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## Theory of Multiphonon Absorption due to Anharmonicity in Crystals

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A theory of multiphonon absorption due to anharmonicity in crystals is presented, employing a Green's-function technique. In contrast to previous theories, we do *not* expand the lattice-interaction potential in powers of displacements. We are therefore able to obtain a single expression for the absorption coefficient  $\alpha$ , which includes various classes of contributions to infinite order in phonons, and which is valid for all frequencies in the multiphonon regime. The results involve just the displacement-correlation tensor of the lattice, and the Fourier components of the interatomic potential  $v$ . Simplified expressions are obtained for isotropic models, and specific choices of  $v$ . Within the Einstein model, one finds an exponential behavior,  $\alpha(\omega) \sim e^{-\sigma\omega}$ ; predicted values of  $\sigma$  within the model are found to be in good agreement with recent experimental data on alkali halides. A general technique for evaluating  $\alpha$ , the method of convolutions, is elaborated. Predictions regarding the frequency and temperature dependence of  $\alpha$  are discussed and compared with other work.

### I. INTRODUCTION

Multiphonon absorption in crystals has its origin in two types of physical interactions: anharmonicity and higher-order electric moments.<sup>1</sup> While the electric-moment interaction allows for direct excitation of phonons by light, the anharmonic interaction must act in conjunction with the electric-moment interaction to produce absorption. A number of papers have calculated the absorption due to anharmonicity<sup>2</sup> and higher-order electric moments<sup>3</sup> separately, as well as in combination with each other.<sup>4</sup> From the results of these calculations it is not evident under just what conditions anharmonic effects, as opposed to those due to higher-order electric moments, dominate. In recent work on the latter question, it was found<sup>5</sup> that, for low-

order multiphonon processes, either mechanism may dominate within a range of actual representative materials.

There has been much interest recently in connection with highly transparent ultrapure infrared materials, which, for example, are necessary to provide relatively distortion-free optical elements for high-power laser applications.<sup>6</sup> In practice, the useful frequency range of such materials is the many-phonon regime above the fundamental phonon frequency, but well below the electronic gap. Past calculations<sup>1-5</sup> of multiphonon effects have been concerned chiefly with photon frequencies near resonance, and have employed perturbative expansions of the lattice potential in powers of lattice displacements in order to calculate the quantities of interest. Such methods become extremely

laborious and unwieldy for higher-order phonon processes, where an increasing multiplicity of contributions to a perturbation formalism result. For this reason, it is desirable to introduce an approach to the calculation of multiphonon absorption in the transparent regime of crystals in which the anharmonic potential is *not* expanded in phonon displacements. The latter constitutes the principal objective of the present work.

We here restrict consideration to the linear response to the photon field, for crystals with a nonvanishing dipole moment. The effects of anharmonicity are then considered for transitions mediated by just the dipole portion of the electric moment characterizing intrinsic bulk processes. The treatment is restricted here in this fashion because these conditions constitute a well-known historical problem, and because they provide a relatively simple and transparent framework for the application of the present techniques. However, the techniques to be developed here may, in fact, be easily extended to treating higher-order moments and anharmonicity simultaneously, and to nonlinear effects, aspects of which we intend to pursue in future work. The extension to surface and impurity absorption may be carried out in a similar fashion as well.

The present treatment hinges on the ability to express the full lattice-interaction potential in the form of a sum of interactions between pairs of atoms in the crystal in the form

$$V = \frac{1}{2} \sum_{ljs'} v_{ss'}(\vec{R}_{ls} - \vec{R}_{js'}), \quad (1)$$

where  $v_{ss'}(\vec{R}_{ls} - \vec{R}_{js'})$  is the interaction between the  $s$ th atom in cell  $l$  and the  $s'$ th atom in cell  $j$ , and the sum is restricted to  $ls \neq js'$ . A description of the lattice on the basis of  $V$  alone, while physically intuitive, does involve certain assumptions, such as the complete separation of the electronic motion from the ionic motion<sup>7</sup> (i. e., adiabaticity), and the validity of the point-ion model. We do not consider here the question of justification of this form for  $V$ ; rather, we will assume that such a  $V$  does, in fact, allow for an adequate description of lattice interactions in the infrared.

In Sec. II we express the complex dielectric susceptibility  $\chi$  in terms of a lattice Green's function  $G$ . An exact expression for  $G$  is then derived, in which the principal contribution to the absorption is given by a Green's function  $P(\vec{k}, \omega)$  involving the anharmonic potential  $V_A$ . The evaluation of  $P$  is carried out in the harmonic ensemble, in terms of the displacement-displacement correlation tensor of the lattice and the momentum Fourier coefficients of the potential  $v$ . In Sec. III,  $P$  is further evaluated for a diatomic lattice, for a simplified choice of potentials, and for an Einstein model of

the lattice. Also, the application of a general technique for numerically evaluating  $P$ , the method of convolutions, is described. Finally, the present method and results are discussed and compared with previous ones and with experiment in Sec. IV.

## II. GREEN'S FUNCTION FOR MULTIPHONON ABSORPTION

The interaction between atoms in a crystal lattice may be expressed as<sup>8</sup>

$$V = \frac{1}{2} \sum_{ll's's'} v_{ss'}(\vec{R}_{ls} - \vec{R}_{l's's'}) \\ = \sum_{\vec{q}} \sum_{ll's's'} v_{ss'}^{qs} e^{i\vec{q} \cdot (\vec{R}_l^0 - \vec{R}_{l'}^0)} e^{i\vec{q} \cdot (\vec{u}_{ls} - \vec{u}_{l's's'})}, \quad (2a)$$

where, with  $\vec{k}_s$  the position vector of the  $s$ th atom within a unit cell,

$$v_{ss'}^{qs} = \frac{1}{4} e^{i\vec{q} \cdot (\vec{k}_s - \vec{k}_{s'})} (\bar{v}_{\vec{q}}^{ss'} + \bar{v}_{-\vec{q}}^{ss'}), \quad (2b)$$

where  $\bar{v}_{\vec{q}}$  is the Fourier transform of  $v(\vec{R})$ ,

$$\bar{v}_{\vec{q}}^{ss'} = \sum_{R_l} e^{-i\vec{q} \cdot \vec{R}_l} v_{ss'}(\vec{R}_l). \quad (2c)$$

$\vec{R}_l^0$  is the equilibrium position of lattice atom  $l$ , and  $\vec{u}_l$  its displacement from equilibrium; the terms with  $ls = l's'$  are to be excluded in the sum. The normal modes of the lattice (noninteracting phonons) are determined by the terms in  $V$  quadratic in the  $\vec{u}_l$ 's; the terms linear in the  $\vec{u}_l$ 's may be shown to vanish for periodic lattices.<sup>9</sup> One then defines<sup>7</sup> an anharmonic potential  $V_A$  as the portion of  $V$  containing terms cubic and higher in the  $\vec{u}_l$ 's. For the present purposes we will be concerned primarily with calculating multiphonon transitions involving at least three phonons, in which case the potential  $V_A$  will, in fact, be replaceable with  $V$ .

The phonon Hamiltonian including anharmonicity takes the form ( $\hbar=1$ )

$$H = H_0 + V_A, \quad (3)$$

$$H_0 = \sum_{\vec{k}\alpha} \omega_{\vec{k}\alpha} b_{\vec{k}\alpha}^\dagger b_{\vec{k}\alpha},$$

where  $b_{\vec{k}\alpha}$  are creation-annihilation operators for phonons of wave vector  $\vec{k}$  and branch  $\alpha$ , and  $\omega_{\vec{k}\alpha}$  are the corresponding frequencies. It will be convenient in what follows to work also with operators  $A$ ,  $B$  defined as

$$A_{\vec{k}\alpha}^\dagger = b_{\vec{k}\alpha}^\dagger + b_{-\vec{k}\alpha}^\dagger, \quad (4)$$

$$B_{\vec{k}\alpha}^\dagger = b_{\vec{k}\alpha}^\dagger - b_{-\vec{k}\alpha}^\dagger.$$

The complex dielectric susceptibility  $\chi$  describing the linear response to an external photon field is given by<sup>1</sup>

$$\chi(\vec{k}, \omega) = -G_\omega(M_{\vec{k}}(t); M_{-\vec{k}}(0)), \quad (5)$$

where  $\vec{k}$  and  $\omega$  are the photon wave vector and frequency and  $M_{\vec{k}}$  is the corresponding electric-mo-

ment operator. The notation  $O(t)$  indicates an operator in the Heisenberg representation,

$$O(t) = e^{iHt} O e^{-iHt}; \quad (6)$$

$G$  is the retarded Green's function (GF)

$$G(A(t); B(0)) \equiv -i\theta(t) \langle [A(t), B(0)] \rangle, \quad (7)$$

where  $\theta$  is the Heaviside function and  $\langle \rangle$  indicates a thermal average over the eigenstates of  $H$ ; the notation  $G_\omega$  indicates a Fourier transform with respect to  $\omega$ ,

$$G_\omega = (2\pi)^{-1} \int dt e^{i\omega t} G(t). \quad (8)$$

For simplicity, we have written  $\chi$  for the isotropic case, where  $\chi$  is a scalar; extension to the tensor is straightforward, but would clutter the development with needless notational difficulties, and will not be considered here. Also, we restrict ourselves to a dipole moment characterizing just a single infrared-active (TO) mode of frequency  $\omega_{\vec{k}}$ , namely,

$$M_{\vec{k}} = m_{\vec{k}} A_{\vec{k}}, \quad (9)$$

where we suppress the TO branch index in writing  $A_{\vec{k}}$  and  $\omega_{\vec{k}}$ ;  $m_{\vec{k}}$  is a coupling coefficient which has been displayed in a variety of places<sup>1</sup> and whose explicit form is not of special concern here. One observes that the evaluation of  $\chi$ , and hence the infrared optical properties of the crystal, in the above case involves essentially just the evaluation of the single Green's function  $G(\vec{k}\omega) \equiv G_\omega(A_{\vec{k}}; A_{-\vec{k}})$ .

Application of the equation-of-motion method to the calculation of  $G$  yields the result

$$G(\vec{k}\omega) = [(\pi/\omega_{\vec{k}})(\omega^2 - \omega_{\vec{k}}^2) + \Pi(\vec{k}, \omega)]^{-1}, \quad (10)$$

where  $\Pi$ , known as the proper self-energy function, takes the form

$$\Pi(\vec{k}\omega) = \bar{P}(\vec{k}\omega) / \left( 1 + \frac{\omega_{\vec{k}}}{\pi} \frac{\bar{P}(\vec{k}\omega)}{\omega^2 - \omega_{\vec{k}}^2} \right), \quad (11)$$

where

$$\begin{aligned} \bar{P}(\vec{k}\omega) &= \frac{1}{2} \langle [F_{\vec{k}}, B_{\vec{k}}^\dagger] \rangle + P(\vec{k}\omega), \\ P(\vec{k}\omega) &\equiv G_\omega(F_{\vec{k}}; F_{-\vec{k}}), \\ F_{\vec{k}} &= \frac{1}{2} [B_{\vec{k}}, V_A]. \end{aligned} \quad (12)$$

These results are derived in detail in Appendix A. If one restricts consideration to just the lowest-order contribution to  $\Pi$ , for example, then  $\Pi \approx \bar{P}$ , and

$$G(\vec{k}\omega) \approx [(\pi/\omega_{\vec{k}})(\omega^2 - \omega_{\vec{k}}^2) + \bar{P}(\vec{k}\omega)]^{-1}, \quad (13)$$

where

$$\bar{\omega}_{\vec{k}}^2 = \omega_{\vec{k}}^2 + \langle [F_{\vec{k}}, B_{\vec{k}}^\dagger] \rangle (\omega_{\vec{k}}/\pi) \quad (14)$$

are renormalized frequencies and  $P$  is a "polarization function." Since  $P$  and  $\bar{P}$  themselves involve Green's functions, we have simply succeeded in

expressing our original GF in terms of other more complicated ones.<sup>10</sup> It will therefore be necessary to introduce approximations into the calculation of  $G$  in order to proceed further. For our purposes we are primarily interested in the imaginary part of  $\bar{P}$ , which is the principal function determining the shape of the absorption in the transparent regime. The approximation we will employ in what follows is to evaluate the thermal average in  $P$  over the unperturbed Hamiltonian  $H_0$ , rather than the full  $H (= H_0 + V)$ . As will be pointed out later, it is possible, in principle, to do better than this by employing a cumulant expansion for the averaging, which leads in a first approximation to a set of coupled transcendental equations for GF's of the form  $G(A_{\vec{k}}^*(t); A_{-\vec{k}}(0))$ . Unfortunately, however, the solution of such a set of equations will not, in general, be a practical possibility.

The principal function determining the infrared absorption is the imaginary part of  $\chi$ . This may be seen<sup>11</sup> by expressing the absorption coefficient  $\alpha$ , defined as the probability of absorption per unit length of crystal, as

$$\alpha(\omega) = 4\pi(\omega/c)\kappa_1^{-1}(\omega) \text{Im}\chi(\omega), \quad (15)$$

where  $\kappa_1(\omega)$  is the real part of the refractive index defined from  $\kappa_1(\omega) = \text{Re} \{ [1 + 4\pi[\chi_0 + \chi(\omega)]]^{1/2} \}$ , where  $\chi_0$  is the background dielectric susceptibility.  $\kappa_1$  varies slowly as a function of  $\omega$  in the transparent regime of interest here, so that the shape of the absorption spectrum is determined, essentially, by just  $\text{Im}\chi$  alone. One has, measuring  $\chi$  in units of  $m_{\vec{k}}^2$ ,

$$\text{Im}\chi(\omega) = \text{Im}\Pi \{ [\pi\omega_{\vec{k}}^{-1}(\omega^2 - \omega_{\vec{k}}^2) + \text{Re}\Pi]^2 + (\text{Im}\Pi)^2 \}^{-1/2}, \quad (16a)$$

where

$$\begin{aligned} \text{Re}\Pi &= [\pi\omega_{\vec{k}}^{-1}(\omega^2 - \omega_{\vec{k}}^2) \text{Re}\bar{P} + |\bar{P}|^2] D, \\ \text{Im}\Pi &= [\pi\omega_{\vec{k}}^{-1}(\omega^2 - \omega_{\vec{k}}^2) \text{Im}\bar{P}] D, \end{aligned} \quad (16b)$$

$$D = \frac{\pi\omega_{\vec{k}}^{-1}(\omega^2 - \omega_{\vec{k}}^2)}{[\pi\omega_{\vec{k}}^{-1}(\omega^2 - \omega_{\vec{k}}^2) + \text{Re}\bar{P}]^2 + (\text{Im}\bar{P})^2}.$$

In the limit where  $\omega^2 - \omega_{\vec{k}}^2 \gg |\bar{P}|$ , one obtains  $\Pi \approx \bar{P}$ , so that

$$\text{Im}\chi(\omega) = \frac{\text{Im}\bar{P}(\vec{k}\omega)}{\pi^2\omega_{\vec{k}}^{-2}(\omega^2 - \omega_{\vec{k}}^2)^2 + [\text{Im}\bar{P}(\vec{k}\omega)]^2}, \quad (17a)$$

where

$$\bar{\omega}_{\vec{k}}^2 = \bar{\omega}_{\vec{k}}^2 + \omega_{\vec{k}}\pi^{-1} \text{Re}\bar{P}(\vec{k}\omega) \quad (17b)$$

and where we have used the fact that  $\langle [F_{\vec{k}}, B_{\vec{k}}^\dagger] \rangle$  is real. The latter also enables us to replace  $\text{Im}\bar{P} = \text{Im}P$  in Eqs. (16b), in general. Thus the principal function involved in the absorption line shape is just  $\text{Im}P(\vec{k}\omega)$ . To evaluate this function we first calculate a related quantity, the correlation function

$$\mathcal{F}_{\vec{k}}(t) = \langle F_{\vec{k}}(t) F_{-\vec{k}}(0) \rangle, \quad (18)$$

from which the Green's function  $P(\vec{k}, \omega)$  may be obtained in standard fashion; specifically,<sup>10</sup>

$$\text{Im}P = -\frac{1}{2} \frac{1}{n(\omega) + 1} \mathcal{F}, \quad (19a)$$

$$\text{Re}P = \mathcal{P} \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\mathcal{F}(\omega') d\omega'}{[n(\omega') + 1](\omega' - \omega)},$$

where  $\mathcal{P}$  indicates principal parts integral;

$$n(\omega) = (e^{\beta\omega} - 1)^{-1}, \quad (19b)$$

and the limit  $+i\epsilon$  is employed in evaluating  $P$ .

In the development to follow, we will evaluate  $P$  in the harmonic ensemble. In this approximation, it is clear that only terms cubic or higher can contribute to  $\text{Im}P$  for  $\omega > 2\omega_m$ , where  $\omega_m$  is the maximum phonon frequency. Physically, this just reflects conservation of energy in real phonon processes. (Actually, a more careful examination of the explicit form of  $\text{Im}P$  reveals that the latter condition can be relaxed to  $\omega > \omega_m$ .) Thus one may replace  $V_A$  by  $V$  in the calculation of  $\text{Im}P$  in this regime, a condition which is not *essential* for the evaluation of  $\text{Im}P$ , but which does simplify the algebra considerably. Employing the standard expression for  $\vec{u}_i$  in terms of the  $A$ 's one then obtains

$$\begin{aligned} \mathcal{F}(t) = & \frac{2}{\omega_{\vec{k}}} \sum_{\substack{\vec{q}, \vec{q}', \vec{r}, \vec{r}' \\ \vec{r}, \vec{r}' \neq \vec{q}, \vec{q}'}} (m_r m_{r'})^{-1/2} (\vec{q} \cdot \vec{f}_{\vec{k}-\vec{q}}) (\vec{q}' \cdot \vec{f}_{\vec{k}-\vec{q}'}) v_{\vec{q}}^{rs} v_{\vec{q}'}^{r's'} \sum_{\vec{R}_1, \vec{R}_2, \vec{R}_3} e^{i\vec{q} \cdot \vec{R}_1 - i\vec{q}' \cdot \vec{R}_2 + i\vec{k} \cdot \vec{R}_3} \\ & \times \exp\left\{ -\frac{1}{2} \vec{q} \cdot \vec{C}_{rr}(0, 0) \cdot \vec{q} - \frac{1}{2} \vec{q} \cdot \vec{C}_{ss}(0, 0) \cdot \vec{q} - \frac{1}{2} \vec{q}' \cdot \vec{C}_{r'r'}(0, 0) \cdot \vec{q}' - \frac{1}{2} \vec{q}' \cdot \vec{C}_{s's'}(0, 0) \cdot \vec{q}' + \vec{q} \cdot \vec{C}_{rs}(R_1, 0) \cdot \vec{q} \right. \\ & \left. + \vec{q}' \cdot \vec{C}_{r's'}(R_2, 0) \cdot \vec{q}' + \vec{q} \cdot [\vec{C}_{rr'}(-\vec{R}_3, t) + \vec{C}_{ss'}(\vec{R}_2 - \vec{R}_1 - \vec{R}_3, t) - \vec{C}_{rs'}(\vec{R}_2 - \vec{R}_3, t) - \vec{C}_{s'r'}(-\vec{R}_1 - \vec{R}_3, t)] \cdot \vec{q} \right\}, \quad (23) \end{aligned}$$

where  $\vec{C}$  is the displacement-displacement correlation tensor of the lattice,<sup>12</sup>

$$\vec{C}_{rs}(\vec{R}, t) = \langle \vec{u}_r(\vec{R}, t) \vec{u}_s(0, 0) \rangle, \quad (24)$$

and where we have employed the translational invariance of the crystal in arriving at the result, Eq. (23). For  $\vec{k}=0$ , terms with  $r=s'$  and  $s=r'$  vanish identically and may be omitted from the sum. For crystals with many atoms per unit cell, one requires knowledge of a multiplicity of correlation tensors involving the different varieties of atoms. (For a diatomic lattice, for example, one requires three correlation tensors:  $\vec{C}_{11}$ ,  $\vec{C}_{22}$ , and  $\vec{C}_{12}$ .) Explicitly,  $\vec{C}$  takes the form<sup>8</sup>

$$\begin{aligned} \vec{C}_{rs}(\vec{R}, t) = & \frac{1}{2N} \sum_{\vec{k}_r} \frac{\vec{f}_{\vec{k}_r r} \vec{f}_{\vec{k}_r s}}{(m_r m_s)^{1/2}} \\ & \times [e^{i(\vec{k} \cdot \vec{R} - \omega_{\vec{k}_r} t)} (n_{\vec{k}_r} + 1) + e^{-i(\vec{k} \cdot \vec{R} - \omega_{\vec{k}_r} t)} n_{\vec{k}_r}], \quad (25) \end{aligned}$$

directly

$$\begin{aligned} F_{\vec{k}} = & 2i \sum_{\vec{q}; i, s, s'} v_{\vec{q}}^{ss'} \frac{\vec{q} \cdot \vec{f}_{-\vec{k}-\vec{q}}}{(2N\omega_{-\vec{q}} m_s)^{1/2}} \\ & \times e^{i(\vec{q}-\vec{k}) \cdot \vec{R}_i^0 - i\vec{q} \cdot \vec{R}_i^0} e^{i\vec{q} \cdot (\vec{u}_{i, s} - \vec{u}_{i, s'})}, \quad (20) \end{aligned}$$

where  $\vec{f}$  is the polarization vector of the TO phonon and  $m_s$  the mass of the  $s$ th atom. One notes that the terms with  $s=s'$  vanish for  $\vec{k}=0$ . Using (20),

$$\begin{aligned} \mathcal{F}(t) = & -4 \sum_{\substack{\vec{q}; i, j, j' \\ \vec{q}, \vec{q}', r, r'}} \frac{(\vec{q} \cdot \vec{f}_{-\vec{k}-\vec{q}}) (\vec{q}' \cdot \vec{f}_{\vec{k}-\vec{q}'})}{2N(\omega_{\vec{q}} \omega_{-\vec{q}'} m_s m_{s'})^{1/2}} v_{\vec{q}}^{ss'} v_{\vec{q}'}^{r'r'} \\ & \times \exp[i(\vec{q} - \vec{k}) \cdot \vec{R}_i^0 - i\vec{q}' \cdot \vec{R}_j^0 + i(\vec{q}' + \vec{k}) \cdot \vec{R}_j^0 - i\vec{q}' \cdot \vec{R}_j^0] \\ & \times \langle e^{i\vec{q} \cdot (\vec{u}_{i, s} - \vec{u}_{i, s'})} e^{i\vec{q}' \cdot (\vec{u}_{j, r} - \vec{u}_{j, r'})} \rangle. \quad (21) \end{aligned}$$

The thermal average may be carried out in the  $H_0$  ensemble by application of Glauber's theorem,<sup>12</sup>

$$\begin{aligned} \langle e^{i\vec{A} \cdot \vec{u}_1} e^{-i\vec{B} \cdot \vec{u}_2} \rangle = & \exp\left[-\frac{1}{2} \vec{A} \cdot \langle \vec{u}_1 \vec{u}_1 \rangle \cdot \vec{A} \right. \\ & \left. - \frac{1}{2} \vec{B} \cdot \langle \vec{u}_2 \vec{u}_2 \rangle \cdot \vec{B} + \vec{A} \cdot \langle \vec{u}_1 \vec{u}_2 \rangle \cdot \vec{B} \right], \quad (22) \end{aligned}$$

whence, defining

$$\vec{R}_1 = \vec{R}_i^0 - \vec{R}_j^0, \quad \vec{R}_2 = \vec{R}_j^0 - \vec{R}_j^0, \quad \vec{R}_3 = \vec{R}_j^0 - \vec{R}_i^0,$$

one obtains, using various symmetry relations<sup>8</sup> and switching around labels,

where  $n_{\vec{k}_r} \equiv (e^{\beta\omega_{\vec{k}_r}} - 1)^{-1}$ . Thus, evaluation of  $C$  in full requires, in general, a knowledge of the phonon spectrum and the polarization vectors  $\vec{f}_{\vec{k}_r}$  over the entire Brillouin zone.

We comment briefly on the form of  $\mathcal{F}$  when the thermal average is carried out over  $H$  rather than  $H_0$ . A cumulant expansion for this case shows<sup>13</sup>

$$\begin{aligned} \langle e^{i\vec{A} \cdot \vec{u}_1} e^{-i\vec{B} \cdot \vec{u}_2} \rangle = & \exp\left[-\frac{1}{2} \vec{A} \cdot \langle \vec{u}_1 \vec{u}_1 \rangle \cdot \vec{A} \right. \\ & \left. - \frac{1}{2} \vec{B} \cdot \langle \vec{u}_2 \vec{u}_2 \rangle \cdot \vec{B} + \vec{A} \cdot \langle \vec{u}_1 \vec{u}_2 \rangle \cdot \vec{B} + \dots \right], \quad (26) \end{aligned}$$

where the omitted terms involve terms cubic or higher in the  $\vec{u}$ 's (actually, a term of the form  $\langle \vec{u}_1 \rangle \langle \vec{u}_2 \rangle$  does arise, but it is unimportant because it is time independent). Thus, truncating the series in lowest order, one obtains results of the same form as for the harmonic case. However, since the anharmonic functions of the form  $\langle \vec{u}_1 \vec{u}_2 \rangle$  are unknown, it is necessary to express these, in turn, in terms of GF's for the  $A_{\vec{k}_r}$ 's. This procedure

leads to a rather complicated set of coupled transcendental equations involving all the functions  $G(A_{\vec{k}\nu}^{\pm}; A_{\vec{k}\nu}^{\pm})$ , the solution of which very clearly is either difficult or impossible in the general case. The restriction to harmonic averaging in  $\mathcal{F}$  is thus a practical necessity for actual computations.

### III. EVALUATION OF $P(\vec{k}\omega)$ FOR MODEL SYSTEMS

The results for  $\mathcal{F}(t)$  given in Eq. (23) account for the full complexity of the crystal structure and phonon spectrum of real crystals. In this section we concern ourselves with eliciting just the principal features of the frequency and temperature dependence of  $P(\vec{k}\omega)$ , rather than with those properties associated with the details of the vibrational spectra of real crystals. For this purpose it is useful to specialize to the case of diatomic crys-

tals. Moreover, we simplify the discussion by considering an isotropic model, where the tensor  $\vec{C}$  becomes a scalar.

For the above case it follows directly from Eqs. (20) that for  $\vec{k} = 0$ ,

$$F_0 = 2i \sum_{\vec{q}, \vec{q}'} v_{\vec{q}} \frac{\vec{q} \cdot \vec{W}}{(2N\omega_0)^{1/2}} e^{i\vec{k} \cdot \vec{q}} e^{i\vec{q} \cdot (\vec{R}_1 - \vec{R}_1 + \vec{q}_1 - \vec{q}_1)}, \quad (27)$$

where 1 and 2 label the two atoms in the unit cell,  $\vec{k} \equiv \vec{k}_1 - \vec{k}_2$ ,  $v_{\vec{q}} = \frac{1}{4} (\bar{v}_{\vec{q}}^{12} + \bar{v}_{-\vec{q}}^{12})$ , and

$$\vec{W} \equiv \vec{f}_1 m_1^{-1/2} - \vec{f}_2 m_2^{-1/2}.$$

Of course  $\vec{W}$  can be simplified further<sup>8</sup> for the TO mode at  $\vec{k} = 0$ , but this is unimportant for the present purposes, except to note that  $\vec{W} \neq 0$ . Then for an isotropic model one obtains

$$\mathcal{F}(t) = - \sum_{\vec{q}, \vec{q}', \vec{R}_1, \vec{R}_2, \vec{R}_3} e^{i\vec{q} \cdot \vec{R}_1 - i\vec{q}' \cdot \vec{R}_2} h(\vec{q}, \vec{q}') e^{i\vec{k} \cdot (\vec{q} - \vec{q}')} \exp\left\{-\frac{1}{2}(q^2 + q'^2)[C_{11}(00) + C_{22}(0,0) + q^2 C_{12}(\vec{R}_1, 0) + q'^2 C_{12}(\vec{R}_2, 0)]\right. \\ \left. + \vec{q} \cdot \vec{q}' [C_{11}(-\vec{R}_3, t) + C_{22}(\vec{R}_2 - \vec{R}_1 - \vec{R}_3, t) - C_{12}(\vec{R}_2 - \vec{R}_3, t) - C_{12}(-\vec{R}_1 - \vec{R}_3, t)]\right\}, \quad (28a)$$

where

$$h(\vec{q}, \vec{q}') \equiv (2/\omega_0) W^2 v_{\vec{q}} \vec{q} \cdot \vec{q}' v_{\vec{q}'}^*, \quad (28b)$$

where  $v_a$  is the volume per particle.

The integrations over  $\vec{q}$  and  $\vec{q}'$  can be carried out analytically for a variety of special cases, such as when  $v_{\vec{q}}$  is a sum of Gaussian functions. For the case of a single Gaussian, for example, where  $v_{\vec{q}} = v_0 e^{-R_0^2 q^2}$ , one obtains upon integrating over  $\vec{q}$  and  $\vec{q}'$ ,

$$\mathcal{F}(t) = \frac{-2\pi^3}{\omega_0} \sum_{\vec{R}_i} W^2 |v_0|^2 \frac{\partial}{\partial D'} \left\{ \exp\left[-\left(\frac{a_1 R_1^2 + a_2 R_2^2 - D' \vec{R}_1 \cdot \vec{R}_2}{4a_1 a_2 - D'^2}\right)\right] (4a_1 a_2 - D'^2)^{-3/2} \right\}_{D'=D}, \quad (29a)$$

$$\vec{R} = \vec{R} + \vec{k},$$

where

$$a_1 = \frac{1}{2} [C_{11}(00) + C_{22}(00)] - C_{12}(\vec{R}_1, 0) + R_0^2, \\ a_2 = \frac{1}{2} [C_{11}(00) + C_{22}(00)] - C_{12}(\vec{R}_2, 0) + R_0^2, \quad (29b) \\ D = C_{11}(-\vec{R}_3, t) + C_{22}(\vec{R}_2 - \vec{R}_1 - \vec{R}_3, t) \\ - C_{12}(\vec{R}_2 - \vec{R}_3, t) - C_{12}(-\vec{R}_1 - \vec{R}_3, t).$$

One may derive analogous results for other choices of  $v_{\vec{q}}$ , although the Gaussian form turns out to be especially simple for explicit calculations. It should be noted that the present Gaussian function in  $\vec{R}$  space is of the form  $e^{-A(\vec{R}_i^0 - \vec{R}_j^0 + \vec{q}_i - \vec{q}_j)^2}$ , which thus includes, in general, nonvanishing contributions to all orders of phonon processes. This function should not be confused with those of the form  $e^{-A(\vec{R}_i - \vec{R}_j)^2}$ , where  $\vec{R}_0$  is the intracell equilibrium distance, for which the principal contribution to even-order phonon processes vanishes.

*Einstein model.* This model provides a highly oversimplified view of crystal vibrations, which is

nevertheless often useful for qualitative purposes.<sup>11</sup>

In the model, all correlations between different crystalline sites are neglected; the crystal is characterized by a single vibrational frequency  $\omega_0$  for all  $\vec{k}$ . The correlation function becomes (assuming three equivalent phonon branches)

$$\alpha_0^2 C_{jk}(R_i, t) = C_{jk}^E \Delta(R_i) [e^{-i\omega_0 t} (n_0 + 1) + e^{i\omega_0 t} n_0], \quad (30)$$

$$C_{jk}^E \equiv \frac{3}{2} \frac{\hbar^2}{\omega_0 a_0^2 (m_j m_k)^{1/2}},$$

where  $a_0$  is the lattice constant, in which units we henceforth scale all lengths (e. g.,  $R \leftarrow R/a_0$ ,  $C \leftarrow C/a_0^2$ , etc.). When  $C$  is inserted in the diatomic model for  $\mathcal{F}(t)$  given in Eq. (28), the  $\Delta$  function in (30) enables the sums over the  $\vec{R}_i$  to be carried out straightforwardly. Since the latter sums can be carried out explicitly, it is advisable no longer to restrict the choice of  $v_{\vec{q}}$  as in Eq. (29). Rather we obtain results with just sums over  $\vec{q}$  and  $\vec{q}'$  remain-

ing, but with the choice of  $v_{\vec{q}}$  arbitrary. It is convenient in the present development to neglect the Debye-Waller-like terms<sup>12</sup> involving  $C(0, 0)$  and  $C(\vec{R}_3, 0)$ , as these are generally negligible, except at very high temperatures, for  $v_{\vec{q}}$ 's of range  $v_0/\alpha_0 \gg C_E^{1/2}$ , which is the case of interest here. (If the potential  $v_{\vec{q}}$  does not fall off exponentially, however,

these need be retained to ensure convergence of the  $\vec{q}$  integrals.) Also, it is somewhat simpler to work with the Fourier transform  $\mathcal{F}(\omega)$  directly, before carrying out the sums over  $\vec{R}_i$ . Employing the well-known relations (see Ref. 13) for evaluating transforms of exponentials of the form in Eq. (29), one obtains

$$\mathcal{F}(\omega) = \sum_n \delta(\omega - n\omega_0) A_n, \quad (31)$$

$$A_n \equiv \sum_{\vec{q}, \vec{q}'} e^{i\vec{q} \cdot \vec{R}_1 - i\vec{q}' \cdot \vec{R}_2} h(\vec{q}, \vec{q}') \left(\frac{n_0+1}{n_0}\right)^{n/2} e^{i\vec{R}_3 \cdot (\vec{q} - \vec{q}')}, \quad I_n(2Q[n_0(n_0+1)]^{1/2} \vec{q} \cdot \vec{q}'),$$

$$Q \equiv C_{11}^E \Delta(\vec{R}_3) + C_{22}^E \Delta(\vec{R}_2 - \vec{R}_1 - \vec{R}_3) - C_{12}^E \Delta(\vec{R}_2 - \vec{R}_3) - C_{12}^E \Delta(\vec{R}_1 + \vec{R}_3),$$

where  $I_n$  is the modified Bessel function of order  $n$ . The sums over  $\vec{R}_i$  are straightforward, but somewhat tedious; the final result is ( $n > 0$ ), omitting the  $E$  superscript in  $C_{jk}^E$ ,

$$A_n = \sum_{\vec{q}, \vec{q}'} \{N\Delta(\vec{q} - \vec{q}' + \vec{G}) [I_n((C_{11} + C_{22})Y) - I_n(C_{11}Y) - I_n(C_{22}Y)] + N\Delta(\vec{q} + \vec{q}' + \vec{G}) [I_n(-2C_{12}Y) - 2I_n(-C_{12}Y)] - I_n((C_{11} + C_{22})Y) - I_n(-2C_{12}Y) - 2I_n((C_{22} - C_{12})Y) - 2I_n((C_{11} - C_{12})Y) + I_n((C_{11} + C_{22} - 2C_{12})Y) + 2I_n(C_{11}Y) + 2I_n(C_{22}Y) + 4I_n(-C_{12}Y)\} h(\vec{q}, \vec{q}') e^{i\vec{R}_3 \cdot (\vec{q} - \vec{q}')} (n_0 + 1/n_0)^{n/2}, \quad (32)$$

where

$$Y \equiv 2\vec{q} \cdot \vec{q}' [n_0(n_0+1)]^{1/2}$$

and  $\vec{G}$  is a reciprocal-lattice vector.<sup>11</sup>

Although Eq. (32) is rigorous for the model considered, it is unnecessarily complicated for eliciting a qualitative estimate of the frequency dependence of  $\alpha$ . For the latter purpose, it is preferable to consider a simplified model where only interactions between atoms within the same cell are considered, and restriction is made to the optic vibrations of these atoms. The former amounts to choosing  $\vec{R}_1 = \vec{R}_2 = 0$  in Eq. (28); this is physically reasonable for the optic modes because the short-range potential turns out to yield the dominant contribution to multiphonon absorption. If we now retain the tensor character of  $\vec{C}$  in deriving  $\mathcal{F}$ , then

$$A_n = h_0 \sum_{\vec{q}, \vec{q}'} e^{i\vec{q} \cdot \vec{q}'} v_{\vec{q}} v_{\vec{q}'}^* (\hat{W}_1 \cdot \vec{q})(\hat{W}_1 \cdot \vec{q}') \left(\frac{n_0+1}{n_0}\right)^{n/2} \times I_n(2[n_0(n_0+1)]^{1/2} (C_{11} \vec{f}_1 \cdot \vec{q} \vec{f}_1 \cdot \vec{q}' + C_{22} \vec{f}_2 \cdot \vec{q} \vec{f}_2 \cdot \vec{q}' - 2C_{12} \vec{f}_1 \cdot \vec{q} \vec{f}_2 \cdot \vec{q}')), \quad (33)$$

where

$$h_0 \equiv 2\omega_0^{-1} W^2.$$

We now choose  $\vec{f}_1$  and  $\vec{f}_2$  to lie along the vector  $\kappa$ ; then  $\hat{f}_1 = -\hat{f}_2 = \hat{\kappa}$ ,  $|\vec{f}_1| = (m_2/m_1)^{1/2} |\vec{f}_2|$ , and  $|\vec{f}_1|^2 + |\vec{f}_2|^2 = 1$ .

$$A_n = h_0 \sum_{\vec{q}, \vec{q}'} e^{i\vec{q} \cdot \vec{q}'} v_{\vec{q}} v_{\vec{q}'}^* (\hat{\kappa} \cdot \vec{q})(\hat{\kappa} \cdot \vec{q}') \left(\frac{n_0+1}{n_0}\right)^{n/2} \times I_n(2[n_0(n_0+1)]^{1/2} (\hat{\kappa} \cdot \vec{q})(\hat{\kappa} \cdot \vec{q}') C_E), \quad (34)$$

where

$$C_E = f_1^2 C_{11} + f_2^2 C_{22} - 2f_1 f_2 C_{12} = \frac{3}{2} \frac{\hbar^2}{\mu \omega_0 \alpha_0^2},$$

where  $\mu$  is the reduced mass,  $\mu^{-1} = m_1^{-1} + m_2^{-1}$ . We have again neglected Debye-Waller factors as before, which can be shown to be valid for low temperatures, as long as the anharmonicity parameter  $C_E R_0^2$  (where  $R_0$  is the falloff parameter in the potential) is small compared to unity. At low temperatures we need keep just the lowest-order term in the expansion of  $I_n$ , whence

$$A_n = \frac{1}{4} h_0 \left| \sum_{\vec{q}} e^{i\vec{q} \cdot \hat{\kappa}} v_{\vec{q}} (\hat{\kappa} \cdot \vec{q})^{n+1} \right|^2 \frac{C_E^n (n_0+1)^n}{n!} = \frac{1}{4} h_0 f_n C_E^n (n_0+1)^n / n!, \quad (35)$$

where

$$f_n \equiv \left| \frac{\partial^{n+1}}{\partial r^{n+1}} v(r) \right|_{r=\kappa}^2.$$

Thus the strength of the  $n$ th peak is determined among other things by the square of the  $(n+1)$ th derivative of the interatomic potential in real space, evaluated at the equilibrium separation distance  $\kappa$ . The absorption coefficient involves

$$\alpha(\omega) \propto n^{-3} [1 + n(\omega)]^{-1} A_n. \quad (36)$$

For low temperatures and values of  $\omega$  of interest here, we may approximate  $1+n(\omega)$  by unity; then

$$\ln \alpha = -\ln(n!n^3) + n \ln[C_E(n_0+1)] + \ln(f_n) + \text{const.} \quad (37)$$

An often-used potential for alkali halides is the Born-Mayer potential, where the short-range potential, which yields the dominant contribution to higher-order derivatives in Eq. (35), is of the form

$$v(r) = e^{-\lambda r}, \quad (38)$$

with  $\lambda \approx 16-20$  for most alkali halides, when  $r$  is measured in units of  $a_0$ . Thus,

$$\ln \alpha = -n\{(1/n) \ln(n!n^3) - \ln[C_E(n_0+1)\lambda^2]\} + \text{const.} \quad (39)$$

The factor  $n^{-1} \ln(n!n^3)$  varies from  $\sim 1.8$  to  $\sim 2.1$  for  $n=4$  to  $10$ ; thus  $\alpha$  is very nearly exponential as a function of  $n=\omega/\omega_0$  in this range. Very similar results are obtained for a power law  $v$  as well. Thus within the Einstein model, it can be shown that exponential behavior is satisfied approximately, although not exactly, over fairly large regions of  $\omega$ , and for a variety of interatomic potentials.

Note that if  $v_{\vec{q}}$  does not exist, then strictly speaking one needs to modify  $v(\vec{r})$  before applying the above procedures. For example, one might use  $(r^2 + \gamma^2)^{-m}$  and  $r^m e^{-\gamma r}$  in place of  $r^{-2m}$  and  $r^m$  ( $m > 0$ ), respectively; in the end result, one sets  $\gamma \rightarrow 0$ .

*Convolution expansion for  $\mathcal{F}$ .* In general, neither the Fourier transform with respect to  $t$ , nor the sums over  $\vec{R}_i$  in  $\mathcal{F}$ , can be carried out analytically. On the other hand, the sums over the  $\vec{q}_i$  may be carried out explicitly for certain choices of  $v$ , as already illustrated for the case of a Gaussian  $v_{\vec{q}}$ , for example. Thus, it is of special interest to devise suitably general techniques for evaluating  $\mathcal{F}(\omega)$  which take these observations into account. We consider here one such method, that of the convolution expansion, which appears to be especially promising for actual computations in a variety of cases. We note that variations of this technique have, in fact, been applied previously in some similar problems.<sup>14</sup>

Let us assume that the sums over  $\vec{q}$  and  $\vec{q}'$  in Eqs. (28) have been carried out, yielding a functional of  $D$  which we write in the form

$$\mathcal{F}(t) = \sum_{\vec{R}_1 \vec{R}_2 \vec{R}_3} J(\vec{R}_1, \vec{R}_2, \vec{R}_3, D(\vec{R}_1, \vec{R}_2, \vec{R}_3, t)). \quad (40)$$

Then, expanding  $J$  in a Taylor series in  $D$  yields ( $\omega \neq 0$ )

$$\mathcal{F}(\omega) = \sum_{n=1}^{\infty} \sum_{\vec{R}_1 \vec{R}_2 \vec{R}_3} g_n(\vec{R}_1 \vec{R}_2 \vec{R}_3) \rho_n(\vec{R}_1 \vec{R}_2 \vec{R}_3, \omega), \quad (41a)$$

where

$$g_n = \frac{1}{n!} \left[ \frac{\partial^n J(D)}{\partial D^n} \right]_{D=0},$$

$$\rho_1 = (2\pi)^{-1} \int dt e^{-i\omega t} D(\vec{R}_1, t), \quad (41b)$$

$$\rho_{n+1} = \int d\omega' \rho_n(\omega - \omega') \rho_1(\omega').$$

Here  $\rho_n$  is the  $n$ th convolution of  $D$ . One obtains an alternative expression for  $g_n$  by expanding in powers of  $D$  prior to integrating over  $\vec{q}$  and  $\vec{q}'$ , whence

$$g_n = (1/n!) \int d\vec{q} d\vec{q}' e^{i\vec{q} \cdot \vec{R}_1 - i\vec{q}' \cdot \vec{R}_2 + i\vec{k} \cdot \vec{R}_3} h(\vec{k} \vec{q} \vec{q}') e^{i\vec{k} \cdot (\vec{q} - \vec{q}')} \\ \times \exp\left[-\frac{1}{2}(q^2 + q'^2)[C_{11}(00) + C_{22}(00)]\right] \\ + q^2 C_{12}(\vec{R}_1, 0) + q'^2 C_{12}(\vec{R}_2, 0) \} (\vec{q} \cdot \vec{q}')^n. \quad (42)$$

The choice of whether to first integrate and take derivatives, or integrate directly as in (42), may be dictated entirely as a matter of convenience.

The series (41a) has a number of computational and interpretational advantages in the present case, among which are the following: (a) The function  $\rho_1$  is generally expressible in closed form, while  $D$  is not. (b) The  $\rho_n$  are easily generated from  $\rho_1$  by recursive means on a digital computer, or via analytic approximations.<sup>15</sup> (c) The function  $\rho_1$  is proportional to the dimensionless phonon parameter  $C_0 = \hbar^2/m a_0^2 \omega_0$ , where  $m$  is either the reduced mass or total mass, depending on the vibration of interest, and  $\omega_0$  is a characteristic phonon frequency. Since typically  $C_0 \sim 10^{-4}$ , the series (41a) may be expected to converge quite rapidly in most instances. (d) The function  $\rho_n$  is restricted to a range  $\pm n\omega_m$ , where  $\omega_m$  is the maximum phonon frequency. Thus, for cases when the convolution series is rapidly convergent, the main contribution to the  $n$ -phonon regime comes from just  $\rho_n$  alone. (e) Physically,  $\rho_n$  represents the  $n$ -phonon contribution to  $\mathcal{F}$ , which is the sum of all processes involving exactly  $n$  real or virtual phonons.

The convolution expansion is thus observed to provide a method of evaluating multiphonon absorption which is particularly well suited for physical interpretation in terms of  $n$ -phonon processes, as well as being mathematically advantageous for actual computations.

#### IV. DISCUSSION

We have here presented a theory of multiphonon absorption due to anharmonicity in crystals which accounts for various classes of phonon processes to infinite order. The character of the absorption is determined essentially by just a single correlation function  $\mathcal{F}$  involving an effective anharmonic potential  $F_{\vec{r}}$  describing the decay of the TO phonon  $\omega_{\vec{r}}$ . The function  $\mathcal{F}$  is specified fully once the interatomic potential  $v$  and the displacement-correlation tensors  $\vec{C}$  have been specified. For the

intrinsic bulk case  $\mathcal{F}$  takes the explicit form displayed in Eq. (23). The latter expression for  $\mathcal{F}$  can be simplified further in various instances, as demonstrated in Sec. III in connection with a diatomic crystal, isotropic  $\overline{C}$ , and special choices for  $v_q$ .

In what follows, we discuss some of the implications of the present results, such as with respect to the frequency and temperature dependence of  $\alpha$ . Comparison with experiment and with other theoretical treatments is carried out as well.

*Frequency dependence.* The convolution expansion of Eqs. (41) provides a useful framework within which to investigate various general features of the frequency dependence of  $\alpha(\omega)$ . Perhaps the most obvious, but nevertheless significant, implication of the convolution formalism is the lack of structure in higher-order phonon contributions, a direct consequence of the well-known smoothing effects resulting from repeatedly convoluting a given function.<sup>14</sup> This conclusion is consistent with the general trend of experimental observations<sup>16</sup> on multiphonon absorption, which often display substantial structure for low-order processes, but little or none for higher-order ones. Of course, the presence of very sharp peaks in  $\rho_1(\omega)$ , such as may be associated with Van Hove singularities,<sup>8</sup> will be manifest in an appropriately broadened structure arising in higher convolutions. It is apparent, in any case, that an investigation of just the functions  $\rho_n$  alone for a given lattice model can reveal a good deal of information regarding structure in  $\alpha(\omega)$  vs  $\omega$ . For the detailed spectrum, of course, one must carry out the sums over  $n$  and  $\vec{R}_i$ , weighting the  $\rho_n$  with the appropriate  $g_n$ 's associated with a particular potential  $v$ .

As noted previously, the contribution from each  $\rho_n$  extends over an interval of range  $n\omega_m$ , where  $\omega_m$  is the maximum phonon frequency. Also, at low and intermediate temperatures  $\rho_{n+1}/\rho_n \sim C_E(g_{n+1}/g_n)$ ; since  $C_E \sim 10^{-4}$ , if  $g_{n+1}/g_n \ll C_E^{-1}$  (as is expected to generally be the case in practice), then  $\rho_{n+1} \ll \rho_n$ . Thus the contribution to absorption in the  $n$ -phonon regime  $n\omega_m < \omega < (n+1)\omega_m$  is given to an excellent approximation by just  $\rho_n$  alone. This conclusion does not follow at very high temperatures ( $n_h \gg 1$ ) and, strictly speaking, applies only to the average absorption within a regime when substantial structure is present in  $\rho_1(\omega)$ . All other factors being equal, the decay rate of  $\alpha(\omega)$  vs  $\omega$  should thus vary inversely with  $C_E$ . As an example of experimental evidence<sup>17</sup> in support of this contention, one may compare data for LiF with that for NaCl and KCl. It is found that the decrease per unit phonon in the logarithm of  $\alpha$  is about one and a half times as great for the latter than the former. This is consistent with the observation that if we attribute multiphonon processes to just

TO phonons, then  $C_E$  is about three times as great for LiF than for NaCl and KCl.

Recent experiments<sup>17</sup> indicate that multiphonon absorption in a variety of crystals, especially ionic crystals, vary very nearly exponentially as a function of frequency, over a substantial frequency range. If  $\rho_1$  is a reasonably smooth function, then one can argue very roughly that if  $g_{n+1}/g_n \sim g$  for all  $n$ , then  $\mathcal{F}_{n+1}/\mathcal{F}_n \sim gC$ , which implies an exponential form for  $\alpha$ . Apparently, the condition  $g_{n+1}/g_n \sim g$  is realized in practice, at least in approximate fashion, as discussed in Sec. III.

Although somewhat artificial, the Einstein model should nevertheless be useful in deducing various qualitative information regarding  $\alpha(\omega)$ . For realistic models,  $\rho$  is a continuous function of  $\omega$ , and smoothing of higher-order convolutions would be expected to lead to a corresponding smoothing of  $\alpha(\omega)$ . It is thus reasonable to assume that just the average rather than the particular details of the phonons involved are important for large  $n$ . In this spirit, the curve for  $\alpha$  obtained by continuously connecting the  $\delta$ -function strengths of the Einstein model (value of  $\alpha$  integrated over the  $n$ -phonon regime), defined at integer  $n \equiv \omega/\omega_0$  to all values of  $\omega$ , is expected to provide a qualitatively meaningful picture of the frequency dependence of  $\alpha$  for more general cases as well. The emergence of exponential behavior follows very naturally in the Einstein model, as discussed previously, and arises independently of crystalline effects ( $\overline{G} \neq 0$ ), although crystallinity may be important in determining the absolute magnitude of  $\alpha$ .

Inspection of Eqs. (28) reveals that all else being equal, the absorption decreases faster with increasing  $\omega$  as the falloff parameter ( $R_0$ ) in the potential increases. For a Gaussian or Born-Mayer  $v$  in the Einstein case, this is seen explicitly, as  $\sigma$  is equal to the sum of  $\ln R_0^2$  plus other terms. The details of the absorption depend on the shape of  $v$  as well, although an exponential-like behavior would be expected to arise for most physically reasonable choices of  $v$ .

Existing experimental data on alkali halides<sup>17</sup> implies that for  $T = 0^\circ\text{K}$  and  $\omega \gg \omega_{\text{TO}}$ ,  $\alpha \propto e^{-\sigma(\omega/\omega_{\text{TO}})}$ , with  $\sigma \sim 3.5$  for NaCl, KCl, and KBr, and  $\sigma \sim 2.4$  for LiF. In terms of  $\omega/\omega_{\text{LO}}$  ( $\omega_{\text{LO}}$  is the longitudinal-optical-phonon frequency), in which units the data in Ref. 17 are presented, the corresponding  $\sigma \sim 5.6, 5.2, 5.1,$  and  $5.3$ ; we employ scaling in  $\omega_{\text{TO}}$  here to provide orientation of the multiphonon results with the fundamental resonance peaking at  $\omega_{\text{TO}}$ . We here calculate  $\sigma$  within the Einstein model, and appropriate to the Born-Mayer potential [see Eq. (39)]. Employing the average value of the quantity  $n^{-1} \ln(n^3 n!)$  between  $n = 4$  and  $10$ , and the Born and Huang<sup>18</sup> values for  $\lambda$ , and calculating  $C_E$  employing the  $k=0$  TO phonon  $\omega_{\text{TO}}$  for



$\omega_0$ , one obtains  $\sigma \sim 3.6, 3.6, 4.0,$  and  $2.6$  for the same crystals. The use of  $\omega_{TO}$  for  $\omega_0$  is probably inaccurate, as the optic-phonon frequency varies substantially over the Brillouin zone<sup>19</sup> for alkali halides. It is not unreasonable to guess that an appropriate weighted frequency lies between about  $1.1\omega_{TO}$  to  $1.4\omega_{TO}$ . If  $\omega_0 = 1.2\omega_{TO}$  then one finds  $\sigma \sim 3.2, 3.2, 3.6,$  and  $2.2$  for NaCl, KCl, KBr, and LiF, respectively. Considering the crudeness of the Einstein model, these results appear to be in adequate agreement with experiment. When one employs a power law for  $\nu$  in place of the Born-Mayer potential, the agreement with experiment is much poorer, especially for large  $n$ . This is not surprising, as the power law is conventionally determined from thermodynamic prescriptions requiring just the first few derivatives of  $\nu$ , while in the present case we require accurate values for the higher derivatives of  $\nu$  as well.

*Temperature dependence.* The explicit temperature variation of  $\text{Im}P$  obtained here is exactly equivalent to that of existing work<sup>1-4</sup> when differences in notation are accounted for, in the low-temperature limit ( $n\bar{\nu} \lesssim 1$ ). Essentially, an  $n$ -phonon process contributes a term proportional to the absorption. It should be emphasized that for calculations applicable to real crystals one must also incorporate thermal expansion and self-energy effects on the phonon spectrum, as discussed by Cowley,<sup>4</sup> for example. Such may be done either from first principles, or in a semiphenomenological fashion, as in calculations by Namjoshi,<sup>19</sup> for example.

At very high temperatures ( $n\bar{\nu} \gg 1$ ), the Debye-Waller-like factors in Eqs. (28), which constitute a temperature-dependent "vertex renormalization,"<sup>20</sup> become significant. This renormalization is not accounted for in theories employing expansions in  $\bar{\nu}$ . Our results show that the  $n\bar{\nu}^{-1}$  dependence predicted in this limit by the latter theories is, in fact, cut down by exponential factors of the form  $e^{-n\bar{\nu}}$ . For the Einstein model, for example, let us examine the effect of retaining Debye-Waller factors in a typical term in  $A_n$ , such as the first in Eq. (32). One needs to evaluate ( $\bar{G} = 0$ )

$$A \equiv \int d\bar{q} I_n (2q^2 C_E n_0) e^{-2n_0 C_E q^2} \nu_{\bar{q}}^2. \quad (43)$$

For purposes of illustration the potential  $\nu_{\bar{q}} = q^{-1/2} e^{-R_0^2 q^2}$  enables the integral to be evaluated explicitly, whence

$$A = \left( \frac{n_0 C_E}{(R_0^4 + R_0^2 n_0 C_E)^{1/2} + R_0^2 + n_0 C_E} \right)^n \frac{1}{(R_0^4 + R_0^2 n_0 C_E)^{1/2}}. \quad (44)$$

Thus, for  $k_B T / \omega_0 > R_0^2 / C_E$ , the dependence of  $A(T)$  on  $T$  and  $n$  becomes relatively weak. In practice, temperatures where  $A$  deviates substantially from

$n_0^{-1}$  may or may not be reached prior to melting, depending on the particular values of  $R_0$  and  $C_E$  for the crystal concerned.

*Comparison with other work.* The expressions for lower-order processes in  $\text{Im}P$  can be shown to be equivalent to existing results<sup>1-4</sup> obtained by various authors utilizing what amounts to perturbation theory for the Green's functions  $\langle\langle a_{\bar{q}}^\dagger(t); a_{\bar{q}}(0) \rangle\rangle$ . In contrast to the latter works, however, we here obtain a single unified expression for the damping ( $\text{Im}\Pi \sim \text{Im}P$ ) which contains phonon processes summed to all orders.

Recently, several simplified theories of multiphonon absorption have been presented. Sparks and Sham<sup>21</sup> consider  $n$ -phonon splitting processes at a single vertex. The resulting expressions are evaluated by assuming the major contribution to involve just a single critical-point phonon  $\omega_c$ , a concept not far removed from an Einstein approach, in practice. It can be seen from the convolution expansion that under the same conditions where just  $\rho_n$  dominates the  $n$ -phonon regime, the splitting process mentioned yields the dominant contribution to  $\alpha$ . In another recent treatment by Hellwarth *et al.*,<sup>22</sup> an Einstein-like model, where only discrete phonon transitions within a unit cell are allowed, is employed. Both treatments appear to obtain the exponential-like behavior as here. Mills and Maradudin<sup>23</sup> have also obtained an exponential behavior, within a classical model. The agreement between the various theories is not surprising, in view of the similarity of assumptions regarding the suppression of phonon dispersion. Also, the fact that crystallinity plays a minor role in determining the exponential behavior allows for considerable leeway in the choice of models. The predicted temperature dependences<sup>21,22</sup> are also equivalent, with the exception of the very-high-temperature regime, where the present approach leads to the modifications discussed previously.

It should be noted that the present approximations leading to Eq. (23) account for contributions to  $\alpha$  from just processes occurring at a single vertex, similar to those in the treatment in Ref. (21). Presumably, processes involving repeated vertices could be accounted for by employing vertex corrections, as suggested recently by Sparks and Sham.<sup>24</sup> The latter authors find corrections which, as an upper estimate, appear to modify the results for  $n = 1-6$  by changing  $\sigma \rightarrow \sigma'(\omega)$ , where  $\sigma' - \sigma \lesssim -0.3$ . This suggests that for alkali halides, where  $\sigma \sim 3.5$ , one obtains a reasonable estimate of the frequency dependence by omitting vertex corrections all together, although these may be important for large  $n$ , or if very accurate results are required.

We have not here treated the contribution of

higher-order electric moments<sup>3</sup> to  $\alpha$ . In general, these could be equal in importance to the anharmonicity effects.<sup>5</sup> However, the rather good agreement with experiment achieved in their absence in the case of alkali halides suggests that the effects might be small in these crystals. Hellwarth<sup>22</sup> has calculated electric-moment contributions within his model, finding them to be small except for highly anharmonic crystals, such as LiF. The methods of the present paper are well suited for calculating absorption due to electric moments acting separately,<sup>25</sup> as well as in combination with anharmonic interactions.

In closing, it should be remarked that multiphonon absorption in real crystals involves important contributions due to extrinsic as well as intrinsic, and surface as well as bulk processes.<sup>6,16</sup> The present methods can be adapted to treat the latter effects, although the resulting expressions could well become difficult to evaluate, due to a lack of translational invariance in one or more crystal dimensions.

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#### APPENDIX

The retarded Green's function for the phonon operators  $A_{\mathbf{k}\alpha}^{\pm}(t) = b_{\mathbf{k}\alpha}^{\pm}(t) + b_{\mathbf{k}\alpha}^{\pm\dagger}(t)$  is defined as

$$iG_{\mathbf{k}\alpha}^{\pm, \alpha'}(t-t') = \theta(t-t') \langle [A_{\mathbf{k}\alpha}^{\pm}(t), A_{\mathbf{k}\alpha'}^{\pm\dagger}(t')] \rangle. \quad (\text{A1})$$

In the development that follows we suppress the branch index  $\alpha$  for notational simplicity. We will here follow closely the procedures and notation employed in Ref. 26, which treats a slightly more general problem, and obtains results equivalent to, but in a different form from, those derived here.

To derive Dyson's equation [Eqs. (10)–(12)] we first differentiate  $G_{\mathbf{k}\alpha}^{\pm}(t-t')$  with respect to  $t$ , and the Green's function generated by this operation with respect to  $t'$ . Time derivatives of  $A_{\mathbf{k}}^{\pm}(t)$  that appear are reexpressed in terms of the original  $A_{\mathbf{k}}^{\pm}(t)$  operators by using the equations of motion as determined by the full anharmonic Hamiltonian

$$H = \sum_{\mathbf{k}} \omega_{\mathbf{k}} b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + V_A.$$

To carry out these operations, we first take the second derivative of  $G_{\mathbf{k}\alpha}^{\pm}(t-t')$  with respect to  $t$ , which gives

$$i \frac{d^2}{dt^2} G_{\mathbf{k}\alpha}^{\pm}(t-t') = \frac{d}{dt} \{ \delta(t-t') \langle [A_{\mathbf{k}}^{\pm}(t), A_{\mathbf{k}}^{\pm\dagger}(t')] \rangle \} + \delta(t-t') \langle [\dot{A}_{\mathbf{k}}^{\pm}(t), A_{\mathbf{k}}^{\pm\dagger}(t')] \rangle + (t-t') \langle [\ddot{A}_{\mathbf{k}}^{\pm}(t), A_{\mathbf{k}}^{\pm\dagger}(t')] \rangle. \quad (\text{A2})$$

Using the equations of motion, the required time derivatives of  $A_{\mathbf{k}}^{\pm}(t)$  are found to be ( $\hbar=1$ )

$$i\dot{A}_{\mathbf{k}}^{\pm}(t) = [A_{\mathbf{k}}^{\pm}(t), H] = \omega_{\mathbf{k}} B_{\mathbf{k}}^{\pm}(t) + [A_{\mathbf{k}}^{\pm}(t), V_A] = \omega_{\mathbf{k}} B_{\mathbf{k}}^{\pm}(t), \quad (\text{A3})$$

$$i\ddot{A}_{\mathbf{k}}^{\pm}(t) = -i\omega_{\mathbf{k}} [B_{\mathbf{k}}^{\pm}(t), H] = \omega_{\mathbf{k}} \{ -i\omega_{\mathbf{k}} A_{\mathbf{k}}^{\pm}(t) - i[B_{\mathbf{k}}^{\pm}(t), V_A] \}$$

or, using the definition in Eqs. (12) for  $F_{\mathbf{k}}$ ,

$$\ddot{A}_{\mathbf{k}}^{\pm}(t) = -\omega_{\mathbf{k}} A_{\mathbf{k}}^{\pm}(t) - 2\omega_{\mathbf{k}} F_{\mathbf{k}}^{\pm}.$$

Taking the Fourier transform of Eq. (A2) with respect to  $t$  gives

$$i \int_{-\infty}^{\infty} e^{i\omega t} \ddot{G}_{\mathbf{k}\alpha}^{\pm}(t-t') dt = \int_{-\infty}^{\infty} e^{i\omega t} \frac{d}{dt} \{ \delta(t-t') \langle [A_{\mathbf{k}}^{\pm}(t), A_{\mathbf{k}}^{\pm\dagger}(t')] \rangle \} dt + \int_{-\infty}^{\infty} e^{i\omega t} \{ \delta(t-t') \langle [\dot{A}_{\mathbf{k}}^{\pm}(t), A_{\mathbf{k}}^{\pm\dagger}(t')] \rangle + \theta(t-t') \langle [\ddot{A}_{\mathbf{k}}^{\pm}(t), A_{\mathbf{k}}^{\pm\dagger}(t')] \rangle \} dt. \quad (\text{A4})$$

Upon integrating by parts, the first term on the right-hand side of Eq. (A4) may be seen to vanish, so that

$$-2\pi i \omega^2 G_{\mathbf{k}\alpha}^{\pm}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \{ \delta(t) \{ -i\omega_{\mathbf{k}} \langle [B_{\mathbf{k}}^{\pm}(t), A_{\mathbf{k}}^{\pm\dagger}(0)] \rangle - i \langle [[A_{\mathbf{k}}^{\pm}(t), V_A], A_{\mathbf{k}}^{\pm\dagger}] \rangle \} + \theta(t) \{ -\omega_{\mathbf{k}}^2 \langle [A_{\mathbf{k}}^{\pm}(t), A_{\mathbf{k}}^{\pm\dagger}(0)] \rangle - \omega_{\mathbf{k}} \langle [2F_{\mathbf{k}}^{\pm}(t), A_{\mathbf{k}}^{\pm\dagger}(0)] \rangle \} \}. \quad (\text{A5})$$

Using

$$G_{\mathbf{k}}^0(\omega) = \frac{\omega_{\mathbf{k}} \pi^{-1}}{(\omega^2 - \omega_{\mathbf{k}}^2 + i\epsilon)},$$

the equation of motion for the Green's function

$G_{\mathbf{k}\alpha}^{\pm}(\omega)$  may be expressed in terms of the GF  $\langle\langle F_{\mathbf{k}}, A_{\mathbf{k}}^{\pm\dagger} \rangle\rangle_{\omega}$  as

$$G_{\mathbf{k}\alpha}^{\pm}(\omega) = G_{\mathbf{k}}^0(\omega) [ \delta_{\mathbf{k}, \mathbf{k}'} + \langle\langle F_{\mathbf{k}}, A_{\mathbf{k}}^{\pm\dagger} \rangle\rangle_{\omega} ]. \quad (\text{A6})$$

Having defined the GF on the right-hand side of

Eq. (A6) as

$$i\langle\langle F_{\mathbf{k}}^*(t), A_{\mathbf{k}}^\dagger(t') \rangle\rangle = \theta(t-t')\langle\langle F_{\mathbf{k}}^*(t), A_{\mathbf{k}}^\dagger(t') \rangle\rangle, \quad (\text{A7})$$

we proceed, as before, first taking the second derivative of  $\langle\langle F_{\mathbf{k}}^*(t), A_{\mathbf{k}}^\dagger(t') \rangle\rangle$  with respect to  $t'$ , then reexpressing  $A_{\mathbf{k}}^\dagger(t')$  via the equations of motion, and finally Fourier transforming with respect to  $\tau = t - t'$ . These procedures give for the GF in Eq. (A7)

$$\begin{aligned} & \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \frac{d^2}{d\tau^2} \langle\langle F_{\mathbf{k}}^*(0), A_{\mathbf{k}}^\dagger(-\tau) \rangle\rangle \\ &= \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \{ -i\omega \delta(\tau) \langle\langle F_{\mathbf{k}}^*(\tau), A_{\mathbf{k}}^\dagger(0) \rangle\rangle \\ & \quad - \delta(\tau) \langle\langle F_{\mathbf{k}}^*(\tau), i\omega_{\mathbf{k}} B_{\mathbf{k}}^\dagger(0) \rangle\rangle \end{aligned}$$

$$\begin{aligned} & + \theta(\tau) \{ \langle\langle F_{\mathbf{k}}^*(\tau), -\omega_{\mathbf{k}}^2 A_{\mathbf{k}}^\dagger(0) \rangle\rangle \\ & \quad + \omega_{\mathbf{k}} \langle\langle F_{\mathbf{k}}^*(\tau), -2F_{\mathbf{k}}^\dagger(0) \rangle\rangle \}. \quad (\text{A8}) \end{aligned}$$

The equal-time commutator of  $F_{\mathbf{k}}^*(0)$  with  $A_{\mathbf{k}}^\dagger(0)$  vanishes, so that

$$\begin{aligned} \mathcal{P}_{\mathbf{k}\mathbf{k}}^*(\omega) &= [G_{\mathbf{k}}^0(\omega)]^{-1} \langle\langle F_{\mathbf{k}}^*, A_{\mathbf{k}}^\dagger \rangle\rangle_{\omega} \\ &= \frac{1}{2} \langle\langle F_{\mathbf{k}}, B_{\mathbf{k}}^\dagger \rangle\rangle_{\tau=0} + \langle\langle F_{\mathbf{k}}^*, F_{\mathbf{k}} \rangle\rangle_{\omega}. \quad (\text{A9}) \end{aligned}$$

Using (A6) and (A10), the equation of motion for the Green's function  $G_{\mathbf{k}\mathbf{k}}^*(\omega)$  may be written

$$G_{\mathbf{k}\mathbf{k}}^*(\omega) = \delta_{\mathbf{k}\mathbf{k}} G_{\mathbf{k}}^0(\omega) + G_{\mathbf{k}}^0(\omega) \mathcal{P}_{\mathbf{k}\mathbf{k}}^*(\omega) G_{\mathbf{k}}^0(\omega), \quad (\text{A10})$$

from which Eqs. (10)–(12) of the text follow directly.

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