T Matrix for a Substitutional Impurity in Diatomic fcc and bcc Lattices

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The phonon scattering T matrix is analyzed according to the irreducible representations of the point group pertaining to the perturbation caused by a substitutional impurity in the diatomic fcc and bcc lattices. The effects due to change in mass at the impurity site and the changes in the nearest-neighbor central- and noncentral-force constants for the impurity–host-crystal interaction are taken into account. Relations between lattice Green's functions are derived for the nearest-neighbor interactions in the pure lattice. Simple expressions for the irreducible representations of the T matrix are obtained, by assuming only central forces.

I. INTRODUCTION

MUCH attention has been drawn in recent years towards the study of static and dynamic properties of crystals containing substitutional-impurity atoms. The behavior of the phonon scattering T matrix for the defect is investigated in a number of such studies. The evaluation of the T matrix is of central importance for calculating the phonon relaxation times in transport theory.[1] The elastic properties[2] and the infrared lattice-vibration absorption[3] due to gap and resonance modes in imperfect solids may also be investigated using this formulation. The resonance denominator of the T matrix determines the condition of occurrence and the frequencies of these resonance and gap modes. The explanation of several other phenomena, e.g., the first-order Raman scattering,[4] the Mössbauer effect, and the second-order Doppler shift,[5] involves the evaluation of the perturbed Green's functions, which may be determined easily if we know the elements of the T matrix.

Several attempts[1,6] have been made to analyze the T matrix in some realistic models, where effects due to changes in mass and nearest-neighbor force constants were taken into account. The change in the noncentral force interactions were also included in later publications. Benedek and Nardelli[7] have studied the case of a single impurity in a lattice having rock-salt structure. One substitutional impurity in a monatomic bcc lattice has been discussed by Yussouff and Mahanty.[8] However, their results are in error because of their neglect of some nonvanishing elements of the perturbation matrix (see Sec. IV). Mannheim[9] has studied the optic-active F_{1u} modes in the case of monatomic bcc and fcc lattices. Recently,[3,10] numerical calculations of some of the T matrix elements have been made. It is therefore interesting to analzye the T matrix in some other realistic cases.

In the present paper, the T matrix accounting for the phonon scattering is worked out according to the irreducible representations of the point group which pertains to a single-substitutional-impurity perturbation in the case of diatomic fcc and bcc lattices. We take into account the effects due to change in mass at the impurity site, and the changes in the nearest-neighbor central and noncentral force constants for the impurity–host-crystal interaction.

A brief account of the dynamics of the perturbed crystal with the reduction of the T matrix into various irreducible representations is presented in Sec. II. We block-diagonalize the 39-dimensional T matrix of fcc lattice and the 27-dimensional T matrix of bcc lattice, using the lattice-site symmetries in Secs. III and IV, respectively. For simplifying the calculations, relations between the lattice Green's functions are derived for nearest-neighbor forces in a diatomic lattice in the Appendix. These relations are utilized to obtain simple expressions for the different irreducible representations, especially the optic-active F_{1u} modes, for the case of central forces only in Secs. III and IV.

II. THEORY

The time-independent equation of motion for a perturbed crystal may be written in matrix form as[3]

$$[L_0+P(\omega^2)]\Psi=\omega^2\Psi, \tag{1}$$

where $L_0=M_0^{-1/2}\Phi_0M_0^{-1/2}$ is the dynamical matrix of the perfect host lattice and $P(\omega^2)$ is the perturbation matrix, explicitly given by

$$P(\omega^2)=-\omega^2M_0^{-1/2}\Delta MM_0^{-1/2}+M_0^{-1/2}\Delta\Phi M_0^{-1/2}. \tag{2}$$

Here M_0 and Φ_0 are the mass and force constant matrices of the perfect lattice, and ΔM and $\Delta\Phi$ are the corresponding perturbation matrices due to the presence of defect atoms in the lattice. Ψ is a column vector related to the usual displacement-column vector U by

$$U=M_0^{-1/2}\Psi. \tag{3}$$

[1] M. V. Klein, Phys. Rev. **141**, 716 (1966).
[2] G. Benedek and G. F. Nardelli, Phys. Rev. **167**, 837 (1968).
[3] G. Benedek and A. A. Maradudin, J. Phys. Chem. Solids **29**, 423 (1968).
[4] G. Benedek and G. F. Nardelli, Phys. Rev. **154**, 872 (1967).
[5] P. D. Mannheim and A. Simopoulos, Phys. Rev. **165**, 845 (1968).
[6] T. P. Martin, Phys. Rev. **160**, 686 (1967).
[7] G. Benedek and G. F. Nardelli, Phys. Rev. **155**, 1004 (1967).
[8] M. Yussouff and J. Mahanty, Proc. Phys. Soc. (London) **90**, 519 (1967).
[9] P. D. Mannheim, Phys. Rev. **165**, 1011 (1968).
[10] R. F. Caldwell and M. V. Klein, Phys. Rev. **158**, 851 (1967).

In diatomic cubic lattices, L_0 is a $6N\times6N$ matrix, where N is the number of unit cells in the crystal. The $6N$ solutions of Eq. (1), i.e., the eigenvectors and the eigenvalues, may be written as $\{\Psi_\lambda\}$ and $\{\omega_\lambda{}^2\}$, where λ is an index running from 1 to $6N$. These eigenvectors $\{\Psi_\lambda\}$ satisfy the orthonormality condition,

$$(\Psi_\lambda, M_0{}^{-1/2}(M_0+\Delta M)\Psi_{\lambda'})=\delta_{\lambda\lambda'}. \tag{4}$$

The perturbation matrix $P(\omega^2)$ is a $3n\times3n$ matrix, where n is the number of the atoms (including the impurity atom) directly disturbed by the presence of the defect atom. The $3n\times3n$ subspace, which is the space of $P(\omega^2)$, will be the target of our study. The T matrix satisfies the equation

$$T(z)=P(\omega^2)-P(\omega^2)G(z)T(z), \tag{5}$$

where $G(z)$ is the Green's-function matrix operator for the unperturbed lattice defined by

$$G(z)=(L_0-zI)^{-1}. \tag{6}$$

Here, z is the complex frequency $z=\omega^2+2i\omega\eta$ in the limit as $\eta\longrightarrow0^+$. The formal solution of Eq. (5) is

$$T(z)=P(\omega^2)[I+G(z)P(\omega^2)]^{-1}. \tag{7}$$

The introduction of the symmetry coordinates according to the various irreducible representations of the point group of the impurity site block-diagonalizes simultaneously the two matrices $P(\omega^2)$ and $G(z)$ [$=g(z)$ in the subspace $3n\times3n$]. Consequently, the inverse matrix appearing in the expression of T matrix, can be expressed as

$$[I+g(z)P(\omega^2)]^{-1}=\sum_\Gamma\sum_{m,m'}|\Gamma,m)(\Gamma,m|\times[I+g(z)P(\omega^2)]^{-1}|\Gamma,m')(\Gamma,m'|, \tag{8}$$

where $|\Gamma,m)$ denotes the normalized symmetry coordinate, which transforms according to the first row of the irreducible representation Γ. The index m has values from 1 to $n(\Gamma)$, where $n(\Gamma)$ is the number of times the irreducible representation Γ occurs in $P(\omega^2)$. Each of the projected inverse matrices appearing in Eq. (8) may be written as

$$(\Gamma|[I+g(z)P(\omega^2)]^{-1}|\Gamma)=N_\Gamma(z)/D_\Gamma(z), \tag{9}$$

where $D_\Gamma(z)$ is the resonance denominator

$$\det|I+g(z)P(\omega^2)|, \tag{10}$$

coming from the representation Γ, and $N_\Gamma(z)$ is the corresponding adjoint matrix $\mathrm{adj}|I+g(z)P(\omega^2)|$. We may therefore write for the irreducible representation $T_\Gamma(z)$ of the T matrix

$$T_\Gamma(z)=P_\Gamma(\omega^2)N_\Gamma(z)/D_\Gamma(z), \tag{11}$$

where $P_\Gamma(\omega^2)$ is the abbreviation for $(\Gamma|P(\omega^2)|\Gamma)$, the matrix element of $P(\omega^2)$ for the representation Γ. Similarly, we hereafter abbreviate $(\Gamma|g(z)|\Gamma)$ by $g_\Gamma(z)$. The T matrix may thus be written as

$$T(z)=\sum_\Gamma|\Gamma)T_\Gamma(z)(\Gamma|. \tag{12}$$

III. DIATOMIC FCC LATTICE

The elements of the 39×39 perturbation matrix $P(\omega^2)$ for the fcc lattice are as follows:

$$\begin{aligned}
&p_{ii}(\mathbf{0},\mathbf{0})=-\epsilon\omega^2+4(\lambda+2\lambda'),\\
&p_{ij}(\mathbf{0},\mathbf{0})=0,\\
&p_{ii}(\mathbf{0},\mathbf{R}_n)=-\tfrac{1}{2}\chi^{1/2}(\lambda+\lambda'), && \text{if} \quad n_i\neq0\\
&\qquad\qquad=-\chi^{1/2}\lambda', && \text{for} \quad n_i=0;\\
&p_{ij}(\mathbf{0},\mathbf{R}_n)=-\tfrac{1}{2}\chi^{1/2}(\lambda-\lambda')n_in_j,\\
&p_{ii}(\mathbf{R}_n,\mathbf{R}_n)=\tfrac{1}{2}\chi(\lambda+\lambda'), && \text{if} \quad n_i\neq0\\
&\qquad\qquad=\chi\lambda', && \text{for} \quad n_i=0;
\end{aligned}$$

and

$$p_{ij}(\mathbf{R}_n,\mathbf{R}_n)=\tfrac{1}{2}\chi(\lambda-\lambda')n_in_j, \qquad i,j=1,2,3 \tag{13}$$

where ϵ is the mass-change parameter$=\Delta M/M_\pm$ and $\chi=M_\pm/M_\mp$ is the ratio of the masses of the ions of two host sublattices. $\lambda=\Delta\gamma/M_\pm$ and $\lambda'=\Delta\gamma'/M_\pm$ are changes in the central and noncentral nearest-neighbor force constants, repsectively, in units of squared frequency. $\mathbf{R}_n$, the lattice vector of the immediate neighbors of the impurity site at the origin, is given by

$$|\mathbf{R}_n|=(a/\sqrt{2})(n_1,n_2,n_3), \tag{14}$$

where one of the numbers of the index triple $(n_1n_2n_3)$ has value zero, and each of the remaining two may have values ±1. The constant a is the lattice spacing. In Eq. (13), the upper signs apply when the impurity occupies a positive-ion site, and the lower signs when it occupies a negative-ion site.

The irreducible representations for an impurity site having symmetry O_h in the fcc lattice are

$$\Gamma=4F_{1u}+2F_{2u}+2F_{1g}+2F_{2g}+2E_g+E_u+A_{2u}+A_{1g}+A_{2g}. \tag{15}$$

The necessary symmetry coordinates, i.e., the symmetrized linear combinations of the 39 ionic displacements in the space of the impurity ion, have been worked out by Dettmann and Ludwig.[11] However, their results for the irreducible representations $2E_g$ and E_u are in error. They have been corrected and presented in Table I. After using the corrected normalized-symmetry coordinates for block-diagonalizing the perturbation matrix $P(\omega^2)$, we obtain the following matrix

[11] K. Dettmann and W. Ludwig, Phys. Condensed Matter **2**, 241 (1964).

elements for the various irreducible representations:

$$P_{F_{1u}}(\omega^2)=\begin{bmatrix} -\epsilon\omega^2+4(\lambda+2\lambda') & -2\chi^{1/2}\lambda' & -(2\chi)^{1/2}(\lambda+\lambda') & (2\chi)^{1/2}(\lambda-\lambda') \\ -2\chi^{1/2}\lambda' & \chi\lambda' & 0 & 0 \\ -(2\chi)^{1/2}(\lambda+\lambda') & 0 & \tfrac{1}{2}\chi(\lambda+\lambda') & -\tfrac{1}{2}\chi(\lambda-\lambda') \\ (2\chi)^{1/2}(\lambda-\lambda') & 0 & -\tfrac{1}{2}\chi(\lambda-\lambda') & \tfrac{1}{2}\chi(\lambda+\lambda') \end{bmatrix},$$

$$P_{F_{2u}}(\omega^2)=\tfrac{1}{2}\chi\begin{pmatrix} \lambda+\lambda' & -(\lambda-\lambda') \\ -(\lambda-\lambda') & \lambda+\lambda' \end{pmatrix},$$

$$P_{F_{1g}}(\omega^2)=\chi\begin{pmatrix} \lambda' & 0 \\ 0 & \lambda' \end{pmatrix}, \quad P_{F_{2g}}(\omega^2)=\chi\begin{pmatrix} \lambda' & 0 \\ 0 & \lambda \end{pmatrix},$$

$$P_{E_{2g}}(\omega^2)=\tfrac{1}{4}\chi\begin{pmatrix} 3\lambda+\lambda' & -\sqrt{3}(\lambda-\lambda') \\ -\sqrt{3}(\lambda-\lambda') & \lambda+3\lambda' \end{pmatrix},$$

$$P_{E_u}(\omega^2)=\chi\lambda', \quad P_{A_{2u}}(\omega^2)=\chi\lambda', \quad P_{A_{2g}}(\omega^2)=\chi\lambda', \quad P_{A_{1g}}(\omega^2)=\chi\lambda. \tag{16}$$

From Eq. (16), one may note that for central forces only, i.e., for $\lambda'=0$, the matrix elements of $P(\omega^2)$ for the irreducible representations F_{1g}, E_u, A_{2u}, and A_{2g} vanish, and therefore these symmetry motions of the ions of the impurity space are absent.

The projected matrix elements of the Green's function $g(z)$ are as follows:

$$g_{F_{1u}}(z)=\begin{bmatrix} g_0 & 2g_1 & 8^{1/2}g_2 & 8^{1/2}g_3 \\ 2g_1 & 2g_5+g_{11} & 8^{1/2}(g_6+g_7) & 2\sqrt{2}g_8 \\ 8^{1/2}g_2 & 8^{1/2}(g_6+g_7) & g_4+g_5+2g_9+2g_{13}+2g_{14} & 2g_8+g_{15} \\ 8^{1/2}g_3 & 2\sqrt{2}g_8 & 2g_8+g_{15} & g_4-g_5+2g_{10}-2g_{16}+2g_{17} \end{bmatrix},$$

$$g_{F_{2u}}(z)=\begin{pmatrix} g_4+g_5+2g_9-2g_{13}-2g_{14} & -2g_8+g_{15} \\ -2g_8+g_{15} & g_4-g_5+2g_{10}+2g_{16}-2g_{17} \end{pmatrix},$$

$$g_{F_{1g}}(z)=\begin{pmatrix} g_{12}-2g_{16}-2g_{17} & -2g_6+2g_7+2g_8 \\ -2g_6+2g_7+2g_8 & -g_4-g_5+2g_9-g_{15} \end{pmatrix},$$

$$g_{F_{2g}}(z)=\begin{pmatrix} g_{12}+2g_{16}+2g_{17} & 2g_6-2g_7+2g_8 \\ 2g_6-2g_7+2g_8 & -g_4-g_5+2g_9+g_{15} \end{pmatrix},$$

$$g_{E_g}(z)=\begin{pmatrix} -g_4+g_5-2g_8+2g_{10}-2g_{13}+2g_{14}+\tfrac{1}{2}g_{15}+g_{16}+g_{17} & \tfrac{1}{2}\sqrt{3}(-g_{15}+2g_{16}+2g_{17}) \\ \tfrac{1}{2}\sqrt{3}(-g_{15}+2g_{16}+2g_{17}) & -g_4+g_5-2g_8+2g_{10}+2g_{13}-2g_{14}-\tfrac{1}{2}g_{15}-g_{16}-g_{17} \end{pmatrix},$$

$$g_{E_u}(z)=-2g_5+g_{11}+2g_{16}-2g_{17}, \quad g_{A_{2u}}(z)=-2g_5+g_{11}-4g_{16}+4g_{17},$$

$$g_{A_{2g}}(z)=-g_4+g_5+4g_8+2g_{10}-2g_{13}+2g_{14}-g_{15}-2g_{16}-2g_{17},$$

$$g_{A_{1g}}(z)=-g_4+g_5+4g_8+2g_{10}+2g_{13}-2g_{14}+g_{15}+2g_{16}+2g_{17}, \tag{17}$$

where the different combinations of the elements of the Green's-function matrix $g(z)$, are given by

$$g_\mu^{\pm}(z)=\frac{\Omega}{(2\pi)^3}\sum_{s=1}^{6}\int_{\mathrm{BZ}}\frac{j_\mu^{\pm}(\mathbf{k}|s)}{\omega_{\mathbf{k},s}^2-z}d\mathbf{k}. \tag{18}$$

TABLE I. Unnormalized symmetry coordinates according to the irreducible representations $2E_g$ and E_u for an impurity site having O_h symmetry in the fcc lattice.

$\mathbf{R}_n$	0 0 0	$\frac{1}{2}a$ $\frac{1}{2}a$ 0	$\frac{1}{2}a$ 0 $\frac{1}{2}a$	0 $\frac{1}{2}a$ $\frac{1}{2}a$	$\frac{1}{2}a$ $-\frac{1}{2}a$ 0	0 $-\frac{1}{2}a$ $\frac{1}{2}a$	$-\frac{1}{2}a$ 0 $\frac{1}{2}a$
$2E_g$	0 0 0	−1 −1 0	1 0 0	0 1 0	−1 1 0	0 −1 0	−1 0 0
	0 0 0	1 1 0	1 0 −2	0 1 −2	1 −1 0	0 −1 −2	−1 0 −2
	0 0 0	−1 1 0	1 0 2	0 −1 −2	−1 −1 0	0 1 −2	−1 0 2
	0 0 0	1 −1 0	1 0 0	0 −1 0	1 1 0	0 1 0	−1 0 0
E_u	0 0 0	0 0 0	0 −1 0	1 0 0	0 0 0	−1 0 0	0 1 0
	0 0 0	0 0 −2	0 1 0	1 0 0	0 0 2	−1 0 0	0 −1 0

Ω is the primitive unit cell volume of the lattice, the number s indices the six polarization branches, and $\mathbf{k}$ and $\omega_{\mathbf{k},s}$ are the wave vector and frequency of the normal mode of the perfect lattice, respectively. The integration is to be taken over the first Brillouin zone (BZ). The $j_\mu{}^{\pm}(\mathbf{k}|s)$ for $\mu=0$ to 17, have the following expressions:

$$
\begin{aligned}
&j_0{}^{\pm}(\mathbf{k}|s)=|e_\alpha(\pm|\mathbf{k},s)|^2,\\
&j_1{}^{\pm}(\mathbf{k}|s)=e_\alpha(\mp|\mathbf{k},s)e_\alpha{}^*(\pm|\mathbf{k},s)\cos(\tfrac{1}{2}k_\beta a)\cos(\tfrac{1}{2}k_\gamma a),\\
&j_2{}^{\pm}(\mathbf{k}|s)=e_\alpha(\mp|\mathbf{k},s)e_\alpha{}^*(\pm|\mathbf{k},s)\cos(\tfrac{1}{2}k_\alpha a)\cos(\tfrac{1}{2}k_\beta a),\\
&j_3{}^{\pm}(\mathbf{k}|s)=e_\alpha(\mp|\mathbf{k},s)e_\beta{}^*(\pm|\mathbf{k},s)\sin(\tfrac{1}{2}k_\alpha a)\sin(\tfrac{1}{2}k_\beta a),\\
&j_4{}^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\cos(k_\alpha a)\cos(k_\beta a),\\
&j_5{}^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\cos(k_\beta a),\\
&j_6{}^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\cos(\tfrac{1}{2}k_\alpha a)\cos(\tfrac{1}{2}k_\beta a),\\
&j_7{}^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\cos(\tfrac{1}{2}k_\alpha a)\cos(\tfrac{1}{2}k_\beta a)\cos(k_\gamma a),\\
&j_8{}^{\pm}(\mathbf{k}|s)=e_\alpha(\mp|\mathbf{k},s)e_\beta{}^*(\mp|\mathbf{k},s)\sin(\tfrac{1}{2}k_\alpha a)\sin(\tfrac{1}{2}k_\beta a)\cos(\tfrac{1}{2}k_\gamma a),\\
&j_9{}^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\cos^2(\tfrac{1}{2}k_\alpha a),\\
&j_{10}{}^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\sin^2(\tfrac{1}{2}k_\alpha a),\\
&j_{11}{}^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2[1+\cos(k_\beta a)\cos(k_\gamma a)],\\
&j_{12}{}^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2[1-\cos(k_\beta a)\cos(k_\gamma a)],\\
&j_{13}{}^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\cos(\tfrac{1}{2}k_\beta a)\cos(\tfrac{1}{2}k_\gamma a),\\
&j_{14}{}^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\cos(k_\alpha a)\cos(\tfrac{1}{2}k_\beta a)\cos(\tfrac{1}{2}k_\gamma a),\\
&j_{15}{}^{\pm}(\mathbf{k}|s)=e_\alpha(\mp|\mathbf{k},s)e_\beta{}^*(\mp|\mathbf{k},s)\sin(k_\alpha a)\sin(k_\beta a),\\
&j_{16}{}^{\pm}(\mathbf{k}|s)=e_\alpha(\mp|\mathbf{k},s)e_\beta{}^*(\mp|\mathbf{k},s)\sin(\tfrac{1}{2}k_\alpha a)\sin(\tfrac{1}{2}k_\beta a)\cos(k_\gamma a),\\
&j_{17}{}^{\pm}(\mathbf{k}|s)=e_\alpha(\mp|\mathbf{k},s)e_\beta{}^*(\mp|\mathbf{k},s)\sin(\tfrac{1}{2}k_\alpha a)\sin(\tfrac{1}{2}k_\beta a),
\end{aligned}
$$

$$(\alpha,\beta,\gamma=1,2,3 \quad \text{but} \quad \alpha\neq\beta\neq\gamma) \tag{19}$$

where $e_\alpha(\pm|\mathbf{k},s)$ are the Cartesian components of the polarization vector at the two different sites of the unit cell of the host lattice. The polarization vector $\mathbf{e}(\mp|\mathbf{k},s)$ should be multiplied by a phase factor $e^{i\mathbf{k}\cdot\mathbf{R}_n}$ to compare it with the components of the eigenvectors $e_\alpha(\mathbf{k}|\mathbf{y}_j)$ of Born and Huang.[12]

We may now write the different irreducible representations $T_\Gamma(z)$ of the T matrix after using Eqs. (9) and (11) as follows:

$$T_{A_{1g}}(z)=\chi\lambda[1+\chi\lambda(-g_4+g_5+4g_8+2g_{10}+2g_{13}-2g_{14}+g_{15}+2g_{16}+2g_{17})]^{-1}, \tag{20}$$

$$T_{A_{2g}}(z)=\chi\lambda'[1+\chi\lambda'(-g_4+g_5+4g_8+2g_{10}-2g_{13}+2g_{14}-g_{15}-2g_{16}-2g_{17})]^{-1}, \tag{21}$$

$$T_{A_{2u}}(z)=\chi\lambda'[1-\chi\lambda'(2g_5-g_{11}+4g_{16}-4g_{17})]^{-1}, \tag{22}$$

$$T_{E_u}(z)=\chi\lambda'[1-\chi\lambda'(2g_5-g_{11}-2g_{16}+2g_{17})]^{-1}, \tag{23}$$

$$T_{E_{2g}}(z)=\frac{\chi}{4D_{E_{2g}}(z)}\begin{pmatrix} 3\lambda+\lambda'+4\chi\lambda\lambda' g_{E_{2g}}{}^{22} & -\sqrt{3}(\lambda-\lambda')-4\chi\lambda\lambda' g_{E_{2g}}{}^{12} \\ -\sqrt{3}(\lambda-\lambda')-4\chi\lambda\lambda' g_{E_{2g}}{}^{12} & \lambda+3\lambda'+4\chi\lambda\lambda' g_{E_{2g}}{}^{11}\end{pmatrix}, \tag{24a}$$

where

$$D_{E_{2g}}(z)=1+\chi[(\lambda+\lambda')(-g_4+g_5-2g_8+2g_{10})-(\lambda-\lambda')(g_{13}-g_{14}-g_{15}+g_{16}+g_{17})]+\chi^2\lambda\lambda'[(-g_4+g_5-2g_8+2g_{10})^2$$
$$-4(g_{16}+g_{17})^2-g_{15}{}^2+2g_{15}(g_{16}+g_{17})-4(g_{13}-g_{14})(g_{13}-g_{14}-\tfrac{1}{2}g_{15}-g_{16}-g_{17})]. \tag{24b}$$

$$T_{F_{2g}}(z)=\frac{\chi}{D_{F_{2g}}(z)}\begin{pmatrix} \lambda'+\chi\lambda\lambda' g_{F_{2g}}{}^{22} & -\chi\lambda\lambda' g_{F_{2g}}{}^{12} \\ -\chi\lambda\lambda' g_{F_{2g}}{}^{12} & \lambda+\chi\lambda\lambda' g_{F_{2g}}{}^{11}\end{pmatrix}, \tag{25a}$$

where

$$D_{F_{2g}}(z)=1+\chi[\lambda(-g_4-g_5+2g_9+g_{15})+\lambda'(g_{12}+2g_{16}+2g_{17})]+\chi\lambda\lambda'[(g_{12}+2g_{16}+2g_{17})(-g_4-g_5+2g_9+g_{15})$$
$$-4(g_6-g_7+g_8)^2]. \tag{25b}$$

$$T_{F_{1g}}(z)=\frac{\chi\lambda'}{D_{F_{1g}}(z)}\begin{pmatrix} 1+\chi\lambda' g_{F_{1g}}{}^{22} & -\chi\lambda' g_{F_{1g}}{}^{12} \\ -\chi\lambda' g_{F_{1g}}{}^{12} & 1+\chi\lambda' g_{F_{1g}}{}^{11}\end{pmatrix}, \tag{26a}$$

[12] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), p. 298.

where

$$D_{F_{1g}}(z)=1-\chi\lambda'[g_4+g_5-g_{12}+g_{15}-2(g_9-g_{16}-g_{17})]+\chi^2\lambda'^2[(g_{12}-2g_{16}-2g_{17}) \times(-g_4-g_5+2g_9-g_{15})-4(g_6-g_7-g_8)^2]. \quad (26b)$$

$$T_{F_{2u}}(z)=\frac{\chi}{2D_{F_{2u}}(z)}\begin{pmatrix} \lambda+\lambda'+2\chi\lambda\lambda' g_{F_{2u}}{}^{22} & -\lambda+\lambda'-2\chi\lambda\lambda' g_{F_{2u}}{}^{12} \\ -\lambda+\lambda'-2\chi\lambda\lambda' g_{F_{2u}}{}^{12} & \lambda+\lambda'+2\chi\lambda\lambda' g_{F_{2u}}{}^{11}\end{pmatrix}, \quad (27a)$$

where

$$D_{F_{2u}}(z)=1+\chi[(\lambda+\lambda')(g_4+g_9+g_{10}-g_{13}-g_{14}+g_{16}-g_{17})+(\lambda-\lambda')(2g_8-g_{15})] +\chi^2\lambda\lambda'[(g_4+g_5+2g_9-2g_{13}-2g_{14})(g_4-g_5+2g_{10}+2g_{16}-2g_{17})-(2g_8-g_{15})^2]. \quad (27b)$$

In these $T_\Gamma(z)$ matrices, $g_\Gamma{}^{ij}$ denote the matrix elements of the corresponding projected Green's function of the representation Γ, i.e., $g_\Gamma(z)$.

For the optic-active $4F_{1u}$ modes we have

$$T_{F_{1u}}(z)=Q/D_{F_{1u}}(z), \quad (28)$$

where the matrix elements Q_{ij} of the 4×4 Q matrix are given by

$$Q_{ij}=P_{ij}+\sum_{k\neq j}\sum_{p\neq i}(\Delta P_{ip})_{jk}g_{pk}+\sum_{n>m}\sum_{k>p}\sum(\Box P_{jpk})_{imn} \times(\Delta g_{pk})_{mn}+|P_{F_{1u}}(z)|\Box g_{ij}, \quad (29)$$

where i, j, k, m, n, p, etc.$=1, 2, 3, 4$.

Here P_{ij} or g_{ij} are the matrix elements of the 4×4 matrices $P_{F_{1u}}(z)$ or $g_{F_{1u}}(z)$. $(\Delta P_{ip})_{jk}$ or $(\Delta g_{ip})_{jk}$ are the 2×2 subdeterminants containing the matrix elements of the two rows or columns ip and the two columns or rows jk of $P_{F_{1u}}(z)$ or $g_{F_{1u}}(z)$. $(\Box P_{jpk})_{imn}$ is the 3×3 subdeterminant containing the matrix elements of the three rows or columns jpk and the three columns or rows imn. In writing these subdeterminants the orders of the rows and columns should be kept in mind. One interchange in the rows (or columns) means a multiplication of the subdeterminant by -1 once. $\Box g_{ij}$ or $\Box P_{ij}$ are the cofactors of the matrix elements g_{ij} or P_{ij}. $|P_{F_{1u}}(z)|$ is the determinant of $P_{F_{1u}}(z)$. The subdeterminants of the projected perturbation matrix $P_{F_{1u}}(z)$may be simplified to have the following values:

$$\begin{aligned}
&(\Delta P_{12})_{12}=\chi\lambda'[4(\lambda+2\lambda')-\epsilon\omega^2],\\
&(\Delta P_{13})_{13}=\tfrac{1}{2}\chi(\lambda+\lambda')[4\lambda'-\epsilon\omega^2],\\
&(\Delta P_{14})_{14}=2\chi\lambda'(5\lambda+\lambda')-\tfrac{1}{2}\chi(\lambda+\lambda')\epsilon\omega^2,\\
&(\Delta P_{23})_{23}=(\Delta P_{24})_{24}=\tfrac{1}{2}\chi^2\lambda'(\lambda+\lambda'),\\
&(\Delta P_{34})_{34}=\chi^2\lambda\lambda', \qquad (\Delta P_{14})_{34}=-(2\chi)^{3/2}\lambda\lambda',\\
&(\Delta P_{12})_{13}=-2^{3/2}\chi\lambda'(\lambda+\lambda'), \qquad (\Delta P_{13})_{23}=-\chi^{3/2}\lambda'(\lambda+\lambda'),\\
&(\Delta P_{12})_{14}=2^{3/2}\chi\lambda'(\lambda-\lambda'), \qquad (\Delta P_{13})_{24}=\chi^{3/2}\lambda'(\lambda-\lambda'),\\
&(\Delta P_{12})_{23}=(2\chi)^{1/2}\chi\lambda'(\lambda+\lambda'),\\
&(\Delta P_{23})_{24}=-\tfrac{1}{2}\chi^2\lambda'(\lambda-\lambda'),\\
&(\Delta P_{12})_{24}=-(2\chi)^{1/2}\chi\lambda'(\lambda-\lambda'),\\
&(\Delta P_{12})_{34}=(\Delta P_{13})_{34}=(\Delta P_{23})_{34}=(\Delta P_{24})_{34}\\
&\qquad=(\Delta P_{14})_{23}=(\Delta P_{14})_{24}=0, \quad (30)
\end{aligned}$$

and

$$\begin{aligned}
&(\Box P_{234})_{234}=\Box P_{11}=\chi^3\lambda\lambda'^2,\\
&(\Box P_{234})_{134}=-\Box P_{12}=-2\chi^{5/2}\lambda\lambda'^2,\\
&(\Box P_{134})_{134}=\Box P_{22}=\chi^2\lambda\lambda'(4\lambda'-\epsilon\omega^2),\\
&(\Box P_{324})_{124}=-\Box P_{13}=-(2\chi)^{3/2}\chi\lambda\lambda'^2,\\
&(\Box P_{124})_{124}=\Box P_{33}=\tfrac{1}{2}\chi^2\lambda'[16\lambda\lambda'-\epsilon\omega^2(\lambda+\lambda')],\\
&(\Box P_{123})_{123}=\Box P_{44}=-\tfrac{1}{2}\chi^2\lambda'(\lambda+\lambda')\epsilon\omega^2,\\
&(\Box P_{314})_{214}=-\Box P_{23}=-4.2^{1/2}\chi^2\lambda\lambda'^2,\\
&(\Box P_{312})_{412}=-\Box P_{34}=\tfrac{1}{2}\chi^2\lambda'(\lambda-\lambda')\epsilon\omega^2,\\
&(\Box P_{423})_{123}=-(\Box P_{413})_{213}=\Box P_{14}=\Box P_{24}=0. \quad (31)
\end{aligned}$$

The resonance denominator

$$D_{F_{1u}}(z)=1+\sum_i\sum_j g_{ij}P_{ij}+\sum_{n>m}\sum\sum_{j>i}(\Delta g_{mn})_{ij}(\Delta P_{mn})_{ij} +\sum_i\sum_j\Box g_{ij}\Box P_{ij}+|P_{F_{1u}}(z)||g_{F_{1u}}(z)|, \quad (32a)$$

where the second term

$$\sum_i\sum_j g_{ij}P_{ij}=[4(\lambda+2\lambda')-\epsilon\omega^2]g_0-8\chi^{1/2}[\lambda(g_2-g_3) +\lambda'(g_1+g_2+g_3)]+\chi(\lambda+\lambda')(g_4+g_9+g_{10} +g_{13}+g_{14}-g_{16}+g_{17})+\chi\lambda'(2g_5+g_{11}) -\chi(\lambda-\lambda')(2g_8+g_{15}), \quad (32b)$$

and the fifth term simplifies to the form

$$|P_{F_{1u}}(z)||g_{F_{1u}}(z)|=-\chi^3\lambda\lambda'^2\epsilon\omega^2\sum_j g_{1j}\Box g_{1j}. \quad (32c)$$

The third and fourth terms, which are too lengthy to reproduce here, may be written after using values of $(\Delta P_{mn})_{ij}$ and $\Box P_{ij}$, given by Eqs. (30) and (31), and the Green's-function matrix $g_{F_{1u}}(z)$.

For the fcc diatomic lattice the relations between the various Green's functions may be written after using Eqs. (A6)–(A8) of the Appendix. Equation (A6) reduces to the form

$$4[(\eta+2\eta')g_0-\chi^{1/2}\{\eta'g_1+(\eta+\eta')g_2-(\eta-\eta')g_3\}] =1+\omega^2g_0. \quad (33)$$

If we substitute the two values $(a/\sqrt{2})(0,\eta_\beta,\eta_\gamma)$ and $(a/\sqrt{2})(\eta_\alpha,\eta_\beta,0)$ for $|\mathbf{R}_n'|$, in Eq. (A7), we have

$$4(\eta+2\eta')g_1-\chi^{1/2}[2\eta'(2g_5+g_{11})+4(\eta+\eta')(g_6+g_7) -4(\eta-\eta')g_8]=\omega^2 g_1, \quad (34)$$

and

$$4(\eta+2\eta')g_2-\chi^{1/2}[2\eta'(g_6+g_7)+\tfrac{1}{2}(\eta+\eta')(g_4+g_5+2g_9 +2g_{13}+2g_{14})-\tfrac{1}{2}(\eta-\eta')(2g_8+g_{15})]=\omega^2 g_2. \quad (35)$$

The choice of $|\mathbf{R}_n'|=(a/\sqrt{2})(\eta_\alpha,0,\eta_\gamma)$ in Eq. (A8) gives

$$4(\eta+2\eta')g_3-\chi^{1/2}[2\eta' g_8+\tfrac{1}{2}(\eta+\eta')(2g_8+g_{15}) -\tfrac{1}{2}(\eta-\eta')(g_4-g_5+2g_{10}-2g_{16}+2g_{17})]=\omega^2 g_3. \quad (36)$$

In these relations $\eta=\gamma/M_\pm$ and $\eta'=\gamma'/M_\pm$, where γ and γ' are the central- and noncentral-force constants of the pure lattice.

The problem is immensely simplified if we confine ourselves to central forces only. For this particular case the use of the above relations between the Green's functions help us a lot, and the 4×4 matrix $P_{F_{1u}}(z)$ reduces to a 3×3 one. For this particular case we have

$$T_{F_{1u}}(z)=\frac{1}{D_{F_{1u}}(z)}\begin{bmatrix}Q_{11} & Q_{12} & Q_{13}\\ Q_{21} & Q_{22} & Q_{23}\\ Q_{31} & Q_{32} & Q_{33}\end{bmatrix},$$

where

$$Q_{11}=(4\lambda-\epsilon\omega^2)-(\lambda\epsilon\omega^4/4\eta^2)(1+\omega^2 g_0)+(\lambda/\eta)\epsilon\omega^2 \times[\omega^2 g_0-4\eta\chi^{1/2}(g_2-g_3)],$$

$$Q_{12}=Q_{21}=-(2\chi)^{1/2}\lambda[1+(\epsilon\omega^2/4\eta)(1+\omega^2 g_0-4\eta g_0)],$$

$$Q_{13}=Q_{31}=(2\chi)^{1/2}\lambda[1+(\epsilon\omega^2/4\eta)(1+\omega^2 g_0-4\eta g_0)],$$

$$Q_{22}=Q_{33}=\tfrac{1}{2}(\chi\lambda)(1-\epsilon\omega^2 g_0),$$

and

$$Q_{23}=Q_{32}=-\tfrac{1}{2}(\chi\lambda)(1-\epsilon\omega^2 g_0). \quad (37)$$

The resonance denominator

$$D_{F_{1u}}(z)=1+(4\lambda-\epsilon\omega^2)g_0+(\lambda/4\eta^2) \times[(1+\epsilon)\omega^2+4\eta(2-\epsilon\omega^2 g_0)][1+\omega^2 g_0-4\eta g_0] +4\lambda\chi^{1/2}(1-\epsilon\omega^2 g_0)(g_2-g_3). \quad (38)$$

For the monatomic-fcc lattice this denominator reduces to Eq. (31) of Mannheim.[9] The other nonvanishing irreducible representations $T_\Gamma(z)$ are:

$$T_{F_{2u}}(z)=\frac{\chi\lambda}{D_{F_{2u}}(z)}\begin{pmatrix}1 & -1\\ -1 & 1\end{pmatrix}, \quad (39)$$

where

$$D_{F_{2u}}(z)=1+\chi\lambda(g_4+2g_8+g_9+g_{10}-g_{13}-g_{14} -g_{15}+g_{16}-g_{17}). \quad (40)$$

$$T_{F_{2g}}(z)=\chi\lambda[1-\chi\lambda(g_4+g_5-2g_9-g_{15})]^{-1}, \quad (41)$$

$$T_{A_{1g}}(z)=\chi\lambda[1-\chi\lambda(g_4-g_5-4g_8-2g_{10}-2g_{13} +2g_{14}-g_{15}-2g_{16}-2g_{17}]^{-1}, \quad (42)$$

and

$$T_{E_{2g}}(z)=\frac{\chi}{D_{E_{2g}}(z)}\begin{pmatrix}3\lambda & -\sqrt{3}\lambda\\ -\sqrt{3}\lambda & \lambda\end{pmatrix}, \quad (43a)$$

where

$$D_{E_{2g}}(z)=1-\chi\lambda(g_4-g_5+2g_8-2g_{10}+g_{13}-g_{14} -g_{15}+g_{16}+g_{17}). \quad (43b)$$

IV. DIATOMIC BCC LATTICE

The matrix elements of the 27×27 perturbation matrix $P(\omega^2)$ in the CsCl structure are

$$\begin{aligned}p_{ii}(\mathbf{0},\mathbf{0})&=-\epsilon\omega^2+\tfrac{1}{3}8(\lambda+2\lambda'),\\ p_{ij}(\mathbf{0},\mathbf{0})&=0,\\ p_{ii}(\mathbf{0},\mathbf{0})&=-\tfrac{1}{3}\chi^{1/2}(\lambda+2\lambda'),\\ p_{ij}(\mathbf{0},\mathbf{R}_n)&=-\tfrac{1}{3}\chi^{1/2}(\lambda-\lambda')n_i n_j,\\ p_{ii}(\mathbf{R}_n,\mathbf{R}_n)&=\tfrac{1}{3}\chi(\lambda+2\lambda'),\\ p_{ij}(\mathbf{R}_n,\mathbf{R}_n)&=\tfrac{1}{3}\chi(\lambda-\lambda')n_i n_j,\\ &\qquad(i,j=1,2,3)\end{aligned} \quad (44)$$

where $|\mathbf{R}_n|=(a/\sqrt{3})(n_1,n_2,n_3)$ and each of the numbers of the set $\{n\}$ may have values ±1. Yussouff and Mahanty[8] have considered the case of substitutional impurity in the monatomic bcc lattice. They neglected the matrix elements $p_{ij}(\mathbf{R}_n,\mathbf{R}_n)$, which are, in fact, nonvanishing elements.[13] The inclusion of these matrix elements in $P(\omega^2)$ alters significantly the final results.

The various irreducible representations for a substitutional impurity having O_h symmetry in bcc lattice are

$$\Gamma=3F_{1u}+2F_{2g}+F_{1g}+F_{2u}+E_g+E_u+A_{2u}+A_{1g}. \quad (45)$$

The perturbation matrix $P(\omega^2)$ has the following

[13] Dr. M. Yussouff has accepted this correction (private communication).

matrix elements for these irreducible representations:

$$P_{F_{1u}}(\omega^2)=\tfrac{1}{3}\begin{bmatrix}-3\epsilon\omega^2+8(\lambda+2\lambda') & -(8\chi)^{1/2}(\lambda+2\lambda') & -4(\chi)^{1/2}(\lambda-\lambda')\\ -(8\chi)^{1/2}(\lambda+2\lambda') & \chi(\lambda+2\lambda') & \sqrt{2}\chi(\lambda-\lambda')\\ -4\chi^{1/2}(\lambda-\lambda') & \sqrt{2}\chi(\lambda-\lambda') & \chi(2\lambda+\lambda')\end{bmatrix},$$

$$P_{F_{2g}}(\omega^2)=\tfrac{1}{3}\chi\begin{pmatrix}\lambda+2\lambda' & \sqrt{2}(\lambda-\lambda')\\ \sqrt{2}(\lambda-\lambda') & 2\lambda+\lambda'\end{pmatrix},$$

$$P_{F_{1g}}(\omega^2)=\chi\lambda',\quad P_{F_{2u}}(\omega^2)=\chi\lambda',\quad P_{E_g}(\omega^2)=\chi\lambda',$$

$$P_{E_u}(\omega^2)=\chi\lambda',\quad P_{A_{2u}}(\omega^2)=\chi\lambda,\quad P_{A_{1g}}(\omega^2)=\chi\lambda. \tag{46}$$

For central forces only, we observe that the matrix elements for the irreducible representations F_{1g}, F_{2u}, E_g, and E_u vanish, and these symmetry motions are not present. These results are different from those of Yussouff and Mahanty,[8] who have shown that all the irreducible representations contribute in this particular case.

The projected Green's functions for these irreducible representations are

$$g_{F_{1u}}(z)=\begin{bmatrix}g_0 & 8^{1/2}g_1 & -4g_2\\ 8^{1/2}g_1 & g_3+g_5+g_6+2g_7+2g_8 & -\sqrt{2}(g_9+g_{10})\\ -4g_2 & -\sqrt{2}(g_9+g_{10}) & g_4+g_5-g_6+g_9-g_{10}\end{bmatrix},$$

$$g_{F_{2g}}(z)=\begin{pmatrix}g_4-g_5+g_6+2g_7-2g_8 & -\sqrt{2}(g_9-g_{10})\\ -\sqrt{2}(g_9-g_{10}) & g_3-g_5-g_6+g_9+g_{10}\end{pmatrix},$$

$$g_{F_{1g}}(z)=g_3-g_5-g_6-g_9-g_{10},$$

$$g_{F_{2u}}(z)=g_4+g_5-g_6-g_9+g_{10},$$

$$g_{E_g}(z)=g_4-g_5+g_6-2g_7+2g_8-g_9-g_{10},$$

$$g_{E_u}(z)=g_3+g_5+g_6-2g_7-2g_8-g_9+g_{10},$$

$$g_{A_{2u}}(z)=g_3+g_5+g_6-2g_7-2g_8+2g_9-2g_{10},$$

$$g_{A_{1g}}(z)=g_4-g_5+g_6-2g_7+2g_8+2g_9+2g_{10}. \tag{47}$$

Again, the Green's functions $g_\mu^{\pm}(z)$ are the complex-valued integrals given by Eq. (18). Now, however, $j_\mu^{\pm}(\mathbf{k}|s)$ for $\mu=0$–10 has the following expressions:

$$j_0^{\pm}(\mathbf{k}|s)=|e_\alpha(\pm|\mathbf{k},s)|^2,$$

$$j_1^{\pm}(\mathbf{k}|s)=e_\alpha(\pm|\mathbf{k},s)e_\alpha^*(\mp|\mathbf{k},s)\cos(\tfrac{1}{2}k_1a)\cos(\tfrac{1}{2}k_2a)\cos(\tfrac{1}{2}k_3a),$$

$$j_2^{\pm}(\mathbf{k}|s)=e_\alpha(\pm|\mathbf{k},s)e_\beta^*(\mp|\mathbf{k},s)\sin(\tfrac{1}{2}k_\alpha a)\sin(\tfrac{1}{2}k_\beta a)\cos(\tfrac{1}{2}k_\gamma a),$$

$$j_3^{\pm}(\mathbf{k}|s)=2|e_\alpha(\mp|\mathbf{k},s)|^2\cos^2(\tfrac{1}{2}k_\alpha a),$$

$$j_4^{\pm}(\mathbf{k}|s)=2|e_\alpha(\mp|\mathbf{k},s)|^2\sin^2(\tfrac{1}{2}k_\alpha a),$$

$$j_5^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\cos(k_1a)\cos(k_2a)\cos(k_3a),$$

$$j_6^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\cos(k_\beta a)\cos(k_\gamma a),$$

$$j_7^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\cos(k_\alpha a)\cos(k_\beta a),$$

$$j_8^{\pm}(\mathbf{k}|s)=|e_\alpha(\mp|\mathbf{k},s)|^2\cos(k_\beta a),$$

$$j_9^{\pm}(\mathbf{k}|s)=e_\alpha(\mp|\mathbf{k},s)e_\beta^*(\mp|\mathbf{k},s)\sin(k_\alpha a)\sin(k_\beta a),$$

$$j_{10}^{\pm}(\mathbf{k}|s)=e_\alpha(\mp|\mathbf{k},s)e_\beta^*(\mp|\mathbf{k},s)\sin(k_\alpha a)\sin(k_\beta a)\cos(k_\gamma a), \tag{48}$$

where $\alpha, \beta, \gamma = 1, 2, 3$, and $\alpha \neq \beta \neq \gamma$. Again, the polarization vector $\mathbf{e}(\mp|k,s)$ should be multiplied by a phase factor $e^{i\mathbf{k}\cdot\mathbf{R}_n}$ to compare it with that of Born and Huang.[12]

The different irreducible representations $T_\Gamma(z)$ may again be written down as

$$T_{A_{1g}}(z) = \chi\lambda[1+\chi\lambda(g_4-g_5+g_6-2g_7+2g_8+2g_9+2g_{10})]^{-1}, \tag{49}$$

$$T_{A_{2u}}(z) = \chi\lambda[1+\chi\lambda(g_3+g_5+g_6-2g_7-2g_8+2g_9-2g_{10})]^{-1}, \tag{50}$$

$$T_{E_u}(z) = \chi\lambda'[1+\chi\lambda'(g_3+g_5+g_6-2g_7-2g_8-g_9+g_{10})]^{-1}, \tag{51}$$

$$T_{E_g}(z) = \chi\lambda'[1+\chi\lambda'(g_4-g_5+g_6-2g_7+2g_8-g_9-g_{10})]^{-1}, \tag{52}$$

$$T_{F_{2u}}(z) = \chi\lambda'[1+\chi\lambda'(g_4+g_5-g_6-g_9+g_{10})]^{-1}, \tag{53}$$

$$T_{F_{1g}}(z) = \chi\lambda'[1+\chi\lambda'(g_3-g_5-g_6-g_9-g_{10})]^{-1}, \tag{54}$$

$$T_{F_{2g}}(z) = \frac{\chi}{2D_{F_{2g}}(z)}\begin{pmatrix} \lambda+2\lambda'+3\chi\lambda\lambda' g_{F_{2g}}{}^{22} & \sqrt{2}(\lambda-\lambda')-3\chi\lambda\lambda' g_{F_{2g}}{}^{12} \\ \sqrt{2}(\lambda-\lambda')-3\chi\lambda\lambda' g_{F_{2g}}{}^{12} & 2\lambda+\lambda'+3\chi\lambda\lambda' g_{F_{2g}}{}^{11} \end{pmatrix}, \tag{55a}$$

where

$$D_{F_{2g}}(z) = 1+(\tfrac{1}{3}\chi)[(2\lambda+\lambda')g_3+(\lambda+2\lambda')(g_4+2g_7-2g_8)-3(\lambda+\lambda')g_5-(\lambda-\lambda')g_6-(2\lambda-5\lambda')g_9+3(2\lambda-\lambda')g_{10}] \\ +\chi^2\lambda\lambda'[(g_4-g_5+g_6+2g_7-2g_8)(g_3-g_5-g_6+g_9+g_{10})-2(g_9-g_{10})^2]. \tag{55b}$$

Here $g_{F_{2g}}{}^{ij}$ are the matrix elements of $g_{F_{2g}}(z)$.

For the optic-active modes $3F_{1u}$, we have

$$T_{F_{1u}}(z) = Q/D_{F_{1u}}(z), \tag{56}$$

where the elements Q_{ij} of the matrix Q are given by

$$Q_{ij} = P_{ij} + \sum_{k\neq i}\sum_{m\neq j}(\Delta P_{ik})_{jm} g_{mk} + |P_{F_{1u}}(z)|\,\Delta g_{ij} \tag{57}$$

in which Δg_{ij} are the cofactors of the elements g_{ij} of the matrix $g_{F_{1u}}(z)$, and $|P_{F_{1u}}(z)|$ is the determinant of $P_{F_{1u}}(z)$. The subdeterminants $(\Delta P_{ik})_{jm}$, which are to be written as discussed in Sec. III, are given by

$$(\Delta P_{23})_{23} = \chi^2\lambda\lambda', \quad (\Delta P_{13})_{32} = (2\chi)^{3/2}\lambda\lambda', \\ (\Delta P_{13})_{13} = \tfrac{1}{3}\chi[24\lambda\lambda' - \epsilon\omega^2(2\lambda+\lambda')], \quad (\Delta P_{12})_{23} = 0, \\ (\Delta P_{12})_{12} = -\tfrac{1}{3}\chi(\lambda+2\lambda')\epsilon\omega^2, \quad \text{and} \quad (\Delta P_{21})_{13} = \tfrac{1}{3}\sqrt{2}\chi(\lambda-\lambda')\epsilon\omega^2. \tag{58}$$

The resonance denominator

$$D_{F_{1u}}(z) = 1+\sum_i\sum_j P_{ij}g_{ij} + \sum_{k\neq i}\sum_{p\neq j}(\Delta P_{ik})_{pj}(\Delta g_{ik})_{pj} + |P_{F_{1u}}(z)|\,|g_{F_{1u}}(z)|, \tag{59a}$$

where

$$\sum_i\sum_j P_{ij}g_{ij} = [-\epsilon\omega^2+(8/3)(\lambda+2\lambda')]g_0 - (16/3)\chi^{1/2}[(\lambda+2\lambda')g_1-2(\lambda-\lambda')g_2] \\ +(\tfrac{1}{3}\chi)[(\lambda+2\lambda')g_3+(2\lambda+\lambda')g_4+3(\lambda+\lambda')g_5-(\lambda-\lambda')g_6+2(\lambda+2\lambda')(g_7+g_8)-(2\lambda-5\lambda')g_9-3(2\lambda-\lambda')g_{10}], \tag{59b}$$

$$\sum_{k\neq i}\sum_{p\neq j}(\Delta P_{ik})_{pj}(\Delta g_{ik})_{pj} = \chi\lambda\lambda'[\chi\Delta g_{11}+8\Delta g_{22}+4(2\chi)^{1/2}\Delta g_{12}] - \tfrac{1}{3}\chi\epsilon\omega^2[(2\lambda+\lambda')\Delta g_{22}+(\lambda+2\lambda')\Delta g_{33} \\ -2^{3/2}(\lambda-\lambda')\Delta g_{23}], \tag{59c}$$

and

$$|P_{F_{1u}}(z)|\,|g_{F_{1u}}(z)| = -\chi\lambda\lambda'\epsilon\omega^2[g_0\Delta g_{11}+8^{1/2}g_1\Delta g_{12}-4g_2\Delta g_{13}]. \tag{59d}$$

Again, Eqs. (A6)–(A8) of the Appendix give the following relations between the Green's functions:

$$(8/3)\{(\eta+2\eta')g_0-\chi^{1/2}[(\eta+2\eta')g_1-2(\eta-\eta')g_2]\} = 1+\omega^2 g_0, \quad (60)$$

$$(8^{1/2}/3)[8(\eta+2\eta')g_1-\chi^{1/2}\{(\eta+2\eta')(g_3+g_5+g_6 +2g_7+2g_8)-2(\eta-\eta')(g_9+g_{10})\}]=\omega^2 g_1, \quad (61)$$

and

$$(4/3)[8(\eta+2\eta')g_2 -\chi^{1/2}\{(\eta+2\eta')(g_9+g_{10}) -(\eta-\eta')(g_4+g_5-g_6+g_9-g_{10})\}]=\omega^2 g_2, \quad (62)$$

where $\eta=\gamma/M_{\pm}$ and $\eta'=\gamma'/M_{\pm}$.

For the particular case of central forces only, we have

$$T_{F_{1u}}(z)=Q/D_{F_{1u}}(z), \quad (63)$$

where the explicit forms of the matrix elements Q_{ij} are

$$Q_{11}=((8\lambda/3)-\epsilon\omega^2)-\frac{3\lambda}{8\eta^2}\epsilon\omega^4(1+\omega^2 g_0)+\frac{\lambda}{\eta}\epsilon\omega^2 \times\left[\omega^2 g_0-\frac{8\eta}{3}\chi^{1/2}(g_1-2g_2)\right],$$

$$Q_{12}=Q_{21}=-(8\chi)^{1/2}\tfrac{1}{3}\lambda\left[1+\frac{3\epsilon\omega^2}{8\eta}\left(1+\omega^2 g_0-\frac{8\eta}{3}g_0\right)\right],$$

$$Q_{13}=Q_{31}=-4\chi^{1/2}\tfrac{1}{3}\lambda\left[1+\frac{3\epsilon\omega^2}{8\eta}\left(1+\omega^2 g_0-\frac{8\eta}{3}g_0\right)\right],$$

$$Q_{22}=\tfrac{1}{3}\chi\lambda(1-\epsilon\omega^2 g_0), \quad Q_{33}=\tfrac{2}{3}\chi\lambda(1-\epsilon\omega^2 g_0),$$

and

$$Q_{23}=Q_{32}=2^{1/2}\chi\tfrac{1}{3}\lambda(1-\epsilon\omega^2 g_0). \quad (64)$$

The resonance denominator

$$D_{F_{1u}}(z)=1+(8\lambda/3-\epsilon\omega^2)g_0+(3\lambda/8\eta^2) \times[(16\eta/3)+(1+\epsilon)\omega^2-(8\eta/3)\epsilon\omega^2 g_0] \times[1+\omega^2 g_0-(8\eta/3)g_0]+(8\lambda/3) \times\chi^{1/2}(1-\epsilon\omega^2 g_0)(g_1-2g_2). \quad (65)$$

Again for the monatomic bcc lattice this determinant reduces to that of Mannheim.[9] The other nonvanishing contributions to the T matrix are from the irreducible representations $T_{A_{1g}}(z)$, $T_{A_{2u}}(z)$, and $T_{F_{2g}}(z)$ which are given by Eqs. (49), (50), and (55).

Out of these, $T_{F_{2g}}(z)$ simplifies to

$$T_{F_{2g}}(z)=\frac{\chi\lambda}{3D_{F_{2g}}(z)}\begin{pmatrix}1 & \sqrt{2}\\ \sqrt{2} & 1\end{pmatrix},$$

where

$$D_{F_{2g}}(z)=1+(\chi\lambda/3)(2g_3+g_4-3g_5-g_6+2g_7 -2g_8-2g_9+6g_{10}). \quad (66)$$

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APPENDIX: RELATIONS BETWEEN GREEN'S FUNCTIONS

The time-independent equation of motion for a pure diatomic lattice may be written as

$$\sum_{\beta,\kappa'} C_{\alpha\beta}(\mathbf{k})_{\kappa\kappa'} e_\beta\left(\frac{\kappa'}{\mathbf{k},s}\right)=\omega_{\mathbf{k},s}^2 e_\alpha\left(\frac{\kappa}{\mathbf{k},s}\right), \quad (A1)$$

where the Fourier-transformed dynamical matrix

$$C_{\alpha\beta}(\mathbf{k})_{\kappa\kappa'}$$

is defined by

$$C_{\alpha\beta}(\mathbf{k})_{\kappa\kappa'}=\sum_{\bar{l}} L_{\alpha\beta}{}^0(\bar{l})_{\kappa\kappa'} e^{-i\mathbf{k}\cdot\mathbf{R}(\bar{l})}. \quad (A2)$$

Here $\bar{l}=l-l'$, $\mathbf{R}(\bar{l})=\mathbf{R}(l,\kappa)-\mathbf{R}(l',\kappa')$, and $\mathbf{R}(l,\kappa)=\mathbf{R}(l)+\mathbf{R}(\kappa)$, where $\mathbf{R}(l)$ is the lattice vector of the cell (l), and $\mathbf{R}(\kappa)$ is the position vector of atom κ with respect to the cell (l).

$$L_{\alpha\beta}{}^0(\bar{l})_{\kappa\kappa'}$$

are the elements of the dynamical matrix L^0 of Eq. (1). The eigenvalues of the matrix C are the squared frequencies $\omega_{\mathbf{k},s}{}^2$, and the eigenvectors $e_\alpha(\kappa/\mathbf{k},s)$ are the Cartesian components of the polarization vectors $\mathbf{e}(\kappa/\mathbf{k},s)$. They are orthonormal and normalized as

$$\sum_{\kappa,\alpha} e_\alpha{}^*(\kappa/\mathbf{k},s')e_\alpha(\kappa/\mathbf{k},s)=\delta_{ss'}, \quad (A3)$$

$$\sum_s e_\alpha{}^*(\kappa'/\mathbf{k},s)e_\beta(\kappa/\mathbf{k},s)=\delta_{\alpha\beta}\delta_{\kappa\kappa'}. \quad (A4)$$

The eigenvectors of Eq. (A1) should be multiplied by the phase factors $e^{i\mathbf{k}\cdot\mathbf{R}(\kappa)}$ to compare them with the eigenvectors $e_\alpha(k|\mathbf{y}_j)$ of Born and Huang.[12]

For nearest-neighbor forces only, we may write Eq. (A1) as

$$\sum_\beta L_{\alpha\beta}{}^0(\mathbf{0},\mathbf{0})e_\beta(\pm|\mathbf{k},s)+\sum_{\mathbf{R}_n} e^{-i\mathbf{k}\cdot\mathbf{R}_n}\sum_\beta L_{\alpha\beta}{}^0(\mathbf{0},\mathbf{R}_n) \times e_\beta(\mp|\mathbf{k},s)=\omega_{\mathbf{k},s}{}^2 e_\alpha(\pm|\mathbf{k},s), \quad (A5)$$

where the two different sites of the unit cell are represented by $+$ or $-$, and $\mathbf{R}_n$ denote the position vectors of the nearest neighbors of the ion $(+)$ or $(-)$ at origin.

Multiplying (A5) by $e_\alpha^*(\pm|\mathbf{k},s)$, dividing by $(\omega_{\mathbf{k},s}^2-\omega^2)$, and then integrating over the first Brillouin zone in k space, we have

$$L_{\alpha\alpha}^0(\mathbf{0},\mathbf{0})g_0+\sum_{\mathbf{R}_n}L_{\alpha\alpha}^0(\mathbf{0},\mathbf{R}_n)g_{\alpha\alpha}(R_n)$$
$$+\sum_{\mathbf{R}_n}\sum_{\beta\neq\alpha}L_{\alpha\beta}^0(\mathbf{0},\mathbf{R}_n)g_{\alpha\beta}(R_n)=1+\omega^2 g_{\alpha\alpha}(\pm). \quad \text{(A6)}$$

In writing Eq. (A6), the symmetry properties of the Green's functions $g_{\alpha\beta}(R_n)$ and the elements of the dynamical matrix have been kept in mind. The pertinent Green's functions are defined below.

Multiplying Eq. (A5) by $e_\alpha^*(\mp|\mathbf{k},s)e^{i\mathbf{k}\cdot\mathbf{R}_n'}$, where $\mathbf{R}_n'$ denotes one of the nearest-neighboring sites, and by repeating the process we find

$$L_{\alpha\alpha}^0(\mathbf{0},\mathbf{0})g_{\alpha\alpha}(\mp)+\sum_{\mathbf{R}_n}L_{\alpha\alpha}^0(\mathbf{0},\mathbf{R}_n)g_{\alpha\alpha}(|\mathbf{R}_n-\mathbf{R}_n'|)$$
$$+\sum_{\mathbf{R}_n}\sum_{\beta\neq\alpha}L_{\alpha\beta}^0(\mathbf{0},\mathbf{R}_n)g_{\alpha\beta}(|\mathbf{R}_n-\mathbf{R}_n'|)=\omega^2 g_{\alpha\alpha}(R_n'). \quad \text{(A7)}$$

Again repeating the process after multiplying (A5) by $e_\gamma^*(\mp|\mathbf{k},s)e^{i\mathbf{k}\cdot\mathbf{R}_n'}$, one gets

$$L_{\alpha\alpha}^0(\mathbf{0},\mathbf{0})g_{\alpha\gamma}(\mp)+\sum_{\mathbf{R}_n}L_{\alpha\alpha}^0(\mathbf{0},\mathbf{R}_n)g_{\alpha\gamma}(|\mathbf{R}_n-\mathbf{R}_n'|)$$
$$+\sum_{\mathbf{R}_n}\sum_{\beta\neq\alpha}L_{\alpha\beta}^0(\mathbf{0},\mathbf{R}_n)g_{\beta\gamma}(|\mathbf{R}_n-\mathbf{R}_n'|)=\omega^2 g_{\alpha\gamma}(R_n'). \quad \text{(A8)}$$

In these relations the various Green's functions $g_{\alpha\alpha}(\pm)$, $g_{\alpha\alpha}(\mp)$, $g_{\alpha\gamma}(\mp)$, and $g_{\alpha\beta}(|\mathbf{R}_n-\mathbf{R}_n'|)$ are obtained from Eq. (18) after using the following values for $j^\pm(\mathbf{k}|s)$:

$$j_{\alpha\alpha}^\pm(\pm)=j_0^\pm=e_\alpha(\pm|\mathbf{k},s)e_\alpha^*(\pm|\mathbf{k},s), \quad \text{(A9)}$$
$$j_{\alpha\alpha}^\pm(\mp)=e_\alpha(\pm|\mathbf{k},s)e_{,\alpha}^*(\mp|\mathbf{k},s)e^{i\mathbf{k}\cdot\mathbf{R}_n'}, \quad \text{(A10)}$$
$$j_{\alpha\gamma}^\pm(\mp)=e_\alpha(\pm|\mathbf{k},s)e_\gamma^*(\mp|\mathbf{k},s)e^{i\mathbf{k}\cdot\mathbf{R}_n'}, \quad \text{(A11)}$$

and

$$j_{\alpha\beta}(|\mathbf{R}_n-\mathbf{R}_n'|)=e_\alpha(R_n|\mathbf{k},s)e_\beta^*(R_n'|\mathbf{k},s)e^{-i\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_n')}. \quad \text{(A12)}$$