*Research sponsored by Air Force Office of Scientific Research, Office of Aerospace Research, USAF, under Grant No. AFOSR 70-1936. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon.

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Dielectric Susceptibility and Infrared Absorption in Cubic Crystals Containing Substitutional Impurities

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Using thermodynamic double-time Green's-function methods and Kubo formalism, theoretical expressions are obtained for the dielectric susceptibility and infrared-absorption coefficient of a Bravais crystal containing randomly distributed substitutional impurities. Mass changes as well as force-constant changes between the impurity atoms and the host-lattice atoms are explicitly included. It is found that these expressions contain some nondiagonal contributions in addition to the usual diagonal contributions. For phonons of small half-width, the linear absorption coefficient is proportional to the half-width, which in turn varies as the square of the sum of the mass and force-constant changes. Contributions due to localized modes are also obtained.

I. INTRODUCTION

It is well known that the introduction of defects into crystals greatly modifies their optical and dynamical properties.[1,2] Such modifications are largest in the vicinity of the defects. Comprehensive literature[3] is available discussing the dynamics of crystal lattices with defects, both theoretically and experimentally. The Mössbauer effect from the impurity has been used to investigate the mean-square amplitude and energy of the defect atom.[4] However, these properties are not very sensitive to details of the spectrum because they involve averages over all the perturbed modes. Another method, based on the measurement of optical absorption by one-phonon processes, appears to present a much simpler method to study the motion of defects because of the direct link between the absorption line shape and the structure of the phonon spectrum of the impure crystal. Such impurity absorption is known to occur in covalent crystals such as diamond where, by symmetry, there are no one-phonon transitions in a perfect crystal.[5]

In recent years, there has been considerable interest in the study of the optical absorption of crystals with impurities in the far-infrared region using various models and approximations.[6–10] Most of the theoretical work has been restricted to the treatment of the so-called mass-defect approximation in which the defect consists of one substitutional atom whose mass is different from that of the host atoms. This difference characterizes the perturbation due to the impurity. The force constants linking the impurity to its neighbors remain unchanged. This seems somewhat unreasonable since in actual practice introduction of defects modifies the force constants between the impurity atom and the host atoms. Recently, some results[11–17] have been obtained on the nature of perturbed modes in the vicinity of defects due to force-constant changes between the impurities and their nearest neighbors for low impurity concentration. It would be of interest to investigate the infrared absorption in a crystal containing substitutional impurities, taking into account the change in force constants associated with the impurities in addition to the change in mass.

The object of this paper is to investigate the behavior of a disordered crystal containing substitutional impurities under external radiation. Using the method of thermodynamic double-time Green's functions[18] and Kubo formalism,[19] expressions are obtained for the dielectric susceptibility and the linear absorption coefficient for a harmonic Bravais crystal containing randomly distributed substitutional impurities in the low-concentration limit. Changes in mass and force constants due to the introduction of the impurities in the host crystal are taken into account explicitly. The absorption due to localized modes is also discussed. This study provides convenient formulas for defect-induced optical absorption. The analysis is based on a harmonic model of the crystal with up to second-order terms in the dipole-moment expansion.

II. GENERAL FORMALISM

The response of a crystal to an external field is conveniently described by the dielectric susceptibility. Using Kubo formalism, the general expression for the dielectric susceptibility tensor $\chi_{\mu\nu}(\omega)$ can be written[18,19]

$$\chi_{\mu\nu}(\omega) = -\lim_{\epsilon\to 0} 2\pi G_{\mu\nu}(\omega + i\epsilon) \quad , \tag{1}$$

where $G_{\mu\nu}(\omega)$ is the Fourier transform of the retarded double-time Green's function defined by[18]

$$G_{\mu\nu}(t-t') = \langle\langle M_\mu(t); M_\nu(t')\rangle\rangle$$
$$= -i\theta(t-t')\langle [M_\mu(t), M_\nu(t')]\rangle \quad . \tag{2}$$

Here $\theta(t)$ is the usual step function and M_μ is the μth component of the crystal dipole-moment operator in the Heisenberg representation. The angular brackets denote the thermal average over the canonical ensemble described by the crystal Hamiltonian, namely,

$$\langle 0\rangle = \mathrm{Tr}(e^{-\beta H}\, 0)/\mathrm{Tr}(e^{-\beta H}) \quad , \tag{3}$$

in which $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the absolute temperature, and H is the Hamiltonian of the system. The dipole moment $\vec{M}$ of the crystal depends on the lattice configuration and may be expanded in a phonon series as[20]

$$M_\mu = \sum_{n\geq 1} \sum_{k_1, k_2, \ldots, k_n} M_\mu(k_1, k_2, \ldots, k_n) A_{k_1} A_{k_2} \cdots A_{k_n} \quad , \tag{4}$$

where $M_\mu\,(k_1, k_2, \ldots, k_n)$ are the Fourier transforms of the expansion coefficients in terms of ionic displacements and $A_k = a_k + a_{-k}{}^\dagger = A_{-k}{}^\dagger$, $a_k{}^\dagger$, and a_k being the creation and annihilation operators of wave vector k. We use one index k for both $\vec{k}j$, where $\vec{k}$ is the wave vector and j is the polarization branch. With the help of Eqs. (2) and (4), Eq. (1) can be written

$$\chi_{\mu\nu}(\omega) = \sum_{n,m\geq 1} \chi_{\mu\nu}^{(n,m)}(\omega) \quad , \tag{5}$$

$$\chi_{\mu\nu}^{(n,m)}(\omega) = -\lim_{\epsilon\to 0} 2\pi \sum_{k_1,\ldots,k_n} \sum_{k'_1,\ldots,k'_m} M_\mu(k_1, \ldots, k_n) \times M_\nu(k'_1, \ldots, k'_m)\, G_{k_1,\ldots,k_n,k'_1,\ldots,k'_m}(\omega + i\epsilon), \tag{6}$$

where $G(\omega)$ is the Fourier transform of the Green's function and is given by

$$G_{k_1,\ldots,k_n,k'_1,\ldots,k'_m}(\omega) = \langle\langle A_{k_1}(t), \ldots, A_{k_n}(t); A_{k'_1}(t'), \ldots, A_{k'_m}(t')\rangle\rangle_\omega \quad . \tag{7}$$

The linear absorption coefficient $\alpha(\omega)$ of the crystal as a function of frequency ω is given by[1]

$$\alpha(\omega) = -\,(4\pi\omega/c)\,\mathrm{Im}\chi_{\mu\nu}(\omega) \,, \tag{8}$$

where Im stands for the imaginary part and c is the velocity of light.

The determination of the dielectric susceptibility and the absorption coefficient thus involves the evaluation of Green's functions for a suitable model of the crystal Hamiltonian. Here we use a harmonic model of the crystal in which the explicit form of the Green's functions can easily be obtained. In the crystal dipole-moment expansion, terms up to second order are considered. Szigeti[21] has pointed out that the interaction of these electric-moment terms gives rise to anharmonic interactions and to the side bands of the main absorption peaks.

III. HAMILTONIAN AND GREEN'S FUNCTIONS

We consider a three-dimensional Bravais harmonic crystal with a total of N atoms such that $N-n$ lattice sites are occupied by atoms of mass M, while n sites are occupied by randomly distributed substitutional impurities each of mass M'. We assume that the force constants between the host atoms and an impurity atom are changed due to the introduction of the impurity. If the impurity concentration (n/N) is quite small, the impurity-impurity interaction may be neglected. The change in force constants between impurity and host atoms may be assumed to be restricted only to nearest neighbors. The Hamiltonian of such a system in the harmonic approximation can be written

$$H=\sum_{l\alpha}^{N}\frac{p_\alpha^2(l)}{2M}+\tfrac{1}{2}\sum_{l\alpha}^{N}\sum_{l'\beta}^{N}\phi_{\alpha\beta}(l,l')u_\alpha(l)u_\beta(l')+\sum_{i\alpha}^{n}\left(\frac{1}{2M'}-\frac{1}{2M}\right)p_\alpha^2(i)+\tfrac{1}{2}\sum_{l\alpha}\sum_{l'\beta}\Delta\phi_{\alpha\beta}(l,l')u_\alpha(l)u_\beta(l')\;, \quad (9)$$

where $u_\alpha(l)$ is the α-Cartesian component of the displacement of the lth atom from its equilibrium position, $p_\alpha(l)$ is the α component of the momentum of the lth atom, M and M' are the masses of the host and impurity atoms, $\phi_{\alpha\beta}(l,l')$ is the component of the harmonic force constants between the atoms l and l', and $\Delta\phi_{\alpha\beta}(l,l')\,[=\phi'_{\alpha\beta}(l,l')-\phi_{\alpha\beta}(l,l')]$ represents the change in the force constant resulting from the introduction of impurities. The primed ϕ's denote the force constants in presence of impurities. The summation over l and l' in the last term is nonvanishing only if either l or l' corresponds to the site of an impurity atom.

We now define the weighted harmonic mean M_0 of the masses of all the atoms by the relation

$$1/M_0=f/M'+(1-f)/M\;, \quad (10)$$

where $f=n/N$. Introducing this equation into Eq. (9) and expressing the momentum and displacement vectors in terms of phonon-creation and phonon-annihilation operators in the usual manner, the Hamiltonian in the second-quantized form can be written

$$H=\sum\nolimits_k \hbar\omega_k(a_k^\dagger a_k+\tfrac{1}{2})+H'\;, \quad (11)$$

where H' is the perturbation part of the Hamiltonian due to the introduction of impurities, and is given by

$$H'=-\hbar\sum_{k_1,k_2}[C(k_1,k_2)B_{k_1}B_{k_2}-D(k_1,k_2)A_{k_1}A_{k_2}] \qquad (\vec{k}_1\neq\vec{k}_2)\;, \quad (12)$$

with

$$B_k=a_k-a_{-k}^\dagger=-B_{-k}^\dagger\;,$$

$$C(k_1,k_2)=\frac{1}{2\mu}\frac{M_0}{N}(\omega_{k_1}\omega_{k_2})^{1/2}\vec{e}(k_1)\cdot\vec{e}(k_2)\times\left(\sum_{l}^{N}e^{i(\vec{k}_1+\vec{k}_2)\cdot\vec{R}(l)}-\sum_{i}^{n}e^{i(\vec{k}_1+\vec{k}_1)\cdot\vec{R}(i)}\right), \quad (13a)$$

and

$$D(k_1,k_2)=\frac{1}{4N}\sum_{l\alpha}\sum_{l'\beta}\frac{\Delta\phi_{\alpha\beta}(l,l')}{M_0(\omega_{k_1}\omega_{k_2})^{1/2}}e_\alpha(k_1)e_\beta(k_2)\times e^{i[\vec{k}_1\cdot\vec{R}(l)+\vec{k}_2\cdot\vec{R}(l')]}\;. \quad (13b)$$

Here ω_k is the angular frequency of the normal mode of wave vector k, $\vec{e}(k)$ is the polarization vector, $\vec{R}(l)$ is the equilibrium position vector of the lth atom, and $\mu=MM'/(M'-M)$. Using the relation[2]

$$\Delta\phi_{\alpha\beta}(l,l)=-\sum_{l'}{}'\Delta\phi_{\alpha\beta}(l,l')\;, \quad (13c)$$

where the prime on the sum denotes that the term with $l=l'$ is excluded, $D(k_1,k_2)$ can be written

$$D(k_1,k_2)=\frac{1}{4}\sum_{\alpha\beta}\frac{1}{M_0}\frac{e_\alpha(k_1)e_\beta(k_2)}{(\omega_{k_1}\omega_{k_2})^{1/2}}\sum_{ll'}{}'\frac{1}{N}\Delta\phi_{\alpha\beta}(l,l')\times e^{i(\vec{k}_1+\vec{k}_2)\cdot\vec{R}(l)}(e^{i\vec{k}_2\cdot[\vec{R}(l)-\vec{R}(l')]}-1), \quad (13d)$$

where, as mentioned earlier, the lattice points l and l' refer to the impurity and its nearest neighbors.

To evaluate the one-particle Green's function

$$G_{kk'}(t-t')=\langle\langle A_k(t);A_{k'}^\dagger(t')\rangle\rangle \quad (14)$$

appearing in Eq. (6), we introduce the Green's function

$$F_{kk'}(t-t')=\langle\langle B_k(t);A_{k'}^\dagger(t')\rangle\rangle\;. \quad (15)$$

Differentiating these Green's functions twice with respect to the time argument t and Fourier transforming the result, $G_{kk'}(\omega)$ is found to be

$$(\omega^2-\omega_k^2)G_{kk'}(\omega)=\omega_k\delta_{kk'}/\pi+(4/\pi)C(-k,k')+(\omega_k/\pi)\langle\langle L_k(t);A_{k'}^\dagger(t')\rangle\rangle_\omega\;, \quad (16)$$

where

$$L_k(t)=4\pi\sum_{k_1}\left(D(-k,k_1)+(\omega_{k_1}/\omega_k)C(-k,k_1)+(4/\omega_k)\sum_{k_2}C(-k,k_2)D(-k_2,k_1)\right)A_{k_1}\;. \quad (17)$$

Considering the equation of motion for the Green's function that appears on the right-hand side of Eq. (16) with respect to the time argument t' and substituting the resulting expression into Eq. (16), the Green's function $G_{kk'}(\omega)$ can be written in the form of Dyson's equation:

$$G_{kk'}(\omega)=\delta_{kk'}G^0_{kk}(\omega)+G^0_{kk}(\omega)\tilde{P}(k,k',\omega)G^0_{kk'}(\omega)+4g_{kk}(\omega)C(-k,k')$$
$$=\delta_{kk'}G^0_{kk}(\omega)+G^0_{kk}(\omega)\,\Pi(k,k',\omega)G_{kk'}(\omega)+4g_{kk}(\omega)C(-k,k')\,,\tag{18}$$

where

$$G^0_{kk}(\omega)=\frac{\omega_k}{\pi(\omega^2-\omega_k^2)}\,,\qquad g^0_{kk}(\omega)=\frac{1}{\pi(\omega^2-\omega_k^2)}\,,$$

and the polarization operator $\Pi\,(k,k',\omega)$ is given by

$$\Pi\,(k,k',\omega)=\tilde{P}(k,k',\omega)[1+G^0_{k'k'}(\omega)\tilde{P}(k,k',\omega)]^{-1}\,,\tag{19}$$

with

$$\tilde{P}(k,k',\omega)=\tfrac{1}{2}\{\langle[L_k(t),\ B^\dagger_{k'}(t')]\rangle+(\omega/\omega_k)\times\langle[L_k(t),\ A^\dagger_{k'}(t')]\rangle+(4/\omega_k)\textstyle\sum_{k_1}C(k,\,-k_1)\times\langle[L_k(t),\ B^\dagger_{k_1}(t')]\rangle\}_{t=t'}+\tfrac{1}{2}\langle\langle L_k(t);\ L^\dagger_{k'}(t')\rangle\rangle\,.\tag{20}$$

If the frequencies ω are far from the zeros of the denominator in Eq. (19), one may expand the right-hand side in a power series in $\tilde{P}(k,k',\omega)$. Retaining only the first term, i.e., $\Pi(k,k',\omega)\simeq\tilde{P}(k,k',\omega)$, Eq. (18) can be written

$$G_{kk'}(\omega)=\frac{\omega_k[\delta_{kk'}+(4/\omega_k)C(-k,k')]}{\pi[\omega^2-\tilde{\omega}_k^2-2\omega_kP(k,k',\omega)]}\,,\tag{21}$$

where $\tilde{\omega}_k$ is the renormalized frequency of the mode k in the lowest-order approximation of the perturbation theory and is given by

$$\tilde{\omega}_k^2=\omega_k^2+(\omega_k/2\pi)\{\langle[L_k(t),\ B^\dagger_{k'}(t')]\rangle^0+(\omega/\omega_k)\langle[L_k(t),\ A^\dagger_{k'}(t')]\rangle^0+(4/\omega_k)\textstyle\sum_{k_1}C(k,\,-k_1)\langle[L_k(t),\ B^\dagger_{k_1}(t')]\rangle^0\}\,,\quad t=t',\quad \omega\simeq\tilde{\omega}_k\tag{22}$$

and

$$P(k,k',\omega)=(1/2\pi)\langle\langle L_k(t);\ L^\dagger_{k'}(t')\rangle\rangle\,.\tag{23}$$

The superscript 0 denotes that in the determination of the occupation numbers $N_k=\langle A^\dagger_kA_k\rangle$, commutation relations are evaluated by means of the zeroth-order Green's function

$$\tilde{G}^0_{kk'}(\omega)=\omega_k\delta_{kk'}/\pi(\omega^2-\tilde{\omega}_k^2)\,.\tag{24}$$

The self-energy operator $P(k,k',\omega)$ can be evaluated in successive approximations, i.e.,

$$P(k,k',\omega)=P_0(k,k',\omega)+P_1(k,k',\omega)+\cdots\,,\tag{25}$$

where the subscripts 0 and 1 indicate that the Green's functions appearing in Eq. (23) must be obtained in the lowest- and first-order approximations, respectively.

In the first-order approximation, the Green's function (21) can be evaluated by replacing P by P_0. The frequency distribution of the corresponding zeroth-order Green's function [Eq. (24)] can be described by the zeroth-order renormalized Hamiltonian

$$H^0_{\text{ren}}=\tfrac{1}{4}\hbar\textstyle\sum_k[(\tilde{\omega}_k^2/\omega_k)A^\dagger_kA_k+\omega_kB^\dagger_kB_k]\,.\tag{26}$$

$P_0(k,k',\omega)$ can easily be evaluated from Eqs. (17) and (23) via the Hamiltonian (26). For small $\epsilon(\to+0)$, the Green's function (21) becomes

$$G_{kk'}(\omega+i\epsilon)=\frac{\omega_k\xi_{kk'}}{\pi[\omega^2-\epsilon^2_{kk'}(\omega)+2i\omega_k\Gamma_{kk'}(\omega)]}\,,\tag{27}$$

where

$$\epsilon^2_{kk'}(\omega)=\omega_k^2+2\omega_k\Delta_{kk'}(\omega)\tag{28a}$$

and

$$\xi_{kk'}=\delta_{kk'}+(4/\omega_k)C(-k,k')\,.\tag{28b}$$

Here $\Delta_{kk'}(\omega)$ and $\Gamma_{kk'}(\omega)$ are the shift and width of the response function and are given by

$$\Delta_{kk'}(\omega)=16\mathcal{P}\textstyle\sum_{k_1}\alpha(-k,k_1)\alpha^\dagger(k',k_1)\,\omega_{k_1}/(\omega^2-\tilde{\omega}^2_{k_1})\,,\tag{29}$$

and

$$\Gamma_{kk'}(\omega)=8\pi\textstyle\sum_{k_1}\alpha(-k,k_1)\alpha^\dagger(k',k_1)(\omega_{k_1}/\tilde{\omega}_{k_1})\times[\delta(\omega-\tilde{\omega}_{k_1})-\delta(\omega+\tilde{\omega}_{k_1})]\,,\tag{30}$$

where

$$\alpha(k_1,k_2)=4[D(k_1,k_2)+(\omega_{k_2}/\omega_{k_1})C(k_1,k_2)+(4/\omega_k)\textstyle\sum_{k_2'}C(k_1,k_2')D(-k_2',k_2)]\tag{31}$$

and $\mathcal{P}$ denotes the principal part.

To evaluate the two-particle Green's function

$$\Gamma^{(1)}_{k_1k_2k_1'k_2'}(t-t')=\langle\langle A_{k_1}(t)A_{k_2}(t);\ A^\dagger_{k_1'}(t')A^\dagger_{k_2'}(t')\rangle\rangle\,,\tag{32a}$$

we introduce the following Green's functions:

$$\Gamma^{(2)}_{k_1k_2k_1'k_2'}(t-t')=\langle\langle B_{k_1}(t)A_{k_2}(t);\ A^\dagger_{k_1'}(t')A^\dagger_{k_2'}(t')\rangle\rangle\,,\tag{32b}$$

$$\Gamma^{(3)}_{k_1k_2k_1'k_2'}(t-t')=\langle\langle A_{k_1}(t)B_{k_2}(t);A^\dagger_{k_1'}(t')A^\dagger_{k_2'}(t')\rangle\rangle\,,\tag{32c}$$

and

$$\Gamma^{(4)}_{k_1k_2k_1'k_2'}(t-t')=\langle\langle B_{k_1}(t)B_{k_2}(t);\ A^\dagger_{k_1'}(t')A^\dagger_{k_2'}(t')\rangle\rangle\,.\tag{32d}$$

Writing their equations of motion with the help of the zeroth-order renormalized Hamiltonian (26) and solving for $\Gamma^{(1)}$, we get

$$\Gamma^{(1)}_{k_1k_2k_1'k_2'}(\omega)=\frac{1}{2\pi}\sum_{\pm}(N_{k_2}\pm N_{k_1})\frac{\omega_{k1}\omega_{k2}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}}\times\frac{\tilde{\omega}_{k1}\pm\tilde{\omega}_{k2}}{\omega^2-(\tilde{\omega}_{k_1}\pm\tilde{\omega}_{k2})^2}(\delta_{k_1k_1'}\delta_{k_2k_2'}+\delta_{k_1k_2'}\delta_{k_2k_1'})\,,\tag{33}$$

where

$$N_k = \langle A_k^\dagger A_k \rangle \, \omega / \tilde{\omega}_k \; .$$

Here we have evaluated the Green's functions (14) and (32a) in the lowest-order approximation of the polarization operator. If the imaginary part of $P_0(k, k', \omega)$ in Eq. (27) becomes zero for some $\epsilon_k (\neq \tilde{\omega}_k)$, its value should be evaluated in first-order approximation, i.e., by considering higher-order terms in Eq. (25). It can be shown that the values of these Green's functions are still given by Eqs. (27) and (33) except for the replacement of $\tilde{\omega}_k$ by ϵ_k.

IV. DIELECTRIC SUSCEPTIBILITY

Equations (5) and (6) show that the total dielectric susceptibility of a harmonic crystal containing randomly distributed substitutional impurities with nonlinear dipole moments up to second order is determined by one- and two-particle Green's functions. In the formalism based on the successive approximations, using the renormalized Hamiltonian [Eq. (26)], contributions due to the Green's functions with an odd number of operators will be zero. The dielectric susceptibility (5) can therefore be written

$$\chi_{\mu\nu}(\omega) = \chi_{\mu\nu}^{(1,1)}(\omega) + \chi_{\mu\nu}^{(2,2)}(\omega) \; , \tag{34}$$

where $\chi_{\mu\nu}^{(1,1)}(\omega)$, with the help of Eq. (27), is given by

$$\chi_{\mu\nu}^{(1,1)}(\omega) = -2\pi \sum_{k_1,k_1'} \frac{M_\mu(k_1) M_\nu(k_1') \xi_{k_1 k_1'}}{\omega^2 - \epsilon_{k_1 k_1'}^2(\omega) + 2 i \omega_k \Gamma_{k_1 k_1'}(\omega)} \; . \tag{35}$$

Similarly, substituting the value of the two-particle Green's function from Eq. (33), the expression for $\chi_{\mu\nu}^{(2,2)}(\omega)$ is given by

$$\chi_{\mu\nu}^{(2,2)}(\omega) = -\lim_{\epsilon \to 0} 2 \sum_{k_1,k_1'} M_\mu(k_1, k_1') M_\nu(-k_1, -k_1') \times \frac{\omega_{k_1}\omega_{k_1'}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_1'}} \sum_{\pm} (N_{k_1'} \pm N_{k_1}) \frac{\tilde{\omega}_{k_1} \pm \tilde{\omega}_{k_1'}}{(\omega + i\epsilon)^2 - (\tilde{\omega}_{k_1} \pm \tilde{\omega}_{k_1'})^2} \; . \tag{36}$$

Equation (36) gives the contribution to the dielectric susceptibility due to the nonlinear second-order dipole moment. For a perfect lattice in which $C(k_1, k_1')$ and $D(k_1, k_1')$ vanish, expressions (35) and (36) become equivalent to those obtained by Wehner[22] and Bilz.[23]

V. ABSORPTION COEFFICIENT

The linear absorption coefficient (8) will now be evaluated for one- and two-phonon processes, i.e., considering first- and second-order dipole-moment terms in Eq. (4). Substituting the imaginary parts of the dielectric susceptibilities from Eqs. (35) and (36) into Eq. (8), we obtain

$$\alpha(\omega) = \frac{4\pi\omega}{c} \left(\sum_{k_1,k_1'} \frac{4\pi\omega_{k_1}^2 M_\mu(k_1) M_\mu(k_1') \xi_{k_1 k_1'} \Gamma_{k_1 k_1'}(\omega)}{[\omega^2 - \epsilon_{k_1 k_2'}^2(\omega)]^2 + 4\omega_{k_1}^2 \Gamma_{k_1 k_1'}^2(\omega)} \right) + \pi \sum_{k_1,k_1'} |M_\mu(k_1, k_1')|^2 \frac{\omega_{k_1}\omega_{k_1'}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_1'}} \sum_{\pm} (N_{k_1'} \pm N_{k_1}) \times [\delta(\omega - \omega_{k_1} \mp \omega_{k_1'}) - \delta(\omega + \omega_{k_1} \pm \omega_{k_1'})] \; . \tag{37}$$

In the above expression, contributions due to localized modes which exist outside the band frequencies of the crystal have not been included. In the event of there being localized modes, their contribution to the linear absorption coefficient $\alpha(\omega)$ can be calculated by finding the imaginary part of the Green's function (21) for $\omega > \omega_{\max}$ ($\omega_{\max}$ is the maximum frequency of the band modes). In the lowest-order approximation, Eq. (21) can in this case be written

$$G_{kk'}(\omega) = \frac{\xi_{kk'} \tilde{G}_{kk}^0(\omega)}{1 - 2\tilde{G}_{kk}^0(\omega) P_0(k, k', \omega)} \; . \tag{38}$$

We are interested in the imaginary part of the Green's function (38). Near resonance, where the denominator of Eq. (38) is zero, we may expand the denominator as

$$G_{kk'}(\omega) = \frac{-\xi_{kk'} \tilde{G}_{kk}^0(\omega)}{\omega - \omega_l} \times \left(\frac{d}{d\omega} [2\tilde{G}_{kk}^0(\omega) P_0(k, k', \omega)] \right)_{\omega = \omega_l} \; . \tag{39}$$

The imaginary part can be evaluated by replacing $\omega \to \omega + i\epsilon$ and letting ϵ tend to zero. Using the relation

$$\frac{1}{x \pm i\epsilon} = \mathcal{P} \frac{1}{x} \mp i\pi\delta(x) \; , \tag{40}$$

we obtain

$$\mathrm{Im} G_{kk'}(\omega) = \pi \xi_{kk'} \tilde{G}_{kk}^0(\omega_l) \delta(\omega - \omega_l) \Big/ 2 \left(\frac{d}{d\omega} [\tilde{G}_{kk}^0(\omega) P_0(k, k', \omega)] \right)_{\omega = \omega_l} \; , \tag{41}$$

where ω_l is the localized mode frequency. Therefore, we must add to Eq. (37) the term

$$\alpha_{1oc}(\omega) = \frac{2\pi^2 \omega_l}{c} \sum_{k_1,k_1'} M_\mu(k_1) M_\mu(k_1') \xi_{k_1 k_1'} \tilde{G}_{kk}^0(\omega_l) \Big/ \left(\frac{d}{d\omega} [\tilde{G}_{k_1 k_1}^0(\omega) P_0(k_1, k_1', \omega)] \right)_{\omega = \omega_l} \delta(\omega - \omega_l) \; , \tag{42}$$

which gives a δ-function line shape. This will be broadened due to anharmonic effects. It may be pointed out that in obtaining Eq. (42) we have considered the localized modes for the one-phonon Green's function only for simplicity.

VI. DISCUSSION

In the present paper, we have derived expressions for infrared absorption due to randomly distributed substitutional impurities in a Bravais crystal considering the change in the force-constants. The expression (37) shows that the absorption can be expressed as the sum of two terms, diagonal and nondiagonal contributions. The diagonal contribution $(\vec{k}_1=\vec{k}_1')$ arises from force-constant changes, while the nondiagonal contribution $(\vec{k}_1\neq\vec{k}_1')$ depends upon mass and force-constant changes. $\Gamma_{k_1k_1'}(\omega)$, which measures the width of the response function, depends upon terms proportional to the square of the sum of the mass and force-constant changes. In the harmonic approximation, $\Gamma_{k_1k_1'}(\omega)$ is independent of temperature. Using some suitable lattice-dynamical model, its magnitude can be evaluated in the high- and low-frequency regions. In the limiting case when $\Gamma_{k_1k_1'}(\omega)$ is small, one can neglect the second term in the denominator of the first term of Eq. (37), and the linear absorption coefficient becomes proportional to the width and hence inversely proportional to the phonon lifetime. The second term in Eq. (37) gives the contribution to the absorption due to higher-order terms in the dipole moment. This term gives the dominant contribution to the absorption in covalent crystals where the first-order dipole moment (with no charged impurities) is zero. It describes the temperature dependence of the absorption coefficient, and the high-temperature limit is proportional to T. To first order in the difference of the impurity force constant from those of a perfect lattice, the third term in Eq. (31) can be neglected. For small values of $(M'-M)$ and $\Delta\phi_{\alpha\beta}$ Eq. (31) shows that the mass change and force-constant change make reinforcing or canceling contributions to the absorption depending on whether they are of equal or of opposite signs. Krumhansl and Mathew[24] have shown that in the case of a linear atomic chain, atomic-mass and force-constant changes cause reinforcing or canceling contributions to the relaxation rate according to whether they are of equal or opposite signs, respectively. Recently, we[25] have also developed a similar formalism for the infrared-absorption coefficient in an anharmonic crystal considering dipole moments up to second order. It is found that the absorption coefficient due to crystal anharmonicity is proportional to T^2 in the high-temperature range, which agrees with experimental results.[26,27] It should be noted that the values of the one- and two-particle Green's functions have been obtained here in successive approximations. This is expected to be applicable for low impurity concentration.

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