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Theory of impurity-induced infrared absorption in cubic crystals

S. S. Jaswal
University of Nebraska

J. M. Wadehra
University of Nebraska, ad5541@wayne.edu

Theory of impurity-induced infrared absorption in cubic crystals

S. S. Jaswal and J. M. Wadehra*

Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68508

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A method to calculate the infrared absorption due to a very low concentration of defects in a diatomic cubic crystal is developed directly from the basic absorption equation in quantum mechanics when the impurity produces changes in mass and short-range force constants. It is shown that the absorption is due to the modes of T_{1u} symmetry about the defect and is proportional to the square of the projection of the amplitudes of the ions in the defect space onto the transverse-optic modes at the zone center as determined by the perturbation. A procedure to calculate the amplitudes of the ion in the defect space for a given mode is outlined. The present method gives more physical insight into the problem than most of the Green's-function formalisms used in the field.

Several authors have studied theoretically the problem of infrared absorption due to a very low concentration of impurities in a crystal using various Green's-function formalisms of the many-body theory.[1-5] Following our work on the mass-defect problem[6] we develop here a method to calculate the infrared absorption in a crystal due to a very low concentration of impurities directly from the basic absorption equation given by Lax and Burstein[7] when the impurity involves changes in the mass as well as short-range force constants.

Martin[4] has essentially shown that, for the wavelength of electromagnetic radiation very long compared to the interatomic spacing, the absorption-coefficient expression of Lax and Burstein[7] reduces to

$$\alpha(\omega_f) = \frac{2\pi^2 D}{3n(\omega_f)c}\left(\frac{n_\infty^2 + 2}{3}\right)^2 \left| \hat{\lambda} \cdot \sum_{l\kappa} e_\kappa \vec{\chi}(l\kappa \,|\, f) \right|^2 g(\omega_f)$$

(1)

for phonons in the harmonic approximation, where D is the defect concentration, $n(\omega_f)$ is the index of refraction, c is the velocity of light in vacuum, n_∞ is the long-wavelength limit of the high-frequency index of refraction, $\hat{\lambda}$ is the unit vector in the direction of polarization of the incident electromagnetic radiation, $\vec{\chi}(l\kappa|f)$ is the amplitude of the κth ion in the lth unit cell corresponding to the impurity-mode frequency ω_f, e_κ is the charge on the κth ion, and $g(\omega_f)$ is the phonon density of states. This expression is expected to give reasonable results for frequencies away from the restsrahlen band. For a very low defect concentration $n(\omega_f)$, n_∞ and the density of states (except for the local modes) of the imperfect crystal are essentially the same as those of the perfect crystal. Thus the effect of the impurity on the infrared absorption is contained in

$$A = \left| \hat{\lambda} \cdot \sum_{l\kappa} e_\kappa \vec{\chi}(l\kappa|f) \right|^2 ,$$

which is the square of the projection of the dipole moment of the imperfect crystal on the direction of polarization of the incident radiation. We outline below a method to calculate this quantity.

$\chi_\alpha(l\kappa|f)$ is determined by the equations of motion of the perturbed crystal,

$$\sum_{\beta l'\kappa'} \left[\omega_f^2 \delta_{\alpha\beta}\delta_{ll'}\delta_{\kappa\kappa'} M_\kappa - \phi_{\alpha\beta}^0\binom{ll'}{\kappa\kappa'} \right]\chi_\beta(l'\kappa'\,|\,f)$$

$$= \sum_{\beta l'\kappa'} \Delta_{\alpha\beta}\binom{ll'}{\kappa\kappa'}\chi_\beta(l'\kappa'\,|\,f) ,$$

(2)

where M_κ is the mass of the κth-type ion in the perfect crystal, $\phi_{\alpha\beta}^0\binom{ll'}{\kappa\kappa'}$ are the force constants of the unperturbed crystal, and $\Delta_{\alpha\beta}\binom{ll'}{\kappa\kappa'}$ is the perturbation due to the change in mass and force constants, i.e.,

$$\Delta_{\alpha\beta}\binom{ll'}{\kappa\kappa'} = \Delta\phi_{\alpha\beta}\binom{ll'}{\kappa\kappa'} - \omega_f^2 \delta_{\alpha\beta}\delta_{ll'}\delta_{\kappa\kappa'}\Delta M_\kappa .$$

The Greek subscripts α, β, etc., refer to the three Cartesian axes x, y, and z. In terms of the Green's functions of the perfect crystal and perturbation $\underline{\Delta}$, the amplitude is given by

$$\underline{\chi} = \underline{G}\,\underline{\Delta}\,\underline{\chi}$$

(3)

in matrix form. The Green's-function matrix $\underline{G}$ is given by

$$G_{\alpha\beta}\binom{ll'}{\kappa\kappa'}; \omega = \frac{1}{N}\sum_{\vec{k}j} \frac{1}{(M_\kappa M_{\kappa'})^{1/2}} \frac{e_\alpha(\kappa|\,\substack{\vec{k}\\j})e_\beta^*(\kappa'|\,\substack{\vec{k}\\j})}{\omega^2 - \omega_j^2(\vec{k})}$$

$$\times \exp\left\{2\pi i\vec{k}\cdot\left[\vec{r}\binom{l}{\kappa} - \vec{r}\binom{l'}{\kappa'}\right]\right\} ,$$

(4)

where N is the number of unit cells in the crystal, $\vec{e}(\kappa|\substack{\vec{k}\\j})$ and $\omega_j(\vec{k})$ are the eigenvectors and eigenfrequencies, respectively, of the pure crystal corresponding to wave vector $\vec{k}$ and the phonon dispersion branch j, and $\vec{r}\binom{l}{\kappa}$ is the equilibrium position of the κth ion in the lth unit cell.

The frequencies of the impurity modes are given by the secular equation

$$|\underline{1} - \underline{G}\,\underline{\Delta}| = 0 \; . \tag{5}$$

This can be block diagonalized by the symmetry coordinate matrix, and one gets the secular equations of lower dimensionalities corresponding to the various irreducible representations of the point group of the impurity.

Now from Eq. (3) we have

$$\sum_l \chi_\gamma(l\kappa|f) = \sum_{\substack{l'l'' \\ \kappa'\kappa''\beta\lambda}} G_{\gamma\beta}\!\left(\begin{matrix}ll' \\ \kappa\kappa'\end{matrix}; \omega_f\right) \Delta_{\beta\lambda}\!\left(\begin{matrix}l'l'' \\ \kappa'\kappa''\end{matrix}\right) \chi_\lambda(l''\kappa''|f) . \tag{6}$$

After some simplifications Eq. (6) becomes

$$\sum_l \chi_\gamma(l\kappa|f) = \sum_j \frac{e_\gamma(\kappa|{}^0_j)}{(M_\kappa)^{1/2}[\omega_f^2 - \omega_j^2(0)]} S(f,j) \equiv \chi_\gamma(\kappa|f) , \tag{7}$$

where

$$S(f,j) = \sum_{\alpha l'\kappa'} \frac{e_\alpha^*(\kappa'|{}^0_j)}{(M_{\kappa'})^{1/2}} (\underline{\Delta}\,\underline{\chi})_\alpha^{l'\kappa',f} . $$

For a diatomic ionic crystal

$$A = \left| \hat{\lambda} \cdot \sum_{l\kappa} e_\kappa \vec{\chi}(l\kappa|f) \right|^2 = e_{\mathrm{eff}}^2 \{\hat{\lambda} \cdot [\vec{\chi}(+|f) - \vec{\chi}(-|f)]\}^2 , \tag{8}$$

where e_{eff}, the magnitude of the effective charge on each ion, including the impurity in the crystal, is assumed to be the same throughout the crystal. Since the electromagnetic radiation is transverse in nature, Eq. (8) can be written as
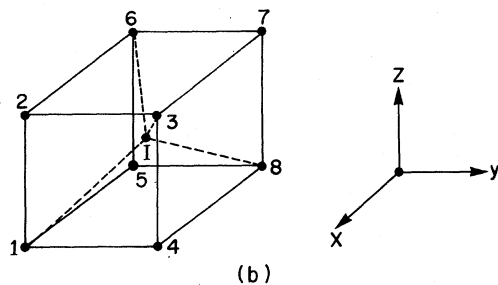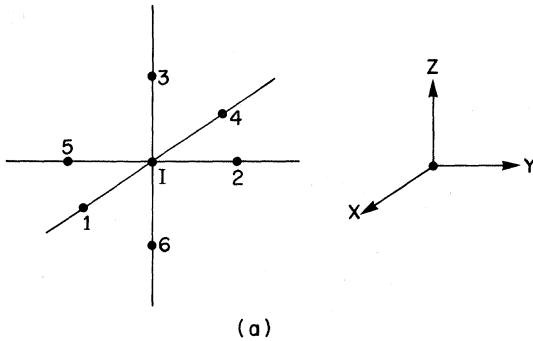

(a)

(b)

FIG. 1. (a) Impurity (I) and its six nearest neighbors $(1,2,\cdots,6)$ in a NaCl-structure crystal; (b) impurity (I) and its eight nearest neighbors $(1,2,\cdots,8)$ in a CsCl-structure crystal.

$$A = e_{\mathrm{eff}}^2 \sum_j^{\mathrm{TO}} \frac{|S(f,j)|^2}{[\omega_f^2 - \omega_j^2(0)]^2} \left| \frac{\vec{e}(+|{}^0_j)}{\sqrt{M_+}} - \frac{\vec{e}(-|{}^0_j)}{\sqrt{M_-}} \right|^2 , \tag{9}$$

where the summation is over the transverse-optic (TO) modes at the Γ point ($\vec{k}=0$). For a diatomic cubic crystal and a TO branch

$$\left| \frac{\vec{e}(+|{}^0_j)}{\sqrt{M_+}} - \frac{\vec{e}(-|{}^0_j)}{\sqrt{M_-}} \right|^2 = \frac{M_- + M_+}{M_- M_+} \equiv \mu . \tag{10}$$

Therefore

$$A = \frac{e_{\mathrm{eff}}^2 \mu}{(\omega_f^2 - \omega_{\mathrm{TO}}^2)^2} \sum_j^{\mathrm{TO}} |S(f,j)|^2 , \tag{11}$$

where

$$S(f,j) = \sum_{\alpha l'\kappa'} \frac{e_\alpha^*(\kappa'|{}^0_j)}{(M_{\kappa'})^{1/2}} (\underline{\Delta}\,\underline{\chi})_\alpha^{l'\kappa',f} . \tag{12}$$

We find from Eq. (11) that the problem of getting absorption coefficients boils down to calculating $S(f,j)$. For the impurity involving the mass change and the changes in short-range force constants $\underline{\Delta}$ is a relatively small matrix involving the impurity and some of its neighbors. Thus $S(f,j)$ is determined by the amplitudes of the impurity and its neighbors affected by the perturbation. Hence the infrared absorption due to an impurity in a crystal depends on the projections of the impurity-mode amplitudes of the ions in the defect space onto the corresponding TO mode amplitudes at the Γ point, as determined by the perturbation $\underline{\Delta}$.

Group theory can be used to simplify the calculation of $S(f,j)$. We see from Eq. (3) that the normal modes of the imperfect crystal can be classified in terms of the irreducible representations of the symmetry coordinates of the ions in the defect space. With the perturbation limited to the nearest neighbors of the impurity, the defect spaces for NaCl structure and CsCl structure are shown in Fig. 1. If we denote the displacements of the impurity (I) and its neighbors $(1, 2, \ldots)$ by $\vec{u}^I$, $\vec{u}^1$, $\vec{u}^2$, etc., the vector spaces formed by these displacements for the two structures transform according to the following irreducible representations of the O_h group:

$$\Gamma(\mathrm{NaCl}) = A_{1g} + E_g + T_{1g} + 3T_{1u} + T_{2g} + T_{2u} ,$$

$$\Gamma(\mathrm{CsCl}) = A_{1g} + A_{1u} + E_g + E_u + T_{1g} + 3T_{1u} + 2T_{2g} + T_{2u} .$$

The symmetry coordinates $\underline{X}$ for the two structures, as given by the reduction of their vector spaces,

TABLE I. Symmetry coordinates of an impurity and its nearest neighbors in the NaCl-structure crystals.

Rep.	Coord.																							u
A_{1g}	X_1	0	0	0	$1/\sqrt{6}$	0	0	0	$1/\sqrt{6}$	0	0	0	$1/\sqrt{6}$	$-1/\sqrt{6}$	0	0	0	$-1/\sqrt{6}$	0	0	0	$-1/\sqrt{6}$	U_x^I
E_g	X_2	0	0	0	0	0	0	0	$\tfrac{1}{2}$	0	0	0	$-1/2$	0	0	0	0	$-1/2$	0	0	0	$1/2$	U_y^I
	Y_2	0	0	0	$-1/\sqrt{3}$	0	0	0	$1/\sqrt{12}$	0	0	0	$1/\sqrt{12}$	$1/\sqrt{3}$	0	0	0	$-1/\sqrt{12}$	0	0	0	$-1/\sqrt{12}$	U_z^I
T_{1g}	X_3	0	0	0	0	$\tfrac{1}{2}$	0	$-\tfrac{1}{2}$	0	0	0	0	0	0	$-\tfrac{1}{2}$	0	$\tfrac{1}{2}$	0	0	0	0	0	U_x^1
	Y_3	0	0	0	0	0	$\tfrac{1}{2}$	0	0	0	$-\tfrac{1}{2}$	0	0	0	0	$-\tfrac{1}{2}$	0	0	0	$\tfrac{1}{2}$	0	0	U_y^1
	Z_3	0	0	0	0	0	0	0	0	$\tfrac{1}{2}$	0	$-\tfrac{1}{2}$	0	0	0	0	0	$-\tfrac{1}{2}$	0	$\tfrac{1}{2}$	0	0	U_z^1
T_{1u}	X_4	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	U_x^2
	X_5	0	0	0	$1/\sqrt{2}$	0	0	0	0	0	0	0	0	$1/\sqrt{2}$	0	0	0	0	0	0	0	0	U_y^2
	X_6	0	0	0	0	0	0	$\tfrac{1}{2}$	0	0	$\tfrac{1}{2}$	0	0	0	0	0	$\tfrac{1}{2}$	0	0	$\tfrac{1}{2}$	0	0	U_z^2
	Y_4	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	U_x^3
	Y_5	0	0	0	0	0	0	0	$1/\sqrt{2}$	0	0	0	0	0	0	0	0	$1/\sqrt{2}$	0	0	0	0	U_y^3
	Y_6	0	0	0	0	$\tfrac{1}{2}$	0	0	0	0	0	$\tfrac{1}{2}$	0	0	$\tfrac{1}{2}$	0	0	0	0	0	$\tfrac{1}{2}$	0	U_z^3
	Z_4	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	U_x^4
	Z_5	0	0	0	0	0	0	0	0	0	0	0	$1/\sqrt{2}$	0	0	0	0	0	0	0	0	$1/\sqrt{2}$	U_y^4
	Z_6	0	0	0	0	0	$\tfrac{1}{2}$	0	0	$\tfrac{1}{2}$	0	0	0	0	0	$\tfrac{1}{2}$	0	0	$\tfrac{1}{2}$	0	0	0	U_z^4
T_{2g}	X_7	0	0	0	0	$\tfrac{1}{2}$	0	$\tfrac{1}{2}$	0	0	0	0	0	0	$-\tfrac{1}{2}$	0	$-\tfrac{1}{2}$	0	0	0	0	0	U_x^5
	Y_7	0	0	0	0	0	$\tfrac{1}{2}$	0	0	0	$\tfrac{1}{2}$	0	0	0	0	$-\tfrac{1}{2}$	0	0	0	$-\tfrac{1}{2}$	0	0	U_y^5
	Z_7	0	0	0	0	0	0	0	0	$\tfrac{1}{2}$	0	$\tfrac{1}{2}$	0	0	0	0	0	$-\tfrac{1}{2}$	0	$-\tfrac{1}{2}$	0	0	U_z^5
T_{2u}	X_8	0	0	0	0	0	0	$\tfrac{1}{2}$	0	0	$-\tfrac{1}{2}$	0	0	0	0	0	$\tfrac{1}{2}$	0	0	$-\tfrac{1}{2}$	0	0	U_x^6
	Y_8	0	0	0	0	$\tfrac{1}{2}$	0	0	0	0	0	$-\tfrac{1}{2}$	0	0	$\tfrac{1}{2}$	0	0	0	0	0	$-\tfrac{1}{2}$	0	U_y^6
	Z_8	0	0	0	0	0	$\tfrac{1}{2}$	0	0	$-\tfrac{1}{2}$	0	0	0	0	0	$\tfrac{1}{2}$	0	0	$-\tfrac{1}{2}$	0	0	0	U_z^6

are listed in Tables I and II in the form

$$\underline{X} = \underline{S}\,\underline{u}\,. \tag{13}$$

The fact that $\underline{G}$ and $\underline{\Delta}$ are invariant under the operations of the point group of the defect space implies that (a) the forms of $\underline{G}$ and $\underline{\Delta}$ can be found by group theory and (b) matrix $\underline{S}$ block diagonalizes $\underline{G}$ and $\underline{\Delta}$ with each block along the diagonal belonging to a particular irreducible representation. For a given irreducible representation the dimensionality of a block in a block-diagonalized matrix is equal to the number of times that representation appears in the reduction of the vector space, and the number of times that block is repeated along the diagonal is equal to the dimensionality of the representation. Block diagonalization of $\underline{G}$ and $\underline{\Delta}$ implies that the secular equation breaks up into smaller determinants corresponding to the blocks along the diagonal. Further diagonalization of a block determines the frequencies and the symmetry coordinates, and the latter determine the amplitudes of the various ions in the defect space vibrating in a particular mode by $\underline{u} = \underline{\tilde{S}}\,\underline{X}$. For example, the T_{1u} irreducible representation appears thrice in the reduction of either of the two vector spaces. Therefore the block diagonalization in either case gives three identical secular equations corresponding to the threefold degeneracy of the T_{1u} modes. The dimensionality of the determinant in these secular equations is three. The diagonalization of the matrix corresponding to this determinant gives

three symmetry coordinates a, b, and c corresponding to each eigenvalue. If we form $\underline{X}$ by substituting a, b, and c, respectively, for X_4, X_5, and X_6 and zeros for the other elements in Table I, $\underline{u} = \underline{\tilde{S}}\,\underline{X}$ gives the amplitudes $\chi_\alpha(l\kappa|f)$ of the ions in the defect space for that particular T_{1u} mode in a crystal of NaCl structure. The amplitudes $\chi_\alpha(l\kappa|f)$ for this example are listed in Table III. Thus Tables I and II can be used to find the amplitudes of the ions in the defect space for the various modes in terms of the appropriate symmetry coordinates.

With this knowledge of $\bar{\chi}(l\kappa|f)$ and $\underline{\Delta}$ from group theory it can be shown that $S(f, j)$ is zero for all modes except the ones with T_{1u} symmetry. The symmetry coordinates a, b, and c for the T_{1u} modes can be calculated from the equations of motion and the normalization condition as shown below.

The equation of motion can be rewritten as follows:

$$\underline{S}\,\underline{\chi} = \underline{S}\,\underline{G}\,\underline{\tilde{S}}\,\underline{S}\,\underline{\Delta}\,\underline{\tilde{S}}\,\underline{S}\,\underline{\chi}\,. \tag{14}$$

$\underline{S}$ block diagonalizes $\underline{G}$ and $\underline{\Delta}$ and, if $\underline{\chi}$ corresponds to the amplitudes $\bar{\chi}(l\kappa|f)$ for a T_{1u} mode, Eq. (14) is of the form

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \alpha \begin{pmatrix} a \\ b \\ c \end{pmatrix}, \tag{15}$$

where α is a (3×3) matrix and is the product of the

TABLE II. Symmetry coordinates of an impurity and its nearest neighbors in the CsCl-structure crystals.

A_{1g}	X_1	0	0	0	$\frac{1}{2\sqrt6}$	$\frac{-1}{2\sqrt6}$	$\frac{-1}{2\sqrt6}$	$\frac{1}{2\sqrt6}$	$\frac{-1}{2\sqrt6}$	$\frac{1}{2\sqrt6}$	$\frac{1}{2\sqrt6}$	$\frac{1}{2\sqrt6}$	$\frac{1}{2\sqrt6}$	$\frac{1}{2\sqrt6}$	$\frac{1}{2\sqrt6}$
A_{1u}	X_2	0	0	0	$\frac{1}{2\sqrt6}$	$\frac{-1}{2\sqrt6}$	$\frac{-1}{2\sqrt6}$	$\frac{-1}{2\sqrt6}$	$\frac{1}{2\sqrt6}$	$\frac{-1}{2\sqrt6}$	$\frac{1}{2\sqrt6}$	$\frac{1}{2\sqrt6}$	$\frac{1}{2\sqrt6}$	$\frac{-1}{2\sqrt6}$	$\frac{-1}{2\sqrt6}$
E_g	X_3	0	0	0	$\frac14$	$\frac14$	0	$\frac14$	$\frac14$	0	$\frac14$	$-\frac14$	0	$\frac14$	$-\frac14$
	Y_3	0	0	0	$1/4\sqrt3$	$-1/4\sqrt3$	$1/2\sqrt3$	$1/4\sqrt3$	$-1/4\sqrt3$	$-1/2\sqrt3$	$1/4\sqrt3$	$1/4\sqrt3$	$-1/2\sqrt3$	$1/4\sqrt3$	$1/4\sqrt3$
E_u	X_4	0	0	0	$\frac14$	0	$\frac14$	$-\frac14$	0	$\frac14$	$\frac14$	0	$-\frac14$	$-\frac14$	0
	Y_4	0	0	0	$1/4\sqrt3$	$1/2\sqrt3$	$-1/4\sqrt3$	$-1/4\sqrt3$	$-1/2\sqrt3$	$-1/4\sqrt3$	$1/4\sqrt3$	$-1/2\sqrt3$	$1/4\sqrt3$	$-1/4\sqrt3$	$1/2\sqrt3$
T_{1g}	X_5	0	0	0	$\frac14$	$\frac14$	0	$\frac14$	$\frac14$	0	$-\frac14$	$\frac14$	0	$-\frac14$	$\frac14$
	Y_5	0	0	0	$\frac14$	0	$\frac14$	$-\frac14$	0	$\frac14$	$-\frac14$	0	$\frac14$	$\frac14$	0
	Z_5	0	0	0	0	$-\frac14$	$\frac14$	0	$\frac14$	$\frac14$	0	$\frac14$	$-\frac14$	0	$-\frac14$
T_{1u}	X_6	1	0	0	0	0	0	0	0	0	0	0	0	0	0
	X_7	0	0	0	$1/2\sqrt2$	0	0	$1/2\sqrt2$	0	0	$1/2\sqrt2$	0	0	$1/2\sqrt2$	0
	X_8	0	0	0	0	$\frac14$	$\frac14$	0	$\frac14$	$-\frac14$	0	$-\frac14$	$-\frac14$	0	$-\frac14$
	Y_6	0	1	0	0	0	0	0	0	0	0	0	0	0	0
	Y_7	0	0	0	0	$1/2\sqrt2$	0	0	$1/2\sqrt2$	0	0	$1/2\sqrt2$	0	0	$1/2\sqrt2$
	Y_8	0	0	0	$\frac14$	0	$-\frac14$	$\frac14$	0	$\frac14$	$-\frac14$	0	$-\frac14$	$-\frac14$	0
	Z_6	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	Z_7	0	0	0	0	0	$1/2\sqrt2$	0	0	$1/2\sqrt2$	0	0	$1/2\sqrt2$	0	0
	Z_8	0	0	0	$\frac14$	$-\frac14$	0	$-\frac14$	$\frac14$	0	$-\frac14$	$-\frac14$	0	$\frac14$	$\frac14$
T_{2g}	X_9	0	0	0	$1/2\sqrt2$	0	0	$-1/2\sqrt2$	0	0	$1/2\sqrt2$	0	0	$-1/2\sqrt2$	0
	X_{10}	0	0	0	0	$\frac14$	$+\frac14$	0	$-\frac14$	$+\frac14$	0	$-\frac14$	$-\frac14$	0	$\frac14$
	Y_9	0	0	0	0	$1/2\sqrt2$	0	0	$-1/2\sqrt2$	0	0	$1/2\sqrt2$	0	0	$-1/2\sqrt2$
	Y_{10}	0	0	0	$-\frac14$	0	$\frac14$	$\frac14$	0	$\frac14$	$\frac14$	0	$\frac14$	$-\frac14$	0
	Z_9	0	0	0	0	0	$1/2\sqrt2$	0	0	$-1/2\sqrt2$	0	0	$1/2\sqrt2$	0	0
	Z_{10}	0	0	0	$\frac14$	$-\frac14$	0	$\frac14$	$-\frac14$	0	$-\frac14$	$-\frac14$	0	$-\frac14$	$-\frac14$
T_{2u}	X_{11}	0	0	0	$\frac14$	$\frac14$	0	$-\frac14$	$-\frac14$	0	$-\frac14$	$\frac14$	0	$\frac14$	$-\frac14$
	Y_{11}	0	0	0	$\frac14$	0	$\frac14$	$\frac14$	0	$-\frac14$	$-\frac14$	0	$\frac14$	$-\frac14$	0
	Z_{11}	0	0	0	0	$-\frac14$	$\frac14$	0	$-\frac14$	$-\frac14$	0	$+\frac14$	$-\frac14$	0	$\frac14$

(3×3) blocks along the diagonals of $\underline{G}$ and $\underline{\Delta}$. If the impurity is at the negative-ion site, the normalization condition is

$$\sum_{\alpha l\kappa} M_\kappa |\chi_\alpha(l\kappa|f)|^2 - \epsilon_- M_- |\vec{\chi}(I|f)|^2 = 1 , \qquad (16)$$

where $\epsilon_- = (M_- - M'_-)/M_-$ and $\vec{\chi}(I|f)$ is the amplitude of the impurity ion of mass M'_-. In matrix form Eq. (16) becomes

$$(\underline{\tilde\chi}\,\underline{\tilde\Delta})\underline{G}'\underline{\Delta}\,\underline{\chi} - \epsilon_- M_- |\vec{\chi}(I,f)|^2 = 1 , \qquad (17)$$

where

$$G'_{\alpha\beta}\!\left(\!{ll' \atop \kappa\kappa'};\omega_f\right) = \frac{1}{N}\sum_{kj}\frac{e_\alpha(\kappa|{\vec k \atop j})e_\beta^*(\kappa'|{\vec k \atop j})}{[\omega_f^2 - \omega_j^2(\vec k)]^2}\frac{1}{(M_\kappa M_{\kappa'})^{1/2}}$$

$$\times \exp\!\left\{2\pi i\vec k\cdot\left[\vec r\!\left({l \atop \kappa}\right) - \vec r\!\left({l' \atop \kappa'}\right)\right]\right\}. \qquad (18)$$

Equation (17) can be rewritten as

$$\underline{\tilde\chi}\,\underline{\tilde S}\,\underline{S}\,\underline{\tilde\Delta}\,\underline{\tilde S}\,\underline{S}\,\underline{G}'\underline{\tilde S}\,\underline{S}\,\underline{\Delta}\,\underline{\tilde S}\,\underline{S}\,\underline{\chi} - \epsilon_- M_-|\vec\chi(I|f)|^2 = 1 \qquad (19)$$

or

$$(a\ b\ c)\,\mathcal{B}\!\begin{pmatrix} a \\ b \\ c \end{pmatrix} - \epsilon_- M_- a^2 = 1 , \qquad (20)$$

$$
\begin{bmatrix}
-\frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & \frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & \frac{1}{2\sqrt6} & \frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & \frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} \\[4pt]
\frac{1}{2\sqrt6} & \frac{1}{2\sqrt6} & \frac{1}{2\sqrt6} & \frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & \frac{1}{2\sqrt6} & \frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} & \frac{1}{2\sqrt6} & -\frac{1}{2\sqrt6} \\[4pt]
0 & -\frac14 & \frac14 & 0 & -\frac14 & \frac14 & 0 & -\frac14 & -\frac14 & 0 & -\frac14 & -\frac14 & 0 \\[4pt]
\frac{1}{2\sqrt3} & -\frac{1}{4\sqrt3} & -\frac{1}{4\sqrt3} & \frac{1}{2\sqrt3} & -\frac{1}{4\sqrt3} & -\frac{1}{4\sqrt3} & -\frac{1}{2\sqrt3} & -\frac{1}{4\sqrt3} & \frac{1}{4\sqrt3} & -\frac{1}{2\sqrt3} & -\frac{1}{4\sqrt3} & \frac{1}{4\sqrt3} & \frac{1}{2\sqrt3} \\[4pt]
-\frac14 & \frac14 & 0 & -\frac14 & -\frac14 & 0 & -\frac14 & \frac14 & 0 & \frac14 & -\frac14 & 0 & \frac14 \\[4pt]
\frac{1}{4\sqrt3} & \frac{1}{4\sqrt3} & -\frac{1}{2\sqrt3} & \frac{1}{4\sqrt3} & -\frac{1}{4\sqrt3} & \frac{1}{2\sqrt3} & \frac{1}{4\sqrt3} & \frac{1}{4\sqrt3} & \frac{1}{2\sqrt3} & -\frac{1}{4\sqrt3} & -\frac{1}{4\sqrt3} & -\frac{1}{2\sqrt3} & -\frac{1}{4\sqrt3} \\[4pt]
0 & \frac14 & -\frac14 & 0 & \frac14 & -\frac14 & 0 & -\frac14 & -\frac14 & 0 & -\frac14 & -\frac14 & 0 \\[4pt]
\frac14 & \frac14 & 0 & -\frac14 & -\frac14 & 0 & -\frac14 & -\frac14 & 0 & -\frac14 & \frac14 & 0 & -\frac14 \\[4pt]
-\frac14 & 0 & -\frac14 & \frac14 & 0 & \frac14 & \frac14 & 0 & \frac14 & -\frac14 & 0 & -\frac14 & -\frac14 \\[4pt]
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\[4pt]
0 & \frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 \\[4pt]
\frac14 & 0 & -\frac14 & -\frac14 & 0 & -\frac14 & \frac14 & 0 & \frac14 & \frac14 & 0 & \frac14 & -\frac14 \\[4pt]
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\[4pt]
0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 \\[4pt]
+\frac14 & -\frac14 & 0 & -\frac14 & -\frac14 & 0 & \frac14 & \frac14 & 0 & -\frac14 & \frac14 & 0 & \frac14 \\[4pt]
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\[4pt]
\frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} \\[4pt]
0 & -\frac14 & -\frac14 & 0 & \frac14 & \frac14 & 0 & \frac14 & -\frac14 & 0 & -\frac14 & \frac14 & 0 \\[4pt]
0 & -\frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 & -\frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 \\[4pt]
-\frac14 & 0 & \frac14 & +\frac14 & 0 & -\frac14 & +\frac14 & 0 & -\frac14 & -\frac14 & 0 & \frac14 & -\frac14 \\[4pt]
0 & 0 & -\frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 & -\frac{1}{2\sqrt2} & 0 & 0 & -\frac{1}{2\sqrt2} & 0 \\[4pt]
\frac14 & -\frac14 & 0 & -\frac14 & \frac14 & 0 & -\frac14 & \frac14 & 0 & -\frac14 & -\frac14 & 0 & -\frac14 \\[4pt]
-\frac{1}{2\sqrt2} & 0 & 0 & -\frac{1}{2\sqrt2} & 0 & 0 & \frac{1}{2\sqrt2} & 0 & 0 & -\frac{1}{2\sqrt2} & 0 & 0 & -\frac{1}{2\sqrt2} \\[4pt]
0 & \frac14 & \frac14 & 0 & \frac14 & \frac14 & 0 & -\frac14 & \frac14 & 0 & -\frac14 & \frac14 & 0 \\[4pt]
0 & -\frac14 & \frac14 & 0 & \frac14 & -\frac14 & 0 & \frac14 & \frac14 & 0 & -\frac14 & -\frac14 & 0 \\[4pt]
-\frac14 & -\frac14 & 0 & \frac14 & -\frac14 & 0 & -\frac14 & \frac14 & 0 & \frac14 & \frac14 & 0 & -\frac14 \\[4pt]
\frac14 & 0 & \frac14 & -\frac14 & 0 & \frac14 & \frac14 & 0 & -\frac14 & \frac14 & 0 & -\frac14 & -\frac14
\end{bmatrix}
\begin{bmatrix}
U_x^I \\ U_y^I \\ U_z^I \\ U_x^1 \\ U_y^1 \\ U_z^1 \\ U_x^2 \\ U_y^2 \\ U_z^2 \\ U_x^3 \\ U_y^3 \\ U_z^3 \\ U_x^4 \\ U_y^4 \\ U_z^4 \\ U_x^5 \\ U_y^5 \\ U_z^5 \\ U_x^6 \\ U_y^6 \\ U_z^6 \\ U_x^7 \\ U_y^7 \\ U_z^7 \\ U_x^8 \\ U_y^8 \\ U_z^8
\end{bmatrix}
$$

where $\mathfrak{G}$ is a (3×3) matrix.

Equations (15) and (20) can be solved for a, b, and c in terms of the eigenvectors and eigenfrequencies of the unperturbed crystal and the perturbation Δ. Thus we can solve for A from Eq. (11) and hence the absorption coefficient $\alpha(\omega_f)$ from Eq. (1).

In conclusion, we have developed a method to calculate the infrared absorption in a diatomic cubic crystal due to a very low concentration of impurities when the impurity involves changes in the mass and short-range force constants. In this method one sees clearly the various physical processes involved in this problem, which is usually not possible in most of the Green's-function formalisms used in this field.

TABLE III. Amplitudes of the impurity ion (I) and its six nearest neighbors $(1, 2, \ldots, 6)$ in a crystal of NaCl structure for a T_{1u} mode.

$l\kappa$ \ α	$\chi_\alpha(l\kappa \mid T_{1u})$		
	x	y	z
I	a	0	0
1	$b/\sqrt2$	0	0
2	$\frac12 c$	0	0
3	$\frac12 c$	0	0
4	$b/\sqrt2$	0	0
5	$\frac12 c$	0	0
6	$\frac12 c$	0	0

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