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Theoretical Study of the Long-Wavelength Optical Properties of NaCl, KCl, KBr, and KI

John R. Hardy
University of Nebraska - Lincoln

A. M. Karo
Lawrence Livermore National Laboratory, Livermore, California

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J. R. Hardy
Behlen Laboratory of Physics, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0111

A. M. Karo
Lawrence Livermore National Laboratory, Livermore, California 94550
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We have made a detailed theoretical study of the long-wavelength absorption of NaCl, KCl, KBr, and KI, associated with two-phonon difference processes caused by third-order anharmonic terms in the lattice potential energy. It was found that a simple nearest-neighbor approximation to the anharmonicity, combined with lattice-dynamical eigenfrequencies and eigenvectors generated with the use of a deformation dipole model, can generally account for most of the observed absorption. This agreement was obtained without the use of any disposable parameters, as the form of the first-neighbor potential was predetermined. It was also found that discrepancies between theory and experiment can generally be explained by invoking three-phonon processes and, when these contributions are subtracted from the experimental data, the resultant agreement between theory and experiment is excellent. The effects of lifetime broadening of the final-state phonons were also considered. At the longer wavelengths these may be responsible for part of the discrepancy between theory and experiment. Specifically, for NaCl at 3.09 mm, clear evidence was found of an anomalous contribution to the measured absorption which could have such an origin. However, for KI, which has a "window" in its two-phonon absorption at long wavelengths, it is clear that the three-phonon absorption is dominant at low frequencies. Our findings enable us to present certain criteria as to the requirements necessary for a material to possess high transparency in the millimeter-wavelength region. In addition to obtaining theoretical results for the long-wavelength absorption of the four crystals studied, we have also calculated their damping functions over the whole two-phonon range and we thus present results for both summation and difference processes.

I. INTRODUCTION

Some years ago[1] there was much interest in high-transparency window materials for electromagnetic radiation in the micrometer spectral region, specifically at 10.6 μm. A similar problem has now arisen for the intense millimeter radiation produced by such devices as gyrotrons and free-electron lasers. In both frequency ranges the ultimate limit on the performance of any given material is set by its intrinsic absorption. To avoid any electronic contribution, either from free carriers or band-to-band transitions, it is necessary to use large-band-gap insulators of which the easiest to study theoretically are alkali halides. Extensive work[1] has clearly established that the level, temperature, and frequency dependence of the observed absorption, for hyperpure materials in the micrometer region, are consistent with theoretical predictions for intrinsic multiphonon sum band (4–6 depending on the material) absorption. The millimeter region has received only cursory theoretical attention, although there exists a significant amount of experimental data,[2–5] most of it 15–20 years old. The object of this paper is to attempt a systematic theoretical interpretation of these data. The problem differs from that presented by micrometer absorption, in that intrinsic millimeter absorption must be associated with difference processes: processes in which phonons are both created and destroyed. As a consequence, *all* orders of process can, in principle, contribute to absorption at a given frequency. This contrasts with the situation for micrometer absorption where the absorption is generally dominated by one process, the order depending on the frequency. This is primarily a consequence of the requirement of energy conservation; e.g., if the radiation frequency is more than 4 times and less than 5 times the maximum lattice frequency, the lowest order process possible is a five-phonon process. This will dominate the absorption as it is the strongest allowed process.

In the millimeter region, since energy conserva-

tion permits all orders to contribute, we expect the lowest- (second-, and possibly third-) order processes to be dominant, since the coupling to these is strongest. For such processes, and indeed for all difference processes, the density of allowed final states is radically different from that for the corresponding summation bands. This combination of dominance by low-order processes and radically different density of states renders inapplicable the approaches developed for theoretical work on micrometer absorption. Specifically, it rules out the use of simple approximations and requires that the phonon frequencies and eigenvectors employed be derived from a realistic lattice-dynamical model of the system under study.

Experimentally, it appears that both two- and three-phonon contributions are generally present in the millimeter region for alkali halides.[3–5] In this paper we shall present results for the two-phonon absorption obtained using a standard set of semiempirical potentials.[6] These results set a "base line" by effectively specifying how much two-phonon absorption *must be* present at any given frequency. Changes in the potential can raise or lower the overall level of absorption for a given crystal but they cannot change the *relative* levels at different frequencies. Thus, if a given potential produces good agreement between theory and experiment at frequencies where two-phonon absorption is clearly dominant, it *automatically* follows that the two-phonon absorption predicted for the millimeter region must be present. Moreover, in "harder" materials (such as ceramics), which have Debye temperatures well above room temperature, three-phonon difference band absorption will be strongly suppressed and the limiting difference band absorption will be dominated by two-phonon processes.

II. THEORY

The general expression for the dielectric constant at a frequency Ω of an ionic crystal with only one transverse-optic resonance is[7]

$$\epsilon(\Omega)=\epsilon_\infty+\frac{(\epsilon_0-\epsilon_\infty)[\omega^2(\overset{0}{j})+2\omega(\overset{0}{j})\Delta(\overset{0}{j},0)]}{\omega^2(\overset{0}{j})-\Omega^2+2\omega(\overset{0}{j})[\Delta(\overset{0}{j},\Omega)-i\Gamma(\overset{0}{j},\Omega)]}\ , \tag{1}$$

where ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, $\omega(\overset{0}{j})$ is the transverse-optic mode frequency; Δ and $i\Gamma$ are the real and imaginary parts of the transverse-optic phonon self-energy. At low frequencies the imaginary part of $\epsilon(\Omega)$, $\epsilon''(\Omega)$ is given by

$$\epsilon''(\Omega)\simeq 2\frac{(\epsilon_0-\epsilon_\infty)}{\omega(\overset{0}{j})}\Gamma(\overset{0}{j},\Omega) \tag{2}$$

and the extinction coefficient

$$\kappa(\Omega)\simeq\frac{\epsilon''(\Omega)}{2\sqrt{\epsilon_0}}\ . \tag{3}$$

At some of the higher frequencies for which we shall present results we did not make the approximation of setting $\Omega=0$ when deriving Eq. (2) from Eq. (1) and, for consistency, used $\sqrt{\epsilon(\Omega)}$ calculated from Eq. (1), neglecting Δ and Γ, in place of $\sqrt{\epsilon_0}$.

Combining Eqs. (2) and (3) we have

$$\kappa(\Omega)=\frac{(\epsilon_0-\epsilon_\infty)}{\sqrt{\epsilon_0}\,\omega(\overset{0}{j})}\Gamma(\overset{0}{j},\Omega)\ . \tag{4}$$

This is the theoretical quantity which will be compared with experiment.

Thus far the discussion is general; we become specific when we decide which contributions to Γ we include. In this paper we shall only consider the lowest order or two-phonon decay. Moreover, since we are concentrating our attention on the millimeter and submillimeter spectral region, the only significant contribution to Γ comes from two-phonon difference processes in which the virtual optic phonon, created by the external field, decays by the simultaneous creation of one phonon and the the destruction of a second.

The total expression for Γ, including both creation, destruction, and double creation is (in rad/sec)

$$\begin{aligned}\Gamma(\overset{0}{j},\Omega)=&\frac{\pi\hbar(m_1+m_2)}{4\omega(\overset{0}{j})m_1m_2}\lim_{\substack{N\to\infty\\ \Delta\Omega\to 0}}\frac{1}{N\Delta\Omega}\\ &\times\int_\Omega^{\Omega+\Delta\Omega}d\Omega'\sum_{\substack{\vec{q}\\ jj'}}\left\{\psi'''(r_0)[e_x(1\,|\,\overset{\vec{q}}{j})e_x(2\,|\,\overset{-\vec{q}}{j'})-e_x(2\,|\,\overset{\vec{q}}{j})e_x(1\,|\,\overset{-\vec{q}}{j'})]\sin 2\pi q_x r_0\right\}^2\\ &\times[m_1m_2\omega(\overset{\vec{q}}{j})\omega(\overset{-\vec{q}}{j'})]^{-1}\{[n(\overset{\vec{q}}{j})+n(\overset{-\vec{q}}{j'})+1]\delta(\Omega'-\omega(\overset{\vec{q}}{j})-\omega(\overset{-\vec{q}}{j'}))\\ &+|n(\overset{\vec{q}}{j})-n(\overset{-\vec{q}}{j'})|\,\delta(\Omega'-|\omega(\overset{\vec{q}}{j})-\omega(\overset{-\vec{q}}{j'})|)\}\ .\end{aligned} \tag{5}$$

In Eq. (5) m_1 and m_2 are the positive and negative ion masses, $e_x(k \mid \vec{q}_j)$ is the x component of the eigenvector for ion k for the jth mode of wave vector $\vec{q}$, the n's are phonon occupation numbers, N is the number of unit cells, and $\psi'''(r_0)$ is the third derivative of the first-neighbor potential $\psi(r)$, evaluated at $r=r_0$ the equilibrium nearest-neighbor distance.

In order to apply this result to a specific system two things are needed: the lattice-dynamical eigendata (eigenfrequencies and eigenvectors) and an estimate of the third derivative of the first-neighbor interionic potential which appears in Eq. (4). It should be noted that, implicit in Eq. (4), is the assumption that only first-neighbor anharmonicity need be considered. We have also retained only those anharmonic terms that relate to bond compression; those involving anharmonic shears are typically an order of magnitude smaller and thus comparable with, or less than, the uncertainty in the compression terms. While they can be included formally, the additional complication and expenditure of computer time is not justified at the present level of accuracy, i.e., $\pm 10\%$. It should be noted that this does *not* preclude decays involving pairs of transverse phonons. Although their eigenvectors are orthogonal to their *propagation directions* they are not, in general, orthogonal to the nearest-neighbor *bond axes.* Thus, the eigenvector component products in Eq. (5) will be finite for these processes.

In order to evaluate the necessary third derivative we follow the approach of Eldridge and Staal,[8] which they found to give good agreement between the theoretical and experimental optical constants of sodium chloride in the region of the fundamental optical absorption frequency. We consider the first-neighbor potential to be composed of the attractive Coulomb interaction between the two ions and a short-range Born-Mayer repulsion. We further assume that the latter potential is the only short-range interaction present and that its two disposable parameters may be determined from the observed lattice constant and compressibility assuming that the lattice is in static equilibrium. The resultant parameters are given by Tosi[6] for all the alkali halides, and those for sodium chloride were used by Eldridge and Staal. A more refined approach would be to allow for short-range interactions between more distant neighbors and to take appropriate derivatives of the *free* energy. However, this would be much more laborious and Eldridge and Staal's results suggest that the effects of these refinements tend to cancel. Our main purpose is to present a *consistent* set of calculations for a sequence of crystals, and thus we must use the *same* procedure for each; that of Eldridge and Staal is both simple and, at least for sodium chloride, proven. Moreover, the effect of second-neighbor anharmonicity on Γ is only secondary, since it can be shown that it provides no direct contribution to the matrix element in Eq. (5).

In order to generate the eigendata we used a deformation dipole model with short range forces acting between first neighbors and between second-neighbor negative ions. The various model parameters are determined by fitting the following observed data: the high and low-frequency dielectric constants, the lattice constant, the compressibility, the infrared dispersion frequency, and the elastic constant C_{44}. The details of these calculations are described extensively elsewhere.[9]

III. SPECIFIC STUDIES

As was mentioned in the Introduction, experimental data on optical constants in the millimeter and submillimeter regions are sparse; our choice of materials to study was largely dictated by the existence of such data. We thus selected sodium chloride (NaCl), potassium chloride (KCl), potassium bromide (KBr), and potassium iodide (KI). Also, this sequence provides an excellent sample of typical ionic pairs within the alkali halide sequence; specifically, the former pair have comparable ionic masses, while the latter show a wide disparity.

The calculations of contributions to Γ were made for a sample of 64 000 wave vectors $\vec{q}$, within the first Brillouin zone, and the results were "binned" into histogram steps of 0.03×10^{13} rad/sec along the frequency axis. The results for the four crystals, each at a temperature of 300 K, are shown in Fig. 1 for the frequency range from 0 to $\sim 0.7\times10^{13}$ rad/sec. Over this spectral range the contributions come entirely from two-phonon difference processes. The two final-state phonons are unbroadened, except artificially by the width of the histogram steps. This artificial width can, in principle, be reduced to arbitrarily low limits by increasing the density of sample wave vectors; the limitation is solely a practical matter of computer time. In practice, we have found in the past that infinite crystal results can be obtained by smoothing a curve through histograms of the type presented here; indeed such a curve for NaCl has already been published as part of a standard com-

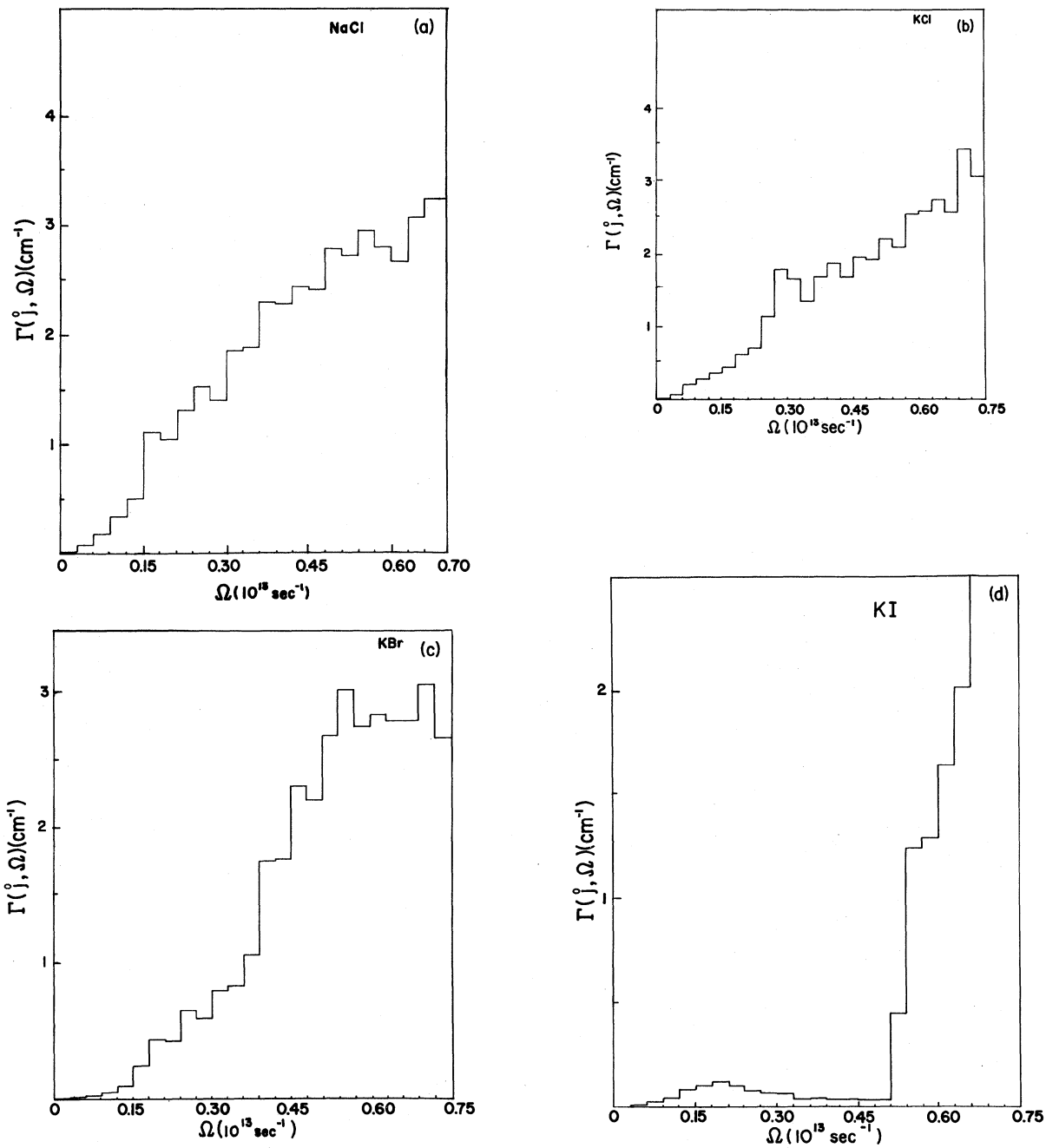

FIG. 1. Low-frequency damping functions due to two-phonon difference processes for NaCl, KCl, KBr, and KI at 300 K.

pilation [Ref. 9; Fig. 36(b)]. However, for the present purposes, it is necessary to use the histogram data since, certainly in the millimeter region ($\omega \lesssim 10^{12}$ rad/sec), one needs to average out "chatter" due to finite mesh size. Moreover, in this spectral range, one cannot smooth by using Lorentzians instead of delta functions for the line shapes. This would lead to finite absorption for *negative* frequencies. This is unphysical, and implies incorrect behavior of the predicted absorption for small positive frequencies. It is thus better to use the histogram data which have the correct limiting behavior $\Gamma \rightarrow 0$ as $\omega \rightarrow 0$. This point should be stressed since, should lifetime effects for the

final-state phonons be significant, then they will have to be treated in a manner which ensures overall energy conservation. The presence of negative frequency absorption reflects the failure of a Lorentzian convolution of Γ to satisfy this requirement. More generally, it would seem that such a convolution is only reliable when $\omega \gtrsim \gamma$ where γ is the Lorentzian half-width. Eldridge and Staal[8] appear to have addressed this problem by convoluting with a Lorentzian of variable width such that $\gamma \rightarrow 0$ as $\omega \rightarrow 0$. Thus in the very low-frequency region, the effect of convolution, or final-state broadening, becomes increasingly less important.

Most recently Sparks *et al.*[10] have invoked this final-state broadening as a means of relaxing the rather stringent selection rules imposed by strict energy and momentum conservation.

It can be seen from Fig. 1 that there is a drastic and surprising change in behavior for KBr and KI, as compared with NaCl and KCl. The latter pair of crystals show broadly similar behavior; the only significant difference occurs at the lowest frequencies, where Γ for NaCl drops (in relative terms) somewhat more rapidly. This can be traced to the fact that, for KCl, the calculated dispersion curves[9] reflect the near-equality of the ionic masses and show a number of points of near-contact between optic and acoustic branches of the same symmetry. As a consequence "interband" transitions, involving an optic and an acoustic phonon, become allowed at lower frequencies than is the case for NaCl, for which the more disparate masses introduce somewhat wider gaps. Such transitions, if energetically allowed, are in general not suppressed by other selection rules and beome dominant at higher frequencies. However, once the frequency is reduced below that of the lowest optic-acoustic gap *at any specific wave vector,* the only transitions allowed are "forbidden" transitions: intraband optic-optic and acoustic-acoustic and forbidden interband transitions, e.g., TO$-$LA. Any such differences must involve phonons from different branches close to some degeneracy line (or point) and their total contribution can only be obtained accurately by the present type of numerical calculation. This is evident if one examines the dispersion curves along symmetry directions for either NaCl or KCl. The number of line and point degeneracies is vast; each represents a potential contribution and many such contributions (e.g., forbidden interband transitions) may be weighted by matrix elements which have to be known precisely; i.e., they cannot be approximated by the symmetry line (or point) value since that is zero. Given these factors, any analytic approximation to these forbidden processes would appear to be extremely difficult and unreliable. Since these represent the only allowed processes at millimeter frequencies, it would appear that calculations of the present type are essential to establish the intrinsic two-phonon absorption in this spectral range, for both these systems and any other system.

The behavior for KBr represents an interesting "transition regime." The frequency spectrum now has a small absolute gap and, at frequencies below the width of this gap, all interband transitions are forbidden by energy conservation. The effect of this is to further depress the damping at low frequencies, and one starts to see a hint of the drastic change that is manifest for KI. For this latter material the magnitude of the absolute gap width is much larger and coincides with that at which the damping becomes almost negligible. This implies that intraband transitions are drastically suppressed. The reason for this is that the ionic masses have become so different that "optic" vibrations involve almost exclusively motions of the light atoms and "acoustic" vibrations are confined mainly to the heavy atoms. In these circumstances the eigenvector products in Eq. (5) will be very small for either optic-optic or acoustic-acoustic combinations. (This is graphically illustrated by Figs. 9$-$12 of Ref. 9, where the two densities of states, weighted respectively by the squares of the positive-ion and negative-ion eigenvector components, are shown for the sodium halides.) This effect should be starting to show in KBr, or, for that matter, in NaCl. However, the effects of mass disparity in these systems may well be partially offset by force constant changes. For KI the 3:1 mass ratio dominates and, possibly assisted by the "softness" and polarizability of the I^-, produces a large measure of sublattice "decoupling" in optic and acoustic motions.

In Figs. 2 and 3 we show the full two-phonon damping functions for all four crystals; the former displaying the difference bands and the latter the summation bands. The data in Fig. 1 represent much magnified displays of the low-frequency parts of the data in Fig. 2.

The overall agreement between the present results and those of other workers[7,8,11–14] appears to be very reasonable. The best comparison is with the data of Eldridge and co-workers for NaCl (Ref. 8) and KI (Ref. 11). For the former crystal, such differences as exist must be due primarily to differ-

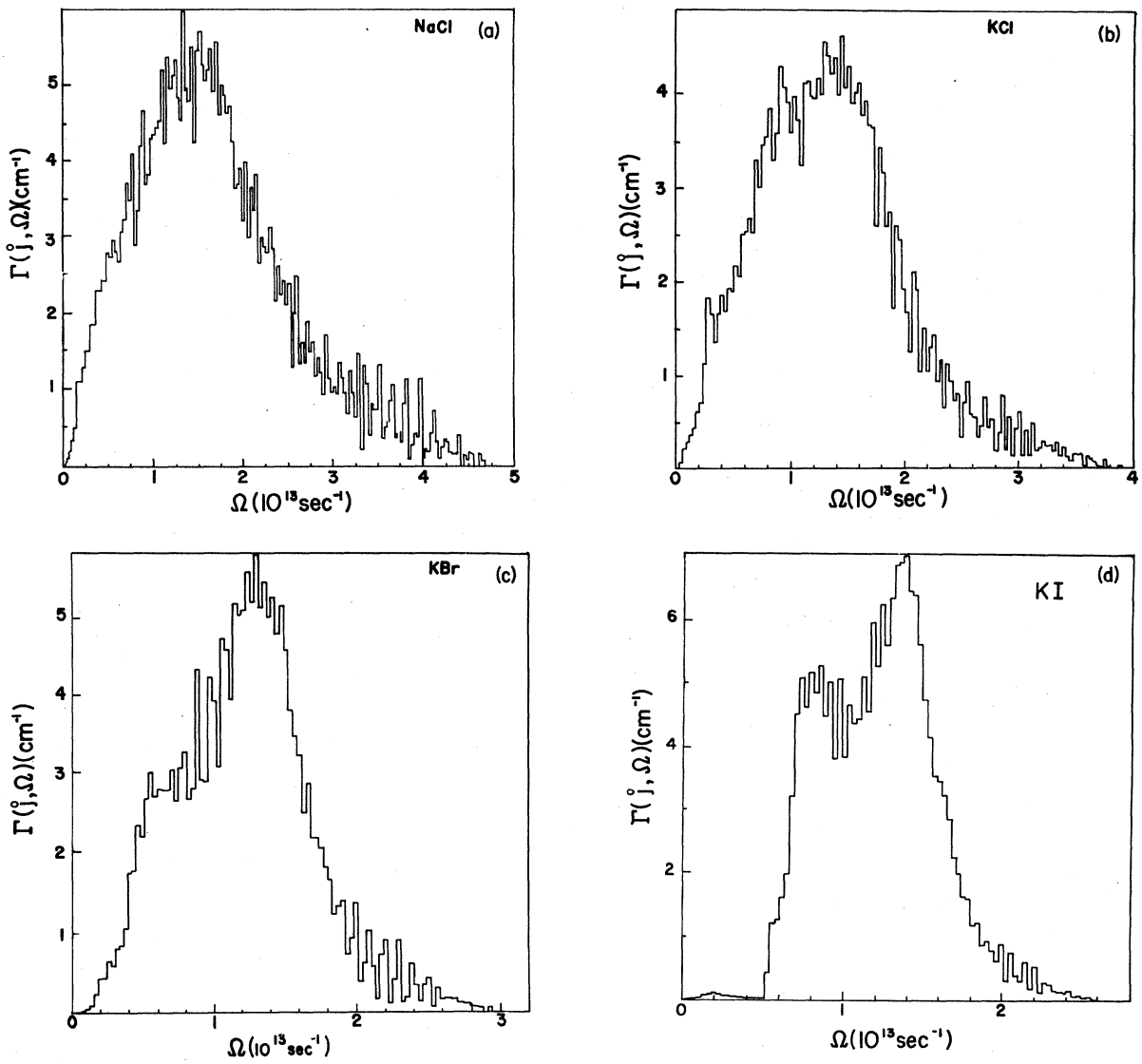

FIG. 2. Damping functions for NaCl, KCl, KBr, and KI: two-phonon difference processes at 300 K.

ences in the lattice-dynamical models. For the latter there are similar primary differences, but there is also another primary difference in the absolute level of absorption. This arises from the use of a different form for the third derivative of the first-neighbor potential mentioned earlier, and discussed in more detail in the next section. This results in a lower value for this derivative and, consequently, $\sim 25\%$ smaller Γ values. There may also be more subtle effects for KI arising from the inclusion of anharmonic bond shearing effects by Eldridge and Kembry[11] which we have neglected. For NaCl, although Eldridge and Staal's work automatically includes these effects, at room temperature the associated combination of derivatives is essentially zero, and thus they should not contribute to discrepancies between our results and those of Eldridge and Staal.[8] For KI this is not the case, and weak effects ($5-10\%$) could be present, but appear to be completely overwhelmed by the primary effects.

For KBr there appears to be about the same degree of agreement with earlier work[12,13] as exists for KI. For KCl there seems to be little, if any, earlier work with which to compare and the present results may be the first for this material.

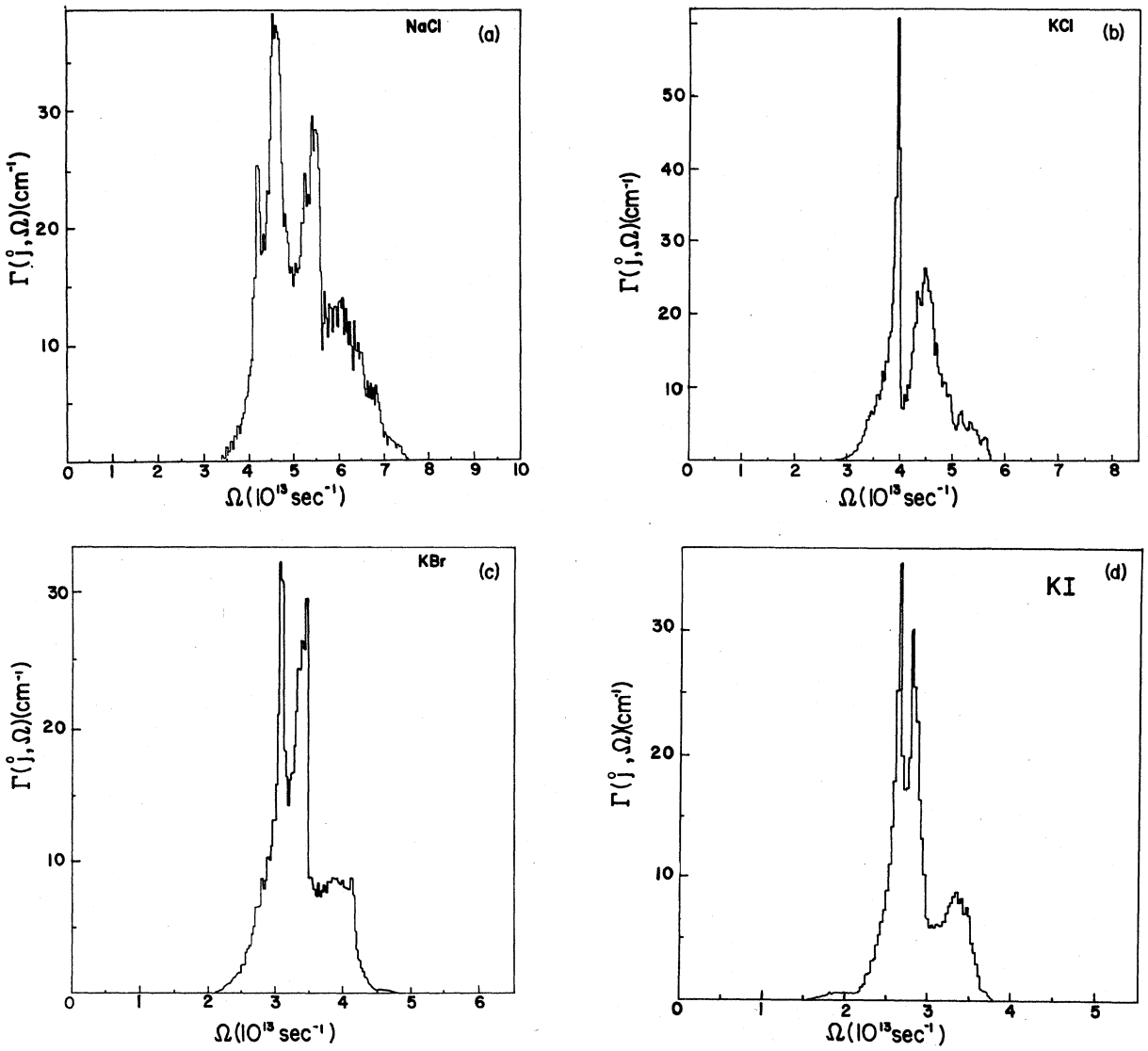

FIG. 3. Damping functions for NaCl, KCl, KBr, and KI; two-phonon summation processes at 300 K.

IV. DETERMINATION OF THE PARAMETERS

As stated earlier, the third derivatives of the nearest-neighbor potentials were calculated using the Tosi parameters[6] derived assuming that the lattice is in static equilibrium at 300 K, which is the temperature used in the calculations.

If $\psi(r)$ is the nearest-neighbor potential, then

$$\psi(r)=\frac{-e^2}{r}+Ae^{-r/\rho}\,, \tag{6}$$

where A and ρ characterize the short-range repulsive potential. Thus at the equilibrium separation r_0,

$$\psi'''(r_0)=\frac{6e^2}{r_0^4}-\frac{Ae^{-r_0/\rho}}{\rho^3}\,. \tag{7}$$

However, from the static equilibrium condition,

$$\frac{-\alpha_m e^2}{6r_0^2}=\frac{-1}{\rho}Ae^{-r_0/\rho}\,, \tag{8}$$

where α_m is the Madelung constant. Thus

$$\psi'''(r_0)=\frac{e^2}{r_0^4}\left[\frac{-\alpha_m}{6}\left[\frac{r_0}{\rho}\right]^2+6\right]\,. \tag{9}$$

The resultant derivatives and their associated input are shown in Table I. Note that there is a

TABLE I. Input parameters for calculation of the two-phonon damping.

Crystal	NaCl	KCl	KBr	KI
Nearest-neighbor distance r_0 (10^{-8} cm)	2.820[a]	3.147[a]	3.298[a]	3.533[a]
Screening radius ρ (10^{-8} cm)	0.321[a]	0.326[a]	0.336[a]	0.348[a]
Observed transverse-optic resonance wave number (cm^{-1})	163[b]	141[b]	114[b]	102[b]
Third derivative of first-neighbor potential $\psi'''(r_0)$ (10^{-12} ergs/cm^3)	−6.0112	−4.9727	−4.3019	−3.5566
Ionic masses (10^{-24} g)				
m_1	38.175[b]	64.930[b]	64.930[b]	64.930[b]
m_2	58.871[b]	58.871[b]	132.691[b]	210.729[b]
Static dielectric constant ϵ_0	5.92[b]	4.85[b]	4.91[b]	5.12[b]
High frequency dielectric constant ϵ_∞	2.33[b]	2.16[b]	2.35[b]	2.64[b]

[a]Reference 6, Tables VII and VIII.
[b]Reference 9, Table VII b.

slight difference between our value of ψ''' for NaCl and that given by Eldridge and Staal[8]; this probably reflects the use of the Fumi value for r_0. For KI, there is a substantial ($\sim 10\%$) difference between our value and that given by Eldridge and Kembry.[11] However, this simply reflects the difference in the Coulomb contributions.

V. COMPARISON OF THEORY AND EXPERIMENT

In Table II we show specific comparisons between the theoretical and experimental extinction coefficients (κ) for all four materials at several wavelengths between 300 μm and 3.09 mm. The general agreement between theory and experiment can be considered satisfactory, except for the heavier halides at the longer wavelengths. The discrepancies elsewhere should be viewed with caution, given the extreme sensitivity of these absolute values of κ to the potential derivatives ψ''' which could well be in error by $\sim 10\%$. Moreover, as the wavelength increases, the experimental values are subject to increasing uncertainty. However, Stolen and Dransfeld[4] also studied the temperature dependence of the absorption of these crystals. At room temperature and above the present calculations would predict a linear dependence on temperature (T) because the phonon occupation numbers in Eq. (5) are proportional to T in this range. Stolen and Dransfeld found that the data could be fitted by

$$\kappa = AT + BT^2 \tag{10}$$

at ~ 300 K and above; this suggests the presence of some three-phonon absorption. At the shorter wavelengths ($\sim 300-500$ μm) the proportion of three-phonon absorption they infer appears to be almost exactly what is needed to remove the discrepancies between our predicted two-phonon absorption and experiment (see Table II). However, at longer wavelengths, their results indicate that A in Eq. (10) is essentially zero, with the implication that there is no two-phonon absorption at those wavelengths; whereas our results indicate that not merely is two-phonon absorption present, it is generally dominant.

A possible resolution of this paradox is suggested by a reexamination of Stolen and Dransfeld's analysis of Dötsch and Happ's data for NaCl at 3.09 mm (Fig. 7 of Ref. 4). This is one of the cases where they find $A \simeq 0$. However, in drawing this conclusion, they appear to have used only the data for $T \gtrsim 300$ K. Thus we have reanalyzed Dötsch and Happ's data, following Stolen and Dransfeld's procedure of plotting κ/T versus T, but using *all* the 3.09 mm data. The result is shown in Fig. 4. The plot appears to show *two* linear regions, not one; the upper being relatively steep and the lower almost flat. Moreover, when we extrapolate the lower region to 0 K and multi-

TABLE II. Comparison of calculated room-temperature two-phonon extinction with experiment at selected longer wavelengths. Unless stated otherwise, the experimental data come from Table I of Ref. 4.

Crystal	Wavelength (μm)	Extinction coefficient κ Theoretical two-phonon component	Experiment
NaCl	320	2.81×10^{-2}	3.23×10^{-2}
		(2.45×10^{-2})[a]	
	500	1.91×10^{-2}	2.43×10^{-2}
		(1.82×10^{-2})[a]	
	1020	9.5×10^{-3}	8.4×10^{-3}
	3090	1.1×10^{-3}	$(\sim1.7\times10^{-3})$[b]
		$+2\times10^{-4}$	
		three phonon[c]	
KCl	320	2.17×10^{-2}	2.65×10^{-2}
		(1.92×10^{-2})[a]	
	500	1.35×10^{-2}	1.83×10^{-2}
		(1.36×10^{-2})[a]	
	900	4.5×10^{-3}	1.07×10^{-2}
		(7.8×10^{-3})[a]	
	3090	1.2×10^{-3}	$(\sim1.8\times10^{-3})$[d]
KBr	320	3.18×10^{-2}	3.72×10^{-2}
		(2.86×10^{-2})[a]	
	500	1.00×10^{-2}	1.43×10^{-2}
		(7.2×10^{-3})[a]	
	900	3.4×10^{-3}	5.2×10^{-3}
	3090	2×10^{-4}	$(\sim7\times10^{-4})$[e]
KI	320	1.64×10^{-2}	2.27×10^{-2}
		(1.36×10^{-2})[a]	
	500	6×10^{-4}	8.4×10^{-3}
		$+\ 8.2\times10^{-3}$	
		three-phonon[f]	
	900	1.2×10^{-3}	
	3090	2×10^{-4}	
		$+\ 1.1\times10^{-3}$	
		three-phonon[f]	

[a]Values shown in parentheses in this column are estimates of the *experimental* two-phonon contribution from Figs. 4–7 of Ref. 4 and, for KCl, from R. Stolen, Thesis, University of California, Berkeley, 1965 (unpublished).
[b]Estimated from Fig. 2 of Ref. 3.
[c]Reference 8, and private communication from J. E. Eldridge.
[d]Estimated from Fig. 2 of Ref. 2.
[e]Also estimated from Fig. 2 of Ref. 2, but by extrapolation.
[f]Reference 16, and private communication from J. E. Eldridge.

ply the intercept by 300 K, the resultant κ value is $\sim10^{-3}$, in excellent agreement with the predicted value in Table II (1.1×10^{-3}). On this basis we would argue that the two-phonon absorption is in the classical limit, even at temperatures ~100 K,

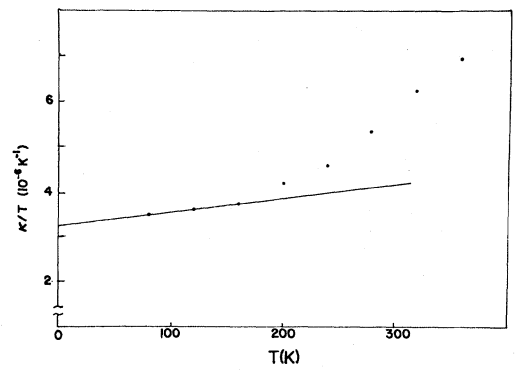

FIG. 4. Plot of the 3.09-mm extinction coefficient κ divided by temperature T for NaCl at 300 K. The points are the experimental values from Ref. 3: The lower linear region is indicated by the straight line which is extrapolated to 0 K.

and that apparently there are two T^2 contributions, of which Stolen and Dransfeld indentified only the steeper one. This led them to infer that two-phonon absorption was essentially absent. However, were this to be the case, one can see from their "model" calculations (Fig. 10 of Ref. 4) that κ/T should drop sharply *below* the linear extrapolation as quantum effects become important; it can be seen from Fig. 2 that the reverse is true. We now observe that if the *low-temperature* linear region of the κ/T plot is extrapolated to 300 K, then the additional absorption, over and above the two-phonon contribution, is $\sim10\%$ of the total measured absorption; this agrees very well with the value calculated by Eldridge and Staal[8] for the *intrinsic* three-phonon absorption at this temperature and wavelength. It would thus appear that the residual excess absorption at 300 K has some other origin. The most likely explanation is that the two phonons involved in the decay of the optic phonon themselves decay "smearing out" the frequency delta functions into regions where the density of final states is low, as described by Bilz[15], this is the "lifetime effect" alluded to previously.

It is also apparent from Table 4-1 of Ref. 15 that once one admits of the need to follow the two phonons involved in the decay of the virtual transverse-optic phonon through further anharmonic interactions, independent decay is not their only possible behavior. However, most possibilities, including independent decay, would appear to be proportional to T at high temperatures; this, combined with the T dependence of the initial two-phonon decay, will give an overall T^2 dependence in their contributions to Γ. Thus, the anomalous high-temperature absorption could

come from one or more of these processes; the most obvious being simple decay of the two phonons.

It is not immediately obvious why the "classical" regime for these processes is not reached until $T \sim 200-250$ K. The most likely explanation is that they only become significant when *all* phonon numbers have reached the classical limit. This is supported by the close agreement between the temperature just cited and the Debye temperature for NaCl.

In the light of this discussion for NaCl, we are inclined to believe that other apparent discrepancies between our results and those of Stolen and Dransfeld (see Table II) have basically the same origins. In particular their raw data for KBr at 900 μm (see Fig. 3 of their paper) seem to be showing the wrong (upward) curvature at lower temperatures.

The foregoing analysis leads us to believe that, for NaCl and KCl, the discrepancies between two-phonon theory and experiment are due mainly to final state broadening and, to a lesser degree, to genuine three-phonon absorption; the relative importance of the latter increasing markedly at the shorter wavelengths.

For KBr and KI the results in Table II indicate excellent agreement between predicted and observed two-phonon contributions except at the longer wavelengths. It is likely that the T^2 contribution to κ (at the longer wavelengths) comes mainly from intrinsic three-phonon absorption. The results for KBr at 3.09 mm and for KI at 500 μm clearly indicate that the observed absorption is dominated by higher-order processes. However, it may well be that no one explanation fits all the data. Fortunately, calculations of the three-phonon absorption in KI made by Eldridge and Staal[16] provide a sound basis for understanding the intrinsic absorption in this material. It appears (see Table II), that, at 500 μm and beyond, the absorption is basically due to intrinsic three-phonon difference processes. However, comparison between theoretical and existing experimental κ values[4,5] should be made with caution for the longer wavelengths since the experimental values may well contain significant contributions from impurities.

There remains the problem of the apparently anomalous temperature dependence of the 500 μm absorption; the data apparently vary more rapidly than T^2. This could be explained by the presence of even higher-order processes; however, we already have excellent agreement between theory and experiment—additional absorption would destroy this. An intriguing possibility is that this anomalous temperature dependence is due to final state broadening effects on the *three-phonon* process. If there is a strong constraint against two-phonon decay for one or more of these three phonons, then its width will be $\sim T^2$ at room temperature. It thus follows that the absorption could vary as rapidly as T^4. We thus appear to have a reasonable overall understanding of KI; specifically, we can see that its behavior at long wavelengths is radically different from the other three crystals studied and why this is the case.

As regards KBr we are not in a position to be so specific. However, it would appear from examination of Bruce's calculations[13] for this material, that three-phonon damping becomes dominant at longer wavelengths. Specifically, at 3.09 mm $\kappa \sim 3-4 \times 10^{-4}$ for three-phonon processes. This is almost twice the two-phonon contribution and the sum of both is close to the measured value.

VI. CONCLUSIONS

This examination of four typical alkali halides leads us to the following conclusions concerning their intrinsic long-wavelength optical absorption arising from phonon difference processes:

(a) For materials with comparable ionic masses, in which the optic- and acoustic-phonon branches are well overlapped, the largest contribution comes from *two-phonon* difference processes. Superposed on this are are the effects of lifetime broadening on these two phonons which, in regions where the density of final states is low, can enhance the absorption by 30–40 %. Intrinsic three-phonon absorption appears to be relatively unimportant at long wavelengths.

(b) In materials with widely differing ionic masses, which have gaps or near gaps in their frequency spectra, the two-phonon absorption is markedly to very strongly suppressed and the intrinsic three-phonon processes become much enhanced and dominant at long wavelengths. This occurs both because the matrix elements for three-phonon processes are much larger than those for two-phonon processes and because the density of final states for the former is much enhanced. It also appears that final-state lifetime effects may enhance the temperature dependence of the three-phonon processes.

(c) The foregoing results are valid for the alkali halides studied at room temperature because this is

well above their Debye temperatures. At lower temperatures one expects the relative importance of three-phonon absorption and lifetime broadening to be strongly suppressed and two-phonon processes to dominate. However, the results for KI[16] suggest that very low temperatures would be needed.

Simple ceramics, such as MgO, at room temperature are in approximately the same degree of relative thermal agitation as alkali halides at ~ 100 K. Thus the behavior of alkali halides at low temperatures is highly germane to an understanding of that of ceramics at room temperature. In this context our single most important conclusion would appear to be that, by making one ion much heavier, one can open a low frequency "window" in the two-phonon absorption spectrum and, provided one is working well below the Debye temperature of the material, this window will not be significantly blocked by intrinsic three-phonon processes. This "window effect" is so marked that it persists even if it is "bought" by making the material significantly "softer" and heavier.

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