PHYSICAL REVIEW B VOLUME 12, NUMBER 2 15 JULY 1975

Theory of multiphonon absorption in crystals: The wings of internal vibrational modes of molecular impurities

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(Received 13 January 1975)

The correlation-function approach of Bendow, Ying, and Yukon is applied to obtain the multiphonon absorption in the wings of internal vibrational modes of impurities in ionic host crystals. Expansion of the interaction potential in powers of displacements is avoided; we thus obtain expressions containing various classes of phonon processes summed to infinite order. Simplified results for the absorption are obtained by averaging over impurity sites, and by utilizing an Einstein model for the lattice. The results imply that the shape of the multiphonon wing is determined largely by the host-lattice density of states, and that in typical instances the spectrum will display an exponential-like frequency dependence similar to the intrinsic case. The rate of fall off is determined primarily by the range of the impurity-host interaction potential. Explicit results are obtained for a model of a substitutional point impurity in a diatomic host, and applied to the case of OH$^-$ in KCl.

I. INTRODUCTION

A variety of papers have recently investigated intrinsic multiphonon absorption far above the reststrahl in pure crystals. These include both theoretical[1-7] and experimental[8-10] studies of the frequency and temperature dependence of multiphonon absorption. However, extrinsic rather than intrinsic absorption appears to be dominant throughout significant portions of the transparent regime of many state-of-the-art crystals of interest for ir applications.[11] This is evidenced by observed absorption coefficients α which exceed theoretical predictions, often by many orders of magnitude,[12] and by considerable structure which deviates from intrinsic behavior.[13] For ionic crystals, the internal vibrational modes of molecular impurities are an important source of absorption in the ir. For example, contributions to absorption in the mid-ir from impurities such as CO_3^{--}, OH^-, HCO_3^-, ClO_3^-, and NO_2^- in host crystals such as KCl have been investigated extensively.[14] The purpose of the present work is to analyze theoretically the effect of internal vibrational modes of a low concentration of molecular impurities on the residual absorption in the transparent regime of ionic crystals. Our primary interest here will be the high-energy wing of the absorption, which lies many host phonons in frequency above the peak of the impurity-mode absorption. A preliminary report of aspects of the present work has been given previously.[15]

We will adopt the correlation-function approach of Bendow *et al.*,[16] applied previously to intrinsic multiphonon absorption, to treat absorption in the impurity–host-crystal system. Attention will be restricted to absorption due to just linear moments, a procedure which has generally led to good agreement with experiment for intrinsic spectra in ionic crystals. Moreover, we assume a random distribution of noninteracting impurities, and perform averages over impurities at appropriate stages in the development. Such approximations are designed to simplify the calculations, in what otherwise threatens to become an overly complicated problem.

The plan of this paper is as follows: The formal theory is presented in Sec. II, and an expression for α is derived in terms of Green's functions (GF) for the effective multiphonon interaction potential. Employing the harmonic approximation for these GF's, we obtain a simplified result for α in Sec. III. In Sec. IV we calculate the absorption in the high-frequency wing of the impurity mode, within an Einstein model for the host phonons. Various implications of the present treatment are discussed in Sec. V.

II. FORMAL THEORY

We take for the Hamiltonian of the lattice-impurity system

$$
\begin{aligned}
&H = H_0 + V; \quad H_0 = H_0^L + H_0^I; \quad V = V_L + V_I :\\
&H_0^L = \sum_{\vec{k}\alpha} \omega_{\vec{k}\alpha} a^\dagger_{\vec{k}\alpha} a_{\vec{k}\alpha} ,\\
&H_0^I = \sum_{n\beta} \omega_\beta c^\dagger_{n\beta} c_{n\beta} ,\\
&V_L = \sum_{lsl's'} v_L(\vec{r}_{ls} - \vec{r}_{l's'}) - V_L^H ,\\
&V_I = \sum_{lsnr} v_I(\vec{r}_{ls} - \vec{R}_{nr}) .
\end{aligned}
\tag{2.1}
$$

H_0^L and H_0^I are the unperturbed host-lattice and impurity-mode Hamiltonians, V_L is the host-lattice anharmonicity potential, and V_I is the impurity-host-lattice interaction potential. We omit the internal anharmonicity of the impurity, which is responsible principally for absorption at harmonics of the internal modes, a situation which we will not be concerned with here. In Eq. (2.1) $\vec{r}_{ls}$ and $\vec{R}_{nr}$ are the positions of the sth lattice atom in cell l, and of the rth impurity atom at site n, respectively; restrictions of the sums to occupied sites is understood. The a_α's and c_β's are creation-annihilation operators of lattice modes on branch α and of impurity mode β, respectively. V_L^H is the harmonic portion of the lattice interaction energy, which is already contained in H_0^L. The quadratic portion of V_I is taken to be a small perturbation, and thus retained in V. This is motivated by the observation that molecular-impurity modes undergo just small shifts (as low as a few percent) when placed in a host matrix.[17]

We here calculate response to the photon field from linear moments alone. The complex dielectric susceptibility is given by[18]

$$\overleftrightarrow{\chi}(\omega) = (1/\hbar\Omega) G_\omega(\vec{M}(t); \vec{M}(0)) ,$$
$$G_\omega = (2\pi)^{-1} \int dt\, e^{i\omega t} G(t) , \tag{2.2}$$

where G_ω $[G(t)]$ is the retarded GF[16,18] in frequency [time] space for the operators (A, B); Ω is the crystal volume; $\vec{M}(t)$ is the electric moment operator $\vec{M}$ in the Heisenberg representation, with[19]

$$\vec{M} = \sum_{ls} e_s^L \vec{u}_{ls} + \sum_{nr} e_r^I \vec{U}_{nr} , \tag{2.3a}$$

where $\vec{u}_{ls}$ and $\vec{U}_{nr}$ are the displacements from equilibrium of the sth host-lattice atom in cell l and the rth impurity atom at site n. Since we have a dilute concentration of impurity atoms distributed at random, we will utilize the usual normal mode expansion for $\vec{u}_{ls}$; then, taking $N - N_I \approx N$, where N and N_I are the total number of host and impurity atoms, respectively,

$$\vec{M} = (N)^{1/2} \sum_{\alpha s} \vec{m}^L_{\vec{k}\alpha s} A_{\vec{k}\alpha} \delta_{\vec{k}} + \sum_{\beta n r} \vec{m}^I_{\beta r} C_{n\beta} ,$$
$$A_{\vec{k}\alpha} = a_{\vec{k}\alpha} + a^\dagger_{\vec{k}\alpha} ; \quad C_{n\beta} = c_{n\beta} + c^\dagger_{n\beta} , \tag{2.3b}$$
$$\vec{m}^L_{\vec{k}\alpha s} = e_s (2\mu_s \omega_{\vec{k}\alpha})^{-1/2} \vec{f}_{\vec{k}\alpha s} ,$$
$$\vec{m}^I_{\beta r} = e_r (2\mu_r \omega_\beta)^{-1/2} \vec{f}_{\beta r} ,$$

with the e's charges, μ's masses, and f's polarization vectors. Below we will also require the conjugate operators

$$B_{\vec{k}} = a_{\vec{k}\alpha} - a^\dagger_{-\vec{k}\alpha} ; \quad D_{n\beta} = c_{n\beta} - c^\dagger_{n\beta} . \tag{2.4}$$

The absorption coefficient follows for optically isotropic crystals as[20] ($\hbar$, $c = 1$),

$$\alpha(\omega) = \frac{4\pi\omega}{3\eta(\omega)} \operatorname{Im} \sum_\gamma [\overleftrightarrow{\chi}(\omega)]_{\gamma\gamma} , \tag{2.5}$$

where γ indicates Cartesian components and where η is the refractive index, which is slowly varying in the wing regions of interest here.

The calculation of χ proceeds directly from Eqs. (2.2) and (2.3a), whence

$$\overleftrightarrow{\chi}(\omega) = -\frac{1}{\Omega} \Bigg(\sum_{\substack{\alpha s,\\ \alpha' s'}} N \vec{m}^L_{0\alpha s} \vec{m}^L_{0\alpha' s'} g_{11}^{\alpha\alpha'}(00\omega) + \sum_{\substack{\alpha s\\ \beta n r}} (N)^{1/2} \vec{m}^L_{0\alpha s} \vec{m}^I_{\beta r} [g_{12}^{\alpha\beta}(0n\omega) + g_{21}^{\beta\alpha}(n0\omega)] + \sum_{\substack{\beta n r\\ \beta' n' r'}} \vec{m}^I_{\beta r} \vec{m}^I_{\beta' r'} g_{22}^{\beta\beta'}(nn'\omega) \Bigg) , \tag{2.6}$$

where the g's are defined in t space as

$$g_{11}^{\alpha\beta}(\vec{k}\vec{k}'t) = G(A_{\vec{k}\alpha}(t); A_{\vec{k}'\beta}(0)) ,$$
$$g_{12}^{\alpha\beta}(\vec{k}nt) = G(A_{\vec{k}\alpha}(t); C_{n\beta}(0)) ,$$
$$g_{21}^{\alpha\beta}(n\vec{k}t) = G(C_{n\alpha}(t); A_{\vec{k}\beta}(0)) , \tag{2.7}$$
$$g_{22}^{\alpha\beta}(nn't) = G(C_{n\alpha}(t); C_{n\beta}(0)) .$$

g_{11} is the host-lattice GF in the presence of impurities, g_{22} is the impurity-mode GF, and g_{12} and g_{21} are the interacting impurity-lattice GF's. Our objective will be to evaluate these GF's employing approximations appropriate to the multiphonon absorption problem.

Below we will utilize Fourier transforms of the $v(r)$'s defined by[16]

$$v_L(\vec{r}_{ls} - \vec{r}_{l's'}) = \sum_{\vec{q}} (v^L_{\vec{q}})^{ss'} e^{i\vec{q}\cdot(\vec{r}_{ls} - \vec{r}_{l's'})} ,$$
$$(v^L_{\vec{q}})^{ss'} = \tfrac{1}{4} e^{\vec{q}\cdot(\vec{\kappa}_s - \vec{\kappa}_{s'})} (\bar{v}^{ss'}_{\vec{q}} + \bar{v}^{ss'}_{-\vec{q}}) , \tag{2.8}$$
$$\bar{v}^{ss'}_{\vec{q}} = \sum_{\vec{R}_i} e^{-\vec{i}_q \circ \vec{R}_i} v_{ss'}(\vec{R}_i) ,$$

where $\vec{\kappa}_s$ is the position vector of the sth atom in the unit cell; $v^I_{\vec{q}}$ is defined in an obvious analogous fashion.

We now apply the equation-of-motion method[16,21,22] to g_{11}; one obtains directly

$$g_{11}^{\alpha\beta}(\vec{k}\vec{k}'\omega) = g_0(\vec{k}\omega)\, \delta_{\vec{k},-\vec{k}'}\, \delta_{\alpha\beta} + g_0^\alpha(\vec{k}\omega) P_{11}^{\alpha\beta}(\vec{k}\vec{k}'\omega) g_0^\beta(\vec{k}\omega) , \tag{2.9}$$

where g_0 is the unperturbed host-lattice GP, $\delta_{\vec{k},\vec{k}'}$ is zero unless $\vec{k} - \vec{k}'$ is a reciprocal-lattice vector, and

$$g_0^\alpha = \omega_{\vec{k}} / \pi(\omega^2 - \omega^2_{\vec{k}\alpha}) , \quad P_{11}^{\alpha\beta}(\vec{k}\vec{k}'\omega) = 2\pi\{-\tfrac{1}{2}[F^\alpha(\vec{k}), B_{\vec{k}'\beta}] + 2\pi G_\omega(F^\alpha(\vec{k}t); F^\beta(\vec{k}'0))\}, \quad F^\alpha = F_L^\alpha + F_I^\alpha , \tag{2.10}$$
$$F_L^\alpha(\vec{k}) = \tfrac{1}{2}[B_{\vec{k}\alpha}, V_L], \quad F_I^\alpha(\vec{k}) = \tfrac{1}{2}[B_{\vec{k}\alpha}, V_I] .$$

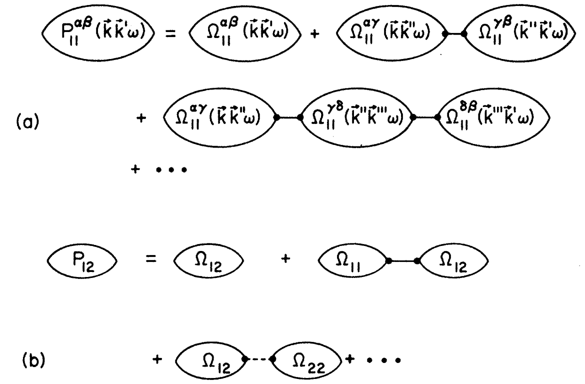

FIG. 1. Relationship between P's and Ω's; the solid horizontal lines represent the noninteracting host GF g_0, and the broken line its impurity counterpart d_0. Some of the indices have been spelled out explicitly in (a), but are omitted in (b).

Since the first term in brackets is real it does not contribute to Imχ in the regimes of interest, and may be henceforth omitted. The F's are the effective interaction potentials responsible for multiphonon absorption. Explicitly,

$$F_L^\alpha(\vec{k}) = 2i \sum_{\vec{q}ll'ss'} e^{i(\vec{q}+\vec{k})\cdot\vec{r}^{\,0}_l - i\vec{q}\cdot\vec{r}^{\,0}_{l'}}(\vec{q}\cdot\vec{f}^{\,\alpha}_{\vec{k}s}) \times (v^L_{\vec{q}})^{ss'}\,(2N\mu_s\omega_{\vec{k}\alpha})^{-1/2} \times[e^{i\vec{q}\cdot(\vec{u}_{ls}-\vec{u}_{l's'})} - i\vec{q}\cdot(\vec{u}_{ls}-\vec{u}_{l's'})]\,, \qquad (2.11)$$

$$F_I^\alpha(\vec{k}) = i \sum_{\vec{q}lnsr} e^{i(\vec{q}+\vec{k})\cdot\vec{r}^{\,0}_l - i\vec{q}\cdot\vec{R}^{0}_n}(\vec{q}\cdot\vec{f}^{\,\alpha}_{\vec{k}s})\,(v^I_{\vec{q}})_{ss'} \times(2N\mu_s\omega_{\vec{k}\alpha})^{-1/2} e^{i\vec{q}\cdot(\vec{u}_{ls}-\vec{U}_{nr})}\;,$$

where $\vec{r}^{\,0}$ and $\vec{R}^0$ are, respectively, the host-lattice and impurity equilibrium positions,

$$\vec{r}_{ls} = \vec{r}^{\,0}_{ls} + \vec{u}_{ls}\,;\quad \vec{R}_n = \vec{R}^0_n + \vec{U}_n\;. \qquad (2.12)$$

For notational simplicity we will omit the superscript "0" in $\vec{r}^{\,0}$ and $\vec{R}^0$ in what follows.

It is useful in certain instances to recast Eq. (2.9) in terms of a function Ω_{11} as

$$g_{11}^{\alpha\beta}(\vec{k}\vec{k}'\omega) = g_0^\alpha(\vec{k}\omega)\,\delta_{\vec{k},-\vec{k}'}\delta_{\alpha\beta} + g_0^\alpha(\vec{k}\omega)\sum_{\vec{k}''\gamma}\Omega_{11}^{\alpha\gamma}(\vec{k}\vec{k}''\omega)\,g_{11}^{\gamma\beta}(\vec{k}''\vec{k}'\omega)\;, \qquad (2.13)$$

where P_{11} is related to Ω_{11} by the graphical representation indicated in Fig. 1(a); Ω_{11} represents all the graphs which cannot be disconnected by breaking a single solid line. In the harmonic approximation, e.g., one has simply $P_{11} = \Omega_{11}$.

A similar analysis to the above yields for g_{22}

$$g_{22}^{\beta\beta'}(nn'\omega) = d_0^\beta(\omega)\,\delta_{nn'}\delta_{\beta\beta'} + d_0^\beta(\omega)\,P_{22}^{\beta\beta'}(nn'\omega)\,d_0^{\beta'}(\omega)\;,$$

$$g_{22}^{\beta\beta'}(nn'\omega) = d_0^\beta(\omega)\,\delta_{nn'}\,\delta_{\beta\beta'} + d_0^\beta(\omega)\sum_{n''\gamma}\Omega_{22}(nn''\omega)\,g_{22}^{\gamma\beta'}(n''n\omega)\;,$$

$$d_0^\beta(\omega) = (\omega_\beta/\pi)\,(\omega^2-\omega_\beta^2)^{-1}\;,$$

$$P_{22}^{\beta\beta'}(\omega) = (2\pi)^2 G_\omega\,(I_n^\beta(t);\,I_{n'}^{\beta'}(0))\;, \qquad (2.14)$$

$$I^\beta(n) = \tfrac{1}{2}[D_{n\beta},\,V_I] = i\sum_{\vec{q}lsr} e^{i\vec{q}\cdot(\vec{r}_l-\vec{R}_n)}\,(\vec{q}\cdot\vec{f}_r)\,(v^I_{\vec{q}})^{sr} \times(2\mu_r\omega_\beta)^{-1/2} e^{i\vec{q}\cdot(\vec{u}_{ls}-\vec{U}_{nr})}\;,$$

where we have used $[D, V_L] = 0$ and have omitted the term in P_{22} proportional to $\langle[I_n^\beta, D_{n'\beta'}]\rangle$, which does not contribute to ImP_{22}. The relation between P_{22} and Ω_{22} is again finally the same as between P_{11} and Ω_{11} [see Fig. 1(a)], and $P_{22} = \Omega_{22}$ in the harmonic approximation.

For the mixed GF g_{12} one obtains

$$g_{12}^{\alpha\delta}(\vec{k}n\omega) = g_0^\alpha(\vec{k}\omega)\,P_{12}^{\alpha\delta}(\vec{k}n\omega)\,d_0^\delta(\omega)\;,$$

$$P_{12}^{\alpha\delta}(\vec{k}n\omega) = (2\pi)^2 G_\omega(F^\alpha(\vec{k}t);\,I_n^\delta(0))\;, \qquad (2.15)$$

$$g_{12}^{\alpha\delta}(\vec{k}n\omega) = \sum_{\substack{\gamma\beta\\ \vec{k}'n'}} g_{11}^{\alpha\gamma}(\vec{k}\vec{k}'\omega)\,\Omega_{12}^{\gamma\beta}(\vec{k}'n'\omega)\,g_{22}^{\beta\delta}(n'n\omega)\;.$$

where the relation between g_{12} and Ω_{12} is indicated graphically in Fig. 1(b).

III. EVALUATION OF Imχ

In this section we obtain an explicit expression for Imχ in terms of displacement-displacement correlators, for the case where the interaction GF's P_{ij} are evaluated in the harmonic approximation. This is the simplest procedure to cut off the infinite chain of equations[21,22] involving the GF's for the interactions V_L and V_I. Extensions to more general approximation schemes will be discussed in Sec. IV. We will utilize averages over impurity sites, a convenient standard approximation,[23] which is most appropriate for a dilute distribution of impurities.

A. Evaluation of g_{11}

In the harmonic approximation $\Omega_{11} = (2\pi)^2 G(F^\alpha; F^\beta)$ [see Eqs. (2.9), (2.10), and (2.13)]; to obtain Imχ we will require Im$G_\omega(F^\alpha; F^\beta)$. It is more convenient for the present purposes to work with the correlator J, related to ImG_ω by[16]

$$J_\omega(A,B) = \langle A(t)B(0)\rangle_\omega = -2[n(\omega)+1]\,\mathrm{Im}G_\omega(A(t);B(0)) \qquad (3.1)$$

where n is the Bose-Einstein function, $n(\omega) = (e^{\beta\omega}-1)^{-1}$, with $\beta = (k_B T)^{-1}$ the inverse temperature. Denoting harmonic approximation by a superscript "0" and suppressing the $\vec{k}$ and t dependences for notational simplicity,

$$\langle F^\alpha F^\beta\rangle^0 = \langle F_L^\alpha F_L^\beta\rangle^0 + \langle F_I^\alpha F_L^\beta\rangle^0 + \langle F_L^\alpha F_I^\beta\rangle^0 + \langle F_I^\alpha F_I^\beta\rangle^0\;. \qquad (3.2)$$

The first term on the left-hand side is just the host-lattice interaction correlator studied in detail in

Ref. 16, which takes the form

$$\langle F_L^\alpha(\vec{k}t)\, F_L^\beta(\vec{k}', 0)\rangle^0 = (1/4\pi^2)\, P_L^{\alpha\beta}(\vec{k}t)\, \delta_{\vec{k},-\vec{k}'}\ , \qquad (3.3)$$

with the function P displayed explicitly in Ref. 16. When an average over impurity sites is performed the host-impurity interaction correlators $\langle F_I F_L\rangle^0$ vanishes if $qv_{\vec{q}}^{L,I} \to 0$ as $q \to 0$, as demonstrated in the Appendix. Thus, within the present approximations the principal task in obtaining g_{11} is the evaluation of the impurity correlator $\langle F_I^\alpha F_I^\beta\rangle_{\text{av}}^0$, where "av" indicates an average over impurity sites.

Utilizing Glauber's theorem[24] one obtains directly

$$\begin{aligned}\langle F_I^\alpha(\vec{k}t)\, F_I^\beta(\vec{k}'0)\rangle &= -\frac{1}{N} \\ &\times \sum_{\substack{\vec{q}lsnr \\ \vec{q}'l's'n'r}} \exp[i(\vec{q}+\vec{k})\cdot\vec{r}_l + i(\vec{q}'+\vec{k}')\cdot\vec{r}_{l'} \\ &- i\vec{q}\cdot\vec{R}_n - i\vec{q}'\cdot\vec{R}_{n'}]\, H_{ll'ss'}^{nn'rr'}(\vec{q}\vec{q}'t)\, (v_{\vec{q}}^I)^{sr}(v_{\vec{q}}^I)^{s'r'} \\ &\times(\vec{q}\cdot\vec{f}_{\vec{k}s}^\alpha)\, (\vec{q}'\cdot\vec{f}_{\vec{k}'s'}^\beta)\, (4\mu_s\,\mu_{s'}\,\omega_{\vec{k}\alpha}\,\omega_{\vec{k}'\beta})^{-1/2}\ , \qquad (3.4)\end{aligned}$$

where

$$\begin{aligned}H = \exp\{ &-\vec{q}\cdot[\overleftrightarrow{C}(lst,\ l's'0) - \overleftrightarrow{C}(lst,\ n'r'0) \\ &- \overleftrightarrow{C}(nrt,\ l's'0) + \overleftrightarrow{C}(nrt;\ n'r'0)]\cdot\vec{q}' + D\}\end{aligned}$$

with the $\overleftrightarrow{C}$'s displacement-displacement correlators; for example,

$$\overleftrightarrow{C}(lst,\, l's'0) = \langle\vec{u}_{ls}(t)\vec{u}_{l's'}(0)\rangle^0\,, \qquad (3.5)$$

with similar expressions for the remaining C's. D is a time-independent Debye-Waller factor which has little influence on $\text{Im}\chi$ at moderate temperatures,[16] and will be omitted henceforth. With the present break up of the Hamiltonian—the mixed host impurity C's vanish identically. Also, if one averages over impurity sites, the host-lattice correlator may be taken to be translationally invariant, i.e.,

$$C(lst;\ l's'0) = C(l-l',\, s,\, t;\, 0s'0) \equiv C_{ss'}^L(l-l',\, t)\,. \qquad (3.6)$$

Neglecting the interactions between impurities implies

$$C(nrt,\, n'r'0) = C_{rr'}^I(t)\delta_{nn'}\,. \qquad (3.7)$$

Thus,

$$H = \exp\{-\vec{q}\cdot[C_{ss'}^L(l-l',\, t) + C_{rr'}^I(t)\delta_{nn'}]\cdot\vec{q}'\}\,. \qquad (3.8)$$

Let us define

$$\Pi_{11}^{\alpha\beta}(\vec{k},\, t) = (4\pi^2/N_i)\langle\langle F_I^\alpha(\vec{k},\, t);\ F_I^\beta(-\vec{k},\, 0)\rangle\rangle_{\text{av}}\ ; \qquad (3.9)$$

with $\Pi(\omega)$ the Fourier transform of $\Pi(t)$, the average over impurity sites in Eq. (3.4) yields, after some algebra

$$-\frac{1}{2[n(\omega)+1]}\langle F_I^\alpha(\vec{k}t)F_I^\beta(\vec{k}'0)\rangle_\omega = \text{Im}\Pi_{11}^{\alpha\beta}(\vec{k}\omega)N_I\,\delta_{\vec{k},-\vec{k}'}, \qquad (3.10)$$

$$\text{Im}\Pi_{11}^{\alpha\beta}(\vec{k}t) = -2\pi^2\sum_{\vec{q}\vec{q}'lsrs'r'} e^{i(\vec{q}+\vec{k})\cdot\vec{r}_l}(v_{\vec{q}}^I)^{sr}(v_{-\vec{q}'}^I)^{s'r'}(\vec{q}\cdot\vec{f}_{\vec{k}s'}^\alpha)(\vec{q}'\cdot\vec{f}_{-\vec{k}s'}^\beta)(4\mu_s\mu_{s'}\omega_{\vec{k}\alpha}\omega_{-\vec{k}\beta})^{-1/2}\, L_{ss'}^{rr'}(l\vec{q}\vec{q},\, t)[n(\omega)+1]^{-1}\delta_{\vec{q},\vec{q}'}\ , \qquad (3.11)$$

$$L_{ss'}^{rr'}(l\vec{q}\vec{q},\, t) = \exp\{\vec{q}\circ[C_{ss'}^L(lt) + C_{rr'}^I(t)]\cdot\vec{q}'\},$$

where N_I is the total number of impurities.

It is instructive to recast the expression for $\text{Im}\Pi_{11}$ in an alternative form, which emphasizes interactions in position space. In Sec. IV we will consider absorption in the wings of the fundamental impurity mode; in this instance we need keep just terms linear in C^I. Restricting consideration to a point impurity at a single site (the cell origin) and a single phonon branch, we may drop the $(\alpha,\, \beta)$ and $(r,\, r')$ indices; then taking $\vec{k}=0$ and assuming the form $\vec{q}\cdot\overleftrightarrow{C}_{ss'}^L\cdot\vec{q}' = (\hat{\eta}_s\cdot\vec{q})(\hat{\eta}_{s'}\cdot\vec{q}')C^L$ for the correlator, we find[25]

$$\begin{aligned}\text{Im}\Pi_{11}^{\alpha\beta}(t) \propto \sum_{jll'ss'n}\frac{1}{j!}&\left(\frac{\partial^{j+2}v(\vec{r}_l - \vec{R}_n + \vec{\kappa}_s + \hat{\eta}_s\zeta + \hat{f}_I\phi)}{\partial\zeta^{j+1}\,\partial\phi}\right)_{\zeta,\phi=0}\left(\frac{\partial^{j+2}v(\vec{r}_{l'} - \vec{R}_n + \vec{\kappa}_{s'} + \hat{\eta}_{s'}\zeta + \hat{f}_I\phi)}{\partial\zeta^{j+1}\,\partial\phi}\right)_{\zeta,\phi=0} \\ &\times C^I(t)[C_{ss'}^L(l-l',\, t)]^j(4\mu_s\mu_{s'}\omega_\alpha\omega_\beta)^{-1/2}[n(\omega)+1]^{-1}. \qquad (3.12)\end{aligned}$$

While the above result is unwieldy in general, it is useful as a starting point for various approximations, such as the noninteracting cell limit, in a diatomic crystal, for which $\vec{r}_l = \vec{r}_{l'} = \vec{R}_n = 0$. For a linear vibration model where $\hat{\eta}_s$ and $\hat{f}_I$ point in the same direction, for example,

$$\text{Im}\Pi_{11} \propto \sum_j \frac{1}{j!}\left(\frac{\partial^{j+2}v^I(r)}{\partial r^{j+2}}\right)_{r=\kappa_s}^2[C^L(t)]^j C^I(t) \qquad (3.13)$$

The jth term is the j-phonon contribution to the absorption; the strength of this term is seen to be determined by the $(j+2)$th derivative of the impurity-host lattice interaction potential in position space, evaluated at their intracell separation distance $|\vec{\kappa}_s - \vec{\kappa}_r| = \kappa_s$. Note that these results are similar to those obtained for the intrinsic multiphonon case in Refs. 7 and 16. This noninteracting cell limit will be considered in greater detail in Sec. IV.

Returning to g_{11}, denoting averages by bars, we thus have

$$\bar{g}_{11}^{\alpha\beta}(\vec{k}\vec{k}'\omega) = g_0^\alpha(\vec{k}\omega)\delta_{\vec{k},-\vec{k}'}\delta_{\alpha\beta} + g_0^\alpha(\vec{k}\omega) \times \sum_\gamma [P^{\alpha\gamma}(\vec{k}\omega) + N_I \Pi_{11}^{\alpha\gamma}(\vec{k}\omega)]\,\bar{g}_{11}^{\gamma\beta}(\vec{k}\vec{k}'\omega) . \tag{3.14}$$

If we neglect the coupling between different branches then

$$g_{11}^\alpha(\vec{k}\vec{k}'\omega) = \frac{\delta_{\vec{k},-\vec{k}'}}{g_0^{-1}(\vec{k}\omega) - P^\alpha(\vec{k}\omega) + N_I \Pi_{11}^\alpha(\vec{k}\omega)} , \tag{3.15}$$

where for notational simplicity we henceforth omit the bars over averaged quantities, except for reasons of clarity within derivations.

B. Evaluation of g_{22}

To evaluate Imχ we require $\sum_{nn'} g_{22}^{\alpha\alpha'}(nn'\omega)$; in keeping with the picture of noninteracting impurities adopted in this section, we take $g_{22}(nn'\omega) = \delta_{nn'} g_{22}(\omega)$. The averaged form of Eq. (2.14) then leads to

$$\begin{aligned} g_{22}^{\beta\beta'}(\omega) &= d_0^\beta(\omega)\delta_{\beta\beta'} + d_0^\beta(\omega)\sum_\gamma N_I \Pi_{22}^{\beta\gamma}(\omega)\, g_{22}^{\gamma\beta'}(\omega) , \\ N_I \Pi_{22}^{\beta\gamma}(\omega) &= \sum_{nn'} \bar{\Omega}_{22}^{\beta\gamma}(nn'\omega) . \end{aligned} \tag{3.16}$$

Utilizing procedures identical to those for Π_{12}, one obtains for ImΠ_{22}

$$\mathrm{Im}\Pi_{22}^{\beta\gamma} = 2\pi^2 \sum_{\vec{q}\vec{q}' l s r s' r'} e^{i\vec{q}\cdot\vec{r}_l}(v_{\vec{q}}^I)^{sr} \times (v_{-\vec{q}'}^I)^{s'r'}(\vec{q}\cdot\vec{f}_r^\beta)(\vec{q}'\cdot\vec{f}_{r'}^\gamma)(4\mu_r\mu_{r'}\omega_\beta\omega_\gamma)^{-1/2} \times L_{ss'}^{rr'}(l\vec{q}\vec{q}'t)[n(\omega)+1]^{-1}\delta_{\vec{q},\vec{q}'} . \tag{3.17}$$

For a single impurity mode the $(\beta\gamma)$ indices may be dropped and one has

$$g_{22}^{\beta\beta'}(\omega) = \delta_{\beta\beta'}/[d_0^\beta(\omega)^{-1} - N_I \Pi_{22}^\beta(\omega)] . \tag{3.18}$$

If anharmonic interactions are neglected in Π_{22}, then g_{22} reduces to the standard harmonic impurity-mode GF.

C. Evaluation of g_{12} and g_{21}

Utilizing $g_{11}(\vec{k}\vec{k}') = \delta_{\vec{k},\vec{k}'} g_{11}(\vec{k})$, and defining Π_{12} through

$$\sum_n \Omega_{12} = -N_I \Pi_{12} ,$$

one has

$$\sum_n g_{12}^{\alpha\delta}(\vec{k}n\omega) = -N_I \sum_{\gamma\beta} g_{11}^{\alpha\beta}(\vec{k}\omega)\,\Pi_{12}^{\gamma\beta}(\vec{k}\omega)\, g_{22}^{\beta\delta}(\omega) ,$$

with

$$\Pi_{12}^{\gamma\beta} = 2\pi^2 \sum_{\vec{q}\vec{q}' l s s' r r'} e^{i(\vec{q}+\vec{k})\cdot\vec{r}_l} \times (v_{\vec{q}}^I)^{sr}(v_{-\vec{q}'}^I)^{s'r'}(\vec{q}\cdot\vec{f}_{\vec{k}s}^\gamma)(\vec{q}'\cdot\vec{f}_{r'}^\beta) \times (4\mu_s\mu_{r'}\omega_{\vec{k}\alpha}\omega_\beta)^{-1/2} L_{ss}^{rr'}(l\vec{q}\vec{q}'t)\,\delta_{\vec{q},\vec{q}'} . \tag{3.19}$$

Perfectly analogous results follow for g_{21} and Π_{21}, which we therefore do not display explicitly.

D. Expression for Imχ

Within the approximations of the present section, the imaginary part of the susceptibility follows directly once Eqs. [(3.15, 18, and 19)] have been inserted into Eq. (2.6). For the present purposes we will be concerned specifically with the absorption in the high-frequency wing of a single impurity mode; then one finds

$$\mathrm{Im}\Delta\chi \cong -\rho_I\Big[\sum_{\alpha\beta s s'} m_{\alpha s}^L m_{\beta s'}^L g_0^\alpha(\omega)\,\mathrm{Im}\Pi_{11}^{\alpha\beta}(\omega) g_0^\beta(\omega) + m_I m_I d_0(\omega)\,\mathrm{Im}\Pi_{22}(\omega) d_0(\omega) - 2\sum_{\alpha s} m_I m_{\alpha s}^L d_0(\omega)\,\mathrm{Im}\Pi_{12}^\alpha(\omega) g_0^\alpha(\omega)\Big] , \tag{3.20}$$

where $\rho_I = N_I/\Omega$ is the impurity concentration and $\Delta\chi = \chi - \chi_L$, with χ_L the intrinsic host-crystal susceptibility.[1–7] If one utilizes the result in Eq. (3.20) and its analogs for the other Π's, for example, then

$$\mathrm{Im}\Pi_{AB}^{\alpha\beta}(\omega) = 2\pi^2 \sum_{\vec{q}\vec{q}' l s s' r r'} e^{i\vec{q}\cdot\vec{r}_l}(v_{\vec{q}}^I)^{sr} \times (v_{-\vec{q}'}^I)^{s'r'}(\vec{q}\cdot\vec{f}_A^\alpha)(\vec{q}'\cdot\vec{f}_B^\beta)(4\mu_A\mu_B\omega_A\omega_B)^{-1/2} \times L_{ss'}^{rr'}(l\vec{q}\vec{q}'\omega)_{AB}\,\delta_{\vec{q},\vec{q}'}[n(\omega)+1]^{-1} , \tag{3.21}$$

where $\mu_{A,B}$, $\omega_{A,B}$, and $\vec{f}_{A,B}^\alpha$ are given in Table I, and $L(\omega)$ is the Fourier transform of $L(t)$ [see Eq. (2.11)]. Depending on the model to be employed and the method of calculation, it may be more ap-

TABLE I. Parameters appearing in Π_{AB}.

	$\mu_{A,B}$	$\omega_{A,B}$	$\vec{f}_{A,B}^\alpha$
$A=1$	μ_s	$\omega_{0\alpha}$	$\vec{f}_{0s}^\alpha$
$A=2$	μ_r	ω_α	$\vec{f}_r^\alpha$
$B=1$	$\mu_{s'}$	$\omega_{0\beta}$	$\vec{f}_{0s'}^\alpha$
$B=2$	$\mu_{r'}$	ω_β	$\vec{f}_{r'}^\beta$

propriate to employ the alternative result for Π_{AB} displayed in Eqs. (3.12) and (3.13) for Π_{11}, for example. In either instance, the above formulas provide a convenient starting point for calculations of impurity wing absorption; all one requires, in addition to various standard parameters, is the unperturbed (harmonic) displacement-displacement correlators for the impurity and the host, and the interaction potential between them, v_I.

IV. WING ABSORPTION OF AN IMPURITY IN AN EINSTEIN LATTICE

A wide variety of papers have utilized Einstein[16] or single-particle models[26] for the lattice to investigate intrinsic multiphonon absorption. Although somewhat artificial, the simplicity of the model makes it useful for a qualitative investigation of multiphonon behavior. In this section we utilize such a model for the lattice to study the absorption in the high-frequency wing of the fundamental ω_I of an impurity mode, at frequencies many host phonons above ω_I ($\omega-\omega_I \gg \omega_{\vec{k}\alpha}$). To elicit the principal physical effects with a minimum of mathematical complexity, we restrict attention to a single-site point-impurity model for a diatomic host crystal, and vibrations of the lattice and impurity which are collinear within each cell.

In the Einstein model only atoms within the same cell are correlated; with three identical branches one obtains[16]

$$\begin{aligned} C^E_{ss'}(lt) &= \delta_l C^E_{ss'}(t) \ , \\ C^E_{ss'}(t) &= C^E_{ss'}[e^{-i\omega_0 t}(n_0+1)+e^{i\omega_0 t}n_0] \ , \qquad (4.1) \\ C^E_{ss'} &= \tfrac{3}{2}\hbar/[\omega_0 a_0^2(\mu_s\mu_{s'})^{1/2}] \ . \end{aligned}$$

The above definitions correspond to scaling all lengths in terms of the lattice constant a_0. If we choose the vibration direction to lie along $\hat{\kappa}_s$, then for the Einstein model each of the Π_{AB}'s in Eqs. (3.20) and (3.21) are proportional to

$$C_0^I \sum_{\substack{j\vec{q}\vec{q}'l \\ nss'}} e^{i\vec{q}\cdot(\vec{r}_l-\vec{R}_n+\vec{\kappa}_s)} e^{i\vec{q}'\cdot(\vec{r}_l-\vec{R}_n+\vec{\kappa}_{s'})} v^s_{\vec{q}} v^{s'}_{\vec{q}'} [(n_E+1)/n_E]^{j/2} I_j\{2[n_E(n_E+1)]^{1/2}(\vec{q}\cdot\hat{\kappa}\kappa_s)(\vec{q}'\cdot\hat{\kappa}\kappa_{s'})C^E_{ss'}\}$$

$$\times(\vec{q}\cdot\hat{\kappa})^2(\vec{q}'\cdot\hat{\kappa})^2 f_A f_B\,\delta(\omega-\omega_I-j\omega_E)\ , \quad n_E=(e^{\beta\omega_E}-1)^{-1} \ , \qquad (4.2a)$$

where we have utilized $f_I^2=1$; with μ_I the reduced mass for the impurity stretching mode,

$$\begin{aligned} C_0^I(t) &= C_0^I e^{i\omega_I t} \\ C_0 &= [n(\omega_I)+1]\hbar/\mu_I\omega_I a_0^2 \ . \end{aligned} \qquad (4.2b)$$

v^s is the interaction between the impurity and host atom s and I_j is the modified Bessel function. The absorption in this model is observed to be a series of δ functions at $\omega-\omega_I=j\omega_E$. To relate this spectrum to behavior characteristic of actual crystals, one generally averages the absorption over a frequency distribution $F(\omega_E)$, which then yields α as a continuous function of frequency (see Ref. 26 for details). In certain instances very similar results may be obtained by simply connecting the δ-function peaks with an exponential envelope function.[27]

Rather than analyze the general Einstein results in Eq. (4.2), we will here specialize to certain simplified limits of the latter. At low temperatures such that $n(\omega_E) \ll 1$, one may expand each Bessel function, and keep just the lowest-order term. Moreover, for the present purposes it is appropriate[28] to consider potentials $v(r)$ which decrease very rapidly with r. This is so because in typical instances the many-phonon terms ($j \gg 1$) will dominate the absorption in the frequency regime of interest here; since these involve repeated derivatives of v, just the short-range portion of v is important. The latter is indeed a very rapidly decreasing function of interatomic distance for typical pair interactions in ionic solids.[28] In this instance the major contribution to the sums over (l, s, s') in Eq. (4.2) will be from the $\mathfrak{N}$ nearest neighbors (nn) of the impurity at cell n; the latter may be approximated as very nearly $\mathfrak{N}$ times the single-cell contribution.[27] When all of the latter considerations have been incorporated into Eq. (4.2), one obtains a result equivalent to that given previously in Eq. (3.13), namely

$$\mathfrak{N}^2 C_0^I \sum_j \frac{1}{j!}\left(\frac{\partial^{j+2}v(r)}{\partial r^{j+2}}\right)^2_{r=\kappa}(C^E_{22})^j$$

$$\times(1+n_E)^j\,\delta(\omega-\omega_I-j\omega_E) \ , \qquad (4.3)$$

where v is the interaction in position space between the impurity at the cell origin and the host atom $s=2$ of the diatomic crystal, and κ their separation distance. Details of the algebra leading to Eq. (4.3) are available in connection with an analogous derivation in Ref. 16, and need not be repeated here.

In the remainder of this section we analyze the simplified limit given by Eq. (4.3) with an eye to extracting the principal properties manifested by the wing absorption. Utilizing Eq. (3.20) one obtains for $\overline{\omega}=\omega-\omega_I \gg \omega_E$

$$\alpha = \alpha_L(\omega)+\alpha_I(\omega) \ ,$$

$$\alpha_L(\omega) = (4\pi\omega/\eta c)\,\mathrm{Im}\,\chi_L(\omega) \ ,$$

$$\alpha_I(\omega) = (4\pi\omega/\eta c)\rho_I \operatorname{Im}\chi_I(\omega) \ ,$$

$$\operatorname{Im}\chi_I(\omega) = [A_1(\omega) + A_2(\omega)(\omega_E^2/\overline{\omega}^2) + A_3(\omega)(\omega_E/\overline{\omega})]F(\overline{\omega})/[n(\omega)+1] \ ,$$

$$A_1 = m_L^2\left(\frac{\omega_E}{\omega^2}\right)^2 \frac{h}{\omega_E \mu_2 a_0^2} \frac{\mu_1}{\mu_1+\mu_2} \ , \qquad (4.4)$$

$$A_2 = m_I^2 \frac{\omega_I^2}{\omega_E^2(\omega+\omega_I)^2} \frac{h}{\omega_I \mu_I a_0^2} \ ,$$

$$A_3 = 2 m_L m_I \frac{\omega_I}{(\omega+\omega_I)\omega^2} \frac{h}{(\omega_I\omega_E\mu_2\mu_I)^{1/2} a_0^2} \left(\frac{\mu_1}{\mu_1+\mu_2}\right)^{1/2} \ ,$$

$$F(\overline{\omega}) = \mathfrak{N}^2 C_0^I \sum_j \frac{1}{j!}\left(\frac{\partial^{j+2} v(r)^2}{\partial r^{j+2}}\right)_\kappa^2 \times (n_E+1)^j (C_{22}^E)^j \delta(\overline{\omega} - j\omega_E) \ ,$$

where $\chi_L(\omega)$ is the standard host-phonon susceptibility treated elsewhere.[1-7] It is not difficult to see that for typical values of parameters the envelope of the high-frequency impurity wing absorption is exponential-like as a function of $\overline{\omega}$, as was shown previously[1-7] to be the case for the intrinsic spectrum, i.e., $\operatorname{Im}\chi_L$ vs ω. To demonstrate this more explicitly, we employ a Born-Mayer form[28] for $v(x) = v_0 e^{-\lambda x}$; in the regime of interest here, we may take $\omega \approx \omega_I$, so that only variations in $\overline{\omega}$ need be considered, yielding for the envelope of the peaks of the impurity absorption

$$\alpha_I(\overline{\omega}) \cong (4\pi\omega_I/\eta c) v_0^2 \lambda^4 e^{-2\lambda\kappa} C_0^I \times \{A_1(\omega_I)\exp[\overline{\omega}\ln Y - \ln(\overline{\omega}!)] + A_2(\omega_I)\exp[\overline{\omega}\ln Y - \ln(\overline{\omega}!) - 2\ln\overline{\omega}] + A_3(\omega_I)\exp[\overline{\omega}\ln Y - \ln(\overline{\omega}!) - \ln\overline{\omega}] \ , \qquad (4.5)$$

$$Y = (n_E+1)C\lambda^2 \ ,$$

where $C = C_{22}^E$ and we have scaled $\overline{\omega}$ in units of ω_E. Thus α_I is a sum of three terms, each of which, for conditions of interest here, will be exponential-like over sufficiently small intervals of $\overline{\omega}$. Clearly, α_I will be closest to exponential for small values of $Y \ll 1$, a condition which is generally met for the case of heavy-ion interactions in ionic solids and for partially covalent solids, where the interatomic potentials appear to be much "softer" than in the ionic case (see Ref. 29), but may not be for light-ion interactions (see Ref. 28). In any case, whenever $Y \ll 1$,

$$\alpha_I(\overline{\omega}) \approx A(\overline{\omega}) e^{-B\overline{\omega}} \ , \quad B = -\ln Y > 0 \ , \qquad (4.6)$$

where $A(\overline{\omega})$ is a slowly varying function of $\overline{\omega}$.

The principal difficulty in applying Eqs. (4.4) and (4.5) to actual cases is that the effective impurity-host interaction $v(x)$ is not accurately known; because of the repeated derivatives in Eq. (4.4), the hardness parameter λ will be especially crucial in determining the multiphonon absorption spectrum. One may conceive of a variety of schemes for deducing this information: For example, measurement of both the TO mode and the compressibility of the compound X^+Y^-, where Y^- is an impurity radical, should provide[30] the effective interaction v between X^+ and Y^-, when thermodynamic prescriptions (such as given by Born and Huang[28]) are applied to determine v. This v could then be utilized in calculating α_I in the host-impurity system $XZ:Y^-$. Unfortunately, however, the experimental data required for the latter and other similar schemes does not appear to be available for typical molecular impurity-host lattice combinations. For this reason, it would not be meaningful at present to attempt quantitative predictions of α_I, or the parameters A and B in Eq. (4.6).

For qualitative purposes, however, it might suffice to utilize typical values of λ characteristic of interatomic interactions in ionic solids, such as those given in Born and Huang,[28] for example. Guidelines for a reasonable choice are few, but one possibility is to approximate the interaction of X^+ with Z^- in $XY:Z^-$ as that of X^+ with a nearly equal mass ion W^- in the crystal XW. Let us apply this prescription of OH^- in KCl; then the closest analogue to the K^+-OH^- interaction is that between K^+ and F^- in KF. We have calculated α as a function of $\overline{\omega}/\omega_E$ for two values of β from Eq. (4.4). For this case one finds that the impurity term A_2 dominates; interpolating to noninteger $\overline{\omega}/\omega_E$,

$$\alpha(\overline{\omega}/\omega_E) \approx \sigma_I \alpha_0 [\lambda^2 C_{22}^E (n_E+1)]^{\overline{\omega}/\omega_E} \left(\frac{\omega_E}{\overline{\omega}}\right)^2 \frac{1}{\Gamma(\overline{\omega}/\omega_E + 1)} \ , \qquad (4.7)$$

$$\alpha_0 = \frac{(\epsilon_0 - \epsilon_\infty)\mathfrak{N}^2}{8\eta c} \frac{e_I^*}{e_L^*} \frac{\mu_E}{\mu_I} \frac{v^2(\kappa)}{\hbar^2} \ .$$

Here Γ is the gamma function; ϵ_∞ and ϵ_0 the high- and low-frequency dielectric constants of the host; e^*'s are effective (transverse) charges; and $\sigma_I = N_I/N$ is the fraction of impurities in the crystal. If we take $e_I^*/e_L^* \sim 1$ and utilize ω_{TO} for ω_E, we obtain $\alpha_0 \approx 2.4\times10^4$ cm^{-1}. In Fig. 2 we display $\alpha/\alpha_0\sigma_I$ vs $\overline{\omega}/\omega_E$ for two values of temperature,[31] and the results are observed to be nearly exponential, as remarked previously. A typical value of wing absorption deduced for this case is $\alpha \sim \sigma_I\times10^{-1}$ cm^{-1} at $\omega - \omega_I = 4\omega_E$, i.e., four host phonons above the impurity mode. In ultrapurified alkali halides $\sigma_I \sim 10^{-6}$ is not unreasonable, for which case one predicts a very small $\alpha(\overline{\omega}/\omega_E = 4) \sim 10^{-7}$ cm^{-1}.

V. CONCLUSIONS AND DISCUSSION

In the present paper we have utilized various approximations to calculate the multiphonon absorption due to internal modes of a low concentration of molecular impurities in ionic crystals. Explicit results were obtained (for an Einstein model

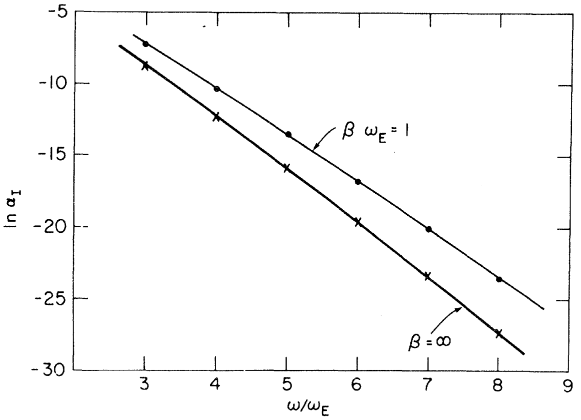

FIG. 2. Logarithm of impurity wing absorption coefficient α_I, scaled in units of $\sigma_I \alpha_0$ (see text) vs dimensionless frequency $\bar{\omega}/\omega_E$, for stretching mode of OH$^-$ in KCl, at two values of temperature.

of the host) from which the absorption may be computed directly, once the impurity-host interaction potential has been specified. Among the principal conclusions:

(a) The shape of the impurity wing is determined largely by the host-lattice correlation; i.e., the host density of states.[32] However, the relative strength of the many-phonon terms in α are governed by the impurity-host interaction potential.

(b) In typical instances the absorption is exponential-like as a function of $\omega - \omega_I$. A variety of terms with differing frequency dependences arise, in contrast to the intrinsic case, but in various limits a dominant exponential behavior will be manifested.

(c) The fall off of α in the wing region is determined by the phonon parameter $\lambda^2 C$, ~0.1 for typical values of parameters. This corresponds to a decrease of somewhat more than an order of magnitude per host-phonon[33] frequency.

(d) The explicit temperature dependence of α is approximately $[n(\omega_E)+1]^j/[n(\omega)+1]$ in the j-phonon regime, identical to that predicted in the intrinsic case.[1-7]

The role of the host-lattice correlation in determining $\alpha_I(\omega > \omega_I)$ may be made clearer by considering a convolution expansion in terms of $C^L(t)$ in Eq. (3.21). Essentially, $\text{Im}\chi(t)$ is a functional of $C^L(t)$ (for simplicity, we consider just a single C^L), so that

$$\text{Im}\chi_\omega = \sum_j \frac{1}{j!} \frac{\partial^j \text{Im}\chi[C^L]}{\partial (C^L)^j} \rho_j(\omega) \tag{5.1}$$

where ρ_j is the jth convolution of C_ω; i.e., $\rho_1 = C_\omega$. It is easily shown that when the position dependence of C is suppressed that ρ_j is, in fact, proportional to the n-phonon density of states of the host.[34] There are a variety of instances in which structure will arise in the ρ_j's, as discussed in detail elsewhere.[35] In general, repeated convolutions tend to wash out any structure in C_ω. If $\lambda^2 C_0$ is sufficiently small, the principal contribution to $\text{Im}\chi_\omega$ in the jth phonon regime will stem from the ρ_j term alone. Thus, we may expect that detailed structure reflecting selection rules will be manifested in the vicinity of the impurity peaks, but that it will be weak or absent as $\omega - \omega_I \gg \omega_{\vec{k}\alpha}$. The latter considerations provide a partial justification for the use of Einstein-type models in the many-phonon regime, although their inadequacy near to and below the peak is patent. Indeed, experimental evidence of the suppression of structure in the intrinsic case is widespread for ionic crystals.[36]

In the paragraphs to follow we point out various limitations of the general formulation in Secs. II and III, as well as the model calculations in Sec. IV. One general feature of our formulation has been the averaging over impurity sites which, for example, suppresses the modifications in the host-lattice correlation which are due to impurities; these may be important in highly localized systems. The crystalline normal mode expansion for the host moment employed in Eq. (2.3) will not, in general take proper account of impurity-host selection rules. However, for the purpose of calculating wing absorption, where $\vec{k}$-selection rules and structure in C^L are suppressed, such effects should be relatively minor.

In the model calculations we have treated the impurity as a structureless entity. If quantitatively accurate results are required, it may well be necessary to include summations over all atoms constituting the impurity, and to utilize the corresponding interactions for each with host atoms, a formidable task indeed. Another factor which requires attention is the determination of the effective charges associated with the various host and impurity vibrations, which can differ significantly from the electronic charge in certain instances (see Ref. 37). These reasons, combined with the simplified phonon spectrum utilized and uncertainties in the host-impurity potential v, probably limit the accuracy of the predicted α's to no better than an order of magnitude. However, it is clear that more elaborate computations are not justified unless detailed information becomes available about the crucial function v.

In this paper we have evaluated the multiphonon interaction GF's $[G(F;F)$, etc.$]$ in the harmonic approximation. Extensions to include the internal anharmonicity of the impurity, and the host-lattice anharmonicity are relatively straightforward.

Cumulant methods show that the simplest approximation including anharmonicity is accomplished essentially by replacement of the harmonic correlators C by their anharmonic counterparts (see Ref. 29). However, if we wish to include the anharmonicity $V_A^{I\text{-}L}$ due to the interaction between the impurities and the lattice, then we must also retain various mixed impurity-host correlators which vanish in the ensemble where $V_A^{I\text{-}L}=0$. Their evaluation requires the solution of a simultaneous set of coupled GF equations; an extensive literature exists on this subject, and need not be pursued further here.[21,23]

One aspect of the temperature dependence of α in the wing region is worthy of further discussion: In Sec. IV we included only the explicit temperature dependence due to thermal occupancies, which imply $\alpha \sim T^{n-1}$ in the n-phonon regime at high $T \gg \omega_E$; this is identical to the T dependence predicted in the intrinsic case, as noted previously in this section. However, it has been pointed out by various authors that the implicit T dependence due to T variation of the phonon spectrum, lattice constant and interaction parameters can substantially affect the overall T dependence of α in the many-phonon regime.[38] The results for typical alkali halides suggest a strong suppression of the implicit T dependence, which agrees with experimental data.[39] With minor modifications, one anticipates the identical effects to arise in the impurity wing case as well.

Finally, we point out various analogies between the present problem and that of phonon-induced sidebands in electronic impurity absorption. In the latter instance the electron-phonon interaction plays a role analogous to that of V_I in the present case. Since the origin of the sidebands in both instances is interaction with host phonons, one expects, on general grounds, that the two spectra will share various features in common. A formal analogy may be seen by comparing to Einstein-lattice results within the configuration-coordinate model of Huang and Rhys.[40] The nth-phonon sideband is proportional to

$$e^{S_1}\left(\frac{n_E+1}{n_E}\right)^{n/2} I_n\left[\left(\frac{n_E}{n_E+1}\right)^{1/2} S_2\right]\delta(\omega-\Delta E-n\omega_E), \tag{5.2}$$

with e^{S_1} a Debye-Waller-like factor, and S_2 an interaction strength measuring the readjustment of the impurity-atom equilibrium positions in the excited electronic state. This result is formally similar to that in Eq. (4.2), except that in the latter a distribution of strengths $S(\vec{q},\vec{q}\,')$ appear, and an appropriately weighted sum over factors such as in Eq. (5.2) need be taken. The similarities are more striking when comparing to the localized-limit results at low temperature, as displayed in Eq. (4.3). Essentially, these differ from the corresponding results in the electronic case just by the appearance of factors of $(\partial^{n+2}v/\partial r^{n+2})_\kappa^2$ (which are unity in the electronic case). The latter factors are a result of a dynamic treatment of the potential V_I, as contrasted with the configuration-coordinate approach, in which certain effects of the interaction are treated implicitly through S_2. Moreover, three different types of terms arise in the present problem due to the sum of $\vec{u}$'s and $\vec{U}$'s in $\vec{M}$, while just a single term corresponding to the $\vec{U}$'s need be considered in the electronic case. Other general similarities may be noted by comparing the shape function in Eq. (4.35) of Pryce in the volume in Ref. 18, for example, with Eq. (5.1) above; both involve similar types of weighted sums over n-phonon densities of states. It would have been possible, of course, to derive results even more closely equivalent to the electronic ones by invoking strict analogues of the models and assumptions utilized in that connection. However, most of these rely significantly on the adiabatic separation of the electronic and lattice motion. Such a separation is highly questionable for most cases of interest in the present problem where the coupling of the vibrations of the impurity with those of the host lattice are concerned. Another motivation for treating V_I dynamically is that one expects the details of the potential to be highly significant in the regime of interest here $(\omega-\omega_I \gg \omega_E)$. Indeed, this is manifested by the appearance of the higher derivatives of v in various expressions for α obtained in this paper.

At present there does not appear to be adequate experimental data for comparison with the theory. For such measurements one requires, in general, crystals which are ultrapure, except for doping with just a single impurity species. The detection technique which appears most promising at present is that of emittance spectroscopy,[41] which should provide both the sensitivity and resolution to successfully probe the multiphonon wing at relatively low values of the impurity concentration. With the substantial recent progress in the ultrapurification of alkali-halide crystals,[11] it should now be possible to perform useful measurements of impurity wing absorption to compare with theory.

ACKNOWLEDGMENT

The authors thank Dr. J. L. Birman for useful discussions during the course of this work.

APPENDIX: EVALUATION OF $\langle F_I F_L\rangle^0$

In this Appendix we demonstrate that $\langle F_I F_L\rangle^0$ vanishes if $qv_{\vec{q}} \to 0$ as $q \to 0$. Explicitly,

$$F_I^{\alpha}(\vec{k}t)\,F_L^{\beta}(\vec{k}'0)=\sum_{\substack{qq'lnl'l''\\ srs's''}}(v_q^I)^{sr}(v_q^L)^{s's''}(\vec{q}\cdot f_{\vec{k}s}^{\beta})(\vec{q}'\cdot f_{\vec{k}'s'}^{\beta})(m_s m_{s'}\omega_{\vec{k}\alpha}\,\omega_{\vec{k}'\beta})^{-1/2}$$

$$\times\exp[i(\vec{q}+\vec{k})\cdot\vec{r}_l-i\vec{q}\circ\vec{R}_n+i(\vec{q}'+\vec{k}')\cdot\vec{r}_{l'}-i\vec{q}'\cdot\vec{r}_{l''}]\,E_{ss's''r}^{ll'l''n}\,, \tag{A1}$$

$$E=\langle e^{i\vec{q}\cdot(\vec{u}_{ls}-\vec{U}_{nr})}\,e^{i\vec{q}'\cdot(\vec{u}_{l's}-\vec{u}_{l''s''})}\rangle^0\,.$$

When the thermal average is carried out by Glauber's theorem, and it is noted that mixed correlators of the form $\langle\vec{u}_{ls}(t)\,\vec{U}_{nr}(0)\rangle^0$ vanish, then E is seen to be independent of (n,r). If we now carry out an average over impurity sites, then $\sum_n e^{i\vec{q}\cdot\vec{R}_n}$ leads to a factor of $\delta(\vec{q})$ in Eq. (A1); thus if $qv_q\rightarrow 0$ for $q\rightarrow 0$, $\langle F_I F_L\rangle^0$ vanishes.

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*Research at NYU supported by AF Cambridge Research Labs (AFSC) under Contract No. F19628-73-C-0100.

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