PHYSICAL REVIEW B VOLUME 18, NUMBER 12 15 DECEMBER 1978

Defect Green's function and *T* matrix for an hcp lattice with a substitutional impurity

Debendranath Sahoo and Hrushi Kesh Sahu
Reactor Research Center, Kalpakkam 603102, India
(Received 19 July 1977)

Starting with a two-neighbor defect space model for a substitutional impurity in an hcp lattice, we apply matrix-partitioning and Green's-function techniques for the study of atomic vibrations in the defect space. Using the fact that the defect site has the point-group symmetry of the Group D_{3h}, we set up and decompose the total representation $\Gamma(D_{3h})$ of the group as $\Gamma(D_{3h}) = 4A_1' \oplus 2A_1'' \oplus 3A_2' \oplus 4A_2'' \oplus 8E' \oplus 5E''$. The symmetry-adapted basis vectors of the 39-dimensional defect space are calculated using the projection operator technique and the projected forms of the Green's function and the perturbation matrices are derived. The formal results obtained here are applicable to a variety of problems in hcp crystals.

I. INTRODUCTION

In the lattice statics of crystals with impurities one is concerned with the local distortion of the lattice around a defect, while in the lattice dynamics of crystals with impurities one is interested mainly in the impurity-induced change in the vibrational modes of the host crystal, i.e., in local and resonance modes. These are of importance in infrared-absorption, Raman-scattering, and Mössbauer-effect experiments. The most convenient theoretical approach to defect problems in crystals is linear-response theory, which leads naturally to the use of crystal Green's functions. We mention in this connection the recent review article by Taylor[1] and the work of Maradudin[2] for the dynamic properties of defect crystals, and the article by Tewary[3] for static properties. Ludwig and Dettmann[4] have applied group theory to certain impurity problems in crystals with structures of the simple cubic, NaCl, CsCl, diamond, zincblende, and CaF_2 types. For these symmetries, Ludwig and Dettmann have supplied tables for the symmetry-adapted basis functions, which greatly simplify the solution of defect problems in lattice statics and dynamics. (Agrawal[5] has corrected an error in their result for the fcc case.) However, no such table is available for solving impurity problems in the hcp structure. The present paper fills this need, and it is hoped that it will facilitate systematic defect calculations in hcp crystals.

We derive, for a hcp crystal, explicit theoretical expressions for the symmetry-reduced crystal Green's function and perturbation matrices which are needed for the analysis of those dynamic or static substitutional-impurity problems which preserve the D_{3h} point symmetry (of the impurity site). We assume that the defects perturb the force constants of the host lattice up to second-nearest neighbors, 12 atoms thus being affected. In Sec. II, we outline the method of our calculation and in Sec. III, we apply the symmetry properties of the hcp lattice to obtain the most general forms of the Green's-function and the force-constant matrices. The defect model is described in Sec. IV, and in Sec. V, we apply group theory to obtain the symmetry-adapted basis vectors of the defect space, and block-diagonalize the perfect-lattice Green's-function and perturbation matrices. Finally, in Sec. 6, we discuss our results and indicate some possible applications. The applications of the theory to the lattice statics of a single vacancy in magnesium is presented in a companion paper.

II. THEORY

Since the theory of the dynamics of a crystal with an impurity atom is well known,[2] we shall merely quote the important results relevant to our purpose.

In matrix form, the time-independent equations of motion of the perturbed crystal reduce to

$$[\omega^2\underline{M} - \underline{\phi} + \delta\underline{L}(\omega)]\underline{U} = 0, \tag{2.1}$$

where the perturbation matrix $\delta\underline{L}(\omega) = -\omega^2\Delta\underline{M} + \Delta\underline{\phi}$, ω is the normal-mode vibration frequency of the defect crystal, $\underline{M}$ and $\underline{\phi}$ are the mass and force-constant matrices of the perfect lattice, and $\Delta\underline{M}$ and $\Delta\underline{\phi}$ are the corresponding perturbation matrices owing to the presence of the defect in the lattice. For the hcp lattice, each of the above matrices is $6N \times 6N$, where N is the number of unit cells in the crystal. The matrix $\delta\underline{L}$ can be written as a 2×2 block matrix in which the only nonvanishing block $\delta\underline{l}$ $(= -\omega^2\delta\underline{M} + \delta\underline{\phi})$ is a $3p \times 3p$ $(p \ll N)$ matrix, p being the number of atoms (including the impurity itself) disturbed by the presence of the impurity. It is this $3p$-dimensional space, the so-called defect space, which will be the object of our study. Basic to the investigation of defect problems are the perfect and the defect crystal Green's function matrices and the phonon-scattering matrix. The relevant blocks of these matrices for the defect-space calculation are the $3p \times 3p$ matrices $\underline{g}(\omega)$, $\underline{g}^*(\omega)$, and $\underline{t}(\omega)$, respectively. These matrices are related to each other by the following equations:

$$\underline{g}^*=(\underline{I}-\underline{g}\delta\underline{l})^{-1}\underline{g}=\underline{g}(\underline{I}-\delta\underline{l}\,\underline{g})^{-1} \tag{2.2}$$

and

$$\underline{t}=\delta\underline{l}(\underline{I}-\underline{g}\delta\underline{l})^{-1}=(\underline{I}-\delta\underline{l}\,\underline{g})^{-1}\delta\underline{l}. \tag{2.3}$$

The introduction of the symmetry coordinates[2] for the various irreducible representations (IR's) of the point group $\mathcal{G}$ of the impurity site (taken as the origin of coordinates) block-diagonalizes the matrices $\underline{g}(\omega)$ and $\delta\underline{l}(\omega)$ simultaneously. A faithful $3p$-dimensional representation of $\mathcal{G}$, called the total representation $\Gamma(\mathcal{G})$, consists of a set of $3p \times 3p$ matrices

$$\mathcal{S}_{\alpha\beta}(l\kappa, l'\kappa'; \underline{S})=S_{\alpha\beta}\delta(\underline{S}^{-1}\vec{\mathrm{x}}(l'\kappa'), \vec{\mathrm{x}}(l\kappa)), \tag{2.4}$$

where $\underline{S}$ is a 3×3 orthogonal matrix effecting the group operation on the individual atomic sites. Here l is the lattice index, κ is the sublattice index, and α, β denote Cartesian components; and $\underline{S}$ is written in the Cartesian coordinate system $\mathcal{K}$ whose origin is at the impurity site. If $\mathcal{G}$ is of order h, there are h such matrices $\underline{S}$ (and hence matrices $\underline{\mathcal{S}}$). The technique of decomposition of $\Gamma(\mathcal{G})$ into its IR's $\Gamma^s(\mathcal{G})$ makes use of the characters $\chi(\underline{S})$ of the elements $\underline{S}$ in $\Gamma(\mathcal{G})$ and the corresponding characters $\chi^s(\underline{S})$ of all the IR's $\Gamma^s(\mathcal{G})$:

$$\Gamma(\mathcal{G})=\sum_s \oplus c_s\Gamma^s(\mathcal{G}), \tag{2.5}$$

where

$$c_s=\frac{1}{h}\sum_{\underline{\mathcal{S}}\in\mathcal{G}} [\chi^s(\underline{S})]^*\chi(\underline{S}). \tag{2.6}$$

The symmetry-reduced form of the matrix $\underline{A}$ (which stands for $\underline{g}$, $\underline{g}^*$, $\delta\underline{l}$, or $\underline{t}$) in the sth IR is given by the expression

$$A^s(a,a')=\psi_\alpha^{sa\lambda}(l\kappa)^*A_{\alpha\beta}(l\kappa, l'\kappa')\psi_\beta^{sa'\lambda}(l'\kappa'), \tag{2.7}$$

where $\vec{\psi}^{sa\lambda}$ is the symmetry-adapted basis vector (*SAV*) for the λth row in the ath occurrence of the sth IR, and the result is independent of λ. In Eq. (2.7) and in the rest of the paper, repeated Cartesian and lattice indices (α, l, κ, etc.) are summed over their respective ranges. There is no summation over λ and s. The range of λ is from 1 to f_s (the dimensionality of the s IR), and that of a is from 1 to c_s. The calculation of the complete orthonormal set $\{\vec{\psi}\}$ is done by means of the standard projection operator technique,[2] for which it is necessary to know the explicit matrix representation $\Gamma^s(\mathcal{G})$ of the sth IR (for $f_s \geq 2$) in the coordinate system $\mathcal{K}$.

The actual calculation of the $c_s \times c_s$ matrix $\underline{A}^s$, involving the multiplication of a $3p \times 3p$ matrix with $3p$-dimensional vectors, is simplified considerably by the following trick. We first calculate

$$\eta_\alpha^{sa\lambda}(l\kappa)=A_{\alpha\beta}(l\kappa, l'\kappa')\psi_\beta^{sa\lambda}(l'\kappa') \tag{2.8}$$

for a particular site $(l\kappa)$. Then for all other sites (LK) which belong to the *same shell* of neighbors (with respect to the defect), the quantity $\eta_\alpha^{sa\lambda}(LK)$ can be computed by means of the relation

$$\vec{\eta}^{\,sa\lambda}(LK)=\sum_{\lambda'=1}^{f_s}\underline{S}\vec{\eta}^{\,sa\lambda'}(l\kappa)\overline{\Gamma}^s_{\lambda'\lambda}(\underline{S}) \times \delta(\underline{S}^{-1}\vec{\mathrm{x}}(LK), \vec{\mathrm{x}}(l\kappa)). \tag{2.9}$$

In this equation $\overline{\Gamma}^s_{\lambda'\lambda}(\underline{S})$ is the $(\lambda'\lambda)$ matrix element of the inverse of the matrix representation $\Gamma^s(\underline{S})$ of the element $\underline{S}$. The proof of Eq. (2.9) is given in Appendix A. Having obtained all the $\vec{\eta}$'s in this manner, the matrix $\underline{A}^s$ is calculated by means of the fomula

$$A^s(a,a')=\psi_\alpha^{sa\lambda}(l\kappa)\eta_\alpha^{sa'\lambda}(l\kappa). \tag{2.10}$$

The fact that the matrix $\underline{A}$ satisfies the relation $A_{\alpha\beta}(l\kappa, l'\kappa')=A_{\beta\alpha}(l'\kappa', l\kappa)$ (permutation symmetry) implies that $\underline{A}^s$ is a symmetric matrix. Thus we need to compute $A^s(a,a')$ only for $a' \geq a$ (or for $a' \leq a$).

The application of an operation $\underline{S}$ on any lattice site yields another site on the same shell of neighbors. This means that the defect space D consists of invariant subspaces D^m, where m is the shell index. In a two-neighbor defect-space model such as the one we are considering here, m takes on only three values: 0, 1, and 2, corresponding, respectively, to the defect, the first, and the second shells. Thus all defect-space calculations can be done separately in each D^m. The following direct-sum decompositions exists

$$D=\sum_m \oplus D^m, \tag{2.11}$$

$$\Gamma(\mathcal{G})=\sum_m \oplus \Gamma^m(\mathcal{G}), \tag{2.12}$$

$$\vec{\psi}^{\,sa\lambda}=\sum_m \oplus \vec{\psi}^{\,sa\lambda m}, \tag{2.13}$$

and

$$\vec{\eta}^{\,sa\lambda}=\sum_m \oplus \vec{\eta}^{\,sa\lambda m}. \tag{2.14}$$

Corresponding to those decompositions, one obviously has the following:

$$c_S = \sum_m c_S^m , \tag{2.15}$$

$$\chi(\underline{S}) = \sum_m \chi^m(\underline{S}) , \tag{2.16}$$

$$c_S^m = \frac{1}{h} \sum_{\underline{S} \in G} [\chi^s(\underline{S})]^* \chi^m(\underline{S}) , \tag{2.17}$$

and

$$A^S(a, a') = \sum_m \psi_\alpha^{Sa\lambda m}(l\kappa) \eta_\alpha^{Sa'\lambda m}(l\kappa) . \tag{2.18}$$

The projected forms of the defect Green's-function matrix and the t matrix are given by equations obtainable from Eqs. (2.2) and (2.3) by making the replacement $g \to g^S$, $g^* \to g^{*S}$, $\delta l \to \delta l^S$, $t \to t^S$, and $I \to I^S$ (the f_s-dimensional unit matrix).

III. hcp LATTICE

A. Coordinate systems

Figure 1 illustrates the choice[6] of the axes of $\mathcal{K}$ (unit vectors $\hat{i}$, $\hat{j}$, $\hat{k}$) and the crystallographic axes (primitive lattice vectors $\vec{a}$, $\vec{b}$, $\vec{c}$), along with all the atom positions up to the second neighbor of the impurity which is supposed to be located at the common origin of the coordinate systems. Of the two atoms in the primitive cell of the perfect lattice, one is located at the origin, i.e., at $\vec{x}(01) = \vec{0}$, and the other at

$$\vec{x}(02) = \tfrac{2}{3}\vec{a} + \tfrac{1}{3}\vec{b} + \tfrac{1}{2}\vec{c} = -(3)^{-1/2} a\hat{j} + \tfrac{1}{2} c\hat{k} .$$

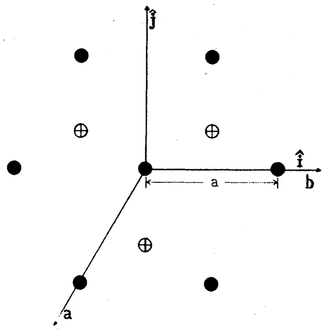

FIG. 1. Orientation of the Cartesian and the crystallographic axes in the diatomic hcp crystal in the basal (XY) plane. The Z axis which coincides with the c axis is perpendicular to the plane of the paper, directed outwards. The black dots represent atoms in the basal plane with a spacing a from the central atom, and the open circles with crosses represent the projections of the six atoms in the $Z = \pm\frac{1}{2}c$ planes.

TABLE I. Atom-index labels and the Cartesian and crystallographic coordinates of all the atoms in the defect space.

Subspace	Atom number	Sublattice index	Crystallographic coordinates			Cartesian coordinates		
D^m	n	κ	l_1	l_2	l_3	x	y	z
D^0	0	1	0	0	0	0	0	0
D^1	1	2	0	0	$\bar{1}$	0	$-a/\sqrt{3}$	$-\frac{1}{2}c$
	2	2	$\bar{1}$	0	$\bar{1}$	$\frac{1}{2}a$	$a/2\sqrt{3}$	$-\frac{1}{2}c$
	3	2	$\bar{1}$	$\bar{1}$	$\bar{1}$	$-\frac{1}{2}a$	$a/2\sqrt{3}$	$-\frac{1}{2}c$
	4	2	0	0	0	0	$-a/\sqrt{3}$	$\frac{1}{2}c$
	5	2	$\bar{1}$	$\bar{1}$	0	$-\frac{1}{2}a$	$a/2\sqrt{3}$	$\frac{1}{2}c$
	6	2	$\bar{1}$	0	0	$\frac{1}{2}a$	$a/2\sqrt{3}$	$\frac{1}{2}c$
D^2	7	1	0	1	0	a	0	0
	8	1	$\bar{1}$	$\bar{1}$	0	$-\frac{1}{2}a$	$\frac{1}{2}\sqrt{3}a$	0
	9	1	1	0	0	$-\frac{1}{2}a$	$-\frac{1}{2}\sqrt{3}a$	0
	10	1	0	$\bar{1}$	0	$-a$	0	0
	11	1	$\bar{1}$	0	0	$\frac{1}{2}a$	$\frac{1}{2}\sqrt{3}a$	0
	12	1	1	1	0	$\frac{1}{2}a$	$-\frac{1}{2}\sqrt{3}a$	0

Here a is the lattice constant in the basal plane, and c is the separation between two adjacent atomic planes parallel to the basal plane.

B. Defect space

The 39-dimensional defect space D consists of three invariant subspaces: D^0, D^1, and D^2. Only the atom at the origin labeled by $n=0$ belongs to D^0; those labeled by $n=1, 2, \ldots, 6$ belong to D^1; and those labeled by $n=7, 8, \ldots, 12$ belong to D^2. Thus D^0 is of dimension 3 and D^1 and D^2 are of dimension 18. Table I gives the relation between the atom indices n, the site indices $(l\kappa)$, and the Cartesian coordinates $x_\alpha(lk)$ of all the atoms in D. We note that if the ratio $c/a<\sqrt{\frac{8}{3}}$, as in the case of Mg, Co, etc., atoms 1–6 are the first neighbors and atoms 7–12 are the second neighbors; while if $c/a>\sqrt{\frac{8}{3}}$, as in the case of Zn, Cd, etc., the role of the two groups of atoms are reversed.

C. Symmetry properties

The group $\mathcal{G}$ for the atom $n=0$ is D_{3h}, the group of the trigonal prism. In Table II we list all the elements of this group and relate our simplified notation to the notations used in the literature to facilitate comparison. In addition to the usual requirements of space-group symmetry (i.e., translational and point-group symmetry), the following restrictions due to the particular D_{6h}^4 space-group structure are worth noting[6]:

$$\underline{\phi}(l1,02)=\underline{\tilde{\phi}}(l1,02)=\underline{\phi}(02,l1) \tag{3.1}$$

and

$$\underline{\phi}(l1,01)=\underline{\tilde{\phi}}(l2,02)=\underline{\phi}(02,l2)\,, \tag{3.2}$$

with similar relations for $\underline{g}$.

TABLE II. Elements of the group D_{3h}. Here $a=\frac{1}{2}\sqrt{3}$, $b=\frac{1}{2}$, $\bar{a}=-a$, and $\bar{b}=-b$.

Our notation	Czachor's notation[a]	Common notation	Matrix operation (international notation)		
S_0	T^{00}	I	x,	y,	z
S_1	T^{02}	$C_3(Z)$	$\bar{b}x+ay$,	$\bar{a}x+\bar{b}y$,	z
S_2	T^{04}	$C_3^{-1}(Z)$	$\bar{b}x+\bar{a}y$,	$ax+\bar{b}y$,	z
S_3	T^{14}	$C_2(1)$	$bx+ay$,	$ax+\bar{b}y$,	$\bar{z}$
S_4	T^{10}	$C_2(2)$	$\bar{x}$,	y,	$\bar{z}$
S_5	T^{12}	$C_2(3)$	$bx+\bar{a}y$,	$\bar{a}x+\bar{b}y$,	$\bar{z}$
S_6	T^{03}	σ_h	x,	y,	$\bar{z}$
S_7	T^{05}	$S_3(Z)$	$\bar{b}x+ay$,	$\bar{a}x+\bar{b}y$,	$\bar{z}$
S_8	T^{01}	$S_3^{-1}(Z)$	$\bar{b}x+\bar{a}y$,	$ax+\bar{b}y$,	$\bar{z}$
S_9	T^{11}	$\sigma_d(1)$	$bx+ay$,	$ax+\bar{b}y$,	z
S_{10}	T^{13}	$\sigma_d(2)$	$\bar{x}$,	y,	z
S_{11}	T^{15}	$\sigma_d(3)$	$bx+\bar{a}y$,	$\bar{a}x+\bar{b}y$,	z

[a] Reference 6.

D. Matrices $\underline{g}$ and $\underline{\phi}$

In obtaining the most general forms of the Green's-function and the force-constant matrices for each shell, it is convenient to write the symmetric and antisymmetric parts of a general 3×3 matrix $\underline{M}$ as

$$\underline{M}=\begin{pmatrix} S_1 & S_4 & S_6 \\ S_4 & S_2 & S_5 \\ S_6 & S_5 & S_3 \end{pmatrix}+\begin{pmatrix} 0 & A_4 & A_6 \\ -A_4 & 0 & A_5 \\ -A_6 & -A_5 & 0 \end{pmatrix}. \tag{3.3}$$

The effect of transforming M by means of the rotation matrices $T^{\mu\nu}$ $(\mu,\nu=0,1,\ldots,5)$ is denoted by

$$\underline{M}^{\mu\nu}=\underline{T}^{\mu\nu}\underline{M}\,\underline{\tilde{T}}^{\mu\nu} \tag{3.4}$$

(where tilde denotes the transposed matrix). Czachor[6] has given the expressions for all the matrices $\underline{M}^{\mu\nu}$ (i.e., the "multiplication table"). Using this multiplication table, the bond invariance under the point-group operations, and Eqs. (3.1) and (3.2), we obtain the most general forms of the matrices $\underline{g}$ and $\underline{\phi}$. For our purpose the force constants up to two neighbors and the Green's functions up to eight neighbors are needed. Let us use the abbreviations

$$\underline{g}(0,n)=\underline{g}(n)\,,$$

$$\underline{g}(01,l\kappa)=\underline{g}(l\kappa)\,,$$

and let $\underline{g}^{(p)}$ denote the Green's function corresponding to the pth shell (note that $\underline{g}^{(0)}(01)$ is the self-term). A similar notation will be used for $\underline{\phi}$. Whenever a superscript appears outside the matrix, it is to be understood that each of the elements of the matrix will depend on the superscript. We shall list now the general forms of the Green's-function matrices up to eight shells of neighbors:

$$\underline{g}^{(0)}(000,1)=\begin{pmatrix} S_1 & 0 & 0 \\ 0 & S_1 & 0 \\ 0 & 0 & S_2 \end{pmatrix}^{(0)},$$

$$\underline{g}^{(1)}(\bar{1}00,2) = \begin{bmatrix} S_1 & \tfrac{1}{2}\sqrt{3}\,(S_1-S_2) & \sqrt{3}\,S_5 \\ \tfrac{1}{2}\sqrt{3}\,(S_1-S_2) & S_2 & S_5 \\ \sqrt{3}\,S_5 & S_5 & S_3 \end{bmatrix}^{(1)},$$

$$\underline{g}^{(2)}(\bar{1}00,1) = \begin{bmatrix} S_1 & \tfrac{1}{2}\sqrt{3}(S_2-S_1) & 0 \\ \tfrac{1}{2}\sqrt{3}(S_2-S_1) & S_2 & 0 \\ 0 & 0 & S_3 \end{bmatrix}^{(2)} + \begin{bmatrix} 0 & A_4 & 0 \\ -A_4 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}^{(2)},$$

$$\underline{g}^{(3)}(\bar{2}\bar{1}0,2) = \begin{bmatrix} S_1 & 0 & 0 \\ 0 & S_2 & S_5 \\ 0 & S_5 & S_3 \end{bmatrix}^{(3)},$$

$$\underline{g}^{(4)}(001,1) = \begin{bmatrix} S_1 & 0 & 0 \\ 0 & S_1 & 0 \\ 0 & 0 & S_3 \end{bmatrix}^{(4)},$$

$$\underline{g}^{(5)}(\bar{2}00,2) = \begin{bmatrix} S_1 & S_4 & S_6 \\ S_4 & S_2 & S_5 \\ S_6 & S_5 & S_3 \end{bmatrix}^{(5)}, \tag{3.5}$$

$$\underline{g}^{(6)}(210,1) = \begin{bmatrix} S_1 & 0 & 0 \\ 0 & S_2 & 0 \\ 0 & 0 & S_3 \end{bmatrix}^{(6)},$$

$$\underline{g}^{(7)}(\bar{1}01,1) = \begin{bmatrix} S_1 & \tfrac{1}{2}\sqrt{3}(S_2-S_1) & S_6 \\ \tfrac{1}{2}\sqrt{3}(S_2-S_1) & S_2 & \sqrt{3}S_6 \\ S_6 & \sqrt{3}S_6 & S_3 \end{bmatrix}^{(7)} + \begin{bmatrix} 0 & A_4 & -\sqrt{3}A_5 \\ -A_4 & 0 & A_5 \\ \sqrt{3}A_5 & -A_5 & 0 \end{bmatrix}^{(7)},$$

$$\underline{g}^{(8)}(\bar{2}00,1) = \begin{bmatrix} S_1 & \tfrac{1}{2}\sqrt{3}(S_2-S_1) & 0 \\ \tfrac{1}{2}\sqrt{3}(S_2-S_1) & S_2 & 0 \\ 0 & 0 & S_3 \end{bmatrix}^{(8)} + \begin{bmatrix} 0 & A_4 & 0 \\ -A_4 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}^{(8)}.$$

The general forms of the matrices $\underline{\phi}^{(p)}$ up to two neighbors, in the notation of Iyengar *et al.*,[7] are

$$\underline{\phi}^{(0)}(000,1) = 6\begin{bmatrix} \alpha+\lambda & 0 & 0 \\ 0 & \alpha+\lambda & 0 \\ 0 & 0 & \gamma+\nu \end{bmatrix},$$

$$\underline{\phi}^{(1)}(\bar{1}00,2) = -\begin{bmatrix} \lambda-\mu & -\sqrt{3}\mu & -\sqrt{3}\sigma \\ -\sqrt{3}\mu & \lambda+\mu & -\sigma \\ -\sqrt{3}\sigma & -\sigma & \nu \end{bmatrix}, \tag{3.6}$$

and

$$\underline{\phi}^{(2)}(\bar{1}00,1) = -\begin{bmatrix} \alpha-\beta & \sqrt{3}\beta & 0 \\ \sqrt{3}\beta & \alpha+\beta & 0 \\ 0 & 0 & \gamma \end{bmatrix} - \begin{bmatrix} 0 & \delta & 0 \\ -\delta & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

It may be noted here that the shell numbering (1, 2) used here corresponds to the case when the c/a ratio is less then the ideal value. If c/a is greater than the ideal value, the shell labels 1 and 2 should be interchanged.

IV. DEFECT MODEL

We assume that the impurity has a mass deficiency ΔM with respect to the host atom, and that the only force constants which are affected by the presence of the impurity are $\underline{\phi}(0,n)$ ($n=1$ to 12) and $\underline{\phi}(n,n)$ ($n=0$ to 12). The elements of the matrix $\delta\underline{l}$ are given below. We have

$$\delta\underline{l}(0,0) = -\omega^2\Delta M\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} - 6\begin{bmatrix} \Delta\alpha+\Delta\lambda & 0 & 0 \\ 0 & \Delta\alpha+\Delta\lambda & 0 \\ 0 & 0 & \Delta\gamma+\Delta\nu \end{bmatrix}, \tag{4.1}$$

$$\begin{aligned} \delta\underline{l}(0,n) &= \delta\underline{\phi}(0,n) \\ &= \delta\underline{\tilde{l}}(n,0) \quad (n=1,2,\ldots,12), \end{aligned} \tag{4.2}$$

$$\begin{aligned} \delta\underline{l}(n,n) &= \delta\underline{\phi}(n,n) \\ &= -\delta\underline{\phi}(0,n) \quad (n=1,2,\ldots,12). \end{aligned} \tag{4.3}$$

It is sufficient to give the general forms of $\delta\underline{l}(0,6)$ and $\delta\underline{l}(0,11)$ alone, since any other $\delta\underline{l}(0,n)$ $(n\neq 0)$ can be obtained from one of these by an appropriate rotation. We have

$$\delta\underline{l}(0,6) = \begin{bmatrix} \Delta\lambda-\Delta\mu & -\sqrt{3}\,\Delta\mu & -\sqrt{3}\Delta\sigma \\ -\sqrt{3}\Delta\mu & \Delta\lambda+\Delta\mu & -\Delta\sigma \\ -\sqrt{3}\Delta\sigma & -\Delta\sigma & \Delta\nu \end{bmatrix} \tag{4.4}$$

and

$$\delta\underline{l}(0,11)=\begin{bmatrix} \Delta\alpha-\Delta\beta & \sqrt{3}\Delta\beta & 0 \\ \sqrt{3}\Delta\beta & \Delta\alpha+\Delta\beta & 0 \\ 0 & 0 & \Delta\gamma \end{bmatrix}. \tag{4.5}$$

Although the matrix $\underline{\phi}(0,11)$ has an antisymmetric part (i.e., the parameter δ), the perturbation matrix $\delta\underline{\phi}(0,11)$ cannot have an antisymmetric part (i.e., $\Delta\delta=0$). This follows from the sum rules

$$\sum_{n=0}^{12}\delta\underline{\phi}(n,11)=0 \quad\text{and}\quad \sum_{n=0}^{12}\delta\underline{\phi}(11,n)=0. \tag{4.6}$$

The only nonvanishing terms in the above sums correspond to $n=0$ and 11. Hence we obtain

$$-\delta\underline{\phi}(11,11)=\delta\underline{\phi}(0,11)=\delta\underline{\phi}(11,0)=\delta\underline{\tilde{\phi}}(0,11). \tag{4.7}$$

V. APPLICATION OF GROUP THEORY

The procedure for obtaining the SAV's and the projected $\underline{A}^s$ matrices (i.e., $\underline{g}^s$ and $\delta\underline{l}$) has been described already in Sec. II. The characters $\chi^m(\underline{S})$ $(m=0,1,2)$ are listed in Table III. The characters $\chi^s(\underline{S})$ may be found in Wilson *et al.*,[8] whose notation for the IR's we follow. We obtain the following decompositions:

$$\Gamma^0(D_{3h})=A_2''\oplus E',$$
$$\Gamma^1(D_{3h})=2A_1'\oplus A_1''\oplus A_2'\oplus 2A_2''\oplus 3E'\oplus 3E'', \tag{5.1}$$
$$\Gamma^2(D_{3h})=2A_1'\oplus A_1''\oplus 2A_2'\oplus A_2''\oplus 4E'\oplus 2E'',$$

and

$$\Gamma(D_{3h})=4A_1'\oplus 2A_1''\oplus 3A_2'\oplus 4A_2''\oplus 8E'\oplus 5E''.$$

Making use of the character table of D_{3h}, and the representation matrices for the IR's E' and E'' with respect to $\mathcal{K}$ which are given in Table IV, we apply the projection operator technique and obtain the complete orthonormal set of vector $\vec{\psi}^{sa\lambda m}$ which are listed in Tables V–VII. It should be noted that in Tables V–VII, the repetition index a is *not* labeled from 1 to c_s^m, but in the following order, respectively: 1 to c_s^0 for D^0; c_s^0+1 to $c_s^0+c_s^1$ for D^1; and $c_s^0+c_s^1+1$ to $c_s^0+c_s^1+c_s^2$ for D^2.

TABLE III. Character table for the total representation Γ^m and Γ.

$\chi_m(\underline{S})$ \ S	S_0	S_1,S_2	S_3,S_4,S_5	S_6	S_7,S_8	S_9,S_{10},S_{11}
	I	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_d$
$\chi_0(\underline{S})$	3	0	−1	1	−2	1
$\chi_1(\underline{S})$	18	0	0	0	0	2
$\chi_2(\underline{S})$	18	0	0	6	0	0
$\chi(\underline{S})$	39	0	−1	7	−2	3

TABLE IV. Matrix elements E'_{mn} $(m,n=1,2)$ of the group elements $\{\underline{S}_i\}$ in the IR E'. Here $a=\frac{1}{2}\sqrt{3}$, $b=\frac{1}{2}$, and the bars above a, b, and 1 denote negative signs.

	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}
E'_{11}	1	$\bar{b}$	$\bar{b}$	b	$\bar{1}$	b	1	$\bar{b}$	$\bar{b}$	b	$\bar{1}$	b
E'_{12}	0	a	$\bar{a}$	a	0	$\bar{a}$	0	a	$\bar{a}$	a	0	$\bar{a}$
E'_{21}	0	$\bar{a}$	a	a	0	$\bar{a}$	0	$\bar{a}$	a	a	0	$\bar{a}$
E'_{22}	1	$\bar{b}$	$\bar{b}$	$\bar{b}$	1	$\bar{b}$	1	$\bar{b}$	$\bar{b}$	$\bar{b}$	1	$\bar{b}$

Omitting tedious details,[9] we list below the projected Green's-function and perturbation matrices. Since these matrices are symmetric, we do not write down the elements of the lower triangles.

$$\underline{g}(A_1')=\begin{bmatrix} C_1 & C_2 & C_3 & C_4 \\ & D_2 & D_3 & D_4 \\ & & O_3 & O_4 \\ & & & P_4 \end{bmatrix},$$

$$\delta\underline{l}(A_1')=\begin{bmatrix} \Delta\lambda-2\Delta\mu & -2\Delta\sigma & 0 & 0 \\ & \Delta\nu & 0 & 0 \\ & & \Delta\alpha+2\Delta\beta & 0 \\ & & & \Delta\alpha-2\Delta\beta \end{bmatrix},$$

$$\underline{g}(A_1'')=\begin{bmatrix} E_1 & E_2 \\ & Q_2 \end{bmatrix},\quad \delta\underline{l}(A_1'')=\begin{bmatrix} \Delta\lambda+2\Delta\mu & 0 \\ & \Delta\gamma \end{bmatrix},$$

$$\underline{g}(A_2')=\begin{bmatrix} F_1 & F_2 & F_3 \\ & -\frac{1}{2}R_2-\frac{1}{2}\sqrt{3}S_2 & -\frac{1}{2}R_3-\frac{1}{2}\sqrt{3}S_3 \\ & & \frac{1}{2}\sqrt{3}R_3-\frac{1}{2}S_3 \end{bmatrix},$$

$$\delta\underline{l}(A_2')=\begin{bmatrix} \Delta\lambda+2\Delta\mu & 0 & 0 \\ & \Delta\alpha-\Delta\beta & -\sqrt{3}\Delta\beta \\ & & \Delta\alpha+\Delta\beta \end{bmatrix},$$

TABLE V. Symmetry-adapted vectors $\vec{\psi}^{sa\lambda 0}$ normalized to unity.

Atom number n	$s=A_2''$ $\lambda=1$ $a=1$	$s=E'$ $\lambda=1$ $a=1$	$s=E'$ $\lambda=2$ $a=1$
0	0	1	0
	0	0	1
	1	0	0

TABLE VI. Symmetry-adapted vectors $\vec{\psi}^{sa\lambda 1}$ normalized to 6. Here $a=\frac{1}{2}\sqrt{3}$, $b=\frac{1}{2}$, $c=2^{-3/2}$, $d=2^{-3/2}\sqrt{3}$, $e=3\times 2^{-3/2}$, $f=2^{-1/2}\sqrt{3}$, $g=2^{-1/2}$, $h=\sqrt{2}$.

$s=$	A_1'		A_1''	A_2'	A_2''		E'			E'			E''			E''		
$\lambda=$	1	1	1	1	1	1	1	1	1	2	2	2	1	1	1	2	2	2
$n \backslash a=$	1	2	1	1	2	3	2	3	4	2	3	4	1	2	3	1	2	3
1	0	0	1	1	0	0	h	0	0	0	0	0	0	0	0	0	0	$\bar{h}$
	1	0	0	0	1	0	0	0	0	0	h	0	h	0	0	0	0	0
	0	1	0	0	0	1	0	0	0	0	0	$\bar{h}$	0	h	0	0	0	0
2	$\bar{a}$	0	$\bar{b}$	$\bar{b}$	$\bar{a}$	0	c	e	0	$\bar{d}$	d	0	d	0	$\bar{d}$	$\bar{e}$	0	$\bar{c}$
	$\bar{b}$	0	a	a	$\bar{b}$	0	$\bar{d}$	d	0	e	c	0	c	0	e	$\bar{d}$	0	d
	0	1	0	0	0	1	0	0	f	0	0	g	0	$\bar{g}$	0	0	f	0
3	a	0	$\bar{b}$	$\bar{b}$	a	0	c	e	0	d	$\bar{d}$	0	$\bar{d}$	0	d	$\bar{e}$	0	$\bar{c}$
	$\bar{b}$	0	$\bar{a}$	$\bar{a}$	$\bar{b}$	0	d	$\bar{d}$	0	e	c	0	c	0	e	d	0	$\bar{d}$
	0	1	0	0	0	1	0	0	$\bar{f}$	0	0	g	0	$\bar{g}$	0	0	$\bar{f}$	0
4	0	0	$\bar{1}$	1	0	0	h	0	0	0	0	0	0	0	0	0	0	h
	1	0	0	0	$\bar{1}$	0	0	0	0	0	h	0	$\bar{h}$	0	0	0	0	0
	0	$\bar{1}$	0	0	0	1	0	0	0	0	0	h	0	h	0	0	0	0
5	a	0	b	$\bar{b}$	$\bar{a}$	0	c	e	0	d	$\bar{d}$	0	d	0	$\bar{d}$	e	0	c
	$\bar{b}$	0	a	$\bar{a}$	b	0	d	$\bar{d}$	0	e	c	0	$\bar{c}$	0	$\bar{e}$	$\bar{d}$	0	d
	0	$\bar{1}$	0	0	0	1	0	0	f	0	0	$\bar{g}$	0	$\bar{g}$	0	0	$\bar{f}$	0
6	$\bar{a}$	0	b	$\bar{b}$	a	0	c	e	0	$\bar{d}$	d	0	$\bar{d}$	0	d	e	0	c
	$\bar{b}$	0	$\bar{a}$	a	b	0	$\bar{d}$	d	0	e	c	0	$\bar{c}$	0	$\bar{e}$	d	0	$\bar{d}$
	0	$\bar{1}$	0	0	0	1	0	0	$\bar{f}$	0	0	$\bar{g}$	0	$\bar{g}$	0	0	$\bar{f}$	0

TABLE VII. Symmetry-adapted vectors $\vec{\psi}^{sa\lambda 2}$ normalized to 6. The symbols a to h have the same meaning as in Table VII.

$s=$	A_1'		A_1''	A_2'		A_2''	E'				E'				E''		E''	
$\lambda=$	1	1	1	1	1	1	1	1	1	1	2	2	2	2	1	1	2	2
$n \backslash a=$	3	4	2	2	3	4	5	6	7	8	5	6	7	8	4	5	4	5
7	1	0	0	$\bar{b}$	a	0	c	$\bar{d}$	d	e	d	$\bar{e}$	$\bar{c}$	$\bar{d}$	0	0	0	0
	0	1	0	$\bar{a}$	$\bar{b}$	0	d	c	$\bar{e}$	d	e	d	d	$\bar{c}$	0	0	0	0
	0	0	1	0	0	1	0	0	0	0	0	0	0	0	$\bar{g}$	$\bar{f}$	$\bar{f}$	g
8	$\bar{b}$	$\bar{a}$	0	1	0	0	h	0	0	0	0	0	g	$\bar{f}$	0	0	0	0
	a	$\bar{b}$	0	0	1	0	0	h	0	0	0	0	f	g	0	0	0	0
	0	0	1	0	0	1	0	0	0	0	0	0	0	0	h	0	0	$\bar{h}$
9	$\bar{b}$	a	0	$\bar{h}$	$\bar{a}$	0	c	d	f	0	$\bar{d}$	$\bar{e}$	g	0	0	0	0	0
	$\bar{a}$	$\bar{b}$	0	a	$\bar{b}$	0	$\bar{d}$	c	0	f	e	$\bar{d}$	0	g	0	0	0	0
	0	0	1	0	0	1	0	0	0	0	0	0	0	0	$\bar{g}$	f	f	g
10	$\bar{1}$	0	0	$\bar{b}$	a	0	c	$\bar{d}$	d	e	$\bar{d}$	e	c	d	0	0	0	0
	0	1	0	a	b	0	$\bar{d}$	$\bar{c}$	e	$\bar{d}$	e	d	d	$\bar{c}$	0	0	0	0
	0	0	$\bar{1}$	0	0	1	0	0	0	0	0	0	0	0	$\bar{g}$	$\bar{f}$	f	$\bar{g}$
11	b	a	0	1	0	0	h	0	0	0	0	0	$\bar{g}$	f	0	0	0	0
	a	$\bar{b}$	0	0	$\bar{1}$	0	0	$\bar{h}$	0	0	0	0	f	g	0	0	0	0
	0	0	$\bar{1}$	0	0	1	0	0	0	0	0	0	0	0	h	0	0	h
12	b	$\bar{a}$	0	$\bar{b}$	$\bar{a}$	0	c	d	f	0	d	e	$\bar{g}$	0	0	0	0	0
	$\bar{a}$	$\bar{b}$	0	$\bar{a}$	b	0	d	$\bar{c}$	0	$\bar{f}$	e	$\bar{d}$	0	g	0	0	0	0
	0	0	$\bar{1}$	0	0	1	0	0	0	0	0	0	0	0	$\bar{g}$	f	$\bar{f}$	$\bar{g}$

$$\underline{g}(A_2'') = \begin{bmatrix} A_1 & A_2 & A_3 & A_4 \\ & G_2 & G_3 & G_4 \\ & & H_3 & H_4 \\ & & & T_4 \end{bmatrix},$$

$$\delta \underline{l}(A_2'') = \begin{bmatrix} 6(\Delta\gamma + \Delta\nu) - \omega^2 \Delta M & 0 & 0 & 0 \\ & \Delta\lambda - 2\Delta\mu & -2\Delta\sigma & 0 \\ & & \Delta\nu & 0 \\ & & & \Delta\gamma \end{bmatrix},$$

$$\underline{g}(E') = \begin{bmatrix} B_1 & B_2 & B_3 & B_4 & B_5 & B_6 & B_7 & B_8 \\ & I_2 & I_3 & I_4 & I_5 & I_6 & I_7 & I_8 \\ & & J_3 & J_4 & J_5 & J_6 & J_7 & J_8 \\ & & & K_4 & K_5 & K_6 & K_7 & K_8 \\ & & & & U_5 & U_6 & U_7 & U_8 \\ & & & & & V_6 & V_7 & V_8 \\ & & & & & & W_7 & W_8 \\ & & & & & & & X_8 \end{bmatrix},$$

$$\delta \underline{l}(E') = \begin{bmatrix} 6(\Delta\alpha + \Delta\lambda) - \omega^2 \Delta M & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ & \Delta\lambda + 2\Delta\mu & 0 & 0 & 0 & 0 & 0 & 0 \\ & & \Delta\lambda - 2\Delta\mu & 2\Delta\sigma & 0 & 0 & 0 & 0 \\ & & & \Delta\nu & 0 & 0 & 0 & 0 \\ & & & & \Delta\alpha - \Delta\beta & -\sqrt{3}\Delta\beta & 0 & 0 \\ & & & & & \Delta\alpha + \Delta\beta & 0 & 0 \\ & & & & & & \Delta\alpha - \Delta\beta & \sqrt{3}\Delta\beta \\ & & & & & & & \Delta\alpha + \Delta\beta \end{bmatrix},$$

$$\underline{g}(E'') = 2^{-1/2} \begin{bmatrix} L_1 & L_2 & L_3 & L_4 & L_5 \\ & M_2 & M_3 & M_4 & M_5 \\ & & N_3 & N_4 & N_5 \\ & & & -\tfrac{1}{2}Y_4 - \tfrac{1}{2}\sqrt{3}Z_4 & -\tfrac{1}{2}Y_5 - \tfrac{1}{2}\sqrt{3}Z_5 \\ & & & & -\tfrac{1}{2}\sqrt{3}Y_5 + \tfrac{1}{2}Z_5 \end{bmatrix},$$

$$\delta \underline{l}(E'') = \begin{bmatrix} \Delta\lambda - 2\Delta\mu & -2\Delta\sigma & 0 & 0 & 0 \\ & \Delta\nu & 0 & 0 & 0 \\ & & \Delta\lambda + 2\Delta\mu & 0 & 0 \\ & & & \Delta\gamma & 0 \\ & & & & \Delta\gamma \end{bmatrix}.$$

The expressions for the symbols $A_1, \ldots, Z_5$ in terms of the Green's-function parameters are given in Appendix B.

Having obtained the projected forms of the matrices $\underline{g}$ and $\delta\underline{l}$ it is trivial to calculate the matrices $\overline{\underline{g}}^{*s}$ and $\overline{\underline{t}}^{s}$, and so we do not write down the explicit expressions for these here.

VI. DISCUSSION

For an isotropic substitutional defect in a diatomic hcp crystal ($\delta\underline{\phi}=0$ in this case), the only modes of vibrations in the defect space which are affected (by the defect) are the A_2'' and E' modes.

The parameter γ in the $\underline{\phi}$ matrix is the bond-bending force constant[9] and is usually much smaller than the parameters α and β which are mainly dependent on the bond-stretching force constants. If it is assumed that $\Delta\gamma \ll \Delta\alpha$ or $\Delta\beta$ and can be neglected, then it can be seen that the IR's A_1'' and E'' do not contain any of the perturbation parameters corresponding to shell number 2. These parameters refer to the first shell in those crystals for which the c/a ratio is larger than the ideal value; hence, for these crystals, there is no contribution to the matrix $\delta\underline{l}$ coming from the A_1'' and E'' modes. (This is true only in the nearest-neighbor approximation.)

The results derived in this paper have a variety of applications in the study of substitutional point defects in hcp crystals. Some of these applications were mentioned in the Introduction. Perhaps the simplest of all such applications is the study of the static relaxation of atoms around a vacancy. We have investigated this problem for the case of magnesium, and our results are reported in the companion paper.

ACKNOWLEDGMENTS

The authors wish to thank G. Venkataraman and V. Balakrishnan for their comments on the manuscript.

APPENDIX A

Proof of Eq.(2.9): Using Eq. (8.7.62) of Ref. 2, the action of the matrix $\underline{\mathcal{S}}(\underline{S})$ on the vector $\vec{\eta}^{\,sa\lambda}$ is given by

$$
\begin{aligned}
&\mathcal{S}_{\mu\alpha}(LK, l\kappa; \underline{S})\eta_\alpha^{sa\lambda}(l\kappa)\\
&\quad=\mathcal{S}_{\mu\alpha}(LK, l\kappa; \underline{S})A_{\alpha\beta}(l\kappa, l'\kappa')\psi_\beta^{sa\lambda}(l'\kappa')\\
&\quad=\mathcal{S}_{\mu\alpha}(LK, l\kappa; \underline{S})A_{\alpha\lambda}(l\kappa, l''\kappa'')\tilde{\mathcal{S}}_{\lambda\nu}(l''\kappa'', L'K'; \underline{S})\\
&\quad\;\;\times\mathcal{S}_{\nu\beta}(L'K', l'\kappa'; \underline{S})\psi_\beta^{sa\lambda}(l'\kappa')\\
&\quad=\sum_{\lambda'=1}^{fs} A_{\mu\nu}(LK, L'K')\psi_\nu^{sa\lambda'}(L'K')\Gamma^s_{\lambda'\lambda}(\underline{S})\\
&\quad=\sum_{\lambda'=1}^{fs} \eta_\mu^{sa\lambda'}(LK)\Gamma^s_{\lambda'\lambda}(\underline{S}).
\end{aligned}
$$

In the second equality, use is made of the fact that the $\mathcal{S}$'s are orthogonal matrices. On employing Eq. (2.4) in the left-hand side, multiplying both sides by the inverse matrix $\bar{\Gamma}^s_{\lambda\lambda''}$, and summing over λ, leads to Eq. (2.9) as required.

APPENDIX B

The expressions for the symbols $A_1, \ldots, Z_5$ used in writing the reduced Green's-function matrices are collected here for ready reference:

$$
\begin{aligned}
A_1&=S_3(0),\\
A_2&=2\times 6^{1/2}S_5(1),\\
A_3&=6^{1/2}S_3(1),\\
A_4&=6^{1/2}S_3(2),\\
B_1&=S_1(0),\\
B_2&=\tfrac{1}{2}\sqrt{3}[-S_1(1)+3S_2(1)],\\
B_3&=\tfrac{1}{2}\sqrt{3}[3S_1(1)-S_2(1)],\\
B_4&=-2\sqrt{3}S_5(1),\\
B_5&=\tfrac{1}{2}\sqrt{3}S_1(2),\\
B_6&=\tfrac{3}{2}[S_1(2)-S_2(2)]-\sqrt{3}A_4(2),\\
B_7&=\tfrac{3}{4}[S_1(2)+S_2(2)]+\tfrac{1}{2}\sqrt{3}A_4(2),\\
B_8&=\tfrac{1}{4}\sqrt{3}[-3S_1(2)+5S_2(2)]-\tfrac{3}{2}A_4(2),\\
C_1&=S_1(0)+S_1(4)+\tfrac{3}{2}[S_1(2)+S_1(7)]\\
&\quad-\tfrac{5}{2}[S_2(2)+S_2(7)]-\sqrt{3}[A_4(2)+A_4(7)],\\
C_2&=-2\sqrt{3}S_6(7)+2A_5(7),\\
C_3&=\tfrac{1}{2}\sqrt{3}[-S_1(1)-S_2(1)-S_1(3)+S_2(3)\\
&\qquad+S_1(5)+S_2(5)]+2S_4(5),\\
C_4&=\tfrac{1}{2}[S_2(3)+S_2(5)]\\
&\quad+\tfrac{3}{2}[S_1(1)+S_1(3)-S_1(5)]-\tfrac{5}{2}S_2(1),\\
D_2&=S_3(0)-S_3(4)+2[S_3(2)-S_3(7)],\\
D_3&=\sqrt{3}[2S_5(1)+S_5(3)+S_5(5)]+S_6(5),\\
D_4&=-2S_5(1)+S_5(3)+S_5(5)-\sqrt{3}S_6(5),\\
E_1&=S_1(0)-S_1(4)+\tfrac{3}{2}[S_2(2)-S_2(7)]\\
&\quad-\tfrac{5}{2}[S_1(2)-S_1(7)]-\sqrt{3}[A_4(2)-A_4(7)],\\
E_2&=-\sqrt{3}[2S_5(1)-S_5(3)+S_5(5)]+S_6(5),\\
F_1&=S_1(0)+S_1(4)+\tfrac{3}{2}[S_2(2)+S_2(7)]\\
&\quad-\tfrac{5}{2}[S_1(2)+S_1(7)]-\sqrt{3}[A_4(2)+A_4(7)],\\
F_2&=\tfrac{1}{2}[S_1(1)+S_1(3)+S_1(5)]\\
&\quad-\tfrac{3}{2}[S_2(1)+S_2(3)-S_2(5)]-\sqrt{3}S_4(5),\\
F_3&=\tfrac{1}{2}\sqrt{3}[-3S_1(1)+S_2(1)+S_1(3)\\
&\qquad+S_2(3)+S_1(5)-S_2(5)]-S_4(5),
\end{aligned}
$$

$$\begin{aligned} G_2 = {} & S_1(0) - S_1(4) + \tfrac{3}{2}[S_1(2) - S_1(7)] \\ & - \tfrac{5}{2}[S_2(2) - S_2(7)] - \sqrt{3}[A_4(2) - A_4(7)], \end{aligned}$$

$$G_3 = 2\sqrt{3}S_6(7) - 2A_5(7),$$

$$G_4 = - 2S_5(1) + S_5(3) + S_5(5) + \sqrt{3}S_6(5),$$

$$H_3 = S_3(0) + S_3(4) + 2[S_3(2) + S_3(7)],$$

$$H_4 = 2[S_3(1) + S_3(3) + S_3(5)],$$

$$\begin{aligned} I_2 = {} & \tfrac{1}{4}\{5[S_1(2) + S_1(7)] - 3[S_2(2) + S_2(7)]\} \\ & + [S_1(0) + S_1(4)] + \tfrac{1}{2}\sqrt{3}[A_4(2) + A_4(7)], \end{aligned}$$

$$\begin{aligned} I_3 = {} & \tfrac{3}{4}[S_1(2) + S_2(2) + S_1(7) + S_2(7)] \\ & - \tfrac{1}{2}\sqrt{3}[A_4(2) + A_4(7)], \end{aligned}$$

$$I_4 = - \sqrt{3}S_6(7) - 3A_5(7),$$

$$\begin{aligned} I_5 = {} & - \tfrac{1}{4}[S_1(1) + S_1(3)] + \tfrac{3}{4}[S_2(1) + S_2(3)] \\ & + \tfrac{1}{2}[S_1(5) + 3S_2(5)] - \sqrt{3}S_5(5), \end{aligned}$$

$$\begin{aligned} I_6 = {} & \tfrac{1}{4}\sqrt{3}[S_1(1) - S_2(1) - S_1(3) - S_2(3)] \\ & + \tfrac{1}{2}\sqrt{3}[S_1(5) - S_2(5)] - S_4(5), \end{aligned}$$

$$I_7 = \sqrt{3}[S_1(1) + \tfrac{1}{2}S_1(3)],$$

$$I_8 = \tfrac{3}{4}[S_1(1) - S_2(1) + S_2(3)],$$

$$\begin{aligned} J_3 = {} & [S_1(0) + S_1(4)] \\ & + \tfrac{1}{4}\{5[S_2(2) + S_2(7)] - 3[S_1(2) + S_1(7)]\} \\ & + \tfrac{1}{2}\sqrt{3}[A_4(2) + A_4(7)], \end{aligned}$$

$$J_4 = - \sqrt{3}S_6(7) + A_5(7),$$

$$J_5 = \tfrac{3}{4}[- S_1(1) + S_1(3) + 3S_2(1) + S_2(3)],$$

$$J_6 = \tfrac{1}{4}\sqrt{3}\{[S_2(1) - S_2(3)] + 3[- S_1(1) + S_1(3)]\},$$

$$J_7 = \tfrac{1}{2}\sqrt{3}[S_1(1) + S_1(3) + 2S_1(5) - S_2(1)] + S_4(5),$$

$$J_8 = - \tfrac{1}{2}S_2(3) + S_2(1) + S_2(5) + \sqrt{3}S_4(5),$$

$$K_4 = - S_3(0) - S_3(7) + S_3(2) + S_3(4),$$

$$K_5 = \tfrac{3}{2}S_5(3),$$

$$K_6 = 2\sqrt{3}S_5(1) - \tfrac{1}{2}\sqrt{3}S_5(3),$$

$$K_7 = - \sqrt{3}S_5(1) + 2S_6(5),$$

$$K_8 = - S_5(1) - S_5(3) + 2S_5(5),$$

$$\begin{aligned} L_1 = {} & - \sqrt{2}S_2(4) + 2^{-3/2}\{5[S_2(2) - S_2(7)] \\ & - 3[S_1(2) - S_1(7)] \\ & + 2\sqrt{3}[A_4(2) - A_4(7)]\}, \end{aligned}$$

$$L_2 = \sqrt{2}[A_5(7) - \sqrt{3}S_6(7)],$$

$$\begin{aligned} L_3 = {} & 2^{-3/2} \times 3[S_1(2) + S_2(2) - S_1(7) - S_2(7)] \\ & - 2^{-1/2} \times \sqrt{3}[A_4(2) - A_4(7)], \end{aligned}$$

$$L_4 = \sqrt{2}\{[S_5(1) + S_5(5)] - \tfrac{1}{2}S_5(3) + \sqrt{3}S_6(5)\}.$$

$$L_5 = - \sqrt{2}[S_3(1) + S_3(3) - 2S_3(5)],$$

$$M_2 = \sqrt{2}[S_3(0) - S_3(2) + S_3(4) - S_3(7)],$$

$$M_3 = - \sqrt{2}[3A_5(7) + \sqrt{3}S_6(7)],$$

$$M_4 = L_5,$$

$$M_5 = \sqrt{6}[S_3(1) - S_3(3)],$$

$$\begin{aligned} N_3 = {} & 2^{-3/2}\{- 3[S_2(2) - S_2(7)] + 5[S_1(2) - S_1(7)] \\ & + 2\sqrt{3}[S_1(0) - S_1(4) + A_4(2) - A_4(7)]\}. \end{aligned}$$

$$N_4 = 3 \times 2^{-1/2}[2S_5(1) + S_5(3)],$$

$$N_5 = - 2^{-1/2}\sqrt{3}S_5(3) + 6^{1/2}[S_5(1) - S_5(5)] + \sqrt{2}S_6(5),$$

$$\begin{aligned} O_3 = {} & S_1(0) + \tfrac{1}{2}[S_1(6) + S_1(8)] \\ & - \tfrac{3}{2}[S_2(2) + S_2(6) + S_2(8)] + \tfrac{5}{2}S_1(2), \end{aligned}$$

$$O_4 = A_4(2) + A_4(8),$$

$$\begin{aligned} P_4 = {} & S_1(0) + \tfrac{1}{2}[S_2(6) - S_2(8)] \\ & + \tfrac{3}{2}[S_1(2) - S_1(6) + S_1(8)] - \tfrac{5}{2}S_2(2), \end{aligned}$$

$$Q_2 = S_3(0) - S_3(8) - 2[S_3(2) - S_3(6)],$$

$$\begin{aligned} R_2 = {} & - \tfrac{1}{2}S_1(0) - \tfrac{1}{4}\{S_1(6) - S_1(8) \\ & + 3[S_2(2) - S_2(6) + S_2(8)] - 5S_1(2)\} \\ & + \tfrac{1}{2}\sqrt{3}[A_4(2) + A_4(8)], \end{aligned}$$

$$\begin{aligned} R_3 = {} & \tfrac{1}{2}\sqrt{3}S_1(0) + \tfrac{1}{4}\sqrt{3}[S_1(6) - S_1(8) + 3[S_2(2) \\ & - S_2(6) + S_2(8) - 5S_1(2)] \\ & + \tfrac{1}{2}[A_4(2) + A_4(8)], \end{aligned}$$

$$\begin{aligned} S_2 = {} & - \tfrac{1}{2}\sqrt{3}S_1(0) \\ & - \tfrac{1}{4}\sqrt{3}\{S_2(6) + S_2(8) - 3[S_1(2) + S_1(6) + S_1(8)] \\ & + 5S_2(2)\} + \tfrac{1}{2}[A_4(2) + A_4(8)], \end{aligned}$$

$$\begin{aligned} S_3 = {} & - \tfrac{1}{2}S_1(0) - \tfrac{1}{4}\{S_2(6) + S_2(8) \\ & - 3[S_1(2) + S_1(6) + S_1(8)] \\ & + 5S_2(2)\} - \tfrac{1}{2}\sqrt{3}[A_4(2) + A_4(8)], \end{aligned}$$

$$T_4 = S_3(0) + S_3(8) + 2[S_3(2) + S_3(6)],$$

$$\begin{aligned} U_5 = {} & \sqrt{2}[8S_1(0) - S_1(2) + 9S_2(2) \\ & + 4S_1(6) + 5S_1(8) - 3S_2(8)] \\ & + 2 \times 6^{1/2}[A_4(8) + A_4(2)], \end{aligned}$$

$$\begin{aligned} U_6 = {} & 6^{1/2} \times [- S_1(2) - S_2(2) + 2S_1(6) \\ & - 2S_2(6) + S_1(8) - S_2(8)], \\ & + 2\sqrt{2}[5A_4(2) - A_4(8)], \end{aligned}$$

$$\begin{aligned} U_7 = {} & 6^{1/2}[- S_1(2) + 3S_2(2) + 3S_1(6) \\ & + 3S_2(6) + 4S_1(8)] - 6\sqrt{2}A_4(2). \end{aligned}$$

$$\begin{aligned} U_8 = {} & \sqrt{3}[3S_1(2) - S_2(2) + S_1(6) \\ & + S_2(6) - 2S_1(8) + 2S_2(8)] \\ & + 2 \times 6^{1/2}[A_4(2) - 2A_4(8)], \end{aligned}$$

$$V_6 = \sqrt{2}[8S_1(0) - 9S_1(2) - S_2(2) + 4S_2(6) + 3S_1(8) - 5S_2(8)] - 2 \times 6^{1/2}[A_4(2) + A_4(8)],$$

$$V_7 = 3\sqrt{2}[-S_1(2) + 3S_2(2) - S_1(6) - S_2(6) + 2S_1(8) - 2S_2(8)] + 2 \times 6^{1/2}[A_4(2) - 2A_4(8)],$$

$$V_8 = 6^{1/2}[-3S_1(2) + S_2(2) + 3S_1(6) + 3S_2(6) - 4S_2(8)] + 6\sqrt{2}A_4(2),$$

$$W_7 = \sqrt{2}[8S_1(0) + 8S_1(2) + 4S_1(6) - 5S_1(8) + 3S_2(8)] + 2 \times 6^{1/2}[A_4(8) - 2A_4(2)],$$

$$W_8 = 6^{1/2}[2S_1(2) + 2S_2(2) - 2S_1(6) + 2S_2(6) + S_1(8) + S_2(8)] + 2\sqrt{2}[A_4(8) + 4A_4(2)],$$

$$X_8 = \sqrt{2}[8S_1(0) - 8S_2(2) + 4S_2(6) - 3S_1(8) + 5S_2(8)] + 2 \times 6^{1/2}[2A_4(2) - A_4(8)],$$

$$Y_4 = 2^{-1/2}[-S_3(0) + S_3(2) + S_3(6) - S_3(8)].$$

$$Y_5 = \sqrt{3}Y_4.$$

$$Z_4 = 2^{-1/2}\sqrt{3}[-S_3(0) - S_3(2) + S_3(6) + S_3(8)],$$

$$Z_5 = -3^{-1/2}Z_4.$$

---

[1] D. W. Taylor, in *Dynamical Properties of Solids*, edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1975), Vol. 2, p. 285.

[2] A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic, New York, 1971).

[3] V. K. Tewary, Adv. Phys. 22, 757 (1973).

[4] K. Dettmann and W. Ludwig, Phys. Kondens. Mater. 2, 24 (1964).

[5] B. K. Agrawal, Phys. Rev. 186, 712 (1969).

[6] A. Czachor, *Inelastic Scattering of Neutrons* (IAEA, Vienna, 1965), p. 181.

[7] P. K. Iyengar, G. Venkataraman, P. R. Vijayaraghavan, and A. P. Roy, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, New York, 1964), p. 223.

[8] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibration* (McGraw-Hill, New York, 1955), p. 98.

[9] Details of calculations, including tables of $\vec{\eta}$ vectors are available, on request, from the authors.