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Vibrational structure of copper and zinc complexes in GaAs: A theoretical analysis

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We have studied the vibrational properties of C and F centers due to copper complexes in GaAs using the Green's-function technique with perturbation models proposed by Gross *et al.* In the nearest-neighbor approximations, all the 33 Green's-function matrix elements involved with the most extended case of the F center have been numerically evaluated with the use of lattice phonons from the eleven-parameter rigid-ion-model (RIM 11) fitted neutron data of GaAs. The observed low-lying resonance modes due to "Cu-V" (C center) and "Zn-V" pairs (with trigonal symmetry) are explained with force-constant softening around the Cu (Zn) impurity and the neighboring arsenic atoms. By incorporating the same perturbation parameters obtained from the trigonal case, we also find a resonance mode for the F center (with rhombic symmetry) in close agreement with the experiments. The trends of force variation due to *two* different pair defects (e.g., Cu-V and Zn-V) in *one* host system (GaAs) can be correlated with the variation of bond ionicity—a result which has already been seen to be significant in the study of isolated charged-impurity vibrations in elemental and compound semiconductors.

I. INTRODUCTION

The vibrational properties of point defects in real solids can be precisely understood if one takes into account the geometric periodic pattern of the host lattice, the maximum solid solubility, the electronic shell structure, and the size of the impurity-host atoms. In diamond and zinc-blende-type crystals, the behavior of the isoelectronic substituents has been extensively studied by local-mode infrared absorption and Raman scattering spectroscopy.[1-4] However, if the substituents are nonisoelectronic, one encounters serious problems due to the concentration of the resulting free carriers. Under these circumstances, it is essential to reduce the free carriers without reducing the impurity concentration, and this is generally accomplished either by double doping during crystal growth, using electron or proton irradiation, introducing intrinsic defects, or by diffusion under conditions where the solubility of the diffusant is controlled by the impurity to be compensated.[1] In all the above methods of compensation, one enhances the possibility of the formation of pairs and/or more complex defect centers of point-group symmetry lower than the host system. The symmetry class of the impurity centers is generally deduced from the behavior of splitting impurity bands in a uniaxially deformed crystal. It is worth mentioning that even with careful analyses of the optical experiments, there remain some uncertainties for assigning the impurity bands (of known symmetry) and this sometimes leads to a seemingly contradictory conclusion.[5,6] On the other hand, the probability for the assigned experimental structure of the impurity center (of known configuration) will be increased if it is also justified through realistic theoretical calculations.[7]

In recent years, a good deal of experimental data on localized vibrational modes due to impurity complexes in zinc-blende-type crystals has been accumulated in the literature.[1-4] The sucess for observing localized vibrational modes has initiated experimentalists to detect resonance modes too; consequently, some experimental speculations are also known for the in-band modes due to copper and zinc complexes in GaAs crystals.[8-11] Gross *et al.*[8-9] have analyzed the absorption and the photoluminescence experiments on copper-diffused GaAs and suggested the possibility of *two* resonance lines [$\omega_r(1) \simeq 0.107\omega_m$ (*C* center) and $\omega_r(2) \simeq 0.154\omega_m$ (*F* center)]. On the other hand, the low-temperature photoluminescence study (of Gilleo *et al.*[11]) on epitaxial GaAs with ionized zinc impurities has speculated a resonance mode ($\omega_r \simeq 0.12\omega_m$), where ω_m is the maximum phonon frequency of the host GaAs crystal. To elucidate the nature of copper complexes, Gross *et al.*[8,9] have made additional investigations regarding the influence of uniaxial compression on the observed lines. It has been confirmed that the $\omega_r(1)$ line is associated with the anisotropic impurity center of *trigonal* symmetry, whereas the $\omega_r(2)$ line is probably due to an impurity center with *rhombic* symmetry. Although the observed dependence of the rate of diffusion of the impurities on the excess arsenic vapor pressure suggested the involvement of vacancies in both the *F* and *C* centers, it did not provide information regarding the number of vacancies involved in each of the above centers. During the measurements of the hole density in crystals saturated with copper in the presence of excess arsenic vapors, Furukawa and Thurmond[12] have suggested the formation of a $\{V_{\rm As}{\rm Cu}_{\rm Ga}V_{\rm As}\}$ impurity complex (where $V_{\rm As}$ stands for the vacancy at the As site and ${\rm Cu}_{\rm Ga}$ is a substitutional copper impurity occupying the Ga site in the GaAs lattice). Since the *F* line is the dominant one in the observed spectra under copper saturation conditions, and the $V_{\rm As}{\rm Cu}_{\rm Ga}V_{\rm As}$ has the rhombic (C_s) symmetry, it was therefore speculated that the *F* line involves a copper impurity at the Ga site and two vacancies, one at each of the As sites (although the rhombic symmetry can be exhibited by other copper complexes also: e.g., $\{{\rm Cu}_{\rm Ga}{\rm Cu}_{\rm Ga}\}$, $\{{\rm Cu}_{\rm Ga}V_{\rm As}{\rm Cu}_{\rm Ga}\}$, $\{V_{\rm Ga}{\rm Cu}_{\rm As}V_{\rm Ga}\}$).

It was pointed out that the *C*-center-producing resonance mode in GaAs is anisotropic and exhibits the trigonal (C_{3v}) symmetry. Again, for such an impurity complex one may think of various possible configurations, including $\{{\rm Cu}_{\rm Ga}V_{\rm As}\}$, $\{{\rm Cu}_i{\rm Cu}_i\}$, etc., and it is quite difficult to select an appropriate one when no conclusive explanation has been furnished experimentally. However, according to Füller and Wolfstrin,[13] the possibility of the reaction between copper interstitial $\{{\rm Cu}_i\}$ and the divacancies that may create (${\rm Cu}_i + V_{\rm Ga}V_{\rm As} \rightarrow {\rm Cu}_{\rm Ga}V_{\rm As}$) a complex ${\rm Cu}_{\rm Ga}V_{\rm As}$, cannot be completely ruled out (cf. Fig. 1).

From a theoretical stand point, most of the vibrational properties of imperfect solids based on the Green's-function technique are concerned with isolated point defects[14–18] (and sometimes only in the mass-defect approximation). Elliot and Pfeuty[19] have made the first implementation of the Green's-function theory to the impurity modes of pair defects with different configurations in the Si lattice. To treat the actual problems with six Green's-function matrix elements, the authors of Ref. 19 were forced to make several approximations in defining the perturbation matrices. In the case of two adjacent impurities with D_{3d} (or C_{3v}) symmetry, for example, they have assumed force-constant changes only in between the impurities, neglecting all other impurity-host-lattice interactions, which were certainly nonzero. Grimm *et al.*[20] have recently extended the "Elliott-Pfeuty" theory to understand the low-lying resonance modes due to defects in GaAs. However, once again, to cope with the complicated mathematics in defining the perturbation for impurity complex of C_s point-group symmetry, they have neglected some nontrivial impurity-host interactions. Quite recently we have developed a complete Green's-function theory by considering appropriate perturbation models for the impurity complexes and lattice phonons from an eleven-parameter—rigid-ion model.[7] Numerical calculations for the localized vibrational modes have been made for almost all the existing cases of pair defects with C_s and C_{3v} point-group symmetries. From the detailed analysis of the localized modes due to *isolated*[21] and *pair* defects[7] in elemental and compound semiconductors, we find that (i) no correlation exists between the force variation and the size of the impurity-host atoms, and (ii) the *increase* or *decrease* of the nearest-neighbor coupling constant for isolated *donor* or *acceptor*, varies in the same sense as does the increase or decrease of the covalency of the bond.

Using the same Green's-function theory, the purpose of the present paper is to find whether or not the observed resonant lines in Cu-diffused GaAs crystals exhibit the same structural models as proposed by Safarov *et al.* for the *C*- and *F*-defect centers. Is the simple empirical law of force variation related to bond ionicity (or covalency)[7] for charged impurities of real significance—and can it be generalized to the pair vibrations producing resonance modes in zinc-blende-type crystals? Starting from the basic theory, we will briefly point out the role of the Green's-function technique for understanding the impurity vibrations in zinc-blende-type crystals in Sec. II. Group-theoretical arguments will be used to obtain the relevant expressions for the resonance denominators in the various irreducible representations pertaining to the appropriate point groups of the impurity centers (cf. Sec. III). Numerical calculations are made for the resonance modes due to copper and zinc impurity complexes in GaAs (cf. Sec. IV) and the results have been compared and discussed with the existing experimental[8–11] and theoretical[20] data.

II. THEORETICAL CONSIDERATIONS

A. Lattice Green's functions

It has been well recognized that most of the vibrational properties of perfect and/or imperfect solids can be adequately described in the harmonic approximation using Green's-function technique. For an excellent survey of the subject matter, we refer to the review articles and monographs by Maradudin.[15–17] We summarize here the relevant part of the theory which will be important for the discussion of the impurity vibrations due to defect complexes in real solids and the application to zinc-blende-type crystals.

Following Maradudin *et al.*,[16] we define the Green's function $\underline{G}(t)$ of the vibrating system as:

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

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, a set of basis vectors $|\,l\kappa\alpha\rangle$ that corresponds to a unit displacement in the αth direction of the κth atom in the lth unit cell, exhibits the property:

$$\langle l\kappa\alpha\,|\,l'\kappa'\beta\rangle=\delta_{ll'}\delta_{\kappa\kappa'}\delta_{\alpha\beta}\ , \tag{2}$$

where δ is the Dirac delta function. Any combination of displacements of the different atoms can be expressed as a vector $|\,u\,\rangle$ and for the $(l\kappa)$ atom in the α direction it is given by $\langle l\kappa\alpha\,|\,u\,\rangle$. The elements of the Green's function $\langle l\kappa\alpha\,|\,\underline{G}(t)\,|\,l'\kappa'\beta\rangle$ in Eq. (1) represent the displacement of the atom $(l\kappa)$ along the α direction due to the force $-\delta(t)$ on the atom $(l'\kappa')$ in the β direction.

The Fourier transform of $\underline{G}(t)$ may be easily seen to satisfy

$$G^{-1}(\omega)=\underline{M}\omega^2-\Phi\ , \tag{3a}$$

or equivalently

$$[\underline{M}^{1/2}\underline{G}(\omega)\underline{M}^{1/2}]^{-1}=\underline{I}\omega^2-\underline{D}\ , \tag{3b}$$

where $\underline{D}=\underline{M}^{-1/2}\underline{\Phi}\underline{M}^{-1/2}$ is called the dynamical matrix.

The complexity of Eqs. (3a) and (3b) in evaluating $\underline{G}(\omega)$ requires a transformation of $\langle l\kappa\alpha\,|\,u\,\rangle$ to a representation that diagonalizes Eq. (3a). From the basic theory of lattice dynamics, the required transformation for periodic lattices is:

$$\langle l\kappa\alpha\,|\,\vec{q}j\,\rangle=N^{-1/2}e_\alpha(\kappa\,|\,\vec{q}j)\exp[-i\vec{q}\cdot\vec{\chi}(l\kappa)]\ , \tag{4}$$

where $\vec{q}$ forms a set of N wave vectors in the first Brillouin zone, j is the polarization index, $\vec{\chi}(l\kappa)$ is the equilibrium position vector of atom $(l\kappa)$, $e_\alpha(\kappa\,|\,\vec{q}j)$ forms the components of the polarization vector for the mode $(\vec{q}j)$ which are orthonormal and complete. If the transformation Eq. (4) is used, it yields

$$\langle\vec{q}j\,|\,\underline{G}(\omega)\,|\,\vec{q}j\,\rangle=[\omega^2-\omega^2(\vec{q}j)]^{-1}\delta_{\vec{q}\,\vec{q}'}\delta_{jj'}\ , \tag{5}$$

where $\omega(\vec{q}j)$ is the phonon frequency of the mode $(\vec{q}j)$.

The component form of the perfect-lattice Green's function in the site representation can be obtained from Eqs. (4) and (5) as

$$\langle l\kappa\alpha\,|\,\underline{G}(\omega)\,|\,l'\kappa'\beta\rangle=\frac{1}{N(M\kappa M\kappa')^{1/2}}\sum_{j\kappa}e_\alpha(\kappa\,|\,\vec{q}j)e^*_\beta(\kappa'\,|\,\vec{q}j)\langle\vec{q}j\,|\,\underline{G}(\omega)\,|\,\vec{q}j\,\rangle\exp\{\,i\vec{q}\cdot[\vec{\chi}(l\kappa)-\vec{\chi}(l'\kappa')]\,\}\ . \tag{6}$$

B. Impurity perturbations

If $\underline{\Gamma}$ is the perturbation on the dynamical matrix $\underline{D}$ of the host lattice [cf. Eq. (3)], then the Green's-function matrix for an imperfect solid $\{\,\underline{U}\,\}$ is defined as

$$\underline{U}^{-1}=\{\,\underline{M}\omega^2-\underline{\Phi}-\underline{\Gamma}\,\}\ , \tag{7a}$$

or equivalently

$$\begin{aligned}\underline{U}&=\underline{G}[\underline{I}-\underline{\Gamma}\underline{G}]^{-1}\\&=\underline{G}[\underline{I}-\underline{\Gamma}\underline{G}]^{-1}\ ,\end{aligned} \tag{7b}$$

The resonance denominator contained in the inverse of the matrix $\{\,\underline{I}-\underline{G}\underline{\Gamma}\,\}^{-1}$ is of central importance for investigating the impurity modes. Again, the size of the Green's-function and perturbation matrices depends upon the space affected by the impurity molecule embedded in a lattice of known crystal structure. Thus for the impurity modes, the condition for the occurrence of nontrivial solutions is

$$\mathrm{Re}\,\|\underline{I}-\underline{g}\underline{\gamma}\|=0\,, \tag{8}$$

where $\underline{g}$ and $\underline{\gamma}$ are the Green's function and perturbation matrices in the impurity space, respectively.

In the region of zero density of phonons, the impurity modes are nonpropagating and are observable as δ-function peaks in the optical experiments. ments. However, if the impurity modes appear at frequencies where the density of phonons is nonzero, such modes can decay into the band continuum and acquire a width,[19]

$$\Delta=2\left[\frac{\mathrm{Im}\,\|\underline{I}-\underline{g}\underline{\gamma}\|}{\dfrac{d}{d\omega^2}\mathrm{Re}\,\|\underline{I}-\underline{g}\underline{\gamma}\|}\right]_{\omega^2=\omega_r^2} \tag{9}$$

The solutions of Eq. (8) for which $\{\Delta<<\omega_{m^2}\}$ is also satisfied will be considered as the true resonant modes and this rules out most of the solutions occuring at the high density of phonons.

III. ANALYSIS OF THE EXPERIMENTAL RESULTS AND THE PROPOSED MODELS FOR THE Cu AND Zn IMPURITY COMPLEXES IN GaAs

A. Vibronic structure of lines

The analysis of vibronic spectra by Safarov *et al.*[10] in copper-doped GaAs has providied evidence for the pure electronic (phononless) transition [accompanied by a simultaneous excitation of a vibrational quantum of energy 3.6 meV ($\sim$29 cm^{-1}) for transition in the *C* centers (C_1, C' lines) and 5.1 meV ($\sim$41 cm^{-1}) for transitions in the *F* centers (F_1, F' lines), respectively.] It is generally believed that the vibronic spectra of impurity centers include both the vibrations of the host-crystal lattice as well as the local vibrations of the impurity. This suggests that the maxima in the vibronic spectra should be reflected in the frequency distribution of the normal modes of the perfect GaAs. However, the detailed analysis of the multiphonon absorption data[22] in terms of characteristic phonon energies have provided confirmation that the frequencies of the impurity modes, although they lie in the range of the acoustic vibrations, they do not coincide with the zone-edge energies of the host GaAs lattice. In Fig. 2, we have displayed the calculated one-phonon density of states using RIM 11 fitted neutron scattering data of GaAs as well as the positions of the resonance lines due to copper and zinc complexes. The perusal of Fig. (2) reveals

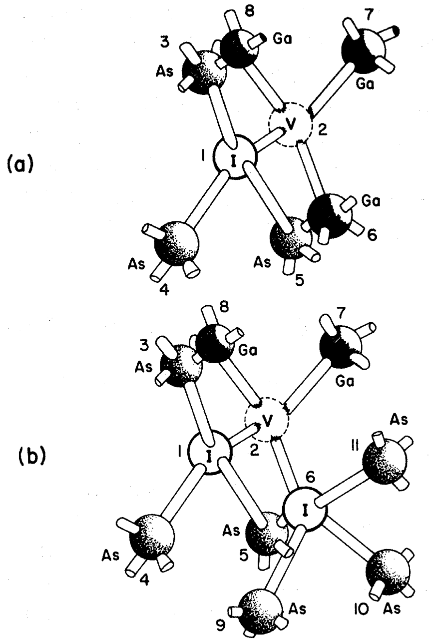

FIG. 1. Perturbation models for the vibrations of *C* (a) and *F* (b) centers in GaAs (after Gross *et al.*) The number of atoms 1,2,3, . . . ,11 and their respective coordinates have been considered with the following notations. (1) *I* (Cu or Zn): $\frac{1}{2}a_0(000)$; 2 *V* (vacancy): $\frac{1}{2}a_0(111)$; (3) As: $\frac{1}{2}a_0(111)$; (4) As: $\frac{1}{2}a_0(111)$; (5) As: $\frac{1}{2}a_0(111)$; (6) Ga (or *I*): $\frac{1}{2}a_0(220)$; (7) Ga: $\frac{1}{2}a_0(022)$; (8) Ga: $\frac{1}{2}a_0(202)$; (9) As: $\frac{1}{2}a_o(131)$; (11) As : $\frac{1}{2}a_0(113)$.

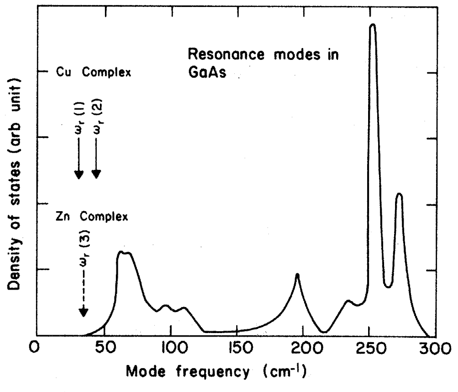

FIG. 2. Calculated one-phonon density of states on the basis of RIM 11 with the parameters of Kunc (Ref. 23). The positions of the impurity modes due to Cu [$\omega_r(1)$, $\omega_r(2)$] and Zn [$\omega_r(3)$] complexes in GaAs have been represented by arrows.

that the *average* transverse acoustic peak occurs at ~ 9.0 meV while the longitudinal acoustic peak lies near ~ 25.0 meV. All this indicates that the observed vibronic structure of the *C* and *F* centers is likely to be due to impurity vibrations rather than the normal vibrations of the GaAs.

From a theoretical standpoint, a low-lying resonance mode can occur only if the mass as well as the rigidity of the bonds of the impurity to the nearest neighbors differs considerably from the values of the corresponding quantities of the replaced host atom. Since the mass of Cu ($M_{\mathrm{Cu}}=63.546$ a.u.) or Zn ($M_{\mathrm{Zn}}=65.37$ a.u.) is smaller than that of the gallium ($M_{\mathrm{Ga}}=69.72$ a.u.) or arsenic atom ($M_{\mathrm{As}}=74.92$ a.u.), these impurities can give rise to resonance mode (when present as a substitutional in GaAs) only if the forces binding them to the neighbors are considerably *softened* compared to those in the perfect lattice. To explain the appearance of the low-frequency local vibrations it is plausible to assume vacancy (or vacancies) in the immediate environment of the substitutional Cu or Zn occupying Ga in GaAs. As pointed out before, the influence of uniaxial compression and the observed splitting pattern of the lines in Cu-doped GaAs has confirmed the symmetry of the *C* centers to be trigonal (oriented along the $\langle 111\rangle$ axis of the crystal). On the basis of the above arguments, it can be considered that the simplified model for the *C* centers consists of a substitutional copper atom occupying a gallium site next to an arsenic vacancy [cf. Fig. 1(a)]. Although, Gross *et al.*[8,9] had suggested orthorhombic-type symmetry for the *F* center (with one of the axes of the center oriented along the [100] axis of the host crystal), they could not propose an appropriate model for it. Based on their own work as well as that of Furukawa and Thurmond,[12] Gross *et al.*[8,9] had speculated that each *F* center can be considered as consisting of a copper impurity and two arsenic vacancies.

Next we will adopt many of the ideas of Gross *et al.*,[8,9] build from them mathematical models for the *C* and *F* centers, and evaluate them in terms of the Green's-function technique.

B. Mathematical models for the Cu and Zn impurity complexes in GaAs

It is known that in zinc-blende-type GaAs every atom $\{\mathrm{Ga}\}$ or $\{\mathrm{As}\}$ is tetrahedrally coordinated and the point-group symmetry is $\{T_d\}$. This symmetry is retained even if an impurity atom (for example, *I*) substitutes for either the $\{\mathrm{Ga}\}$ (number 1) or the $\{\mathrm{As}\}$ (number 2) atom of the GaAs lattice (see Fig. 1). If the impurity (I_{Ga} or I_{As}) forms a complex either with a new impurity atom or with a native defect, the symmetry at the defect site will be reduced. Among other possibilities, the most important situation may occur (a) if the new impurity atom (or vacancy) in the neighborhood of I_{Ga} occupies the nearest As (number 2) site and/or (b) if the impurity occupies the nearest Ga (number 6) site (cf. Fig. 1). In the former case, the symmetry at I_{Ga} will be *trigonal* (C_{3_v}) (the *C* center) whereas in the latter case (b) it reduces to *rhombic* (C_s) (the *F* center). For the most extended impurity complex creating a defect space of 11 involved atoms, we require 33 independent elements of the Green's-function matrix. The determination of these elements has been accomplished using group-theoretic arguments and the transformation properties under operations of the crystal space group.[7] In the Appendix we have given the full size (33×33) matrix involving all the nonzero Green's-function matrix elements. For a special case of an impurity complex comprised of three impurity atoms at 1, 2, and 6 sites (the C_s case), we have considered both the changes of mass at the impurity sites as well as nearest-neighbor—impurity-host interactions. To make the perturbation model more appropriate direct interactions between the impurities by two additional parameters Γ_{12} and Γ_{26} have also been taken into account. For the detailed description of the perturbation model we refer to an earlier paper.[7]

In order to examine the effect of the perturbation on the impurity modes within the bands of the perfect crystal, it is not necessary to work with the full size (24×24 or 33×33) Green's-function and perturbation matrices for the trigonal or rhombic impurity complexes in zinc-blende-type crystals. Since the displacement coordinates of the nearest neighbors form a basis for a reducible representation, it is convenient to work in the $\langle l\kappa\alpha \mid \Gamma_i\rangle$ representation of the normalized symmetry coordinates pertaining to the relevant point group. Here Γ is each one of the irreducible representations contained in the perturbation, and *i* refers to the *i*th partner function of Γ. If we choose the coordinate system to be at a site (for example, number 1) and denote the vector spaces formed by the displacements of impurity molecule and its neighbors as $\underline{u}$, then it transforms according to the following irreducible representations:

$$\Gamma_{C_{3v}}=6A_1+2A_2+8E\ , \tag{10}$$

and

$$\Gamma_{C_s}=19A_1+14A_2\ . \tag{11}$$

The appropriate symmetry coordinates X as required by the reduction of their vector space are given in Tables II and III, respectively, as

$$\underline{X}=\underline{S}\underline{u} \tag{12}$$

Using $\underline{S}$, the matrices $\underline{g}$ and $\underline{\gamma}$ can be reduced to blocks along the diagonal belonging to each of the irreducible representations. The relevant forms of the Green's-function and perturbation matrices have already been given in an earlier paper and the theory has been successfully applied to understand the localized vibrational modes of almost all the existing cases of pair defects (with different configurations) in elemental and compound semiconductors.[7] The detailed analysis of the experimental data suggests that the force perturbation correlation with bond ionicity is not only an important factor for isolated *charged* impurities but is equally significant for pair vibrations also (see Ref. 7 for complete discussions). Here we will use the same concepts to analyze the optical experiments that provide evidence for the resonance modes due to copper and zinc impurity complexes in GaAs.

IV. NUMERICAL COMPUTATIONS AND RESULTS

The Green's-function theory described above can be applied to various possible configurations of impurity vibrations and thus may be helpful in establishing the impurity models for the Cu and Zn complexes in GaAs. We discuss the following cases

A. Vacancy-impurity pairs C_{3v} case

The copper (or zinc) impurity is known to replace Ga in GaAs. Just from a comparison of their respective tetragonal covalent radii (viz., $r_{\text{Cu}}=1.35$ Å, $r_{\text{Zn}}=1.31$ Å, $r_{\text{Ga}}=1.26$ Å, and $r_{\text{As}}=1.18$ Å) one can expect qualitatively that the substitution of Cu (or Zn) for Ga is not going to weaken the rigidity of the bonds between the impurity and the surrounding As atoms. To explain the occurence of low-lying resonant modes due to Cu (or Zn) in GaAs, we must assume at least one lattice defect (e.g., a vacancy or a much smaller impurity) that causes weakening in the Cu (or Zn) defect bonds and thus may give rise to the localized vibrations. As pointed out before, the introduction of an impurity [at the Ga site (for example, 1); cf. Fig. 1(a)] with mass and force-constant changes (in the nearest-neighbor approximation) next to a vacancy [at the As site (for example, 2)] will create a defect space of eight involved atoms with a C_{3v} point-group symmetry. In this symmetry configuration, the impurity center does not move in the A_2 irreducible representation—thus only A_1 and E type modes are expected to be observed in the optical experiments. To elucidate the nature of impurity vibrations (with an appropriate representation) we have numerically solved the determinantal equation [Eq. (8)] by incorporating the involved lattice Green's-function and the perturbation matrices. The lattice phonons and thereby the Green's functions have been calculated using RIM 11 fitted neutron data for GaAs with the parameter values of Kunc.[23] The "impurity-vacancy" pair is regarded in terms of mass change (ϵ_1) as well as force-constant change (t) around the impurity at site 1, while vacancy at site 2 is visualized as $M_2'=0$ and $u=1$ (see Ref. 7 for detailed description of the perturbation models). In Fig. 3, we have displayed the possibility of the occurrence of impurity modes (due to Cu-V pair in GaAs) with the variation of the force-constant-change parameter t. The observed resonance mode due to Cu-V pair (C center) can be seen in our calculation (~ 29 cm^{-1} E mode) with a large force-constant softening ($t\simeq 0.62$) around Cu impurity and the As atoms. The other impurity modes which occur as a result of the graphical solution of Eq. (8) lie at ~ 72 cm^{-1} (E mode), ~ 83 cm^{-1} (A_1 mode), and ~ 113 cm^{-1} (E mode); respectively, (cf. Fig. 3); the region of high density of states (see, e.g., Fig. 2). Similar calculations have been reported for Zn-V pair and the exact fit of the observed resonance $\omega_r(3)$ is achieved with the force-constant softening

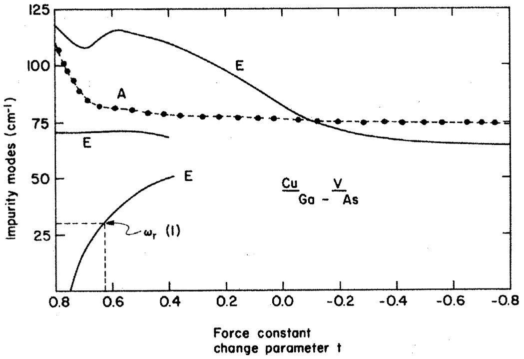

FIG. 3. Variation of impurity modes due to Cu-V pair defect in GaAs with the force-constant-change parameter as described in the text.

($t \simeq 0.6$) around the Zn impurity and the As atoms (cf. Fig. 4). This provides justification to the experimental speculations for the structure of these defect complexes as being "vacancy-impurity" pairs with the trigonal symmetry in GaAs.

B. C_s case

To manifest the observed resonance mode due to the F center to be of rhombic symmetry in GaAs, we have considered various possible defect models (involving Cu), compatible with the symmetry requirements. All except the simplest model with vacancy at the As (site 2) and Cu impurities at sites 1 and 6 (viz., $\mathrm{Cu_{Ga}}V_{\mathrm{As}}\mathrm{Cu_{Ga}}$) have been ruled out. As pointed out before, the impurity complex of C_s point-group symmetry with 11 involved atoms and defect space of size (33×33) will give rise to A_1 and A_2 types of vibrational modes—all optically allowed. With the same perturbation parameters (i.e., $\epsilon_7 = \epsilon_6$ and $t = v \simeq 0.62$) as obtained from the C_{3_v} case, it is worth mentioning that we find a resonance mode $\omega_r(2)$ at 44 cm^{-1} of A_1 symmetry in close agreement with the experiments. This lends support to the reliability of the obtained force variation about the Cu sites and also a good approximation to the expected model for the F center.

V. DISCUSSION AND CONCLUSIONS

Using Green's-function theory with appropriate perturbation models, we have presented a complete theoretical analysis for the vibrational structure of copper and zinc complexes in GaAs. Unlike the earlier calculations of Grimm *et al.*,[20] we have considered here a more elaborate lattice dynamical model for the host GaAs as well as a complete perturbation model for the impurity complex for the C_s symmetry. For the C center (nearest-neighbor Cu-V pair), we find a resonance mode $\{\omega_r(1)\}$ in close agreement with the experimental findings of Gross *et al.*,[8,9] if a large force-constant softening is considered around the Cu—As bonds. Similar calculations have shown the resonance mode $\{\omega_r(3)\}$ for the Zn-V pair but with relatively less softening in the Zn-As couplings. It is worth mentioning that with the same force-constant-change parameters (as obtained from the C_{3_v} case), our theoretical results have also confirmed the occurrence of $\{\omega_r(2)\}$ mode for the F center. The possible model $\{\underline{\mathrm{Cu}}_{\mathrm{Ga}}\underline{V}_{\mathrm{As}}\underline{\mathrm{Cu}}_{\mathrm{Ga}}\}$ with the rhombic symmetry is in corroboration with the earlier theoretical findings,[20] but it is different than the experimental speculations of Safarov *et al.*[10] Copper is known to be a double acceptor in GaAs and its substitution for gallium will introduce excess negative charges. At low-impurity concentration, a vacancy at arsenic can compensate three of them and thus the C center with simple pair $\underline{\mathrm{Cu}}_{\mathrm{Ga}}\underline{V}_{\mathrm{As}}$ defect will be favorable. With higher Cu concentration however, the $\omega_r(1)$ intensity should decrease while the height of $\omega_r(2)$ will increase.[8–10] Consequently, the defect $\mathrm{Cu_{Ga}}V_{\mathrm{As}}\mathrm{Cu_{Ga}}$ can be regarded as a plausible choice for the F center for higher dopants. Quite recently[7] we have pointed out the significance of the bond charge and the bond length for explaining the trends of force perturbation caused by the localized vibration of various isolated and pair impurities in elemental and compound semiconductors. The present results for the resonance modes due to *two* different complexes, Cu-V and Zn-V, in *one* host system lend additional support to our arguments. In highly ionic solids most of the vibrational properties are decided by their ionicity, but we feel, however, that in partially ionic or covalent crystals the bond length and the redistribution of electronic charge density that modify the covalency of the bond (or the strength of the bond) are the important factors.

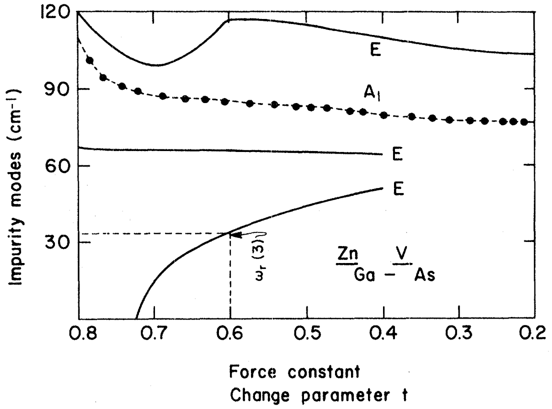

FIG. 4. Same as Fig. (3) but for Zn-V pair defect vibrations in GaAs.

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APPENDIX

We present Tables I–III.

TABLE I. Green's-function matrix for an impurity complex with three defect centers interacting with the nearest-neighbor lattice atoms of zinc-blende-type crystals. The number $g_1, g_2, g_3, \ldots, g_{33}$ within rectangles refers to the elements of the Green's function. The atomic sites 1,2, . . . , 11 are according to Fig. (1). The determination of the matrix elements has been accomplished using group-theoretic arguments and the transformation properties under operations of the crystal space group.

		1			2			3			4			5		
		x	y	z	x	y	z	x	y	z	x	y	z	x	y	z
1	x	g_2	0	0	g_3	g_4	g_4	g_3	g_4	$-g_4$	g_3	$-g_4$	$-g_4$	g_3	$-g_4$	g_4
	y	0	g_2	0	g_4	g_3	g_4	g_4	g_3	$-g_4$	$-g_4$	g_3	g_4	$-g_4$	g_3	$-g_4$
	z	0	0	g_2	g_4	g_4	g_3	$-g_4$	$-g_4$	g_3	$-g_4$	g_4	g_3	g_4	$-g_4$	g_3
2	x	g_3	g_4	g_4	g_1	0	0	g_9	g_{11}	g_{12}	g_{10}	$-g_{12}$	$-g_{12}$	g_9	g_{12}	g_{11}
	y	g_4	g_3	g_4	0	g_1	0	g_{11}	g_9	g_{12}	g_{12}	g_9	g_{11}	$-g_{12}$	g_{10}	$-g_{12}$
	z	g_4	g_4	g_3	0	0	g_1	$-g_{12}$	$-g_{12}$	g_{10}	g_{12}	g_{11}	g_9	g_{11}	g_{12}	g_9
3	x	g_3	g_4	$-g_4$	g_9	g_{11}	$-g_{12}$	g_1	0	0	g_9	g_{12}	$-g_{11}$	g_{10}	$-g_{12}$	g_{12}
	y	g_4	g_3	$-g_4$	g_{11}	g_9	$-g_{12}$	0	g_1	0	$-g_{12}$	g_{10}	g_{12}	g_{12}	g_9	$-g_{11}$
	z	$-g_4$	$-g_4$	g_3	g_{12}	g_{12}	g_{10}	0	0	g_1	$-g_{11}$	$-g_{12}$	g_9	$-g_{12}$	$-g_{11}$	g_9
4	x	g_3	$-g_4$	$-g_4$	g_{10}	g_{12}	g_{12}	g_9	$-g_{12}$	$-g_{11}$	g_1	0	0	g_9	$-g_{11}$	$-g_{12}$
	y	$-g_4$	g_3	g_4	$-g_{12}$	g_9	g_{11}	g_{12}	g_{10}	$-g_{12}$	0	g_1	0	$-g_{11}$	g_9	g_{12}
	z	$-g_4$	g_4	g_3	$-g_{12}$	g_{11}	g_9	$-g_{11}$	g_{12}	g_9	0	0	g_1	g_{12}	$-g_{12}$	g_{10}
5	x	g_3	$-g_4$	g_4	g_9	$-g_{12}$	g_{11}	g_{10}	g_{12}	$-g_{12}$	g_9	$-g_{11}$	g_{12}	g_1	0	0
	y	$-g_4$	g_3	$-g_4$	g_{12}	g_{10}	g_{12}	$-g_{12}$	g_9	$-g_{11}$	$-g_{11}$	g_9	$-g_{12}$	0	g_1	0
	z	g_4	$-g_4$	g_3	g_{11}	$-g_{12}$	g_9	g_{12}	$-g_{11}$	g_9	$-g_{12}$	g_{12}	g_{10}	0	0	g_1
6	x	g_5	g_7	$-g_8$	g_3	g_4	$-g_4$	g_{13}	g_{15}	g_{17}	g_{18}	g_{21}	g_{20}	g_{22}	g_{19}	g_{19}
	y	g_7	g_5	$-g_8$	g_4	g_3	$-g_4$	g_{15}	g_{13}	g_{17}	g_{19}	g_{22}	g_{19}	g_{21}	g_{18}	g_{20}
	z	g_8	g_8	g_6	$-g_4$	$-g_4$	g_3	g_{16}	g_{16}	g_{14}	g_{20}	g_{21}	g_{18}	g_{21}	g_{20}	g_{18}
7	x	g_6	g_8	g_8	g_3	$-g_4$	$-g_4$	g_{18}	g_{21}	g_{20}	g_{14}	g_{16}	g_{16}	g_{18}	g_{20}	g_{21}
	y	$-g_8$	g_5	g_7	$-g_4$	g_3	g_4	g_{19}	g_{22}	g_{19}	g_{17}	g_{13}	g_{15}	g_{20}	g_{18}	g_{21}
	z	$-g_8$	g_7	g_5	$-g_4$	g_4	g_3	g_{20}	g_{21}	g_{18}	g_{17}	g_{15}	g_{13}	g_{19}	g_{19}	g_{22}
8	x	g_5	$-g_8$	g_7	g_3	$-g_4$	g_4	g_{22}	g_{19}	g_{19}	g_{18}	g_{20}	g_{21}	g_{13}	g_{17}	g_{15}
	y	g_8	g_6	g_8	$-g_4$	g_3	$-g_4$	g_{21}	g_{18}	g_{20}	g_{20}	g_{18}	g_{21}	g_{16}	g_{14}	g_{16}
	z	g_7	$-g_8$	g_5	g_4	$-g_4$	g_3	g_{21}	g_{20}	g_{18}	g_{19}	g_{19}	g_{22}	g_{15}	g_{17}	g_{13}
9	x	g_{22}	g_{21}	$-g_{21}$	g_9	$-g_{12}$	$-g_{11}$	g_{23}	g_{26}	g_{26}	g_9	g_{11}	g_{12}	g_{33}	0	0
	y	g_{19}	g_{18}	$-g_{20}$	g_{12}	g_{10}	$-g_{12}$	g_{25}	g_{24}	g_{27}	g_{11}	g_9	g_{12}	0	g_{32}	0
	z	$-g_{19}$	$-g_{20}$	g_{18}	$-g_{11}$	g_{12}	g_9	$-g_{25}$	g_{27}	g_{24}	$-g_{12}$	$-g_{12}$	g_{10}	0	0	g_{32}
10	x	g_{18}	g_{19}	$-g_{20}$	g_{10}	g_{12}	$-g_{12}$	g_{24}	g_{25}	g_{27}	g_{32}	0	0	g_9	g_{11}	g_{12}
	y	g_{21}	g_{22}	$-g_{21}$	$-g_{12}$	g_9	$-g_{11}$	g_{26}	g_{23}	$-g_{26}$	0	g_{33}	0	g_{11}	g_9	g_{12}
	z	$-g_{20}$	$-g_{19}$	g_{18}	g_{12}	$-g_{11}$	g_9	g_{27}	$-g_{25}$	g_{24}	0	0	g_{32}	$-g_{12}$	$-g_{12}$	g_{10}
11	x	g_{13}	g_{15}	$-g_{16}$	g_9	g_{11}	g_{12}	g_{28}	g_{30}	$-g_{31}$	g_{24}	g_{26}	$-g_{27}$	g_{23}	g_{25}	g_{25}
	y	g_{15}	g_{13}	$-g_{16}$	g_{11}	g_9	g_{12}	g_{30}	g_{28}	$-g_{31}$	g_{25}	g_{23}	g_{25}	g_{26}	g_{26}	$-g_{27}$
	z	$-g_{17}$	$-g_{17}$	g_{14}	$-g_{12}$	$-g_{12}$	g_{10}	g_{31}	g_{31}	g_{29}	$-g_{27}$	g_{26}	g_{24}	g_{26}	$-g_{27}$	g_{24}

TABLE I. *(Continued.)*

6			7			8			9			10			11		
x	y	z	x	y	z	x	y	z	x	y	z	x	y	z	x	y	z
g_5	g_7	g_8	g_6	$-g_8$	$-g_8$	g_5	g_8	g_7	g_{22}	g_{19}	$-g_{19}$	g_{18}	g_{21}	$-g_{20}$	g_{13}	g_{15}	$-g_{17}$
g_7	g_5	g_8	g_8	g_5	g_7	$-g_8$	g_6	$-g_8$	g_{21}	g_{18}	$-g_{20}$	g_{19}	g_{22}	$-g_{19}$	g_{15}	g_{13}	$-g_{17}$
$-g_8$	$-g_8$	g_6	g_8	g_7	g_5	g_7	g_8	g_5	$-g_{21}$	$-g_{20}$	g_{18}	$-g_{20}$	$-g_{21}$	g_{18}	$-g_{16}$	$-g_{16}$	g_{14}
g_3	g_4	$-g_4$	g_3	$-g_4$	$-g_4$	g_3	$-g_4$	g_4	g_9	g_{12}	$-g_{11}$	g_{10}	$-g_{12}$	g_{12}	g_9	g_{11}	$-g_{12}$
g_4	g_3	$-g_4$	$-g_4$	g_3	g_4	$-g_4$	g_3	$-g_4$	$-g_{12}$	g_{10}	g_{12}	g_{12}	g_9	$-g_{11}$	g_{11}	g_9	$-g_{12}$
$-g_4$	$-g_4$	g_3	$-g_4$	g_4	g_3	g_4	$-g_4$	g_3	$-g_{11}$	$-g_{12}$	g_9	$-g_{12}$	$-g_{11}$	g_9	g_{12}	g_{12}	g_{10}
g_{13}	g_{15}	g_{16}	g_{18}	g_{19}	g_{20}	g_{22}	g_{21}	g_{21}	g_{23}	g_{25}	$-g_{25}$	g_{24}	g_{26}	g_{27}	g_{28}	g_{30}	g_{31}
g_{15}	g_{13}	g_{16}	g_{21}	g_{22}	g_{21}	g_{19}	g_{18}	g_{20}	g_{26}	g_{24}	g_{27}	g_{25}	g_{23}	$-g_{25}$	g_{30}	g_{28}	g_{31}
g_{17}	g_{17}	g_{14}	g_{20}	g_{19}	g_{18}	g_{19}	g_{20}	g_{18}	g_{26}	g_{27}	g_{24}	g_{27}	$-g_{26}$	g_{24}	$-g_{31}$	$-g_{31}$	g_{29}
g_{18}	g_{19}	g_{20}	g_{14}	g_{17}	g_{17}	g_{18}	g_{20}	g_{19}	g_9	g_{11}	$-g_{12}$	g_{32}	0	0	g_{24}	g_{25}	$-g_{27}$
g_{21}	g_{22}	g_{21}	g_{16}	g_{13}	g_{15}	g_{20}	g_{18}	g_{19}	g_{11}	g_9	$-g_{12}$	0	g_{33}	0	g_{26}	g_{23}	g_{26}
g_{20}	g_{19}	g_{18}	g_{16}	g_{15}	g_{13}	g_{21}	g_{21}	g_{22}	g_{12}	g_{12}	g_{10}	0	0	g_{32}	$-g_{27}$	g_{25}	g_{24}
g_{22}	g_{21}	g_{21}	g_{18}	g_{20}	g_{19}	g_{13}	g_{16}	g_{15}	g_{33}	0	0	g_9	g_{11}	$-g_{12}$	g_{23}	g_{26}	g_{26}
g_{19}	g_{18}	g_{20}	g_{20}	g_{18}	g_{19}	g_{17}	g_{14}	g_{17}	0	g_{32}	0	g_{11}	g_9	$-g_{12}$	g_{25}	g_{24}	$-g_{27}$
g_{19}	g_{20}	g_{18}	g_{21}	g_{21}	g_{22}	g_{15}	g_{16}	g_{13}	0	0	g_{32}	g_{12}	g_{12}	g_{10}	g_{25}	$-g_{27}$	g_{24}
g_2	0	0	g_5	g_8	$-g_7$	g_6	$-g_8$	g_8	g_3	$-g_4$	$-g_4$	g_3	$-g_4$	g_4	g_3	g_4	g_4
0	g_2	0	$-g_8$	g_6	g_8	g_8	g_5	$-g_7$	$-g_4$	g_3	g_4	$-g_4$	g_3	$-g_4$	g_4	g_3	g_4
0	0	g_2	$-g_7$	$-g_8$	g_5	$-g_8$	$-g_7$	g_5	$-g_4$	g_4	g_3	g_4	$-g_4$	g_3	g_4	g_4	g_3
g_5	$-g_8$	$-g_7$	g_2	0	0	g_5	$-g_7$	$-g_8$	g_{13}	g_{17}	$-g_{15}$	g_{18}	g_{20}	$-g_{21}$	g_{22}	g_{19}	$-g_{19}$
g_8	g_6	$-g_8$	0	g_2	0	$-g_7$	g_5	g_8	g_{16}	g_{14}	$-g_{16}$	g_{20}	g_{18}	$-g_{21}$	g_{21}	g_{18}	$-g_{21}$
$-g_7$	g_8	g_5	0	0	g_2	g_8	$-g_8$	g_6	$-g_{15}$	$-g_{17}$	g_{13}	$-g_{19}$	$-g_{19}$	g_{22}	$-g_{21}$	$-g_{20}$	g_{18}
g_6	g_8	$-g_8$	g_5	$-g_7$	$-g_8$	g_2	0	0	g_{18}	g_{20}	$-g_{21}$	g_{14}	g_{16}	g_{16}	g_{18}	g_{21}	$-g_{20}$
$-g_8$	g_5	$-g_7$	$-g_7$	g_5	$-g_8$	0	g_2	0	g_{20}	g_{18}	$-g_{21}$	g_{17}	g_{13}	$-g_{15}$	g_{19}	g_{22}	$-g_{19}$
g_8	$-g_7$	g_5	$-g_8$	g_8	g_6	0	0	g_2	$-g_{19}$	$-g_{19}$	g_{22}	$-g_{17}$	$-g_{15}$	g_{13}	$-g_{20}$	$-g_{21}$	g_{18}
g_3	$-g_4$	$-g_4$	g_{13}	g_{16}	g_{-15}	g_{18}	g_{20}	$-g_{19}$	g_1	0	0	g_9	$-g_{11}$	$-g_{12}$	g_{10}	g_{12}	g_{12}
$-g_4$	g_3	g_4	g_{17}	g_{14}	$-g_{17}$	g_{20}	g_{18}	$-g_{19}$	0	g_1	0	$-g_{11}$	g_9	g_{12}	$-g_{12}$	g_9	g_{11}
$-g_4$	g_4	g_3	$-g_{15}$	$-g_{16}$	g_{13}	$-g_{21}$	$-g_{21}$	g_{22}	0	0	g_1	g_{12}	$-g_{12}$	g_{10}	$-g_{12}$	g_{11}	g_9
g_3	$-g_4$	g_4	g_{18}	g_{20}	$-g_{19}$	g_{14}	g_{17}	$-g_{17}$	g_9	$-g_{11}$	g_{12}	g_1	0	0	g_9	$-g_{12}$	g_{11}
$-g_4$	g_3	$-g_4$	g_{20}	g_{18}	$-g_{19}$	g_{16}	g_{13}	$-g_{15}$	$-g_{11}$	g_9	$-g_{12}$	0	g_1	0	g_{12}	g_{10}	g_{12}
g_4	$-g_4$	g_3	$-g_{21}$	$-g_{21}$	g_{22}	g_{16}	$-g_{15}$	g_{13}	$-g_{12}$	g_{12}	g_{10}	0	0	g_1	g_{11}	$-g_{12}$	g_9
g_3	g_4	g_4	g_{22}	g_{21}	$-g_{21}$	g_{18}	g_{19}	$-g_{20}$	g_{10}	$-g_{12}$	$-g_{12}$	g_9	g_{12}	g_{11}	g_1	0	0
g_4	g_3	g_4	g_{19}	g_{18}	$-g_{20}$	g_{21}	g_{22}	$-g_{21}$	g_{12}	g_9	g_{11}	$-g_{12}$	g_{10}	$-g_{12}$	0	g_1	0
g_4	g_4	g_3	$-g_{19}$	$-g_{21}$	g_{18}	$-g_{20}$	$-g_{19}$	g_{18}	g_{12}	g_{11}	g_9	g_{11}	g_{12}	g_9	0	0	g_1

TABLE II. Eigenvector matrix for C_{3v} point-group symmetry, which can be used to block diagonalize the Green's function and the perturbation matrix of the same symmetry. NF denotes normalization factor.

																										NF	
A_1	X_1	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{3}$	u_x^I
	X_2	0	0	0	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{3}$	u_y^I
	X_3	0	0	0	0	0	0	1	1	0	0	1	1	1	0	1	0	0	0	0	0	0	0	0	0	$\sqrt{6}$	u_z^I
	X_4	0	0	0	0	0	0	0	0	1	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	$\sqrt{3}$	u_x^{II}
	X_5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0	0	1	1	1	0	1	$\sqrt{6}$	u_y^{II}
	X_6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0	0	0	1	0	$\sqrt{3}$	u_z^{II}
A_2	X_7	0	0	0	0	0	0	1	−1	0	0	1	−1	−1	0	1	0	0	0	0	0	0	0	0	0	$\sqrt{6}$	u_x^3
	Y_7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	−1	0	0	1	−1	−1	0	1	$\sqrt{6}$	u_y^3
$E^{(1)}$	X_8	1	−1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_z^3
	X_9	0	0		1	−1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_x^4
	X_{10}	0	0	0	0	0	0	1	−1	0	0	0	1	0	0	−1	0	0	0	0	0	0	0	0	0	2	u_y^4
	X_{11}	0	0	0	0	0	0	0	0	0	1	0	0	0	−1	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_z^4
	X_{12}	0	0	0	0	0	0	−1	1	0	0	2	1	−2	0	−1	0	0	0	0	0	0	0	0	0	$\sqrt{12}$	u_x^5
	X_{13}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	−1	0	0	0	1	0	0	−1	2	u_y^5
	X_{14}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	−1	0	$\sqrt{2}$	u_z^5
	X_{15}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	−1	1	0	0	2	1	−2	0	−1	$\sqrt{12}$	u_x^6
$E^{(2)}$	Y_8	1	1	−2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{6}$	u_y^6
	Y_9	0	0	0	1	1	−2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{6}$	u_z^6
	Y_{10}	0	0	0	0	0	0	−1	−1	0	0	2	−1	2	0	−1	0	0	0	0	0	0	0	0	0	$\sqrt{12}$	u_x^7
	Y_{11}	0	0	0	0	0	0	0	0	−2	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	$\sqrt{6}$	u_y^7
	Y_{12}	0	0	0	0	0	0	−1	−1	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	2	u_z^7
	Y_{13}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	−1	−1	0	0	2	−1	2	0	−1	$\sqrt{12}$	u_x^8
	Y_{14}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	−2	1	0	0	0	1	0	$\sqrt{6}$	u_8^y
	Y_{15}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	−1	−1	0	0	0	1	0	0	1	2	u_z^8

TABLE IIII. Eigenvector matrix for C_s point-group symmetry which can be used to diagonalize the Green's function and the perturbation matrix of the same symmetry. NF denotes normalization factor.

																																			NF	
A_1	X_1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_x^I
	X_2	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	u_y^I
	X_3	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_z^I
	X_4	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	u_x^{II}
	X_5	0	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_y^{II}
	X_6	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	u_z^{II}
	X_7	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_x^3
	X_8	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_y^3
	X_9	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_z^3
	X_{10}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_x^4
	X_{11}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	u_y^4
	X_{12}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_z^4
	X_{13}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_x^5
	X_{14}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_y^5
	X_{15}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	$\sqrt{2}$	u_z^5
	X_{16}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	$\sqrt{2}$	u_x^{III}
	X_{17}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	$\sqrt{2}$	u_y^{III}
	X_{18}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0	$\sqrt{2}$	u_z^{III}
	X_{19}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	u_x^7
A_2	X_{20}	1	−1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_y^7
	X_{21}	0	0	0	1	−1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_z^7
	X_{22}	0	0	0	0	0	0	1	−1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_x^8
	X_{23}	0	0	0	0	0	0	0	0	0	1	0	0	0	−1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_y^8
	X_{24}	0	0	0	0	0	0	0	0	0	0	1	0	−1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_z^8
	X_{25}	0	0	0	0	0	0	0	0	0	0	0	1	0	0	−1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_x^9
	X_{26}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	−1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_y^9
	X_{27}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	−1	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_z^9
	X_{28}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	−1	0	0	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_x^{10}
	X_{29}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	−1	0	0	0	0	0	0	0	0	0	$\sqrt{2}$	u_y^{10}
	X_{30}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	−1	0	0	0	0	$\sqrt{2}$	u_z^{10}
	X_{31}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	−1	0	0	0	0	0	$\sqrt{2}$	u_x^{11}
	X_{32}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	−1	0	0	0	$\sqrt{2}$	u_y^{11}
	X_{33}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	−1	0	$\sqrt{2}$	u_z^{11}

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