

## Theory of microwave absorption in wide-band-gap insulators: The role of thermal phonon lifetimes

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Earlier it has been argued that, in insulating materials, a proper calculation of the contributions to the far-infrared and microwave absorption rate from two-phonon difference processes must take explicit account of the influence of the finite lifetime of the thermal phonons which participate. We explore this issue further here. After initial remarks on the means of incorporating these effects into the computation of the absorption rate, we present numerical studies of the frequency and temperature variations of the low-frequency absorption constant for NaCl and KI, through use of a model which accurately reproduces the phonon spectrum of these materials. Our results provide a reasonable account of the existing data on these materials, and contain predictions that can be tested by further experimental work.

### I. INTRODUCTION

In wide-band-gap insulators, such as the alkali halides, through use of anharmonic perturbation theory one may calculate the contributions from multiphonon processes to the absorption coefficient  $\alpha(\Omega)$  which describes the attenuation of electromagnetic radiation of frequency  $\Omega$  in the material. At moderate temperatures, in general, one expects that two-phonon processes provide the dominant contribution to  $\alpha(\Omega)$  in the far-infrared, though it has been argued that three-phonon processes contribute as well. Particularly in the alkali halides, extensive calculations based on rather sophisticated models have appeared, and these account nicely for infrared absorption data.<sup>1</sup>

Special problems arise at low frequencies, such as those encountered in the very-far-infrared or microwave-frequency regime. The leading contribution to  $\alpha(\Omega)$  clearly has its origin in two-phonon processes, and elementary phase-space considerations suggest that the two-phonon difference process should dominate, since then the whole bath of thermal phonons may contribute to the attenuation rate. But in any material, as the frequency  $\Omega$  approaches zero, one sees easily that such processes fail to conserve energy and wave vector. Let the photon have wave vector  $\mathbf{Q}$  (clearly very close to zero on the scale of the Brillouin zone), and suppose the photon is absorbed by mixing with a phonon of wave vector  $\mathbf{q}$  on branch  $j$  of the phonon dispersion curves, to produce a phonon of wave vector  $\mathbf{q}'$  on branch  $j'$ . We have, if  $\Omega(\mathbf{q},j)$  is the frequency of phonon  $(\mathbf{q},j)$ , the requirement that  $\Omega = \Omega(\mathbf{q},j) - \Omega(\mathbf{q}',j')$  from energy conservation. Near room temperature or above, phonon modes throughout the Brillouin zone are present as thermal excitations, so in general  $\mathbf{q}$  is large. Also  $\mathbf{q}' = \mathbf{q} + \mathbf{Q} \cong \mathbf{q}$  because  $\mathbf{Q}$  is very small. The two-phonon difference process is thus, to excellent approximation, a vertical transition between adjacent phonon bands when  $j \neq j'$ .

Then as  $\Omega \rightarrow 0$ , energy cannot be conserved in such an interband process at a general point in the Brillouin zone. Distinct branches may be degenerate along special lines or at special points in the Brillouin zone, and as  $\Omega \rightarrow 0$  we may conserve energy very near such special features. However, the phase space available for such processes is small. As  $\mathbf{q}$  (and also  $\mathbf{q}'$ ) approach zero,  $\Omega(\mathbf{q},j) - \Omega(\mathbf{q}',j')$  becomes small if  $j$  and  $j'$  refer to acoustical-phonon branches, but upon noting that the velocity of light in the medium is orders of magnitude larger than sound velocities in the solid state, one may show that processes which involve long-wavelength acoustic phonons also fail to conserve energy and wave vector. This rules out intraband processes.

In an earlier paper<sup>2</sup> it was argued that since thermal phonons have finite lifetimes, their energy is not precisely defined, and in such two-phonon difference processes energy is conserved only to within the inverse of the thermal phonon lifetime, which can be the order of  $10 \text{ cm}^{-1}$  or more at room temperature. In many materials the separation between adjacent phonon bands can be this order or slightly more over an appreciable fraction of the Brillouin zone, so relaxation of strict energy conservation "activates" two-phonon difference processes over a significant fraction  $f$  of the Brillouin zone. Quite clearly,  $f$  is independent of  $\Omega$  as  $\Omega \rightarrow 0$ , so in this limit processes near special points and lines which strictly conserve energy are overwhelmed when energy conservation is relaxed. In the earlier paper, calculations carried out by analytic methods based on a crude model of the phonon spectrum accounted for the available data in several alkali halides.

This paper is devoted to a study of this question, on the basis of model calculations which accurately describe the phonon spectrum of two selected alkali halides, NaCl and KI. These two materials have very different phonon spectra. The optical- and acoustical-phonon branches of NaCl overlap in frequency, to produce a density of states that is

smooth with no gaps. In contrast, there is a substantial gap between the two sets of branches in the case of KI. Since intrabranch two-phonon difference processes are forbidden in the alkali halides, and processes in which one phonon is optical and one is acoustical in nature, tend to generate the largest matrix element; it is of interest to compare the results of calculations which incorporate the role of lifetime broadening for these two materials. We shall find that our calculations provide a rather good account of the existing data on these materials, and suggest new experiments be carried out.

In Sec. II we present a theoretical discussion of the means by which one incorporates lifetime broadening of the thermal phonons into the theory. This section is motivated in part by remarks in a recent paper by Hardy and Karo,<sup>3</sup> who have omitted the influence of lifetime broadening in their recent studies. In our view, in the low-frequency regime these results are quantitatively unreliable as a consequence. We elaborate on this point later on. In addition, these authors criticize the method we used earlier to incorporate lifetime broadening into the theory. We shall see in Sec. II that our earlier prescription may be derived in a very straightforward manner, and contrary to the assertion in Ref. 3, it provides us with an approximate expression for the proper self-energy which, when considered as a function of frequency, has the proper analytic structure. We note, incidentally, that in a few of their calculations, Eldridge and Staal<sup>4</sup> introduced the influence of thermal phonon lifetime broadening through a scheme which leads to unphysical properties of the proper self-energy.

## II. SOME THEORETICAL CONSIDERATIONS

We are interested in the absorption coefficient for electromagnetic radiation  $\alpha(\Omega)$ , here defined as the inverse of the distance required for the energy density in a beam to decay to  $1/e$  of its initial value. For radiation whose frequency is well below the *restahl* frequency of the crystal, we may write

$$\alpha(\Omega) = \frac{\Omega}{c(\epsilon_s)^{1/2}} \epsilon_2(\Omega), \quad (2.1)$$

where  $\epsilon_s$  is the static dielectric constant,  $c$  the velocity of light in vacuum, and  $\epsilon_2(\Omega)$  is the imaginary part of the dielectric constant, here assumed small.

In the alkali halides, in the regime where two-phonon processes dominate the absorption, it is a good approximation to ignore the nonlinear terms in the expansion of the crystal electric dipole moment in powers of the atomic displacements. Then the complex frequency-dependent dielectric constant may be written

$$\epsilon(\Omega) = \epsilon_\infty + \frac{4\pi n e^{*2}}{M_r} \frac{1}{\omega_{TO}^2 - \Omega^2 - 2i\omega_{TO}\Gamma_{TO}(\Omega)}, \quad (2.2)$$

where  $\epsilon_\infty$  is the contribution to the dielectric constant from electronic excitations,  $n$  is the number of unit cells per unit volume,  $e^*$  the Born effective charge,  $M_r$  the reduced mass of the unit cell. Then  $\omega_{TO}$  is the (measured) frequency of the zero wave-vector TO phonon (anharmonic corrections are incorporated into  $\omega_{TO}^2$ ), and  $\Gamma_{TO}(\Omega)$

is the imaginary part of the proper self-energy of the TO phonon, evaluated at the frequency  $\Omega$  of the electromagnetic radiation. The properties of this quantity are discussed below.

For frequencies  $\Omega \ll \omega_{TO}$ , Eqs. (2.2) and (2.1) may be combined to give

$$\alpha(\Omega) = \frac{2\Omega(\epsilon_s - \epsilon_\infty)}{c(\epsilon_s)^{1/2}\omega_{TO}} \Gamma_{TO}(\Omega), \quad (2.3)$$

which is the expression we use to compute  $\alpha(\Omega)$ , once  $\Gamma_{TO}(\Omega)$  is determined.

Our task is then to calculate the proper self-energy of the TO phonons, at low frequencies, far off "the energy shell" relevant to evaluating the width of the *restahl* absorption line. This may be accomplished with the diagrammatic perturbation theory outlined some years ago by Maradudin and Fein.<sup>5</sup> Later, we shall rely heavily on the analysis put forward in Sham.<sup>6</sup>

The contribution lowest order in anharmonicity arises from the cubic terms in the expansion of the crystal potential energy in powers of the anharmonic coupling. The diagrammatic representation of this term is given in Fig. 1(a); a selection rule on the anharmonic matrix element<sup>5</sup> applied to the alkali halides shows that the anharmonic matrix element  $V_3$  is nonzero only if the branch index  $j_1$  differs from  $j_2$ .

We shall write out the contribution displayed in Fig. 1(a) explicitly. We use a compact notation, with the simple integers 1 and 2 employed in place of the wave vector  $q$  and branch index  $j$  to label a given phonon mode. We

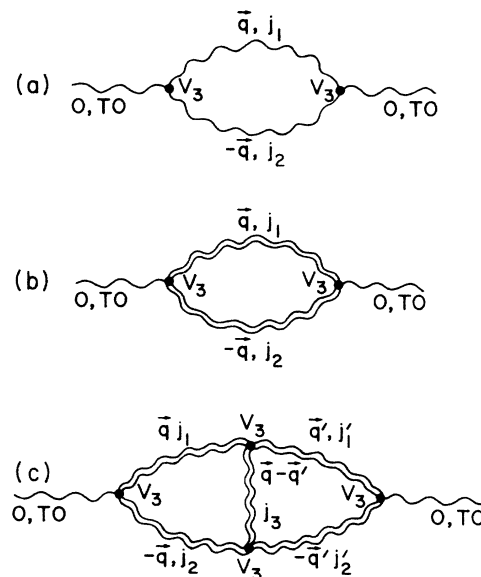


FIG. 1. (a) Lowest-order contribution to the proper self-energy of the  $q=0$  TO phonon. (b) Lifetime effects are incorporated into the theory if dressed phonon propagators (double wavy lines) are incorporated into the calculation of the proper self-energy, rather than the bare propagators illustrated in (a). (c) Higher-order graph, which contributes to the ladder graph approximation to the proper self-energy.

let  $i\omega_l = i2\pi l/\beta$  be the complex Matsubara frequency of the perturbation theory applied to bosons, and in the notation of Ref. 5  $M_{0,TO}(i\omega_l)$  is the proper self-energy of the zero wave-vector TO phonon, evaluated on the imaginary axis of the complex frequency plane. Here  $l$  is an integer and  $\beta = 1/k_B T$ . The diagram of Fig. 1(a) then gives us, using the rules of Ref. 5,

$$M_{0,TO}(i\omega_l) = \frac{18}{\beta} \sum_{1,2} \sum_{l_1} |V_3(0,TO;1;2)|^2 D_1^{(0)}(i\omega_{l_1}) \times D_2^{(0)}(i\omega_l - i\omega_{l_1}), \quad (2.4)$$

$$M_{0,TO}(i\omega_l) = 18 \sum_{1,2} |V_3(0,TO;1;2)|^2 \left[ [n(\omega_2) - n(\omega_1)] \left[ \frac{1}{\omega_1 - \omega_2 - i\omega_l} + \frac{1}{\omega_1 - \omega_2 + i\omega_l} \right] + [1 + n(\omega_1) + n(\omega_2)] \left[ \frac{1}{\omega_1 + \omega_2 + i\omega_l} + \frac{1}{\omega_1 + \omega_2 - i\omega_l} \right] \right], \quad (2.6)$$

and then the object  $\Gamma_{0,TO}(\Omega)$  which appears in Eq. (2.3) is found from the prescription

$$\Gamma_{0,TO}(\Omega) = \frac{1}{i} \text{Im}[M_{0,TO}(\Omega + i\eta)]. \quad (2.7)$$

We shall assume the frequency  $\Omega$  is positive, so the term proportional to  $\delta(\omega_1 + \omega_2 + \Omega)$  is discarded. Very general considerations dictate that  $\Gamma_{0,TO}(\Omega)$  is an odd function of frequency (and hence necessarily vanishes at  $\Omega = 0$ ), so by discarding this term, our attention is restricted to only the domain of positive frequencies. The term in  $\delta(\omega_1 + \omega_2 - \Omega)$  is nonzero, but in the limit  $\Omega \rightarrow 0$ , phase-space considerations show this term is small compared to that generated by the two-phonon difference processes, described by the first two terms in Eq. (2.6). Keeping only these, and noting  $|V_3(0,TO;1;2)|^2$  is invariant under interchange of 1 and 2, gives us

$$\Gamma_{0,TO}(\Omega) = 36\pi \sum_{1,2} |V_3(0,TO;1;2)|^2 [n(\omega_2) - n(\omega_1)] \times \delta(\omega_1 - \omega_2 - \Omega). \quad (2.8)$$

If we attempt to evaluate the expression in Eq. (2.8) for very small values of  $\Omega$ , then we will find the argument that the  $\delta$  function never vanishes (except for the very near vicinity of special lines or points in the Brillouin zone, where branch degeneracy occurs), for the reasons outlined earlier in Sec. I.

The perturbation theoretic expression for  $\Gamma_{0,TO}(\Omega)$  assumes the thermally excited phonons have a perfectly well-defined energy, and that energy is strictly conserved in the decay process. As remarked earlier, these modes have a finite lifetime, and their energy is not well defined as a consequence. Energy is then conserved only to within  $\hbar/\tau_{th}$ , with  $\tau_{th}$  a typical thermal phonon lifetime.

We may build this feature into the theory by replacing the bare phonon propagators in Fig. 1(a) by dressed propagators, as displayed in Fig. 1(b). These propagators describe phonons whose energy is renormalized by anhar-

where selection rules on branch index and wave vector are assumed to be stored in the anharmonic matrix element  $V_3$ , and

$$D_i^{(0)}(i\omega_l) = \frac{2\omega_i}{\omega_i^2 + \omega_l^2} \quad (2.5)$$

is the propagator which describes phonon  $i$ , in the harmonic approximation of lattice dynamics.

It is a straightforward and standard matter<sup>5</sup> to use contour integration to evaluate the sum on  $l_1$  in Eq. (2.4). One finds, with  $n(\omega) = [\exp(\beta\omega) - 1]^{-1}$ ,

monicity (a small and unimportant effect for our purposes), and most importantly their lifetime is finite by virtue of the imaginary part of the proper self-energy incorporated into the dressed propagators.

The expression for the proper self-energy of the zero wave-vector TO phonon still has the form given in Eq. (2.4), but now the unperturbed propagators  $D_i^{(0)}(i\omega_l)$  are replaced by the dressed propagators  $D_i(i\omega_l)$ . We shall evaluate the proper self-energy using the procedure outlined by Sham,<sup>6</sup> for reasons to be discussed shortly. The reader should note that the scheme used by Sham was adapted from the earlier classic paper by Holstein on electron-phonon interactions.<sup>7</sup> Holstein's paper gives a very detailed account of the rationale for the scheme.

Upon using the full phonon propagators in Eq. (2.4), we may employ a contour integration scheme identical to that used to generate Eq. (2.6), to replace the sum on  $i\omega_{l_1}$  by an integration along the real axis of the complex frequency plane. Once again, this procedure is standard. We then let  $i\omega_l \rightarrow \Omega + i\eta$ , to obtain  $M_{0,TO}(\Omega + i\eta)$  from  $M_{0,TO}(i\omega_l)$ .

The expression contains several terms, among them products of two Green's functions  $D_1(\omega' + i\eta)D_2(\omega - \omega' + i\eta)$  evaluated on the same side of the branch cut coincidental with the real axis, and also products  $D_1(\omega' \pm i\eta)D_2(\omega - \omega' \mp i\eta)$  where one partner is the product evaluated above the cut and the other below the cut. Our interest is in phonon pairs where the frequency difference  $(\omega_1 - \omega_2)$  is quite small, and has magnitude comparable to typical inverse lifetime  $\bar{\Gamma}$  of the thermal phonons. It is precisely this limit that is of central interest in Sham's paper, and following him we argue that the dominant contribution to the proper self-energy has its origin in those terms where both members of the pair have frequency arguments which lie on the same side of the branch cut. Furthermore, we may replace such products by an approximate form derived in his paper. Thus, ignoring the small anharmonic frequency shifts, we have

$$D_1(\omega' + i\eta)D_2(\Omega - \omega' + i\eta) = \frac{4\omega_1\omega_2}{[\omega_1^2 - (\omega')^2 - 2i\omega_1\Gamma_1(\omega')][\omega_2^2 - (\omega' - \Omega)^2 - 2i\omega_2\Gamma_2(\Omega - \omega')]} \quad (2.9)$$

and let  $\omega_2 = \omega_1 - \Delta_{12}$ , with  $\Delta_{12} = \omega_1 - \omega_2$ . Assuming  $\Omega$  is small, and our interest is in values of  $\Delta_{12}$  comparable to  $\Gamma_1$  and  $\Gamma_2$ , both of which are small compared to  $\omega_1$  or  $\omega_2$ , we write

$$\begin{aligned} D_1(\omega' + i\eta)D_2(\Omega - \omega' + i\eta) &\cong \frac{4\omega_1^2}{[\omega_1^2 - (\omega')^2 - 2i\omega_1\Gamma_1(\omega')][\omega_1^2 - (\omega')^2 + 2i\omega_1\Gamma_1(\omega') + 2\omega'\Omega - 2\omega_1\Delta_{12}]} \\ &\cong \frac{2i\omega_1[\delta(\omega_1 - \omega') - \delta(\omega_1 + \omega')]}{\omega'\Omega - \omega_1\Delta_{12} + 2i\omega_1\Gamma_1(\omega')} \end{aligned} \quad (2.10)$$

where the reader is referred to the discussions in Refs. 6 and 7 for justification and derivation of the last step.

When Eq. (2.11) is incorporated into the expression for the proper self-energy, after performing some algebra we find

$$M_{0,TO}(\Omega + i\eta) = 18 \sum_{1,2} \frac{|V_3(0, TO; 1, 2)|^2}{\Omega - (\omega_1 - \omega_2) + 2i\bar{\Gamma}(\omega_1)} [n(\omega_1) - n(\omega_1 - \Omega) + n(\omega_2 + \Omega) - n(\omega_1)] \quad (2.11)$$

Here we have taken explicit note of the fact that we have assumed  $\Gamma_1(\omega_1)$  and  $\Gamma_2(\omega_2)$  do not differ greatly in value, so each has been replaced by an average value of the thermal phonon linewidth  $\bar{\Gamma}$ . It is not difficult to obtain a formal expression for the proper self-energy without invoking this assumption, but we shall employ it in the numerical work reported in Sec. III.

Then we have

$$\Gamma_{0,TO}(\Omega) = 18 \sum_{1,2} |V_3(0, TO; 1, 2)|^2 [n(\omega_1) - n(\omega_1 - \Omega) + n(\omega_2 + \Omega) - n(\omega_2)] \frac{\bar{\Gamma}}{(\Omega - \omega_1 + \omega_2)^2 + \bar{\Gamma}^2} \quad (2.12)$$

If we let  $\bar{\Gamma} \rightarrow 0$ , so that the Lorentzian in Eq. (2.13) is replaced by a Dirac  $\delta$  function, we recover Eq. (2.8) from Eq. (2.13). Contrary to the view expressed by Hardy and Karo,<sup>3</sup> we see that indeed lifetime broadening effects are incorporated into the theory by replacing the energy-conserving  $\delta$  function by a Lorentzian. Note that at as  $\Omega \rightarrow 0$ , the right-hand side of Eq. (2.13) always vanishes, so the expression in Eq. (2.13) does not lead to the difficulty in the scheme employed by Eldridge and Staal.<sup>4</sup> In earlier work,<sup>2</sup> a slightly different approximation scheme was used to obtain an expression for  $\Gamma_{0,TO}(\Omega)$ . The resulting form has a somewhat different combination of Bose factors in front of the matrix element and the Lorentzian. We prefer Eq. (2.13), although numerical calculations performed with both expressions give virtually identical results, below  $100 \text{ cm}^{-1}$  for NaCl and KI. Each thermal phonon is described by a spectral density function whose width is  $\bar{\Gamma}$ , and there is no unique prescription for deciding where the Bose functions are to be evaluated. The key issue is to employ a scheme which preserves the proper analytic structure of  $\Gamma_{0,TO}(\Omega)$ , and for small  $\Omega$  the ambiguity is of little quantitative significance.

One issue remains to be explored. This is the role of higher-order corrections to the proper self-energy, over the above dressing the lowest-order graph [Fig. 1(a)] by inserting dressed propagators. A central point of Sham's analysis<sup>6</sup> (and Holstein's study of electron-phonon scattering<sup>7</sup>) is the following. If we consider the particular higher-order graph displayed in Fig. 1(c), quite clearly it contains two additional powers of the anharmonic matrix element  $V_3$ , when compared to the graph in Fig. 1(b). Thus, it should be only a small correction to Fig. 1(b) in the limit of weak anharmonicity. However, the propaga-

tor that describes the additional pair of phonons [labeled  $q_2'j_2'$  and  $-q_2'j_2'$  in Fig. 1(c)] has the form of the Green's-function pair in Eq. (2.11), if the frequency of these two phonons lie close together. If  $\Delta_{12}$  is comparable to  $\Gamma_1(\omega')$  (or possibly smaller), and if  $\Omega$  is small, then the Green's-function product is of order  $V_3^{-2}$ , and the graph displayed in Fig. 1(c) contributes to the self-energy a term quite comparable in magnitude to that from the graph in Fig. 1(b). As Sham has demonstrated, one may construct an infinite sequence of ladder diagrams by iterating the basic structure added to Fig. 1(b) to form Fig. 1(c), and each term in the ladder series has the same order of magnitude as the leading term, Fig. 1(b). To compute the self-energy under these conditions, one must solve an integral equation generated by summing the series; in the appropriate regime of frequency and wave vector, Sham demonstrated the equivalence of this equation to the Boltzman transport equation.

Sham's primary interest was in the application of the analysis to a single branch of acoustical phonons, under conditions where second sound may be supported. In his analysis the parameter analogous to our  $\Delta_{12}$  is  $c_s\{|\mathbf{q} + \mathbf{Q}| - q\} \cong c_s\hat{\mathbf{q}} \cdot \mathbf{Q}$ , where  $c_s$  is the velocity of sound, and  $\mathbf{Q}$  the wave vector of the external driving force of interest (the photon, in our case). Also,  $\mathbf{q}$  is the wave vector of the thermally excited phonon, the analogue of  $(\mathbf{q}j_1)$  in our Fig. 1. Now quite clearly in Sham's case, for *all* choices of  $\mathbf{q}$  anywhere in the Brillouin zone,  $\Delta_{12}$  is smaller than or comparable to  $\Gamma_1(\omega')$ . Thus, when one adds an additional pair of phonon propagators to a given diagram, as in Fig. 1(c), the energy denominator in Eq. (2.11) is small (of order  $V_3^2$ ) for *each* value of  $\mathbf{q}'$  one chooses in performing the sum on  $\mathbf{q}'$ .

Our present situation is very different. While the whole point of our analysis is that inclusion of lifetime broadening breaks down strict energy conservation in the two-phonon difference process and hence allows these to dominate the absorption constant at very low frequencies, at the same time as the pair  $(\mathbf{q}, j_1)$  and  $(-\mathbf{q}, j_2)$  ranges over the entire Brillouin zone, and over all combinations of  $j_1$  and  $j_2$ , most of the phonon frequency differences are very much larger than the thermal phonon spectral width  $\Gamma_1(\omega')$ . Thus, we are in a very different limit than the model system examined by Sham. In our case, only a small fraction of the contributions to the sum over  $\mathbf{q}'$ ,  $j'_1$ , and  $j'_2$  in Fig. 1(c) have energy denominators that are small, in Sham's sense. If, following Sec. I, we let  $f$  be the fraction of points in the Brillouin zone which describe phonon pairs for which  $\Delta_{12}$  is comparable to  $\Gamma_1(\omega')$ , then while the graph in Fig. 1(c) contains near-resonant contributions, the resulting supplement to the proper self-energy is smaller than the graph [Fig. 1(b)] by the factor  $f \ll 1$ . We conclude that for our particular purpose, we can retain only the graph in Fig. 1(b), with little quantitative error.

If we borrow the numerical results to be presented in Sec. III, we may make a crude estimate of  $f$ . Let  $|\bar{V}_3|^2$  be an average value of the square of the anharmonic matrix element, and let  $\bar{\omega}$  be an average phonon frequency of the material. We take the low-frequency limit of Eq. (2.13), replace all quantities by their average, then replace the Bose factors by their high-temperature limit to obtain the crude, approximate value (we use units with  $\hbar=1$ )

$$\Gamma_{0, \text{TO}}(\Omega) \cong \frac{18\Omega |\bar{V}_3|^2 k_B T}{\bar{\omega}^2 \bar{\Gamma}} f. \quad (2.13)$$

(We expect at room temperature and above,  $\bar{\Gamma} \sim T$  and  $f$  to scale with  $\bar{\Gamma}$ , so  $f$  will vary linearly with temperature.) From the golden rule, with a similar crude replacement procedure, we have  $\bar{\Gamma} \sim 2\pi |\bar{V}_3|^2 k_B T / \bar{\omega}^2$ , where the density of states in the golden-rule formula is replaced by the inverse of the average phonon frequency. We thus have

$$\Gamma_{0, \text{TO}}(\Omega) \cong 6\Omega f. \quad (2.14)$$

For NaCl at room temperature, and  $\Omega \cong 5 \text{ cm}^{-1}$ , we shall see in Sec. III that  $\Gamma_{0, \text{TO}}(\Omega) \cong 0.1 \text{ cm}^{-1}$ . Hence,  $f \cong 3 \times 10^{-3} \ll 1$ . An appreciable fraction of the possible transitions in the Brillouin zone are "near resonant," but clearly  $f \ll 1$ .

The above argument that vertex corrections may be ignored rests importantly on the selection rule operative in the alkali halides, which requires the internal phonon pair to be on different branches of the phonon spectrum. This selection rule is operative in any crystal in which each ion sits at a site of inversion symmetry.<sup>5</sup> In crystals of lower symmetry, where intraband scatterings are allowed, we shall realize precisely the situation of concern to Sham, and the role of higher-order corrections must be reexamined.

### III. NUMERICAL RESULTS AND DISCUSSION

We have evaluated the imaginary part of the TO phonon proper self-energy  $\Gamma_{0, \text{TO}}(\Omega)$  using Eq. (2.13) for NaCl and KI, then we used this to calculate the absorption coefficient  $\alpha(\Omega)$  from Eq. (2.3). As already mentioned, these two salts have very different phonon spectra, and it will be of interest to compare the effect of lifetime broadening in the two cases. Central to the evaluation of  $\Gamma_{0, \text{TO}}(\Omega)$  are realistic lattice dynamical models which generate the phonon spectra of these materials. Various phenomenological models that provide good fits to phonon dispersion determined by inelastic neutron scattering exist in the literature,<sup>8</sup> and we have used the 11-parameter shell model proposed by Cowley *et al.*<sup>9</sup> in the work reported here. The parameter values were taken from Raunio and Rolandson<sup>10</sup> for NaCl and from Dolling *et al.*<sup>11</sup> for KI.

Berg and Bell<sup>12</sup> have given explicit expressions for the anharmonic matrix elements  $V_3(0, \text{TO}; \mathbf{q}_1, \omega_1; \mathbf{q}_2, \omega_2)$  in terms of the phonon eigenfrequencies and eigenvectors, along with potential derivatives. These formulas will not be reproduced here. The values of the relevant derivatives of the interionic potentials required were taken from Eldridge and Staal<sup>1</sup> for NaCl, and from Berg and Bell<sup>12</sup> for KI. The Brillouin-zone sum implied in Eq. (2.13) was performed on a grid corresponding to a mesh of 64 000 equally spaced points in the full zone. This grid yields convergence of  $\Gamma_{0, \text{TO}}(\Omega)$  to within 1%, for the far-infrared and microwave frequencies of interest here.

Our only adjustable parameter is then  $\bar{\Gamma}$ , the inverse of the thermal phonon lifetime. In principle, this quantity could be calculated, assuming two-phonon processes dominate, and we would then have a full description of the microwave absorption constant within a picture that ignores all decays to three-phonon final states. While we wish to explore this issue further in future work, at present we shall be content to replace the (frequency-dependent) thermal phonon lifetime by an average value, endowing it with a temperature dependence when appropriate.

In Figs. 2(a) and 2(b), in the low-frequency region, we show the frequency variation of  $\Gamma_{0, \text{TO}}(\Omega)$  at room temperature, for various choices of  $\bar{\Gamma}$ . One sees clearly that in both materials,  $\Gamma_{0, \text{TO}}(\Omega)$ , and hence the absorption constant, are influenced importantly by inclusion of the broadening. Also, the calculated values for KI are more sensitive than those for NaCl, as might be expected from the nature of the phonon spectra of these two salts. At  $\Omega = 4 \text{ cm}^{-1}$ , as  $\bar{\Gamma}$  is varied from  $2 \text{ cm}^{-1}$  to  $15 \text{ cm}^{-1}$ , in NaCl  $\Gamma_{0, \text{TO}}(\Omega)$  varied by only 20%, while it increases by nearly a factor of 2 in KI.

In Figs. 3 and 4 we show similar calculations for the two materials, but now the frequency scale has been expanded to range from 0 to  $100 \text{ cm}^{-1}$ . Qualitatively and quantitatively, at the higher frequencies the results are similar to those of earlier authors, although a dependence on  $\bar{\Gamma}$  clearly remains, especially for KI. Below  $30 \text{ cm}^{-1}$ , our results differ dramatically from those of Hardy and Karo, who find that  $\Gamma_{0, \text{TO}}(\Omega)$  plummets to nearly zero at these low frequencies.

It is striking that in Fig. 2, for both materials  $\Gamma_{0, \text{TO}}(\Omega)$

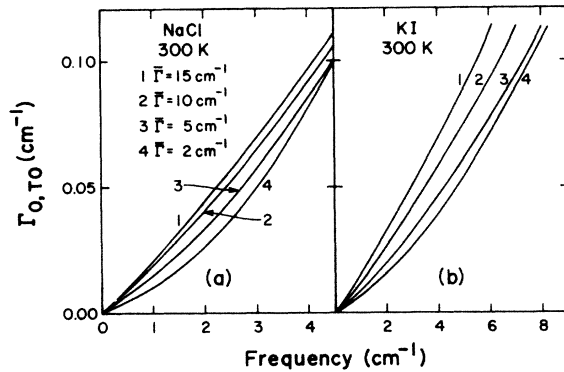


FIG. 2. At low frequencies and at room temperature, we show calculations of  $\Gamma_{0,TO}(\Omega)$  for (a) NaCl and (b) KI, for four selected values of  $\bar{\Gamma}$ .

increases with increasing  $\bar{\Gamma}$ , while at the higher frequencies we see from Figs. 3 and 4 that  $\Gamma_{0,TO}(\Omega)$  is depressed in value as  $\bar{\Gamma}$  becomes larger. It is evident from Fig. 4 that for KI the various curves cross near  $30 \text{ cm}^{-1}$ , and for NaCl we find a similar crossing at  $8 \text{ cm}^{-1}$ .

We understand this behavior as follows. If we consider the contributions from a particular transition that fails to conserve energy by the amount  $\Delta = \omega_{12} - \Omega$ , then from Eq. (2.13) we see that this contribution is weighted by the factor

$$f(\Delta) = \frac{\bar{\Gamma}}{\Delta^2 + \bar{\Gamma}^2}. \quad (3.1)$$

The function  $f(\Delta)$ , considered as a function of  $\bar{\Gamma}$ , has a maximum at  $\bar{\Gamma} = \Delta$ , and is an increasing function of  $\bar{\Gamma}$  when  $\bar{\Gamma} < \Delta$ , and decreases when  $\bar{\Gamma} > \Delta$ . When the frequency  $\Omega$  is raised, a larger fraction of the contribution to  $\Gamma_{0,TO}(\Omega)$  comes from transitions that can conserve energy, i.e., whose energy mismatch  $\Delta$  is smaller than  $\bar{\Gamma}$ . The crossover frequency thus provides a measure of the aver-

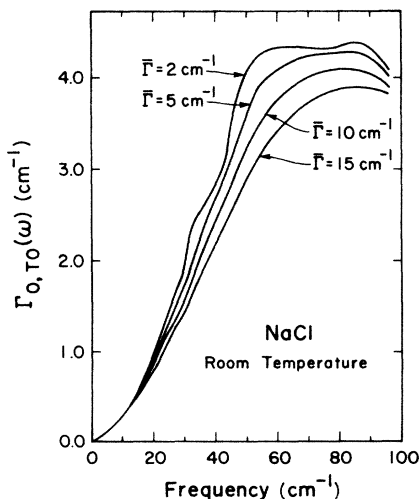


FIG. 3. At room temperature, in the frequency range from 0 to  $100 \text{ cm}^{-1}$ , we show calculations of  $\Gamma_{0,TO}(\Omega)$  for NaCl, again for four values of  $\bar{\Gamma}$ .

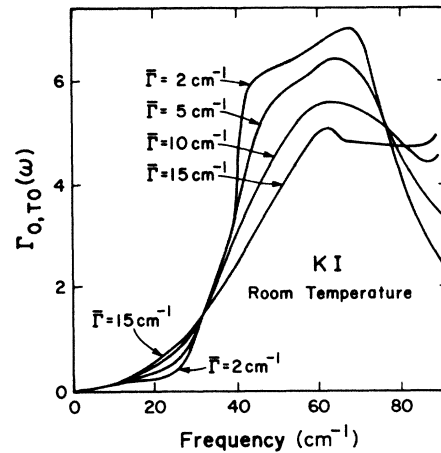


FIG. 4. At room temperature, in the frequency range from 0 to  $100 \text{ cm}^{-1}$ , we show calculations of  $\Gamma_{0,TO}(\Omega)$  for KI, again for four values of  $\bar{\Gamma}$ .

age energy mismatch at low frequencies in the two-phonon difference process, and it is reasonable that this crossover lies at a substantially lower frequency for NaCl than for KI.

We adopt the value  $\bar{\Gamma} = 10 \text{ cm}^{-1}$  as a reasonable average value of the thermal broadening at room temperature, and we now turn to a quantitative comparison between our results and the data of Stolen and Dransfeld.<sup>2</sup> With this value of  $\bar{\Gamma}$ , for KI at room temperature we find  $\alpha = 1.25 \text{ cm}^{-1}$  for radiation with a wavelength of  $500 \mu\text{m}$ . This is within a factor of 2 of the value  $2.1 \text{ cm}^{-1}$  measured by Stolen and Dransfeld.<sup>13</sup> We consider this gratifying, in view of the uncertainty of the value of  $\bar{\Gamma}$ , and our neglect of its dependence on frequency and phonon branch index. In contrast, Hardy and Karo<sup>3</sup> report that their calculation yields  $0.15 \text{ cm}^{-1}$  for  $\alpha$  at this frequency, roughly 15 times smaller than experiment. These authors replace the  $\delta$  function in Eq. (2.8) by a "bin" of width of  $1.67 \text{ cm}^{-1}$ . It is our view that their calculated value of  $\alpha$  at this low frequency is likely to be sensitive to the choice of binwidth, although this possibility was not examined by them. The fact that this is likely follows from the dependence of our calculated linewidths on  $\bar{\Gamma}$ .

To calculate the temperature variation of  $\alpha$ , we must recognize that  $\bar{\Gamma}$  is also temperature dependent. If the dominant contribution to the thermal phonon scattering rate has its origin in two-phonon processes, then near room temperature or above, we may expect that  $\bar{\Gamma}$  will vary linearly with temperature. Thus, we write  $\bar{\Gamma} = AT$ , with  $A$  chosen so that  $\bar{\Gamma} = 10 \text{ cm}^{-1}$  at room temperature. When we adopt this assumption, we then suppose that both  $\alpha$  and  $\bar{\Gamma}$  are dominated by two-phonon processes. This procedure is internally consistent but, as the reader will appreciate shortly, the issue requires further study.

Stolen and Dransfeld find that for NaCl and KI the absorption coefficient has a temperature dependence stronger than linear in  $T$ , provided by the high-temperature behavior of Eq. (2.8). They illustrate this by constructing graphs in the following manner. For various

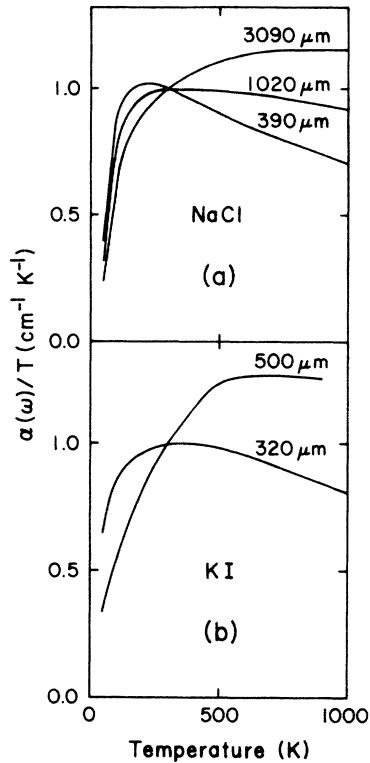


FIG. 5. Following Stolen and Dransfeld (Ref. 13) we plot  $\alpha/T$  vs  $T$  for the frequencies indicated, for (a) NaCl and (b) KI. The curves are normalized so they intersect at  $T=300$  K.

frequencies they plot  $\alpha/T$ , with errors normalized so that at the temperature  $T=300$  K all curves meet at a common point. For KI, only the region below 300 K appears in their plots, while for NaCl it extends slightly above. In Fig. 5 we present the same graphs, as provided by the present calculation. We extend the plots well above 300 K for comparison with future experiments. To the eye, our curves look quite similar, qualitatively to those generated

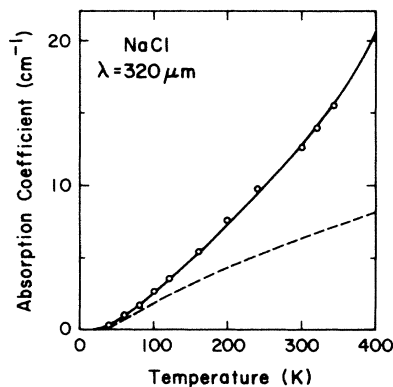


FIG. 6. For NaCl and a wavelength of  $320 \mu\text{m}$ , we directly compare the prediction of our theory (dashed line) with the data (Ref. 13) (open circles). The solid line is constructed as described in the text.

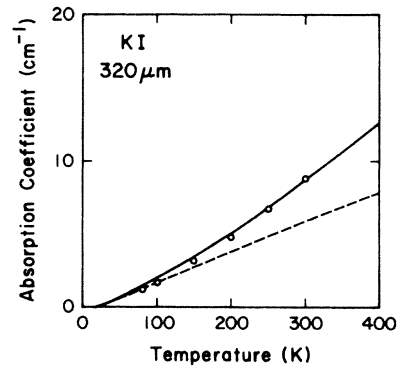


FIG. 7. For KI and a wavelength of  $320 \mu\text{m}$ , we directly compare the prediction of our theory (dashed line) with the data (open circles). The solid line is constructed as described in the text.

from the data. The reader should compare our Fig. 5 with Figs. 5 and 7 of Ref. 13. However, closer inspection shows that the temperature dependence we find for  $\alpha$  is less strong than that obtained by Stolen and Dransfeld.

We illustrate this in Figs. 6 and 7, where for a wavelength of  $320 \mu\text{m}$  we compare our calculations directly with the data. The points are taken from the experimental plots in Ref. 13, and the dashed line is produced by our calculations. While we have a factor of 2 agreement between theory and experiment over the whole temperature range, the temperature variation for  $\alpha$  provided by theory is distinctly weaker than that in the data.

If we examine the discrepancy between theory and experiment in Figs. 6 and 7, the difference between the theoretical and experimental curves exhibits a  $T^2$  temperature variation. The solid curves in Figs. 6 and 7 are calculated by supplementing our theoretical curves by an additional contribution  $BT^2$ . The agreement between the resulting form for  $\alpha$  and the data is remarkable. Since one expects three-phonon contributions to  $\alpha$  to exhibit a  $T^2$  variation, this suggests that three-phonon contributions are more important than thought previously.

#### IV. SUMMARY

In our view the calculations reported here establish clearly that in the far-infrared and microwave-frequency range, a proper calculation of the two-phonon difference contribution to the absorption constant requires inclusion of the influence of the finite lifetime of the thermal phonons on the absorption process.

While we obtain a reasonable account of the data with our calculation, if we regard a factor of 2 agreement between theory and experiment acceptable, important theoretical issues remain to be explored. We require values for  $\bar{\Gamma}$ , calculated for the various phonon branches and at various (low symmetry) points in the Brillouin zone, so one may improve our rather crude procedure which ignores its dependence on branch index and frequency. We have also raised the possibility that three-

phonon processes enter importantly; further study of these contributions would therefore be useful.<sup>14</sup> From the experimental point of view, measurements above room temperature would be most useful, along with studies of the temperature variation of  $\alpha$  at some microwave frequencies.

#### ACKNOWLEDGMENTS

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<sup>1</sup>For an example of such calculations, see the paper by J. E. Eldridge and P. R. Staal, Phys. Rev. B **16**, 4608 (1977).

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<sup>3</sup>J. R. Hardy and A. M. Karo, Phys. Rev. B **26**, 3327 (1982).

<sup>4</sup>in Fig. 8 of Ref. 1, the three-phonon contribution to  $\Gamma_{0,TO}(\Omega)$  is clearly finite in the limit  $\Omega \rightarrow 0$ . A fundamental theorem, quoted in our text, requires this quantity to vanish at  $\Omega = 0$ . Clearly, then, the results reported in this figure are unreliable at low frequencies. We emphasize that the paper of Eldridge and Staal was concerned with higher frequencies, where their "smearing" procedure likely introduced only very little error.

<sup>5</sup>A. A. Maradudin and A. E. Fein, Phys. Rev. **128**, 2589 (1962).

<sup>6</sup>L. J. Sham, Phys. Rev. **156**, 494 (1967).

<sup>7</sup>T. Holstein, Ann. Phys. (N.Y.) **29**, 410 (1964).

<sup>8</sup>See, e.g., the compilation by H. Bilz and W. Kren, in *Phonon Dispersion Relations in Insulators* (Springer-Verlag, Berlin, 1979).

<sup>9</sup>The model is referred to as model VI in R. A. Cowley, W. Cochran, B. N. Brockhouse, and A. D. B. Woods, Phys. Rev. **131**, 1030 (1963).

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<sup>11</sup>G. Dolling, R. A. Cowley, C. Schittenhelm, and I. M. Thorson, Phys. Rev. **147**, 577 (1966).

<sup>12</sup>J. I. Berg and E. E. Bell, Phys. Rev. B **4**, 3572 (1971).

<sup>13</sup>R. Stolen and K. Dransfeld, Phys. Rev. **139**, A1295 (1965).

<sup>14</sup>Eldridge and Staal (Ref. 1) have reported some calculations of the three-phonon contribution to  $\alpha$ , but they provide few details of the procedure. The comment in our Ref. 4 applies to these calculations.