessary in terms of two (Γ_{12} and Γ_{26}) perturbation parameters. The Green's-function matrix elements creating a defect space of eleven involved atoms (see Fig. 1) are thirty-three, which have been evaluated numerically by incorporating the phonons generated by a rigid-ion model of eleven disposable parameters⁴³ (RIM-11).

The paper is organized into six sections: A brief theoretical background of the Green's-function method for studying vibrational properties of the imperfect solids is contained in Sec. II. The use of group theory to simplify the numerical calculations is outlined in Sec. III. Numerical computations for the vibrations of pair defects

with C_{3v} and C_s point-group symmetries in diamond and zinc-blende-type crystals are made, and the results are reported in Sec. IV for explicit impurity complexes. The results are discussed in Sec. V, with concluding remarks presented in Sec. VI. The relevant mathematical results of Sec. III are found in Appendices A and B.

II. BASIC THEORY

The Green's-function method as discussed in several review articles and monographs is followed here for studying the vibrations of various

defect configurations in zinc-blende-type crystals. In the Green's-function theory, the frequencies of the perturbed modes due to the defects can be determined by the condition³⁵

$$\text{Re Det}(I - g\delta l) = 0 \quad (2.1)$$

[valid for frequencies where the density of states is low (or zero) and slowly varying]. Here g and δl are the Green's-function matrix of the perfect lattice and the perturbation matrix in the impurity space (i.e., the space directly affected by the introduction of the defect), respectively.

The matrix elements of the complex Green's function have the usual forms³⁵⁻³⁸:

$$g_{\alpha\beta}(lK; l'K' : \omega^2 - i\xi) = \frac{1}{N(M_K M_{K'})^{1/2}} \sum_{\vec{q}, j} \frac{e_{\alpha}(K|\vec{q}, j)e_{\beta}^*(K'|\vec{q}, j)}{\omega^2 - \omega^2(q, j) - i\xi} \exp\{i\vec{q}[\vec{x}(lK) - \vec{x}(l'K')]\}, \quad (2.2)$$

in terms of the normal-mode frequency $\omega(\vec{q}, j)$ and eigenvector $e_{\alpha}(K|\vec{q}, j)$ (with wave vector \vec{q} and branch index j) of the perfect crystal; M_K denotes the mass of the K th type of atom in a unit cell, N represents the number of unit cells in the crystal, $\vec{x}(lK)$ shows the equilibrium position of the K th atom in the l th unit cell, and ξ is to be understood as a positive infinitesimal.

If the solutions of Eq. (2.1) occur in a frequency region not covered by the host lattice, they are called "localized" or "gap" modes. Their displacement field is large at the impurity and decays rapidly with distance from the defect site. Such modes appear as the delta function peaks in the optical spectra. However, if they lie in a band of frequencies covered by the host, the vibrations are not confined in space around the defect. Such modes are called "quasilocal" or resonant modes and have nonzero width. These modes are considered to be localized modes which acquire width because of the finite density of states around the resonant frequency.

A. Lattice dynamics

In order to treat the vibrational properties of imperfect solids by the Green's-function technique, the knowledge of perfect-lattice phonons is needed from a reliable lattice-dynamical model. In ionic crystals (with rocksalt and cesium-halide structure) several Green's-function calculations⁴ of point defects exist in the literature using the rigid-ion model (RIM), shell model, and breathing shell model. However, in zinc-blende-type crystals almost all the available calculations^{6,9,10} of defect properties use the RIM, although shell-model⁴⁴ and valence-shell-model⁴⁵ fitted lattice phonons in several perfect

systems are known. We understand this reasoning primarily because of the relative simplicity of the RIM, that with fewer parameters it provides practically identical phonon dispersions when compared with those obtained from more complicated models. Again in the shell model⁴⁶ there is, in general, a possibility to select more than one set of model parameters that furnish an equally good fit to the neutron data. The RIM on the other hand, always provides a "homogeneous" set of model parameters, by a least-squares-fitted method.⁴³ (What we actually mean by a "homogeneous" set of model parameters is described in Ref. 42.)

In an earlier study, we have estimated the force variations due to several point defects in various I-VII, II-VI, and III-V compounds using the Green's-function technique in the framework of an eleven-parameter rigid-ion model (RIM-11).⁴³ In order to find some coherence in the force variation, it is worthwhile to treat the vibrations of impurity complexes using the same lattice-dynamical model. The RIM-11 fitted neutron results can be found in the work of Kunc⁴³ for ZnS, ZnSe, GaP, GaAs, and InSb. For the lattice dynamics of ZnTe, CdTe,⁴⁷ InP,⁴⁸ and GaSb,¹⁰ reference is made to the articles by Vandevyver and Plumelle.

B. Green's functions

The size of the Green's-function matrix g and the perturbation matrix δl depend on the space affected by the impurity molecule embedded in a lattice of known crystal structure.³⁵⁻³⁸ In zinc-blende-type crystals,⁷⁻¹⁰ if some impurity (I) substitutes for either the Zn (number 1) or S (number 2) atom of ZnS lattice [see Fig. 1(a)],

the crystal field in the neighborhood of the impurity exhibits T_d symmetry. If, on the other hand, the impurity forms a complex either with a new impurity atom or with native defects of the host lattice, the T_d symmetry at the defect sites (I_{Zn} or I_S) will be disturbed. Among the other possibilities of substitution, the most probable situations may occur (i) when the new impurity atom in the neighborhood of I_{Zn} (say) occupies the nearest S site and/or (ii) if the impurity occupies the nearest Zn (number 6) site to I_{Zn} . In the former case (i) the symmetry at I_{Zn} becomes C_{3v} whereas in the latter case (ii) it reduces to C_s . If force-constant changes are included in the nearest-neighbor approximation, the size of the Green's-function and perturbation matrices becomes 15×15 for the vibrations of a single substitutional impurity with T_d symmetry. However, for the vibrations of impurity complexes with C_{3v} and C_s symmetries, the sizes of the matrices increase to 24×24 and 33×33 , respectively.

In the case of the most extended impurity complex creating a defect space of eleven involved atoms, we require thirty-three independent elements of the Green's-function matrix. The determination of these elements is usually accomplished using group-theoretic arguments, and the transformation properties under operations of the crystal space group.³⁵⁻³⁸ In Table I we have given all the thirty-three elements of the Green's-function required for the full-size 33×33 matrix.⁴⁹ In the actual numerical calculations of the relevant Green's functions, we have incorporated the eigenvectors and eigenvalues generated by the RIM-11, and the Brillouin-zone summations extended over 16 369 points uniformly distributed in the reciprocal space is used. For numerical details we refer to an earlier paper.⁴⁸

C. Perturbation matrix

The case of a single substitutional impurity vibration in zinc-blende-type crystals has been discussed in length elsewhere.^{9,10} Contrary to the findings of Gaur *et al.*,⁹ our results, based on more refined models for the lattice dynamics of perfect crystals and for the defects, have shown that even for isoelectronic substituents the calculated local force variations are quite appreciable and cannot be neglected. In defining the perturbation model for point defects, the first-neighbor short-range tensor force parameters

TABLE I. The Green's-function matrix elements $g_{\alpha\beta}(lK; l'K'; \omega^2 - i\zeta)$ for the most extended case of C_s point-group symmetry in zinc-blende-type crystals.

No. of G.F. matrix elements
$g_1 = g_{xx} (111; 111; \omega^2 - i\zeta)$
$g_2 = g_{xx} (000; 000; \omega^2 - i\zeta)$
$g_3 = g_{xx} (111; 000; \omega^2 - i\zeta)$
$g_4 = g_{xy} (111; 000; \omega^2 - i\zeta)$
$g_5 = g_{xx} (000; 220; \omega^2 - i\zeta)$
$g_6 = g_{xx} (000; 220; \omega^2 - i\zeta)$
$g_7 = g_{xy} (000; 220; \omega^2 - i\zeta)$
$g_8 = g_{xx} (000; 220; \omega^2 - i\zeta)$
$g_9 = g_{xx} (111; \bar{1}\bar{1}1; \omega^2 - i\zeta)$
$g_{10} = g_{xx} (111; \bar{1}\bar{1}1; \omega^2 - i\zeta)$
$g_{11} = g_{xy} (111; \bar{1}\bar{1}1; \omega^2 - i\zeta)$
$g_{12} = g_{xx} (111; \bar{1}\bar{1}1; \omega^2 - i\zeta)$
$g_{13} = g_{xx} (\bar{1}\bar{1}1; 220; \omega^2 - i\zeta)$
$g_{14} = g_{xx} (\bar{1}\bar{1}1; 220; \omega^2 - i\zeta)$
$g_{15} = g_{xy} (\bar{1}\bar{1}1; 220; \omega^2 - i\zeta)$
$g_{16} = g_{xx} (\bar{1}\bar{1}1; 220; \omega^2 - i\zeta)$
$g_{17} = g_{xx} (\bar{1}\bar{1}1; 220; \omega^2 - i\zeta)$
$g_{18} = g_{xx} (1\bar{1}\bar{1}; 220; \omega^2 - i\zeta)$
$g_{19} = g_{xy} (1\bar{1}\bar{1}; 220; \omega^2 - i\zeta)$
$g_{20} = g_{xx} (1\bar{1}\bar{1}; 220; \omega^2 - i\zeta)$
$g_{21} = g_{yy} (1\bar{1}\bar{1}; 220; \omega^2 - i\zeta)$
$g_{22} = g_{yy} (1\bar{1}\bar{1}; 220; \omega^2 - i\zeta)$
$g_{23} = g_{xx} (\bar{1}\bar{1}1; 31\bar{1}; \omega^2 - i\zeta)$
$g_{24} = g_{yy} (\bar{1}\bar{1}1; 31\bar{1}; \omega^2 - i\zeta)$
$g_{25} = g_{xy} (\bar{1}\bar{1}1; 31\bar{1}; \omega^2 - i\zeta)$
$g_{26} = g_{yx} (\bar{1}\bar{1}1; 31\bar{1}; \omega^2 - i\zeta)$
$g_{27} = g_{yx} (\bar{1}\bar{1}1; 31\bar{1}; \omega^2 - i\zeta)$
$g_{28} = g_{xx} (\bar{1}\bar{1}1; 331; \omega^2 - i\zeta)$
$g_{29} = g_{xx} (\bar{1}\bar{1}1; 331; \omega^2 - i\zeta)$
$g_{30} = g_{xy} (\bar{1}\bar{1}1; 331; \omega^2 - i\zeta)$
$g_{31} = g_{xx} (\bar{1}\bar{1}1; 331; \omega^2 - i\zeta)$
$g_{32} = g_{xx} (1\bar{1}\bar{1}; 13\bar{1}; \omega^2 - i\zeta)$
$g_{33} = g_{yy} (1\bar{1}\bar{1}; 13\bar{1}; \omega^2 - i\zeta)$

$$\Phi(\text{Zn}; \text{S}) = \begin{pmatrix} A & B & B \\ B & A & B \\ B & B & A \end{pmatrix} \quad (2.3)$$

of the perfect lattice are considered to be modified such that

$$\Phi(\text{impurity}; \text{S}) = \begin{pmatrix} A' & B' & B' \\ B' & A' & B' \\ B' & B' & A' \end{pmatrix}. \quad (2.4)$$

In order to describe the impurity to be at site 1 (say) by a single dimensionless parameter t , we suppose that A' and B' are proportional to A and B , respectively. Therefore

$$t \equiv (A - A')/A = (B - B')/B = (1 - a). \quad (2.5)$$

Similarly we assume parameters u and v that define variations of nearest-neighbor coupling constants due to substitutional impurities at sites 2 and 6, respectively:

$$u \equiv (A - A'')/A = (B - B'')/B = (1 - b), \quad (2.6)$$

$$v \equiv (A - A''')/A = (B - B''')/B = (1 - c). \quad (2.7)$$

If the three units with isolated impurities at 1, 2, and 6 sites are linked together as shown in Fig. 1(c), it results in the most general defect model of eleven involved atoms in the nearest-neighbor approximation. To make the perturbation model more appropriate, we have also considered the direct interaction in between the impurities by two additional parameters Γ_{12} and Γ_{26} . The force variation is thus given by

$$F_{12} \equiv (1 - ab + \Gamma_{12}) = (u + t - ut + \Gamma_{12}), \quad (2.8)$$

and

$$F_{26} \equiv (1 - bc + \Gamma_{26}) = (u + v - uv + \Gamma_{26}). \quad (2.9)$$

The term F_{12} (or F_{26}) < 0 (or > 0) corresponds to stiffening (or softening) of the bonds 1-2 (or 2-6), respectively. The complete perturbation matrix δl (33×33) has been formed⁴⁹ for a special case of an impurity complex comprised of three impurity centers at 1, 2, and 6 sites, respectively.

III. GROUP-THEORETIC ANALYSIS

In order to find the zeros of the determinantal equation (2.1), group theory is used to simplify the calculations. The introduction of the symmetry coordinates for the impurity molecule that transform according to the irreducible representation s of the site symmetry at the impurity allows the block diagonalization of g and δl . The vector spaces formed by the displacements of the impurity molecule and its neighbors \underline{u} (say) transform according to the following irreducible representations:

$$\Gamma_{T_d} = A_1 + E + F_1 + 3F_2, \quad (3.1)$$

$$\Gamma_{C_{3v}} = 6A_1 + 2A_2 + 8E, \quad (3.2)$$

and

$$\Gamma_{C_s} = 19A_1 + 14A_2. \quad (3.3)$$

The symmetry coordinates \underline{X} as given by the reduction of their vector spaces can be written for T_d , C_{3v} , and C_s point groups in the form

$$\underline{X} = \underline{S} \underline{u}. \quad (3.4)$$

We have constructed⁴⁹ the complete 33×33 eigenvector matrix \underline{S} for C_s symmetry, whereas the form of \underline{S} is known for T_d and C_{3v} symmetry cases from the articles of Ludwig⁵⁰ and of GMIS.⁸

Using \underline{S} one can block-diagonalize g and δl matrices with each block along the diagonal belonging to a particular irreducible representation s . For C_{3v} and C_s point-group symmetries the block-diagonal g and δl matrices in different irreducible representations have the forms given in Appendices A and B respectively.

IV. NUMERICAL COMPUTATION AND RESULTS

The Green's-function theory developed in previous sections may be applied to various possible configurations of impurity vibrations in zinc-blende-type crystals and is equally suitable for diamond-type crystals. By setting $M'_2 = M_2$, $M'_6 = M_1$, and $u = v = \Gamma_{12} = \Gamma_{26} = 0$, one can get results of vibrations for the simplest case of point defect at site 1. If the impurity atom is light as compared to the host-lattice atoms, the vibrational mode of interest will be the triply degenerate localized mode and hence will appear as a single band in optical experiments. The localized pattern will be similar for some light impurity atom substituted for site 2. In earlier studies^{10,51} we have estimated the force variations needed to explain the existing experimental data for various substitutional point defects on either of the 1 or 2 lattice sites. This will help us in analyzing the experimental results of pair modes in diamond or zinc-blende-type crystals. We discuss the following cases:

(a) C_s case. The ion pair with C_s point-group symmetry can give rise to A_1 and A_2 types of vibrational modes, all optically allowed. Since the degeneracies are lifted, six impurity bands are expected for this type of impurity center of very light defect atoms. The effect of a vacancy at site 6 (say) in the pair of C_s symmetry (e.g., $I_1 - V_6$) is to lift the degeneracy of the impurity oscillator at site 1; hence one obtains three non-degenerate modes. We have analyzed the existing experimental data on the basis of our theoretical model, and the perturbation-model parameters needed to explain the vibrations of impurity centers in II-VI and III-V compounds are listed in Table II.

(b) C_{3v} case. In C_{3v} symmetry the impurity center does not move in the A_2 irreducible representation; only A_1 and E types of modes will be observed by optical experiments (ir absorption and Raman scattering). If the impurity atoms are lighter than the substituted ones, four localized modes of vibrations should arise [two because of their movement along their line of joining (1 or A_1^+ , $\leftarrow - \rightarrow$; 4 or A_1^- ; $\rightarrow - \leftarrow$) and two as a result of movement perpendicular (2 or E^+ , $\uparrow \downarrow$; 3 or E^- , \uparrow ,) to it], generally with $\omega_1 > \omega_2 > \omega_3 > \omega_4$.

TABLE II. Localized vibrational modes due to pair defects of C_s point-group symmetry in zinc-blende-type crystals. The underlined atom is the one substituted by those following the colon at sites 1 and 6, respectively.

System	Localized mode frequency (cm^{-1})			t, F_{12}, F_{26}, v (Defect parameters)	t or v (Ref. 10) isolated case	Ref.
	Experimental	Calculated	Mode			
III-V compounds						
<u>GaAs</u> : ⁶ Li, Si	487	484	A_1	0.91	0.90	1
	480	480	A_1	0.847		
	470	475	A_2	-0.513		
	405	406	A_1	0.11	-0.03	
	379	380	A_2			
	374	374	A_1			
<u>GaAs</u> : ⁷ Li, Si	455	453	A_1	0.91	0.90	1
	448	450	A_1	0.847		
	438	442	A_2	-0.513		
	405	405	A_1	0.11	-0.03	
	379	380	A_2			
	374	372	A_1			
<u>GaAs</u> :Si, Cu	399	399	A_1	0.12	-0.03	1
	376	376	A_1	-0.364		
	374	376	A_2	0.225 0.5		
<u>GaAs</u> :Si, Zn	395	395	A_1	0.055	-0.03	1
	382	382	A_1	-0.257		
	378	381	A_2	0.601 0.7		
<u>GaP</u> :Si, Cu	484.2	484	A_1	0.14	0.08	25
	453.8	453	A_1	-0.075		
	453.8	453	A_2	0.625 0.7		
<u>GaP</u> :Si, Zn	478.7	478.7	A_1	0.092	0.08	25
	461.2	462	A_1	-0.035		
	458	462	A_2	0.772 0.8		
II-VI compounds						
<u>ZnSe</u> : ⁷ Li, Al	393	395	A_1	0.985	0.97	31
	383	389	A_1	0.98		
	356?	383	A_2	-0.606		
	373	373	A_1	-0.295	-0.30	
	359	359	A_2			
<u>ZnSe</u> : ⁶ Li, Al	350	349	A_1			31
	424?	416	A_1	0.985	0.97	
	412	414	A_1	0.98		
	390	411	A_2	-0.606		
	373	377	A_1	-0.295	-0.30	
<u>ZnSe</u> :Al, V	359	359	A_2			28(2)
	350	353	A_1			
	388	388	A_1	-0.17	-0.30	
	346	346	A_1	-0.704		
<u>ZnSe</u> :Al, Cu	339(342)	344	A_2	1.0 1.0		28
	377	377	A_1	-0.215	-0.30	
	351.5	351	A_1	-0.543		
	348.0	351	A_2	0.365 0.5		

TABLE II. (Continued.)

System	Experimental	Calculated	Mode	t, F_{12}, F_{26}, v (Defect parameters)	t or v (Ref. 10) isolated case	Ref.
<u>ZnSe</u> : Al, Au	381	381	A_1	-0.187	-0.30	28
	348	348	A_1	-0.602		
	345	348	A_2	0.325 0.5		
<u>ZnTe</u> : Al, V	338(335)	338	A_1	-0.456	-0.51	2
	299	299	A_1	-0.63		
	297	297.7	A_2	1.0 1.0	1.0	
<u>ZnS</u> : Al, V	477	477	A_1	-0.39	-0.76	32
	423	423.9	A_1	-0.911		
	415	418.9	A_2	1.0 1.0	1.0	
<u>ZnS</u> : Al, Cu	462	462	A_1	-0.76	-0.76	32
	438	438.7	A_1	-1.04		
	423	438	A_2	0.42 0.50		
<u>ZnS</u> : Al, Au	465	465	A_1	-0.65	-0.76	32
	427	426	A_1	-1.096		
	423	425	A_2	0.366 0.50		
<u>CdTe</u> : Al, V	326	326	A_1	-0.12	-0.23	27
	287	288	A_1	-0.68		
	282	288	A_2	1.0 1.0	1.0	
<u>CdTe</u> : Al, Cu	310	310	A_1	-0.183	-0.23	27
	294	294	A_1	-0.42		
	291	294	A_2	0.76 0.80		
<u>CdTe</u> : Al, Au	326	326	A_1	-0.12	-0.23	27
	288	288	A_1	-0.68		
	288	288	A_2	0.40 0.60		

However, if one of the pair atoms is relatively heavier than the replaced host atom, only two vibrational modes are to be observed experimentally. The results of our calculations in the mass-defect approximation (MDA) for B (Si or Al) paired with other impurities in elemental (III-V or II-VI) semiconductors are shown in Figs. 2-12. Setting the case of InP and ZnS aside, our results of MDA also suggest the possibility of four LVM's provided that the masses of the pair atoms are very much smaller than those of the host lattice atoms. On the other hand, two modes (3 and 4) fall into the band continuum and only two vibrational modes (1 and 2) are to be seen for $1 > \epsilon_1 > 0$ and $\epsilon_2 < 0$ ($\epsilon_i = (M_i - M'_i)/M_i$, $i = 1, 2$). At $\epsilon_2 = 0$, $\omega_1 = \omega_2$ which eventually gives the MDA value of the LVM frequency for the single impurity vibration at site 1. The absence of modes 3

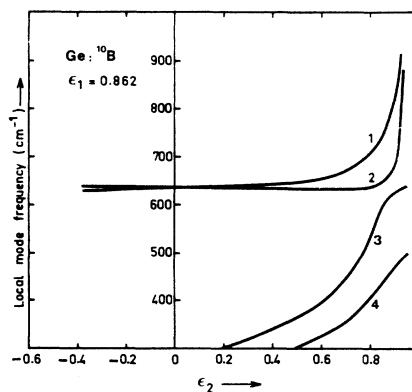


FIG. 2. Localized vibrational modes due to ^{10}B paired with other impurities in Ge lattice in the MDA. The numbers 1, 2, 3, and 4 refer to the different vibrations of the pair defects as described in the text.

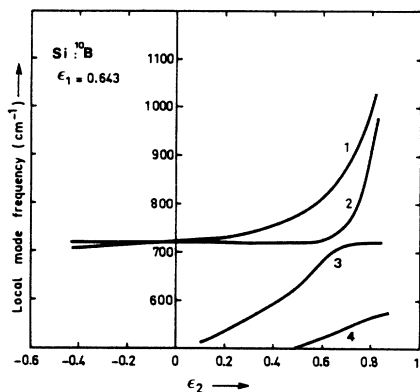


FIG. 3. Same key as Fig. 2 but for an Si lattice.

and 4 and a very small splitting in 1 and 2 vibrations in InP and ZnS crystals are probably evidence for the absence of a large change in force constants about the impurity centers.

The effect of force-constant changes in between the impurity pair is displayed in Fig. 4: It mainly affects, as expected, the modes of impurity vibrations related to the movement of atoms along their line of joining (1 and 4), while the modes related to the movement of atoms perpendicular to it (e.g., 2 and 3) remain almost unchanged. On the other hand, all the vibrational modes are affected with the change of impurity-host interactions (cf. Figs. 7 and 9). A representative list

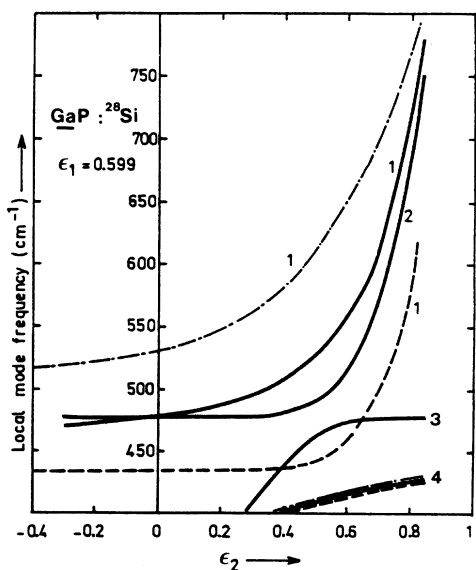


FIG. 4. Localized vibrational modes due to ^{28}Si occupying a Ga site and paired with other impurities replacing P site in GaP lattice. The calculations are represented by— for MDA, --- with $F_{12}=0.4$, and - · - · with $F_{12}=-0.4$, respectively.

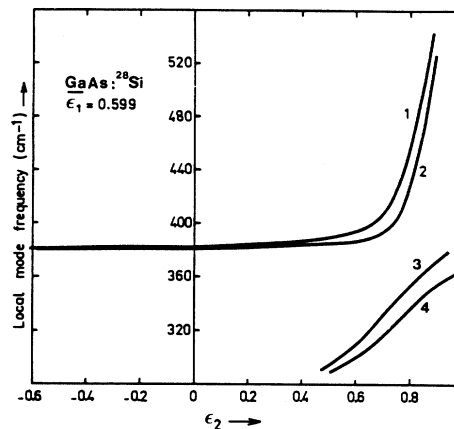


FIG. 5. Localized vibrational modes in the MDA due to ^{28}Si occupying a Ga site and paired with other impurities replacing an As site in a GaAs lattice.

of almost all the existing experimental results on LVM's due to nearest-neighbor pair defects in elemental and compound semiconductors is given in Table III. The calculated results along with the changes in force constants required to correspond with the experimental data have also been included in column three of Table III.

V. DISCUSSION

Before critically analyzing the trends of force variations and consequently the proposed assignment for the vibrational modes of pair defects especially with C_{3v} symmetry, it will be better to point out in brief the behavior of force variations observed earlier for isolated charged impurities in compound semiconductors.^{9,10} For closest mass acceptor (donor) and isoelectronic impurities occupying II or III lattice sites in II-VI or III-V

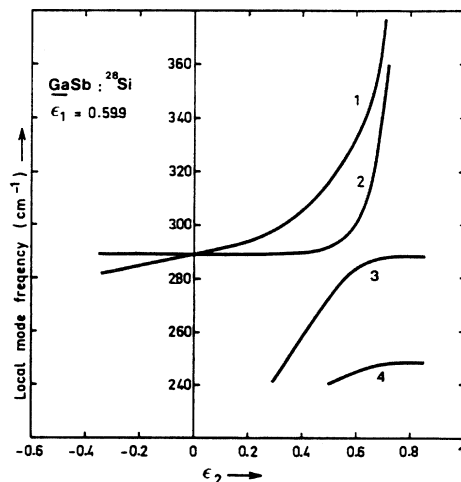


FIG. 6. Same key as Fig. 5 but for GaSb.

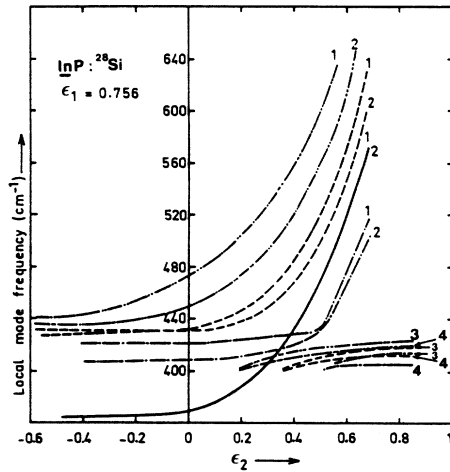


FIG. 7. Localized vibrational modes due to ^{28}Si occupying an In site and paired with other impurities replacing a P site in an InP lattice. The calculations are represented by — for MDA, --- for $t (= F_{12}) = -0.59$, $u = \Gamma_{12} = 0$; - · - · - for $t = -0.59$, $u = 0.4$, $F_{12} = 0.046$; and - · - · - for $t = -0.59$, $u = -0.4$, $F_{12} = -1.226$, respectively.

compounds, we find the following trend of force variations¹⁰:

$$\Delta t^{\text{II or III}} = \begin{cases} t(\text{acceptor}) - t(\text{isoelectronic}) > 0, \\ t(\text{donor}) - t(\text{isoelectronic}) < 0 \end{cases} \quad (5.1)$$

for softening and stiffening, respectively. However, for acceptors occupying VI or V lattice sites the trend of force variation is just the opposite if viewed again in relation to an isoelectronic case: i.e. (with the present notation), for stiffening,

$$\Delta u^{\text{VI or V}} = u(\text{acceptor}) - u(\text{isoelectronic}) < 0 \quad (5.2a)$$

Similarly we suspect a negative trend for donors;

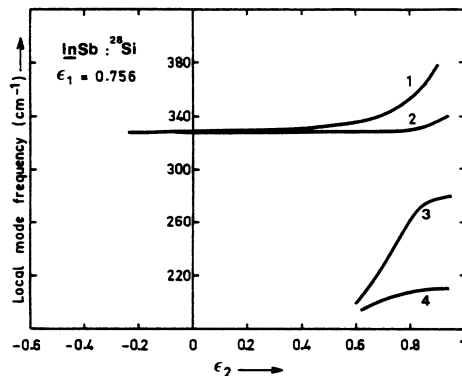


FIG. 8. Localized vibrational modes in the MDA due to ^{28}Si occupying an In site and paired with other impurities replacing an Sb site in an InSb lattice.

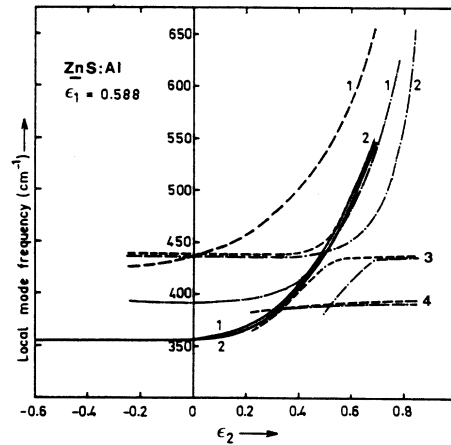


FIG. 9. Localized vibrational modes due to Al occupying a Zn site and paired with other impurities replacing an S site in a ZnS lattice: The calculations are represented by — for MDA: --- for $t (= F_{12}) = -0.76$, $u = \Gamma_{12} = 0$; and - · - · - for $t = -0.76$, $u = 0.4$, $F_{12} = -0.056$.

so that for softening,

$$\Delta u^{\text{VI or V}} = u(\text{donor}) - u(\text{isoelectronic}) > 0. \quad (5.2b)$$

The absolute value of the relative variation for III-V and II-VI compounds lies well within 15–35% and is not related to physical properties such as electronic affinity or the size of the impurity host atoms. However, from Eqs. (5.1), (5.2a), and (5.2b) it can be noted that there is a net correlation between the force perturbation and modification of the bond ionicity (or covalency).⁵¹ It is found that the increase or decrease of force variation due to charged impurities varies in the same sense as does the increase or decrease of the covalency of the bond.⁵² The empirical rule formulated in this way for II-VI or III-V compounds seems to hold reasonably well for charged defects in elemental semiconductors also.⁵³ We discuss the following cases:

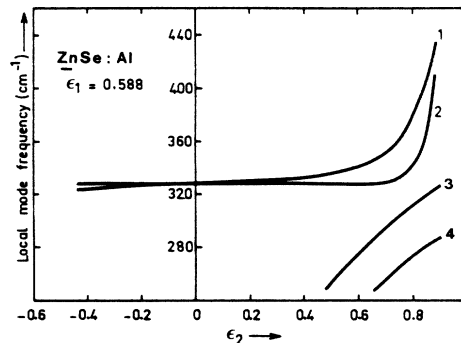


FIG. 10. Same key as Fig. 9 but for ZnSe and only in the MDA.

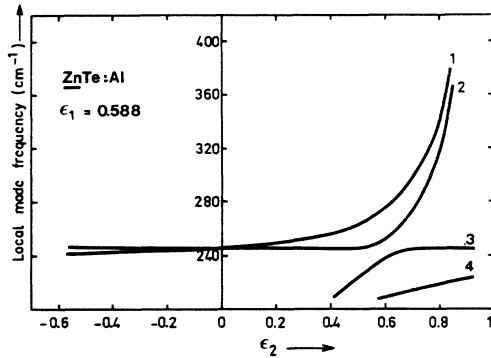


FIG. 11. Same key as Fig. 9 but for ZnTe and only in the MDA.

(a) C_s case. Let us first consider the calculated results of force variations for C_s pair defects based on the above criterion. We have given priority to these pair defects simply because there exists one and only one set of perturbation parameters corresponding to each impurity center that reasonably fits the existing experimental LVM's. Again we have neglected additional force constants (Γ_{12} and Γ_{26}) between 1-2 and 2-6 bonds and have considered only three (t , u , and v) out of five perturbation parameters in these calculations. Since a vacancy at site 6 is visualized as $M'_6=0$ with $v (=F_{26})=1$, we find that "defect-host-vacancy" pair vibrations can be easily fitted by only two adjustable parameters t and u (or F_{12}), which serves as a very good example to find and compare the trends of force variations with isolated charged impurities. Moreover, from each example of an acceptor (donor) at site 1 and a donor (acceptor or vacancy) at

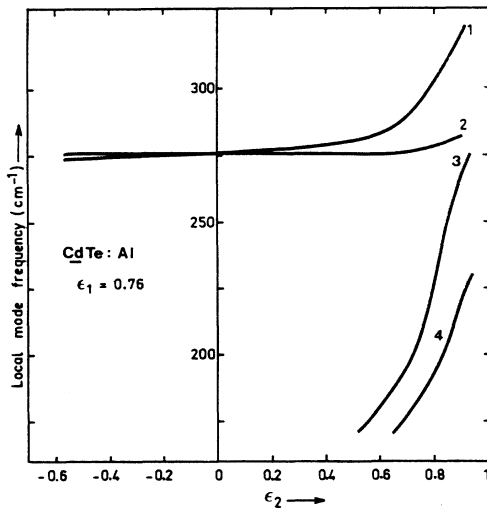


FIG. 12. Same key as Fig. 9 but for CdTe and only in the MDA.

site 6, we have noticed the same trend of softening (stiffening) (for F_{12}) and stiffening (softening) (for F_{26}) related to the decrease or increase of covalency. The values of t and v for the isolated (T_d) case have also been given whenever known (cf., Table II) for better contrast. One may note that isolated force variation values of donor or acceptor impurities have been changed slightly but they are found to be in the same order of magnitude.

Except for the ZnSe:Li, Al system our calculated results have provided very good agreement with the impurity modes observed in different experimental work. Since Dutt *et al.*²⁷⁻²⁹ (and more recently Król *et al.*³²) have realized that the earlier experimental measurements of Mitsuishi *et al.*³¹ have not been satisfactorily analyzed, we too, on the basis of our calculations, feel that the impurity modes in the ZnSe:Li, Al system are to be reinvestigated. In concurrence with our earlier observation of the same force-constant change for different isotopes of an isolated impurity,¹⁰ we find that the same trend still holds true even if the different isotopes are paired with a given impurity atom. This result is supported by the analysis of Talwar and Agrawal⁹ but is in contradiction with the finding of Jain and Prabhakaran.⁵⁴

(b) C_{3v} case. There are two kinds of experimental data known for nearest-neighbor pair defects in elemental and compound semiconductors. In the first category [type (i)] more than two impurity modes have been observed for the pair of very light impurity atoms, whereas in the second kind [type (ii)] only two vibrational modes have been reported for the pair of one light and one heavy impurity atoms. In the Si lattice, especially when B (acceptor) is paired with heavier P, As, and Sb (donors), we find that there exist some controversial and extraneous experimental observations that hinder one from making a definitive assignment to the frequencies of the two types of vibrational modes.^{3,4} The calculated splitting of the two lines A_1 and E in the MDA is very much smaller than the experimental values for each impurity center studied in both elemental and compound semiconductors (cf. Figs. 2-12). Contrary to the C_s case, where only one set of parameters exists, we are able to fit exactly the existing data of LVM's for C_{3v} [type (ii)] case by two equally possible sets of force-constant change parameters (cf. Table III): The first set (a) gives frequency to the mode A_1 smaller than E , whereas in (b) the reverse is assumed; i.e., $\omega_{A_1} > \omega_E$. It is really difficult to determine which set of parameters is more physically plausible in a situation when no con-

TABLE III. Local mode frequency due to pair defects of C_{3v} point-group symmetry in diamond and zinc-blende-type crystals, where the underlined atoms are substituted by those following the colon, respectively.

System	Local mode frequency (cm ⁻¹)		Mode	t, F_{12}, u Defect parameters (parameter set)	t or u (Refs. 10 and 51) Isolated case	Opinion	Ref.	
	Expt.	Calc.						
Type (i) III-V compounds								
<u>GaAs</u> : ²⁸ Si, ²⁸ Si	464	464.6	A_1^+	-0.03	-0.03	Good	1	
	393	424.5	E^+	-0.59				
	367.2	367.8	E^-	-0.54				
		337.8	A_1^-					
	464	464	A_1^+	0.10	-0.03			
	393	393	E^+	-1.015				
	367.2	E^-	-0.47	-0.54	Better			
		A_1^-						
<u>GaAs</u> : ²⁸ Si, ¹⁰ B	685	653	A_1^+	-0.03	-0.03	Good	25	
	596	632	E^+	-0.63				
	384	388	E^-	-0.58	-0.58			
	349	374	A_1^-					
	685	685	A_1^+	-0.003	-0.03			
	596	596	E^+	-1.118				
	384	384	E^-	-0.295	-0.58			Better
	349	365	A_1^-					
<u>GaAs</u> : ²⁸ Si, ¹¹ B	661	628	A_1^+	-0.03	-0.03	Good	26	
	571	605	E^+	-0.63				
	384	388	E^-	-0.58	-0.58			
	349	373	A_1^-					
	661	661	A_1^+	-0.003	-0.03			
	571	572	E^+	-1.118				
	384	383	E^-	-0.295	-0.58			Better
	349	363	A_1^-					
<u>GaP</u> : ²⁸ Si, ¹⁰ B	715	675	A_1^+	0.08	0.08	Good	26	
	621	651	E^+	-0.25				
	464	464	E^-	-0.36	-0.36			
	427	417	A_1^-					
	715	715	A_1^+	0.078	0.08			
	621	621	E^+	-0.462				
	464	464	E^-	-0.244	-0.36			Better
	427	416	A_1^-					

TABLE III. (Continued.)

System	Local mode frequency (cm^{-1})		Mode	t, F_{12}, u Defect parameters (parameter set)	t or u (Refs. 10 and 51) Isolated case	Opinion	Ref.
	Expt.	Calc.					
<u>GaP</u> : $^{28}\text{Si}, ^{11}\text{B}$	693	653	A_1^+	0.08	0.08	Good	26
	595	625	E^+	-0.25			
	464	464	E^-	-0.36			
	427	415	A_1^-		0.08	Better	
	693	692	A_1^+	0.078			
	595	597	E^+	-0.462			
	464	464	E^-	-0.244			
	427	414	A_1^-				
<u>GaP</u> : $^{28}\text{Si}, ^{12}\text{C}$	691	637	A_1^+	0.08	0.08	Good	23
	561	605	E^+	-0.26			
	451(486)	464	E^-	-0.37			
	437?	413	A_1^-		0.08	Better	
	691	691	A_1^+	0.152			
	561	561	E^+	-0.569			
	451(486)	451	E^-	-0.184			
	437?	406	A_1^-				
<u>GaP</u> : $^{28}\text{Si}, ^{28}\text{Si}$	495	495	A_1^+	0.375	0.08	Good	23(24)
	456	456	E^+	-0.113			
	413(430)	413	E^-	-0.475			
			A_1^-		0.08	Better	
		577	A_1^+	-0.10			
	495	495	E^+	-0.622			
	456	456	E^-	-0.475			
	413(430)	405	A_1^-				
Type (ii) Diamond							
<u>SiSi</u> : $^{11}\text{B}, \text{P}$	601	601	A_1	0.198	0.23	Positive	12
				0.306			
	628	628	E	0.135	0.23	Negative	
	601	601	E	0.289			
			0.135				
628	628	A_1	0.135				

TABLE III. (Continued.)

System	Local mode frequency (cm^{-1})		Mode	t, F_{12}, u Defect parameters (parameter set)	t or u (Refs. 10 and 51) Isolated case	Opinion	Ref.
	Expt.	Calc.					
<u>SiSi:</u> ¹⁰ B, P	622	624	A_1	0.198)	0.23	Positive	12
				0.306) (a)			
	653	653	E	0.135)	0.23	Negative	
	622	624	E	0.289)			
653	653	A_1	0.135) (b)				
			0.135)				
<u>SiSi:</u> ¹¹ B, As	604	604	A_1	0.174)	0.23	Positive	3
				0.22) (a)			
	637	636	E	0.056)	0.23	Negative	
	604	604	E	0.285)			
637	636	A_1	-0.018) (b)				
			0.056)				
<u>SiSi:</u> ¹⁰ B, As	625	628	A_1	0.174)	0.23	Positive	3
				0.22) (a)			
	662	662	E	0.056)	0.23	Negative	
	625	628	E	0.285)			
662	662	A_1	-0.018) (b)				
			0.056)				
<u>SiSi:</u> ¹¹ B, Sb	612	612	A_1	0.155)	0.23	Positive	3
				0.166) (a)			
	643	643	E	0.013)	0.23	Negative	
	612	612	E	0.263)			
643	643	A_1	-0.087) (b)				
			0.013)				
<u>SiSi:</u> ¹⁰ B, Sb	635	638	A_1	0.155)	0.23	Positive	3
				0.166) (a)			
	668	668	E	0.013)	0.23	Negative	
	635	638	E	0.263)			
668	668	A_1	-0.087) (b)				
			0.013)				
<u>GeGe:</u> As, ¹¹ B	530	530	A_1	0.189)	0.21	Positive	16
				0.323) (a)			
	557	557	E	0.165)	0.21	Negative	
	530	530	E	0.189)			
557	557	A_1	0.114) (b)				
			0.273)				

TABLE III. (Continued.)

System	Local mode frequency (cm^{-1})		Mode	t, F_{12}, u Defect parameters (parameter set)	t or u (Refs. 10 and 51) Isolated case	Opinion	Ref.		
	Expt.	Calc.							
<u>GeGe:As, ^{10}B</u>		554	A_1	0.189	0.21	Positive	16		
		582	E	0.323					
			E	0.165					
		<i>do</i>	A_1	0.189		0.21	Negative		
				0.114					
				0.273					
<u>GeGe:Ga, P</u>	343	343	A_1	0.084	0.235	Positive	2		
	350	350	E	0.263					
				0.195					
	343	343	E	0.084		0.235	Negative		
	350	350	A_1	0.184					
				0.24					
<u>GeGe:P, In</u>	338	338	A_1	0.172	0.235	Positive	16		
	355	355	E	0.242					
				0.084					
	338	338	E	0.275		0.235	Negative		
	355	355	A_1	0.018					
				0.084					
III-V compounds	337	337	A_1	0.345	0.5	Positive	18		
	350	350	E	0.611					
				-0.54					
	<u>GaAs:^{24}Mg, Te</u>	337	337	E		0.5	0.5	Negative	
		350	350	A_1		0.33			
						-0.34			
335		335	A_1	0.395	0.5	Positive		18	
		344	E	0.574					
				-0.34					
<u>GaAs:^{24}Mg, Se</u>	335	335	E	0.5	0.5	Negative			
		344	A_1	0.33					
				-0.34		0.5	Positive	18	
				0.5					

TABLE III. (Continued.)

System	Local mode frequency (cm^{-1})		Mode	t, F_{12}, u Defect parameters (parameter set)	t or u (Refs. 10 and 51) Isolated case	Opinion	Ref.	
	Expt.	Calc.						
<u>GaAs</u> : ⁶ Li, Te	419	419	A_1	0.723	0.9	Negative	19	
	510	510	E	1.39? (a) -0.13				
	419	419	E	No physical solution	0.9	Negative		
	510	510	A_1	possible				
<u>GaAs</u> : ⁷ Li, Te	391	392	A_1	0.723	0.9	Negative	19	
	475	474	E	1.39? (a) -0.13				
	391	391	E	No physical solution	0.9	Negative		
	475	475	A_1	possible				
II-VI compounds	352.5	352.5	A_1	-0.28	-1.15	Positive	29	
	302	302	E	-1.445 (a) -0.91				
	352.5	352.5	E	-0.28	-1.15	Negative		
	302	302	A_1	-0.514 (b) -1.55				
	331.5	331.5	A_1	-0.23	-1.15	Positive	29	
	305	305	E	-1.386 (a) -0.94				
	331.5	331.5	E	-0.23	-1.15	Negative		
	305	305	A_1	-0.832 (b) -1.27				
	334	334	A_1	-0.03	-0.23	Positive	27	
	279	279	E	-0.824 (a) 0.516				
	<u>CdTe</u> : Al, Sb	334	334	E	-0.637	-0.23	Negative	
		279	279	A_1	0.208 (b) 0.516			

TABLE III. (Continued.)

System	Local mode frequency (cm^{-1})		Mode	t, F_{12}, u Defect parameters (parameter set)	t or u (Refs. 10 and 51) Isolated case	Opinion	Ref.
	Expt.	Calc.					
<u>CdTe:Zn,P</u>	343	343	A_1	-0.135	-1.15	Positive	29
	308	308	E	-1.24			
				-0.975			
	343	343	E	-0.135			
	308	308	A_1	-0.627			
				-1.42			
<u>CdTe:Al,Ag</u>	314	314	A_1	-0.175	-0.23	Negative	27
	293	293	E	-0.485			
				0.23			
	314	314	E	-0.405			
	293	293	A_1	-0.082			
				0.23			
<u>CdTe:Al,Au</u>	313	313	A_1	-0.165	-0.23	Negative	27
	292	292	E	-0.51			
				0.21			
	313	313	E	-0.395			
	292	292	A_1	-0.102			
				0.21			
<u>ZnSe:Al,Ag</u>	381	381	A_1	-0.204	-0.30	Negative	28
	350	350	E	-0.656			
				0.256			
	381	381	E	-0.502			
	350	350	A_1	-0.117			
				0.256			

clusive explanations have been furnished experimentally in assigning the frequencies of the two types of modes.

We first start with the known values of force variations for isolated donor or acceptor (Table III) and analyze the vibrations of "donor-acceptor" light pair defects in III-V compounds. It will provide us with an additional check on the concept of the force variation relation with the bond ionicity (or covalency). Setting the case of GaP^{28}Si , ^{28}Si aside, we have considered in (a) the same values of t and u known for appropriate isolated donor and acceptor impurities (column six, Table III). In defining the force-constant-change

parameter between the donor-acceptor bond [$F_{12} (\equiv t + u - ut + \Gamma_{12})$], we have assumed $\Gamma_{12} = 0$. It is interesting to note that in most of the cases the values of the vibrational modes so obtained are not very far from the experimental results. To obtain the best possible fit for the LVM's, we have varied the three perturbation parameters, and the results are included in (b), Table III. Slight variations in t and u from their corresponding values in the isolated case are seen to be similar as compared to the vibrations of pair defect with C_s point-group symmetry. Since the mass of Si is close to that of P the LVM for GaP^{28}Si has not been experimentally detected, although

the LVM for an isolated Si donor in GaP is known from the ir measurements of Morrison *et al.*²³ and Kachare *et al.*²⁴ (e.g., GaP:²⁸Si at 465 cm⁻¹). However, some additional lines at 495.4, 455.7, 430.4, and 412.8 cm⁻¹ have been observed: The first two were attributed to GaP:²⁸Si, ²⁸Si pairs and the second two were tentatively ascribed to the same defect center. As the expected stiffening around the Si acceptor in GaP is not known, we have therefore tentatively assigned the existing experimental LVM's by two sets of parameters (a) and (b). If the empirical law of force variation noted for isolated and pair defects is also valid for heavier acceptor impurities in III-V compounds, it is believed that the values of set (b) will be better than (a).

Using the same correlation of force variation with bond ionicity (covalency), we have now tentatively assigned the two types of impurity vibrations observed for the second category of C_{3v} defects in elemental and compound semiconductors. The results covering all the specific examples of nearest-neighbor pair defects have been included in Table III [type (ii)]. If the vibrations of the B-P pair defect in an Si lattice are considered on the basis of force variation and bond ionicity, one may find that the "B-P" bond will be much less covalent as compared to the Si-B or P-Si bonds. This corresponds with relatively more softening in between the B-P force constant than the Si-B and P-Si ones, and consequently $\omega_{A_1} < \omega_B$. If the factors related to the change of bond ionicity (covalency) are supposed to be similar and if the donor atom is changed, we find an increase of force variations, especially with the B-As and B-Sb pairs in the Si lattice (maybe due to the increase of the donor size). Strictly speaking, this is equally valid for both sets of parameters; however, we feel positive about the values of set (a). The Li-Te pair defect in GaAs is an exception for which we could fit the existing vibrational-mode frequencies by only one set of parameters with $\omega_{A_1} < \omega_B$. Again the value of force variation between the Li-Te bond is quite unphysical; therefore we believe that the Li atom does not possess the substitutional site and probably occupies an interstitial position or a more complex defect center. In contrast to the softening of bond strength between "acceptor-donor" pairs in IV-IV and III-V compounds, one may find stiffening between the experimentally known "donor-acceptor" pairs in II-VI compounds, and consequently we feel positive about the set of parameter values given in (a) with $\omega_{A_1} > \omega_B$. For Al-Ag and Al-Au centers in II-VI compounds, it is noted that both of the calculated sets of

parameters violate our tentative criteria for determining the type of vibrational modes. Since Dutt *et al.*²⁷⁻²⁹ and Król *et al.*³² have speculated that Au and Ag impurities may also have the interstitial positions, it will be better to assign the observed vibrational modes arising because of Al-Ag_i and Al-Au_i pairs rather than nearest-neighbor substitutional defects in II-VI compounds.

VI. CONCLUDING REMARKS

We have presented the first complete Green's-function theory for studying the vibrations of impurity complexes (involving up to three defect centers) in zinc-blende-type crystals. Explicit numerical calculations have been made for almost all the existing cases of pair defects with C_s and C_{3v} point-group symmetries in elemental and compound semiconductors using appropriate perturbation models and lattice phonons from RIM-11. In order to gain a physical concept of force variations, attention has been given to fit the experimental data for donor-acceptor, acceptor-donor, or donor-host-acceptor (or vacancy) pair vibrations with a minimum possible set of perturbation parameters: For isolated donor and acceptor impurities in compound semiconductors, we found that an increase or decrease of the nearest-neighbor coupling constant varies in the same sense as does the increase or decrease of covalency of the bond.⁵¹ This empirical law partially holds well for charged impurities in elemental semiconductor and is equally valid for pair vibrations, especially when applied in those cases, for which only one solution is theoretically possible. However, if there exist two equally probable sets of perturbation parameters [e.g., C_{3v} pair defects of type (ii)], we prefer the one that proves to be more plausible on the above-based physical criteria. Anyway, this can be checked only through future experimental studies capable of distinguishing the two types of impurity vibrations. It has been revealed from two independent studies^{9,10} of isolated impurity vibrations in zinc-blende-type crystals by the Green's-function technique using different perturbation and lattice-dynamical models that, although the absolute values are different, the basic trend of force variations (for different impurities in similar systems) is found to be quite analogous. We feel that the same trend of force variations, as found in the present work, will be reflected if the entire calculation of pair-defect vibrations is repeated on similar grounds with a different choice of lattice-dynamical models (e.g., shell model or valence shell model, etc.).

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APPENDIX A

The Green's-function and perturbation matrices in different irreducible representations (A_1 and E) for C_{3v} point-group symmetry have the following forms:

(i) For the A_1 irreducible representation,

$$\langle A_1 | g | A_1 \rangle = g(i, j),$$

and

$$\langle A_1 | \delta l | A_1 \rangle = \delta l(i, j) \quad \text{with } i, j = 1, 6.$$

Here $g(i, j)$ and $\delta l(i, j)$ are the symmetric (6×6) matrices. The explicit values for each element have the form

$$\begin{aligned} g(1, 1) &= g_2, \\ g(1, 2) &= (g_3 + 2g_4), \\ g(1, 3) &= \sqrt{2} g_3, \\ g(1, 4) &= (g_3 - 2g_4), \\ g(1, 5) &= \sqrt{2} (g_5 + g_7 - g_8), \\ g(1, 6) &= (g_6 + 2g_8), \\ g(2, 2) &= g_1, \\ g(2, 3) &= \sqrt{2} (g_9 + g_{11} - g_{12}), \\ g(2, 4) &= (g_{10} + 2g_{12}), \\ g(2, 5) &= \sqrt{2} g_3, \\ g(2, 6) &= (g_3 - 2g_4), \\ g(3, 3) &= (g_1 + g_{10} - g_{11} + 2g_{12}), \\ g(3, 4) &= \sqrt{2} (g_9 - g_{12}), \\ g(3, 5) &= (g_{13} + g_{15} + g_{19} + g_{20} + g_{21} + g_{22}), \\ g(3, 6) &= \sqrt{2} (g_{16} + g_{18} + g_{21}), \\ g(4, 4) &= (g_1 - 2g_{11}), \\ g(4, 5) &= \sqrt{2} (g_{17} + g_{18} + g_{19}), \\ g(4, 6) &= (g_{14} + 2g_{20}), \\ g(5, 5) &= (g_2 + g_6 - g_7 + 2g_8), \\ g(5, 6) &= \sqrt{2} (g_5 - g_8), \\ g(6, 6) &= (g_2 - 2g_7), \end{aligned}$$

and

$$\begin{aligned} \delta l(1, 1) &= (M_1 - M'_1)\omega^2 + (3A - 2B)t \\ &\quad + (A + 2B)F_{12}, \\ \delta l(1, 2) &= -(A + 2B)F_{12}, \\ \delta l(2, 2) &= (M_2 - M'_2)\omega^2 + (3A - 2B)u \\ &\quad + (A + 2B)F_{12}, \\ \delta l(1, 3) &= -\sqrt{2} At, \\ \delta l(1, 4) &= (2B - A)t, \\ \delta l(1, 5) &= \delta l(1, 6) = \delta l(2, 3) = \delta l(2, 4) = 0, \\ \delta l(2, 5) &= -\sqrt{2} Au, \\ \delta l(2, 6) &= (2B - A)u, \\ \delta l(3, 3) &= (A + B)t, \\ \delta l(3, 4) &= -\sqrt{2} Bt, \\ \delta l(3, 5) &= 0, \\ \delta l(3, 6) &= 0, \\ \delta l(4, 4) &= At, \\ \delta l(4, 5) &= 0, \\ \delta l(4, 6) &= 0, \\ \delta l(5, 5) &= (A + B)u, \\ \delta l(5, 6) &= -\sqrt{2} Bu, \\ \delta l(6, 6) &= Au. \end{aligned}$$

(ii) For the doubly degenerate E representation, the block form of g and δl matrices will be

$$\langle E | g | E \rangle = g(i, j)$$

and

$$\langle E | \delta l | E \rangle = \delta l(i, j) \quad \text{with } i, j = 1, 8.$$

The explicit matrix elements are

$$\begin{aligned} g(1, 1) &= g_2, \\ g(1, 2) &= g_3 - g_4, \\ g(1, 3) &= \sqrt{2} (g_3 - 3g_4), \\ g(1, 4) &= (g_3 + g_4), \\ g(1, 5) &= -\sqrt{6} (g_3 + g_4), \\ g(1, 6) &= \sqrt{2} (g_5 - 2g_7 - g_8), \\ g(1, 7) &= (g_6 - g_8), \\ g(1, 8) &= -\sqrt{6} (g_5 + g_8), \\ g(2, 2) &= g_1, \\ g(2, 3) &= \sqrt{2} (g_9 - 2g_{11} - g_{12}), \\ g(2, 4) &= (g_{10} - g_{12}), \end{aligned}$$

$$\begin{aligned}
g(2, 5) &= -\sqrt{6} (g_9 + g_{12}), \\
g(2, 6) &= \sqrt{2} (g_3 - 3g_4), \\
g(2, 7) &= (g_3 + g_4), \\
g(2, 8) &= -\sqrt{6} (g_3 + g_4), \\
g(3, 3) &= 0.5(2g_1 - g_{10} - 2g_{11} - 2g_{12}), \\
g(3, 4) &= \sqrt{2} (g_9 + 2g_{12}), \\
g(3, 5) &= -2\sqrt{3} g_{10}, \\
g(3, 6) &= 0.5(2g_{13} - g_{15} - g_{19} \\
&\quad + 2g_{20} - g_{21} - g_{22}), \\
g(3, 7) &= \sqrt{2} (g_{16} + g_{18} - 2g_{21}), \\
g(3, 8) &= 2\sqrt{3} (g_{15} + g_{19} - g_{21} - g_{22}), \\
g(4, 4) &= g_1 + g_{11}, \\
g(4, 5) &= -\sqrt{6} g_9, \\
g(4, 6) &= \sqrt{2} (g_{17} + g_{18} - 2g_{19}), \\
g(4, 7) &= (g_{14} - g_{20}), \\
g(4, 8) &= \sqrt{6} (g_{17} - g_{18}), \\
g(5, 5) &= 0.5(2g_1 + g_{10} + 2g_{11} - 2g_{12}), \\
g(5, 6) &= 2\sqrt{3} (g_{15} - g_{19} + g_{21} - g_{22}), \\
g(5, 7) &= \sqrt{6} (g_{16} - g_{18}), \\
g(5, 8) &= 0.5(2g_{13} + g_{15} - g_{19} \\
&\quad - 2g_{20} - g_{21} + g_{22}), \\
g(6, 6) &= 0.5(2g_2 - g_6 - 2g_7 - 2g_8), \\
g(6, 7) &= \sqrt{2} (g_5 + 2g_8), \\
g(6, 8) &= -2\sqrt{3} g_6, \\
g(7, 7) &= (g_2 + g_7), \\
g(7, 8) &= -\sqrt{6} g_5, \\
g(8, 8) &= 0.5(2g_2 + g_6 + 2g_7 - 2g_8),
\end{aligned}$$

and

$$\begin{aligned}
\delta l(1, 1) &= (M_1 - M_2')\omega^2 + (A - B)F_{12} + (3A + B)t, \\
\delta l(1, 2) &= -(A - B)F_{12}, \\
\delta l(1, 3) &= \sqrt{2} (3B - A)t, \\
\delta l(1, 4) &= -(A + B)t, \\
\delta l(1, 5) &= \sqrt{6} (A + B)t, \\
\delta l(1, 6) &= \delta l(1, 7) = \delta l(1, 8) = \delta l(2, 3) \\
&= \delta l(2, 4) = \delta l(2, 5) = 0, \\
\delta l(2, 2) &= (M_2 - M_2')\omega^2 + (A - B)F_{12} + (3A + B)u, \\
\delta l(2, 6) &= \sqrt{2} (3B - A)u, \\
\delta l(2, 7) &= -(A + B)u,
\end{aligned}$$

$$\begin{aligned}
\delta l(2, 8) &= \sqrt{6} (A + B)u, \\
\delta l(3, 3) &= (A - 0.5B)t, \\
\delta l(3, 4) &= -\sqrt{2} Bt, \\
\delta l(3, 5) &= 2\sqrt{3} Bt, \\
\delta l(3, 6) &= \delta l(3, 7) = \delta l(3, 8) = 0, \\
\delta l(4, 4) &= At, \\
\delta l(4, 5) &= -\sqrt{6} Bt, \\
\delta l(4, 6) &= \delta l(4, 7) = \delta l(4, 8) = 0, \\
\delta l(5, 5) &= (A + 0.5B)t, \\
\delta l(5, 6) &= \delta l(5, 7) = \delta l(5, 8) = 0, \\
\delta l(6, 6) &= (A - 0.5B)u, \\
\delta l(6, 7) &= -\sqrt{2} Bu, \\
\delta l(6, 8) &= 2\sqrt{3} Bu, \\
\delta l(7, 7) &= Au, \\
\delta l(7, 8) &= -\sqrt{6} Bu, \\
\delta l(8, 8) &= (A + 0.5B)u.
\end{aligned}$$

As the impurity molecule does not move in the A_2 irreducible representation, we have not listed the 2×2 g and δl matrix elements.

APPENDIX B

The Green's-function and perturbation matrices in different irreducible representations (A_1 and A_2) for C_s point-group symmetry have the following forms:

(i) For A_1 irreducible representation,

$$\langle A_1 | g | A_1 \rangle = g(i, j),$$

and

$$\langle A_1 | \delta l | A_1 \rangle = \delta l(i, j) \text{ with } i, j = 1, 19.$$

The explicit elements of the symmetric [$g(19 \times 19)$ and $\delta l(19 \times 19)$] matrices have the form

$$\begin{aligned}
g(1, 1) &= g_2, \\
g(1, 2) &= 0, \\
g(1, 3) &= (g_3 + g_4), \\
g(1, 4) &= \sqrt{2} g_4, \\
g(1, 5) &= (g_3 + g_4), \\
g(1, 6) &= -\sqrt{2} g_4, \\
g(1, 7) &= (g_3 - g_4), \\
g(1, 8) &= (g_3 - g_4), \\
g(1, 9) &= 0, \\
g(1, 10) &= (g_5 + g_7),
\end{aligned}$$

$$\begin{aligned}
g(1, 11) &= \sqrt{2} g_8, & g(3, 14) &= 0, \\
g(1, 12) &= (g_6 + g_8), & g(3, 15) &= (g_9 - g_{12}), \\
g(1, 13) &= (g_5 - g_8), & g(3, 16) &= (g_{10} + g_{12}), \\
g(1, 14) &= (g_7 - g_8), & g(3, 17) &= (-g_{11} + g_{12}), \\
g(1, 15) &= (g_{21} + g_{22}), & g(3, 18) &= (g_9 + g_{11}), \\
g(1, 16) &= (g_{18} + g_{19}), & g(3, 19) &= -\sqrt{2} g_{12}, \\
g(1, 17) &= -(g_{19} + g_{20}), & g(4, 4) &= g_1, \\
g(1, 18) &= (g_{13} + g_{15}), & g(4, 5) &= -\sqrt{2} g_{12}, \\
g(1, 19) &= -\sqrt{2} g_{17}, & g(4, 6) &= g_{10}, \\
g(2, 2) &= g_2, & g(4, 7) &= \sqrt{2} g_{12}, \\
g(2, 3) &= \sqrt{2} g_4, & g(4, 8) &= \sqrt{2} g_{11}, \\
g(2, 4) &= g_3, & g(4, 9) &= \sqrt{2} g_9, \\
g(2, 5) &= -\sqrt{2} g_4, & g(4, 10) &= -\sqrt{2} g_4, \\
g(2, 6) &= g_3, & g(4, 11) &= g_3, \\
g(2, 7) &= -\sqrt{2} g_4, & g(4, 12) &= -\sqrt{2} g_4, \\
g(2, 8) &= \sqrt{2} g_4, & g(4, 13) &= \sqrt{2} g_4, \\
g(2, 9) &= \sqrt{2} g_3, & g(4, 14) &= \sqrt{2} g_3, \\
g(2, 10) &= -\sqrt{2} g_8, & g(4, 15) &= -\sqrt{2} g_{11}, \\
g(2, 11) &= g_6, & g(4, 16) &= -\sqrt{2} g_{12}, \\
g(2, 12) &= \sqrt{2} g_8, & g(4, 17) &= \sqrt{2} g_9, \\
g(2, 13) &= \sqrt{2} g_7, & g(4, 18) &= \sqrt{2} g_{12}, \\
g(2, 14) &= \sqrt{2} g_5, & g(4, 19) &= g_{10}, \\
g(2, 15) &= -\sqrt{2} g_{21}, & g(5, 5) &= g_1, \\
g(2, 16) &= -\sqrt{2} g_{20}, & g(5, 6) &= 0, \\
g(2, 17) &= \sqrt{2} g_{18}, & g(5, 7) &= (g_9 - g_{12}), \\
g(2, 18) &= -\sqrt{2} g_{16}, & g(5, 8) &= (g_{10} + g_{12}), \\
g(2, 19) &= g_{14}, & g(5, 9) &= (-g_{11} + g_{12}), \\
g(3, 3) &= g_1, & g(5, 10) &= (g_{13} + g_{15}), \\
g(3, 4) &= 0, & g(5, 11) &= \sqrt{2} g_{16}, \\
g(3, 5) &= (g_9 + g_{11}), & g(5, 12) &= (g_{18} + g_{21}), \\
g(3, 6) &= \sqrt{2} g_{12}, & g(5, 13) &= (g_{19} + g_{22}), \\
g(3, 7) &= (g_{10} + g_{12}), & g(5, 14) &= (g_{20} + g_{21}), \\
g(3, 8) &= (g_9 - g_{12}), & g(5, 15) &= (g_{23} + g_{26}), \\
g(3, 9) &= (g_{11} - g_{12}), & g(5, 16) &= (g_{24} + g_{25}), \\
g(3, 10) &= (g_3 + g_4), & g(5, 17) &= (-g_{25} + g_{27}), \\
g(3, 11) &= -\sqrt{2} g_4, & g(5, 18) &= (g_{28} + g_{30}), \\
g(3, 12) &= (g_3 - g_4), & g(5, 19) &= \sqrt{2} g_{31}, \\
g(3, 13) &= (g_3 - g_4), & g(6, 6) &= g_1,
\end{aligned}$$

$$\begin{aligned}
g(6, 7) &= -\sqrt{2} g_{11}, & g(9, 9) &= (g_1 + g_{10}), \\
g(6, 8) &= -\sqrt{2} g_{12}, & g(9, 10) &= (g_{19} + g_{20}), \\
g(6, 9) &= \sqrt{2} g_9, & g(9, 11) &= \sqrt{2} g_{18}, \\
g(6, 10) &= \sqrt{2} g_{17}, & g(9, 12) &= (g_{16} + g_{21}), \\
g(6, 11) &= g_{14}, & g(9, 13) &= (g_{15} + g_{21}), \\
g(6, 12) &= \sqrt{2} g_{20}, & g(9, 14) &= (g_{13} + g_{22}), \\
g(6, 13) &= \sqrt{2} g_{19}, & g(9, 15) &= g_{12}, \\
g(6, 14) &= \sqrt{2} g_{18}, & g(9, 16) &= g_{12}, \\
g(6, 15) &= -\sqrt{2} g_{26}, & g(9, 17) &= (g_{10} + g_{32}), \\
g(6, 16) &= \sqrt{2} g_{27}, & g(9, 18) &= (g_{25} - g_{27}), \\
g(6, 17) &= \sqrt{2} g_{24}, & g(9, 19) &= \sqrt{2} g_{24}, \\
g(6, 18) &= -\sqrt{2} g_{31}, & g(10, 10) &= g_2, \\
g(6, 19) &= g_{29}, & g(10, 11) &= 0, \\
g(7, 7) &= (g_1 - g_{11}), & g(10, 12) &= (g_5 - g_8), \\
g(7, 8) &= g_9, & g(10, 13) &= (g_6 + g_8), \\
g(7, 9) &= -g_{12}, & g(10, 14) &= (-g_7 + g_8), \\
g(7, 10) &= (g_{18} + g_{19}), & g(10, 15) &= (g_3 - g_4), \\
g(7, 11) &= \sqrt{2} g_{20}, & g(10, 16) &= (g_3 - g_4), \\
g(7, 12) &= (g_{14} + g_{20}), & g(10, 17) &= 0, \\
g(7, 13) &= (g_{17} + g_{18}), & g(10, 18) &= (g_3 + g_4), \\
g(7, 14) &= (g_{17} + g_{19}), & g(10, 19) &= \sqrt{2} g_4, \\
g(7, 15) &= g_9, & g(11, 11) &= g_2, \\
g(7, 16) &= (g_{11} + g_{32}), & g(11, 12) &= -\sqrt{2} g_7, \\
g(7, 17) &= -g_{12}, & g(11, 13) &= -\sqrt{2} g_8, \\
g(7, 18) &= (g_{24} + g_{25}), & g(11, 14) &= \sqrt{2} g_5, \\
g(7, 19) &= -\sqrt{2} g_{27}, & g(11, 15) &= -\sqrt{2} g_4, \\
g(8, 8) &= (g_1 - g_{11}), & g(11, 16) &= \sqrt{2} g_4, \\
g(8, 9) &= g_{12}, & g(11, 17) &= \sqrt{2} g_3, \\
g(8, 10) &= (g_{21} + g_{22}), & g(11, 18) &= \sqrt{2} g_4, \\
g(8, 11) &= \sqrt{2} g_{21}, & g(11, 19) &= g_3, \\
g(8, 12) &= (g_{16} + g_{18}), & g(12, 12) &= (g_2 - g_7), \\
g(8, 13) &= (g_{13} + g_{20}), & g(12, 13) &= g_5, \\
g(8, 14) &= (g_{15} + g_{19}), & g(12, 14) &= -g_8, \\
g(8, 15) &= (g_{11} + g_{33}), & g(12, 15) &= (g_{13} + g_{20}), \\
g(8, 16) &= g_9, & g(12, 16) &= (g_{17} + g_{18}), \\
g(8, 17) &= -g_{12}, & g(12, 17) &= -(g_{15} + g_{21}), \\
g(8, 18) &= (g_{23} + g_{26}), & g(12, 18) &= (g_{19} + g_{22}), \\
g(8, 19) &= \sqrt{2} g_{26}, & g(12, 19) &= -\sqrt{2} g_{19},
\end{aligned}$$

$$\begin{aligned}
g(13, 13) &= (g_2 - g_7), \\
g(13, 14) &= g_8, \\
g(13, 15) &= (g_{16} + g_{18}), \\
g(13, 16) &= (g_{14} + g_{20}), \\
g(13, 17) &= -(g_{16} + g_{21}), \\
g(13, 18) &= (g_{18} + g_{21}), \\
g(13, 19) &= -\sqrt{2} g_{20}, \\
g(14, 14) &= (g_2 + g_6), \\
g(14, 15) &= -(g_{15} + g_{19}), \\
g(14, 16) &= -(g_{17} + g_{19}), \\
g(14, 17) &= (g_{13} + g_{22}), \\
g(14, 18) &= -(g_{20} + g_{21}), \\
g(14, 19) &= \sqrt{2} g_{18}, \\
g(15, 15) &= (g_1 - g_{11}), \\
g(15, 16) &= g_9, \\
g(15, 17) &= -g_{12}, \\
g(15, 18) &= (g_{10} + g_{12}), \\
g(15, 19) &= \sqrt{2} g_{12}, \\
g(16, 16) &= (g_1 - g_{11}), \\
g(16, 17) &= g_{12}, \\
g(16, 18) &= (g_9 - g_{12}), \\
g(16, 19) &= \sqrt{2} g_{11}, \\
g(17, 17) &= (g_1 + g_{10}), \\
g(17, 18) &= (g_{11} - g_{12}), \\
g(17, 19) &= \sqrt{2} g_9, \\
g(18, 18) &= g_1, \\
g(18, 19) &= 0, \\
g(19, 19) &= g_1,
\end{aligned}$$

and

$$\begin{aligned}
\delta l(1, 1) &= (M_1 - M_1')\omega^2 + 3At - Bt + (A + B)F_{12}, \\
\delta l(1, 2) &= -\sqrt{2} B(t - F_{12}), \\
\delta l(1, 3) &= -(A + B)F_{12}, \\
\delta l(1, 4) &= -\sqrt{2} BF_{12}, \\
\delta l(1, 5) &= -(A + B)t, \\
\delta l(1, 6) &= \sqrt{2} Bt, \\
\delta l(1, 7) &= -(A - B)t, \\
\delta l(1, 8) &= -(A - B)t,
\end{aligned}$$

$$\begin{aligned}
\delta l(1, 9) &= \delta l(1, 10) = \delta l(1, 11) = \delta l(1, 12) \\
&= \delta l(1, 13) = \delta l(1, 14) = \delta l(1, 15) \\
&= \delta l(1, 16) = \delta l(1, 17) = \delta l(1, 18) \\
&= \delta l(1, 19) = 0, \\
\delta l(2, 2) &= (M_1 - M_1')\omega^2 + 3At + AF_{12}, \\
\delta l(2, 3) &= -\sqrt{2} BF_{12}, \\
\delta l(2, 4) &= -AF_{12}, \\
\delta l(2, 5) &= \sqrt{2} Bt, \\
\delta l(2, 6) &= -At, \\
\delta l(2, 7) &= \sqrt{2} Bt, \\
\delta l(2, 8) &= -\sqrt{2} Bt, \\
\delta l(2, 9) &= -\sqrt{2} At, \\
\delta l(2, 10) &= \delta l(2, 11) = \delta l(2, 12) = \delta l(2, 13) \\
&= \delta l(2, 14) = \delta l(2, 15) = \delta l(2, 16) \\
&= \delta l(2, 17) = \delta l(2, 18) = \delta l(2, 19) = 0, \\
\delta l(3, 3) &= (M_2 - M_2')\omega^2 + 2Au - 2Bu \\
&\quad + (A + B)(F_{12} + F_{26}), \\
\delta l(3, 4) &= \sqrt{2} B(F_{12} - F_{26}), \\
\delta l(3, 5) &= \delta l(3, 6) = \delta l(3, 7) = \delta l(3, 8) \\
&= \delta l(3, 9) = 0, \\
\delta l(3, 10) &= -(A + B)F_{26}, \\
\delta l(3, 11) &= \sqrt{2} BF_{26}, \\
\delta l(3, 12) &= -(A - B)u, \\
\delta l(3, 13) &= -(A - B)u, \\
\delta l(3, 14) &= \delta l(3, 15) = \delta l(3, 16) = \delta l(3, 17) \\
&= \delta l(3, 18) = \delta l(3, 19) = 0, \\
\delta l(4, 4) &= (M_2 - M_2')\omega^2 + 2Au + A(F_{12} + F_{26}), \\
\delta l(4, 5) &= \delta l(4, 6) = \delta l(4, 7) = \delta l(4, 8) = \delta l(4, 9) = 0, \\
\delta l(4, 10) &= \sqrt{2} BF_{26}, \\
\delta l(4, 11) &= -AF_{26}, \\
\delta l(4, 12) &= \sqrt{2} Bu, \\
\delta l(4, 13) &= -\sqrt{2} Bu, \\
\delta l(4, 14) &= -\sqrt{2} Au, \\
\delta l(4, 15) &= \delta l(4, 16) = \delta l(4, 17) = \delta l(4, 18) \\
&= \delta l(4, 19) = 0, \\
\delta l(5, 5) &= (A + B)t, \\
\delta l(5, 6) &= -\sqrt{2} Bt,
\end{aligned}$$

$$\begin{aligned}
\delta l(5, 7) &= \delta l(5, 8) = \delta l(5, 9) = \delta l(5, 10) \\
&= \delta l(5, 11) = \delta l(5, 12) = \delta l(5, 13) \\
&= \delta l(5, 14) = \delta l(5, 15) = \delta l(5, 16) \\
&= \delta l(5, 17) = \delta l(5, 18) = \delta l(5, 19) = 0, \\
\delta l(6, 6) &= At, \\
\delta l(6, 7) &= \delta l(6, 8) = \delta l(6, 9) = \delta l(6, 10) \\
&= \delta l(6, 11) = \delta l(6, 12) = \delta l(6, 13) \\
&= \delta l(6, 14) = \delta l(6, 15) = \delta l(6, 16) \\
&= \delta l(6, 17) = \delta l(6, 18) = \delta l(6, 19) = 0, \\
\delta l(7, 7) &= At, \\
\delta l(7, 8) &= -Bt, \\
\delta l(7, 9) &= -Bt, \\
\delta l(7, 10) &= \delta l(7, 11) = \delta l(7, 12) = \delta l(7, 13) \\
&= \delta l(7, 14) = \delta l(7, 15) = \delta l(7, 16) \\
&= \delta l(7, 17) = \delta l(7, 18) = \delta l(7, 19) = 0, \\
\delta l(8, 8) &= At, \\
\delta l(8, 9) &= Bt, \\
\delta l(8, 10) &= \delta l(8, 11) = \delta l(8, 12) = \delta l(8, 13) \\
&= \delta l(8, 14) = \delta l(8, 15) = \delta l(8, 16) \\
&= \delta l(8, 17) = \delta l(8, 18) = \delta l(8, 19) = 0, \\
\delta l(9, 9) &= At, \\
\delta l(9, 10) &= \delta l(9, 11) = \delta l(9, 12) = \delta l(9, 13) \\
&= \delta l(9, 14) = \delta l(9, 15) = \delta l(9, 16) \\
&= \delta l(9, 17) = \delta l(9, 18) = \delta l(9, 19) = 0, \\
\delta l(10, 10) &= (M_1 - M'_6)\omega^2 + 3Av - Bv + (A + B)F_{2g}, \\
\delta l(10, 11) &= \sqrt{2} B(v - F_{2g}), \\
\delta l(10, 12) &= \delta l(10, 13) = \delta l(10, 14) = 0, \\
\delta l(10, 15) &= -(A - B)v, \\
\delta l(10, 16) &= -(A - B)v, \\
\delta l(10, 17) &= 0, \\
\delta l(10, 18) &= -(A + B)v, \\
\delta l(10, 19) &= -\sqrt{2} Bv, \\
\delta l(11, 11) &= (M_1 - M'_6)\omega^2 + 3Av + AF_{2g}, \\
\delta l(11, 12) &= \delta l(11, 13) = \delta l(11, 14) = 0, \\
\delta l(11, 15) &= \sqrt{2} Bv, \\
\delta l(11, 16) &= -\sqrt{2} Bv, \\
\delta l(11, 17) &= -\sqrt{2} Av, \\
\delta l(11, 18) &= -\sqrt{2} Bv,
\end{aligned}$$

$$\begin{aligned}
\delta l(11, 19) &= -Av, \\
\delta l(12, 12) &= Au, \\
\delta l(12, 13) &= -Bu, \\
\delta l(12, 14) &= -Bu, \\
\delta l(12, 15) &= \delta l(12, 16) = \delta l(12, 17) \\
&= \delta l(12, 18) = \delta l(12, 19) = 0, \\
\delta l(13, 13) &= Au, \\
\delta l(13, 14) &= Bu, \\
\delta l(13, 15) &= \delta l(13, 16) = \delta l(13, 17) \\
&= \delta l(13, 18) = \delta l(13, 19) = 0, \\
\delta l(14, 14) &= Au, \\
\delta l(14, 15) &= \delta l(14, 16) = \delta l(14, 17) \\
&= \delta l(14, 18) = \delta l(14, 19) = 0, \\
\delta l(15, 15) &= Av, \\
\delta l(15, 16) &= -Bv, \\
\delta l(15, 17) &= -Bv, \\
\delta l(15, 18) &= \delta l(15, 19) = 0, \\
\delta l(16, 16) &= Av, \\
\delta l(16, 17) &= Bv, \\
\delta l(16, 18) &= \delta l(16, 19) = 0, \\
\delta l(17, 17) &= Av, \\
\delta l(17, 18) &= \delta l(17, 19) = 0, \\
\delta l(18, 18) &= (A + B)v, \\
\delta l(18, 19) &= \sqrt{2} Bv, \\
\delta l(19, 19) &= Av.
\end{aligned}$$

(ii) For the A_2 irreducible representation we have

$$\begin{aligned}
\langle A_2 | g | A_2 \rangle &= g(i, j), \\
\langle A_2 | \delta l | A_2 \rangle &= \delta l(i, j), \quad \text{where } i, j = 1, 14
\end{aligned}$$

with the following matrix elements:

$$\begin{aligned}
g(1, 1) &= g_2, \\
g(1, 2) &= (g_3 - g_4), \\
g(1, 3) &= (g_3 - g_4), \\
g(1, 4) &= (g_3 + g_4), \\
g(1, 5) &= -(g_3 + g_4), \\
g(1, 6) &= -2g_4, \\
g(1, 7) &= (g_5 - g_7), \\
g(1, 8) &= (g_6 - g_8), \\
g(1, 9) &= -(g_5 + g_8),
\end{aligned}$$

$$\begin{aligned}
g(1, 10) &= -(g_7 + g_8), & g(4, 12) &= (g_{11} - g_{32}), \\
g(1, 11) &= -(g_{21} - g_{22}), & g(4, 13) &= -g_{12}, \\
g(1, 12) &= -(g_{18} - g_{19}), & g(4, 14) &= (g_{24} - g_{25}), \\
g(1, 13) &= -(g_{19} - g_{20}), & g(5, 5) &= (g_1 + g_{11}), \\
g(1, 14) &= (g_{13} - g_{15}), & g(5, 6) &= -g_{12}, \\
g(2, 2) &= g_1, & g(5, 7) &= (g_{21} - g_{22}), \\
g(2, 3) &= (g_9 - g_{11}), & g(5, 8) &= (g_{16} - g_{18}), \\
g(2, 4) &= (g_{10} - g_{12}), & g(5, 9) &= (g_{13} - g_{20}), \\
g(2, 5) &= -(g_9 + g_{12}), & g(5, 10) &= (g_{15} - g_{19}), \\
g(2, 6) &= -(g_{11} + g_{12}), & g(5, 11) &= -(g_{11} + g_{33}), \\
g(2, 7) &= (g_3 - g_4), & g(5, 12) &= g_9, \\
g(2, 8) &= (g_3 + g_4), & g(5, 13) &= -g_{12}, \\
g(2, 9) &= -(g_3 + g_4), & g(5, 14) &= -(g_{23} - g_{26}), \\
g(2, 10) &= -2g_4, & g(6, 6) &= (g_1 - g_{10}), \\
g(2, 11) &= (g_9 + g_{12}), & g(6, 7) &= -(g_{19} - g_{20}), \\
g(2, 12) &= -(g_{10} - g_{12}), & g(6, 8) &= (g_{16} - g_{21}), \\
g(2, 13) &= -(g_{11} + g_{12}), & g(6, 9) &= (g_{15} - g_{21}), \\
g(2, 14) &= (g_9 - g_{11}), & g(6, 10) &= (g_{13} - g_{22}), \\
g(3, 3) &= g_1, & g(6, 11) &= g_{12}, \\
g(3, 4) &= (g_9 + g_{12}), & g(6, 12) &= g_{12}, \\
g(3, 5) &= -(g_{10} - g_{12}), & g(6, 13) &= (g_{10} - g_{32}), \\
g(3, 6) &= -(g_{11} + g_{12}), & g(6, 14) &= -(g_{25} + g_{27}), \\
g(3, 7) &= (g_{13} - g_{15}), & g(7, 7) &= g_2, \\
g(3, 8) &= (g_{18} - g_{21}), & g(7, 8) &= (g_5 + g_8), \\
g(3, 9) &= (g_{19} - g_{22}), & g(7, 9) &= -(g_6 - g_8), \\
g(3, 10) &= (g_{20} - g_{21}), & g(7, 10) &= -(g_7 + g_8), \\
g(3, 11) &= (g_{23} - g_{26}), & g(7, 11) &= (g_3 + g_4), \\
g(3, 12) &= -(g_{24} - g_{25}), & g(7, 12) &= -(g_3 + g_4), \\
g(3, 13) &= -(g_{25} + g_{27}), & g(7, 13) &= -2g_4, \\
g(3, 14) &= (g_{28} - g_{30}), & g(7, 14) &= (g_3 - g_4), \\
g(4, 4) &= (g_1 + g_{11}), & g(8, 8) &= (g_2 + g_7), \\
g(4, 5) &= -g_9, & g(8, 9) &= -g_5, \\
g(4, 6) &= g_{12}, & g(8, 10) &= g_8, \\
g(4, 7) &= (g_{18} - g_{19}), & g(8, 11) &= (g_{13} - g_{20}), \\
g(4, 8) &= (g_{14} - g_{20}), & g(8, 12) &= (g_{17} - g_{18}), \\
g(4, 9) &= (g_{17} - g_{18}), & g(8, 13) &= -(g_{15} - g_{21}), \\
g(4, 10) &= (g_{17} - g_{19}), & g(8, 14) &= -(g_{19} - g_{22}), \\
g(4, 11) &= g_9, & g(9, 9) &= (g_2 + g_7),
\end{aligned}$$

$$\begin{aligned}
g(9, 10) &= -g_8, \\
g(9, 11) &= (g_{16} - g_{18}), \\
g(9, 12) &= (g_{14} - g_{20}), \\
g(9, 13) &= -(g_{16} - g_{21}), \\
g(9, 14) &= -(g_{18} - g_{21}), \\
g(10, 10) &= (g_2 - g_6), \\
g(10, 11) &= -(g_{15} - g_{19}), \\
g(10, 12) &= -(g_{17} - g_{19}), \\
g(10, 13) &= (g_{13} - g_{22}), \\
g(10, 14) &= (g_{20} - g_{21}), \\
g(11, 11) &= (g_1 + g_{11}), \\
g(11, 12) &= -g_9, \\
g(11, 13) &= g_{12}, \\
g(11, 14) &= (g_{10} - g_{12}), \\
g(12, 12) &= (g_1 + g_{11}), \\
g(12, 13) &= -g_{12}, \\
g(12, 14) &= -(g_9 + g_{12}), \\
g(13, 13) &= (g_1 - g_{10}), \\
g(13, 14) &= -(g_{11} + g_{12}), \\
g(14, 14) &= g_1,
\end{aligned}$$

and

$$\begin{aligned}
\delta l(1, 1) &= (M_1 - M'_1)\omega^2 + 3At + Bt + (A - B)F_{12}, \\
\delta l(1, 2) &= -(A - B)F_{12}, \\
\delta l(1, 3) &= -(A - B)t, \\
\delta l(1, 4) &= -(A + B)t, \\
\delta l(1, 5) &= (A + B)t, \\
\delta l(1, 6) &= 2Bt, \\
\delta l(1, 7) &= \delta l(1, 8) = \delta l(1, 9) = \delta l(1, 10) \\
&= \delta l(1, 11) = \delta l(1, 12) = \delta l(1, 13) \\
&= \delta l(1, 14) = 0, \\
\delta l(2, 2) &= (M_2 - M'_2)\omega^2 + 2Au + 2Bu \\
&\quad + (A - B) \times (F_{12} + F_{26}), \\
\delta l(2, 3) &= \delta l(2, 4) = \delta l(2, 5) = \delta l(2, 6) = 0, \\
\delta l(2, 7) &= -(A - B)F_{26}, \\
\delta l(2, 8) &= -(A + B)u, \\
\delta l(2, 9) &= (A + B)u, \\
\delta l(2, 10) &= 2Bu, \\
\delta l(2, 11) &= \delta l(2, 12) = \delta l(2, 13) = \delta l(2, 14) = 0,
\end{aligned}$$

$$\begin{aligned}
\delta l(3, 3) &= (A - B)t, \\
\delta l(3, 4) &= \delta l(3, 5) = \delta l(3, 6) = \delta l(3, 7) \\
&= \delta l(3, 8) = \delta l(3, 9) = \delta l(3, 10) \\
&= \delta l(3, 11) = \delta l(3, 12) = \delta l(3, 13) \\
&= \delta l(3, 14) = 0,
\end{aligned}$$

$$\begin{aligned}
\delta l(4, 4) &= At, \\
\delta l(4, 5) &= -Bt, \\
\delta l(4, 6) &= -Bt, \\
\delta l(4, 7) &= \delta l(4, 8) = \delta l(4, 9) = \delta l(4, 10) \\
&= \delta l(4, 11) = \delta l(4, 12) = \delta l(4, 13) \\
&= \delta l(4, 14) = 0,
\end{aligned}$$

$$\begin{aligned}
\delta l(5, 5) &= At, \\
\delta l(5, 6) &= Bt, \\
\delta l(5, 7) &= \delta l(5, 8) = \delta l(5, 9) = \delta l(5, 10) \\
&= \delta l(5, 11) = \delta l(5, 12) = \delta l(5, 13) \\
&= \delta l(5, 14) = 0,
\end{aligned}$$

$$\begin{aligned}
\delta l(6, 6) &= At, \\
\delta l(6, 7) &= \delta l(6, 8) = \delta l(6, 9) = \delta l(6, 10) \\
&= \delta l(6, 11) = \delta l(6, 12) = \delta l(6, 13) \\
&= \delta l(6, 14) = 0,
\end{aligned}$$

$$\begin{aligned}
\delta l(7, 7) &= (M_1 - M'_6)\omega^2 + 3Av \\
&\quad + Bv + (A - B)F_{26},
\end{aligned}$$

$$\delta l(7, 8) = \delta l(7, 9) = \delta l(7, 10) = 0,$$

$$\delta l(7, 11) = -(A + B)v,$$

$$\delta l(7, 12) = (A + B)v,$$

$$\delta l(7, 13) = 2Bv,$$

$$\delta l(7, 14) = -(A - B)v,$$

$$\delta l(8, 8) = Au,$$

$$\delta l(8, 9) = -Bu,$$

$$\delta l(8, 10) = -Bu,$$

$$\delta l(8, 11) = \delta l(8, 12) = \delta l(8, 13) = \delta l(8, 14) = 0,$$

$$\delta l(9, 9) = Au,$$

$$\delta l(9, 10) = Bu,$$

$$\delta l(9, 11) = \delta l(9, 12) = \delta l(9, 13) = \delta l(9, 14) = 0,$$

$$\delta l(10, 10) = Au,$$

$$\delta l(10, 11) = \delta l(10, 12) = \delta l(10, 13)$$

$$= \delta l(10, 14) = 0,$$

$$\delta l(11, 11) = Av,$$

$$\delta l(11, 12) = -Bv,$$

$$\delta l(11, 13) = -Bv,$$

$$\delta l(11, 14) = 0,$$

$$\delta l(12, 12) = Av,$$

$$\delta l(12, 13) = Bv,$$

$$\delta l(12, 14) = 0,$$

$$\delta l(13, 13) = Av,$$

$$\delta l(13, 14) = 0,$$

$$\delta l(14, 14) = (A - B)v,$$

where

$$F_{12} = t + u - ut + \Gamma_{12}$$

and

$$F_{26} = u + v - uv + \Gamma_{26}.$$

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- *Visiting Scientist. Permanent address: Department of Physics, University of Allahabad, Allahabad India. Now at: Department of Physics, University of Houston Central Campus, Houston, Texas 77004.
- ¹W. G. Spitzer, in *Festkörperprobleme XI*, edited by O. Madelung (Pergamon, New York, 1971), pp. 1-44.
- ²A. Mitsuishi and A. Manabe, *Oyo Butsurī* **41**, 7 (1972).
- ³R. C. Newman, *Infrared Studies of Crystal Defects* (Taylor and Francis, London, 1973).
- ⁴A. S. Barker and A. J. Sievers, *Rev. Mod. Phys.* (Suppl.) **47**, S1 (1975), and references cited therein.
- ⁵P. G. Dawber and R. J. Elliott, *Proc. Phys. Soc. London* **81**, 453 (1963).
- ⁶S. P. Gaur, J. F. Vetelino, and S. S. Mitra, *J. Phys. Chem. Solids*, **32**, 2737 (1971).
- ⁷R. J. Elliott and P. Pfeuty, *J. Phys. Chem. Solids*, **28**, 1789 (1967).
- ⁸A. Grimm, A. A. Maradudin, I. P. Ipatova, and A. V. Subashiev, *J. Phys. Chem. Solids*, **33**, 775 (1972).
- ⁹D. N. Talwar and Bal K. Agrawal, *Phys. Rev. B* **12**, 1432 (1975).
- ¹⁰M. Vandevyver and P. Plumelle, *Phys. Rev. B* **17**, 675 (1978).
- ¹¹W. G. Spitzer and M. J. Waldner, *J. Appl. Phys.* **36**, 2450 (1965).
- ¹²V. Tsvetov, W. Allred, and W. G. Spitzer, *Appl. Phys. Lett.* **10**, 326 (1967).
- ¹³R. C. Newman and R. S. Smith, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 177.
- ¹⁴V. Tsvetov, W. Allred, and W. G. Spitzer, *Ref. 13*, p. 185.
- ¹⁵A. E. Cosand and W. G. Spitzer, *Appl. Phys. Lett.* **11**, 279 (1967).
- ¹⁶M. R. Brozel, K. Laithwaite, and R. C. Newman, *Radiation Effects in Semiconductors* (Institute of Physics and Physical Society, London, 1977), Ser. No. 31, p. 510, (private communication).
- ¹⁷M. Jouanne, J. F. Morhange, and M. Balkanski, *Phys. Status Solidi B* **92**, 255 (1979); the impurity mode assignments given by these authors are not definitive but rather tentative (private communication).
- ¹⁸P. C. Leung, L. H. Skolnik, W. P. Allred, and W. G. Spitzer, *J. Appl. Phys.* **43**, 4096 (1972).
- ¹⁹W. Hayes, *Phys. Rev.* **138**, A1227 (1965).
- ²⁰O. G. Lorimor and W. G. Spitzer, *J. Appl. Phys.* **38**, 2713 (1967).
- ²¹O. G. Lorimor and W. G. Spitzer, *J. Appl. Phys.* **38**, 3008 (1967).
- ²²O. G. Lorimor and W. G. Spitzer, *J. Appl. Phys.* **37**, 3687 (1966).
- ²³S. R. Morrison and R. C. Newman, *J. Phys. C* **7**, 627 (1974).
- ²⁴A. H. Kachare, W. G. Spitzer, O. G. Lorimor, F. K. Euler, and R. N. Brown, *J. Appl. Phys.* **45**, 5475 (1974).
- ²⁵S. R. Morrison and R. C. Newman, *J. Phys. C* **7**, 619 (1974).
- ²⁶S. R. Morrison, R. C. Newman, and F. Thomson, *J. Phys. C* **7**, 633 (1974).
- ²⁷B. V. Dutt, M. Al-Delaimi, and W. G. Spitzer, *J. Appl. Phys.* **47**, 565 (1976).
- ²⁸B. V. Dutt and W. G. Spitzer, *J. Appl. Phys.* **47**, 573 (1976).
- ²⁹B. V. Dutt and W. G. Spitzer, *J. Appl. Phys.* **48**, 954, 2107 (1977).
- ³⁰A. Manabe, Y. Ikuta, A. Mitsuishi, H. Komiya, and S. Ibuki, *Solid State Commun.* **9**, 1499 (1971).
- ³¹A. Mitsuishi, A. Manabe, H. Yoshinaga, S. Ibuki, and H. Komiya, *Progr. Theor. Phys. Suppl.* **45**, 21 (1970).
- ³²A. Król, M. J. Kozielski, and W. Nazarewicz, *Phys. Status Solidi B* **90**, 649 (1978).
- ³³V. I. Safarov, V. E. Sedov, and T. G. Yugova, *Fiz. Tekh. Poluprovodn.* **4**, 150 (1970) [*Sov. Phys.—Semicond.* **4**, 119 (1970)]; E. F. Gross and V. I. Safarov, *ibid.* **1**, 297 (1967) [*ibid.* **1**, 241 (1967)].
- ³⁴M. A. Gilileo, P. T. Bailey, and D. E. Hill, *Phys. Rev.* **174**, 898 (1968).
- ³⁵A. A. Maradudin, E. W. Montroll, C. H. Weiss, and I. P. Ipatova, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1971), suppl. 3, 2nd edition.
- ³⁶A. A. Maradudin, in *Astrophysics and the Many Body Problem*, 1962 Brandeis Lectures (Benjamin, New York, 1963), Vol. 2.
- ³⁷A. A. Maradudin, *Rep. Prog. Phys.* **28**, 331 (1965).
- ³⁸A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1966), Vol. 18 and 19.
- ³⁹Y. A. Izyumov, *Adv. Phys.* **14**, 569 (1965).
- ⁴⁰R. J. Elliott, J. A. Krumhansl, and P. L. Leath, *Rev. Mod. Phys.* **46**, 465 (1974).
- ⁴¹M. V. Klein, in *Physics of Color Centers*, edited by

- B. Fowler (Academic, New York, 1968), Chap. 7.
- ⁴²P. Plumelle, D. N. Talwar, M. Vandevyver, K. Kunc, and M. Zigone, *Phys. Rev. B* 20, 4199 (1979).
- ⁴³K. Kunc, *Ann. Phys. (Paris)* 8, 319 (1973).
- ⁴⁴B. Prévot, B. Hennion, and B. Dorner, *J. Phys. C* 10, 3999 (1977) and references cited therein.
- ⁴⁵S. S. Jaswal and V. D. Dilly, *Phys. Rev. B* 15, 2366 (1977), and references cited therein.
- ⁴⁶S. Hoshino, Y. Fujii, J. Harada, and J. D. Axe, *J. Phys. Soc. Jpn.* 41, 965 (1976); Technical Report of ISSP Ser. A, No. 746 (1976) (unpublished).
- ⁴⁷P. Plumelle and M. Vandevyver, *Phys. Status Solidi B* 73, 271 (1976).
- ⁴⁸M. Vandevyver and P. Plumelle, *J. Phys. Chem. Solids* 38, 765 (1977).
- ⁴⁹Due to the large size (33×33) of the eigenvector, perturbation, and Green's-function matrices, we have not reproduced them here. However, they can be supplied to the readers on request by the authors.
- ⁵⁰W. Ludwig, in *Recent Developments in Lattice Theory*, *Springer Tracts of Modern Physics*, edited by G. Höhler (Springer, Berlin, 1967), Vol. 43.
- ⁵¹P. Plumelle, D. N. Talwar, M. Vandevyver, K. Kunc, and M. Zigone (unpublished).
- ⁵²In order to understand the force variation relation with the bond ionicity, we consider an example of GaAs with Ga replaced by Al (isoelectronic) and closest mass Mg (acceptor) or Si (donor): Just from comparison of the chemical valences it is clear that the Mg-As bond will be more *ionic* than the Al-As one, whereas Si-As bond will be more *covalent* than Al-As. Applying the same argument to the As site substituted by P (isoelectronic) or Si (acceptor) we see that the Ga-Si bond will be more covalent than the Ga-P one. From the respective force variations (Table III of Ref. 10), one can immediately find that the increase or decrease of the nearest-neighbor force-constant parameter varies exactly with the increase or decrease of the covalency of the bond.
- ⁵³D. N. Talwar and Bal K. Agrawal, *Solid State Commun.* 21, 79 (1977).
- ⁵⁴K. P. Jain and A. K. Prabhakaran, *Phys. Lett.* A46, 175 (1973); *Phys. Rev. B* 8, 1503 (1973).