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Far-Infrared Lattice Absorption in Alkali Halide Crystals*

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Measurements of the absorption between 0.3 and 1.0 mm have been made on NaCl, KCl, KBr, KI, NaI, and LiF between room temperature and 15°K. Present theory explains the absorption in this region as arising from "vertical" transitions from one phonon state to another with the same wave vector but of a higher energy, the energy difference between the two states being the energy of the absorbed photon. At high temperatures such 2-phonon processes should generally lead to a linear temperature dependence of the absorption. Experimentally, however, we found in all cases a strong additional contribution to the absorption which increased as T^2, which we believe to be caused by 3-phonon difference processes. At wavelengths longer than a certain cutoff wavelength, λ_c, depending on the dispersion curves, the linear (2-phonon) contribution disappears, leaving only the T^2 contribution. Comparison of our results with phonon dispersion curves shows that 2-phonon processes involving one longitudinal and one transverse branch do not appear. The results suggest that the observed 2-phonon absorption arises only from transitions between branches of the same polarization.

I. INTRODUCTION

THE absorption of electromagnetic radiation in crystals at frequencies well below the fundamental resonance, i.e., for wavelengths longer than 100 μ, has been studied so far rather incompletely. Rubens and Hertz[1] in their pioneering experiments in 1912 measured the absorption at a wavelength of 300 μ in crystals of NaCl, KCl, and CaF_2 and discovered that the absorption, though strong at room temperature, disappeared on cooling, with the absorption coefficient being roughly proportional to the temperature. From this variation with temperature Ewald[1] concluded later that the absorption may be caused by some anharmonic interaction between the radiation and thermal lattice vibrations. Rather detailed theoretical descriptions[2,3] appeared more recently, and the present experiments were started in order to provide a test for these theories.

The physical mechanism for the absorption process, on which the present theories (see Sec. III A) are based, can be seen most easily with the help of a phonon dispersion diagram of a crystal shown schematically in Fig. 1. Since we are interested in this paper in frequencies well below 10^{13} sec^{-1}, it is clear from the diagram that the only phonons which could be excited directly would be acoustic phonons of long wavelength. Their excitation in perfect crystals with a center of symmetry, however, is made impossible because of their optical inactivity.

The more important contribution to the absorption is expected to arise from "vertical transitions" between 2-phonon states as indicated in Fig. 1 by an arrow: Here one phonon in a lower branch is destroyed while another one with the same momentum but at higher energy is created. The difference in energy $\hbar\omega$ is supplied by the absorbed infrared quantum. The absorption due to this *2-phonon process* is predicted theoretically (see Sec. III A) to increase linearly with temperature.

As far as the frequency dependence is concerned it is clear from Fig. 1 that there should be less or no absorption for frequencies below a certain "cutoff frequency" ω_c, which represents the closest frequency separation of two branches at the zone boundary. Real crystals have, of course, more than two branches and consequently a more complicated frequency dependence would be expected. But in many cases—as will be seen—a cutoff range can still be defined and shows up experimentally.

Our work is restricted to long wavelengths where the 2-phonon *difference* process should apply. For wavelengths shorter than the fundamental resonance (usually around 100 μ) the absorption process is one in which two phonons are created. This 2-phonon *sum* process has been the primary concern of most previous work on infrared absorption in alkali halides.[2,3]

The temperature dependence of the absorption was measured by Klier[4] for LiF. He found it to be quadratic

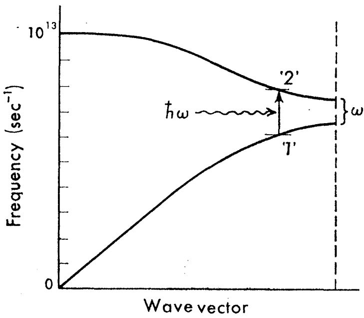

FIG. 1. Simplified dispersion diagram showing one acoustic and one optical branch only. The vertical arrow represents a 2-phonon difference process in which a phonon on branch "1" is destroyed and a phonon on branch "2" of the same wave vector but of higher energy is created.

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[1] H. Rubens and G. Hertz, Berlin. Ber. **14**, 256 (1912). The data have been reproduced in a paper by P. P. Ewald, Naturwiss. **10**, 1057 (1922).

[2] H. Bilz and L. Genzel, Z. Physik **169**, 53 (1962).

[3] V. V. Mitskevich, Fiz. Tverd. Tela **3**, 3036 (1961); **4**, 3035 (1962) [English transls.: Soviet Phys.—Solid State **3**, 2211 (1962); **4**, 2224 (1963)].

[4] M. Klier, Z. Physik **150**, 49 (1958).

between 80 and 600°K, while in NaCl, KCl and CaF_2, according to Rubens and Hertz,[1] as mentioned above, the absorption increases more nearly with the first power of T. Dötsch and Happ[5] extending the experiments on NaCl to a wavelength of a few millimeters observed a dependence closer to T^2 at their longest wavelength of 3 mm.

Room-temperature measurements at variable wavelengths between 0.3 and 3 mm were reported by Genzel, Happ and Weber[6] on NaCl, KCl, and KBr. We will return later to their interesting result that for KBr the absorption increases much faster with frequency than for the two other salts.

The present experiments in the submillimeter range and at temperatures down to 15°K were performed on a number of alkali halide crystals for which the phonon dispersion diagrams have become available, allowing a general comparison with the theory. Our results are reported in Sec. II and generally show in addition to the expected linear contribution at high temperatures a term quadratic in T. The absorption below the cutoff frequency is not at all negligible but still an appreciable fraction of what is observed above the cutoff frequency. Furthermore the temperature dependence below the cutoff is almost purely quadratic in T for all samples which suggests that this strong absorption is caused by a process of the next higher order, i.e., a *3-phonon process*. The nature of this process and the reason for its importance besides the 2-phonon process are described in Sec. III B.

It is also interesting that 2-phonon transitions seem to occur only between the transverse acoustic and transverse optical branches. This simplifies comparison of the experimental results with phonon dispersion curves and facilitates the experimental observation of the cutoff region. The experimental evidence for this empirical "selection rule" will be discussed in Sec. IV.

We have experimental and theoretical reason to believe that the phenomena described here are not caused by impurities. A separate study of the effect of impurities on the far-infrared absorption will be reported in another paper.

II. EXPERIMENTAL RESULTS

The temperature dependence of the far-infrared absorption was studied at wavelengths between 300 μ and 1 mm for NaCl, KCl, KBr, KI, LiF and NaI. In general the temperature ranged between 80 and 300°K, but in some cases it extended from 15 to 420°K. A grating monochromator was used to isolate a band of incoherent radiation from a mercury arc. Wavelength, radiation purity, and bandwidth were checked with a scanning Fabry-Perot interferometer.[7] The bandwidth was about 10% in all cases. After transmission through the sample the radiation was detected by a carbon bolometer,[8] operated at 1.4°K. Only at the longest wavelength of 1 mm was bolometer current noise a major source of error.[9]

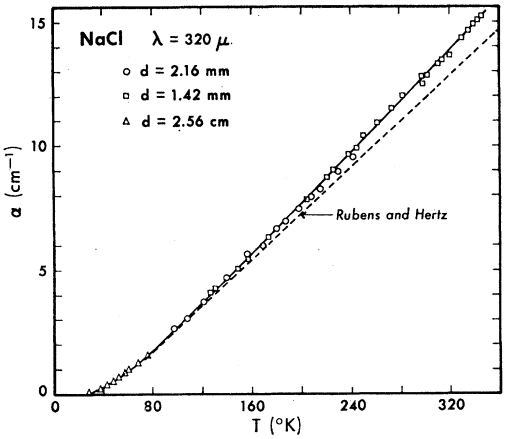

FIG. 2. Typical absorption measurements on NaCl at constant wavelength and for specimens of different thickness *d*.

The alkali halide samples were commercially available[10] as single crystals of cylindrical shape of diameter 2.5 cm, and of varying thickness between 0.1 and 2.5 cm. The samples were located in the gap between 2 light pipes. The use of light pipes has considerable cyrogenic advantages; it poses, however, the following problem: After insertion of the sample into the gap between the

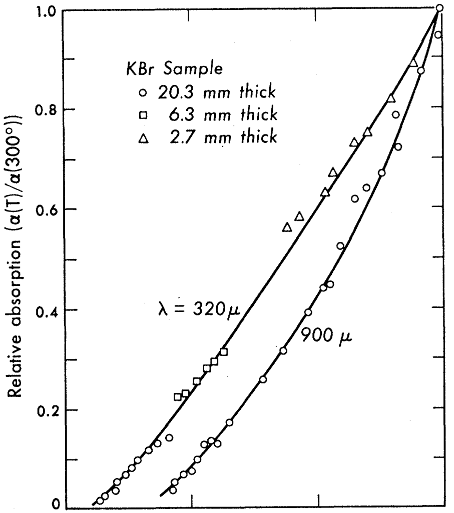

FIG. 3. Absorption in KBr at two different wavelengths.

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[5] H. Dötsch and H. Happ, Z. Physik **177**, 360 (1964).

[6] L. Genzel, H. Happ and R. Weber, Z. Physik **154**, 13 (1959).

[7] K. F. Renk and L. Genzel, Appl. Opt. **1**, 643 (1962). R. Ulrich, K. F. Renk, and L. Genzel, IEEE Trans. Microwave Theory Tech. **11**, 363 (1963).

[8] R. C. Ohlmann, thesis, University of California, Berkeley, 1960 (unpublished).

[9] For more details, see: R. Stolen, thesis, University of California, Berkeley, 1964 (unpublished).

[10] Suppliers: Harshaw Chemical Company, Cleveland, Ohio and Isomet Corporation, Palisades Park, New York.

light pipes, wide-angle radiation is bent more nearly parallel, with the result that the gap is effectively shortened. In all our measurements the readings with the sample out of the beam were corrected accordingly. The temperature of all samples could be varied between 15 and 420°K. Measurements were taken at constant wavelength as the sample temperature varied at a rate of 30° per h.

Figure 2 shows as a representative example the absorption of NaCl at a wavelength of 320 μ for various samples. The previous measurements of Rubens and Hertz[1] are also shown. In Fig. 3 the temperature dependence of the absorption in one material (KBr) but at two different wavelengths is compared. For both wavelengths, 320 and 900 μ, the absorption is normalized to unity at 300°K. It is very obvious that for the longer wavelength of 900 μ, the absorption disappears on cooling more rapidly than at 320 μ.

From Fig. 3 one can see that for the longer wavelength α seems to vary roughly as T^2, while the behavior at the shorter wavelength is more linear in T. We will therefore try to represent the temperature dependence of the absorption by a linear and quadratic term:

$$\alpha = AT + BT^2, \tag{1}$$

with A and B being independent of T. This is the expected temperature dependence at *high temperatures* for a sum of 2- and 3-phonon difference contributions (see Sec. IV). (In this paper, whenever, the temperature dependence is referred to as linear or quadratic it refers to the high-temperature limit only.) How well Eq. (1) represents the experimental temperature dependence, and how large the linear and quadratic contributions are, can best be seen from a plot of (α/T) versus T: For a predominantly linear dependence between α and T, (α/T) will be a constant, while for a quadratic behavior (α/T) will be linear in T. In Figs. 4–7 we have therefore plotted (α/T) as a function of T for KBr, KI, LiF, NaI and NaCl. The solid curves represent our experimental data, normalized again to unity at 300°K. The dashed lines extrapolate the behavior at high temperatures which will be discussed later on. In Fig. 7 we have also included measurements by Dötsch and Happ[5] at $\lambda = 3$ mm. From an inspection of all of these curves it is evident that at high temperatures and long wavelengths the absorption seems to approach a quadratic rather than a linear temperature dependence. Figures 4–7 will be analyzed more fully in Sec. IV.

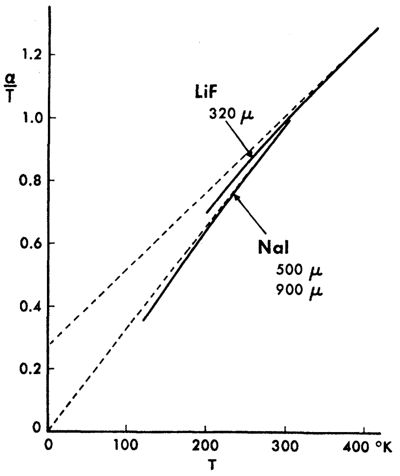

FIG. 6. (α/T) plotted for LiF at 320 μ and for NaI at 500 μ and 900 μ, normalized to 1.0 at 300°K.

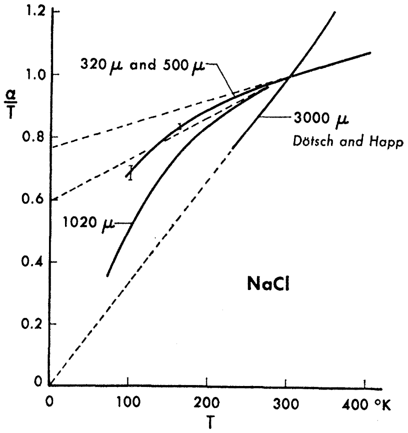

FIG. 7. (α/T) plotted for NaCl at four wavelengths, normalized to 1.0 at 300°K. For 320 μ and 500 μ the data are too close to be resolved.

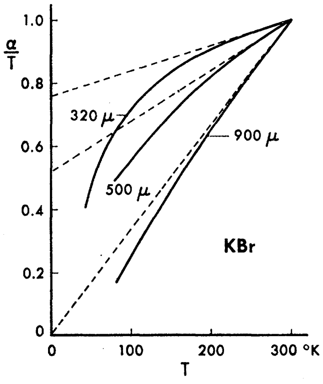

FIG. 4. (α/T) plotted for KBr at three wavelengths, normalized to 1.0 at 300°K.

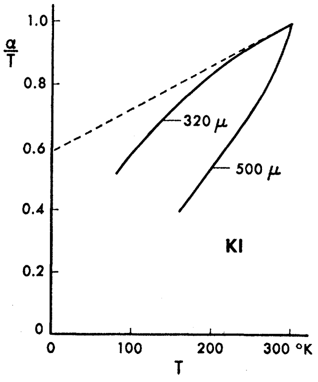

FIG. 5. (α/T) plotted for KI at two wavelengths, normalized to 1.0 at 300°K.

The absolute magnitude of the absorption of the various crystals will not be discussed in this paper. But

TABLE I. Absorption values at 300°K as measured at a few wavelengths.

Crystal	$\lambda[\mu]$	$\alpha[\mathrm{cm}^{-1}]$
NaCl	1020	1.03
	500	6.1
	300	12.7
KBr	900	0.73
	500	3.6
	320	14.6
KCl	900	1.5
	500	4.6
	320	10.4
KI	500	2.1
	320	8.9
LiF	320	3.4
NaI	900	0.97
	500	3.48

for reference, Table I gives the absorption at room temperature and at a few wavelengths for the different alkali halides which we studied.

III. THEORY

In Part A of this section we present an outline for the theoretical treatment of the far infrared absorption in ionic crystals as caused by terms in the lattice potential energy of *third* order in the ionic displacements. The results are similar to the ones published,[2,3,11] but the derivation used here seems to be particularly simple.

An analysis of our experiments in Sec. IV will show, however, that a consideration of these third-order terms alone does only partially—and in several cases not at all—account for the observed absorption. Therefore a brief discussion of *fourth*-order processes is added in Part B.

A. Absorption by 2-Phonon Processes

The lattice potential energy contains a part φ_3 in the third order of the ionic displacements u:

$$\varphi_3=\sum C(1,2,3)u_1u_2u_3\,, \tag{2}$$

where the C's are third-order elastic constants. The summation extends over all ions and includes the components of the u_i's along all three unit vectors. If each displacement u_i is expressed by its expansion into normal modes,[12] Eq. (1) becomes

$$\varphi_3=\sum_{1,2,3} A(1,2,3)Q_1Q_2Q_3\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)\,. \tag{3}$$

The 1,2,3 refer now to normal modes of special wave vector q and branch. The Q's are the amplitudes of the normal modes. $A(1,2,3)$ again contains third-order elastic constants. As is well known these anharmonic terms in the potential energy provide the exchange of energy between the normal modes: Either one phonon decays into two, or two combine to a third.

On application of an electric field the positive and negative ions in the crystal move by a distance $\mathbf{u}_+$ and $\mathbf{u}_-$. Following Huang[12] this motion can be described by a single coordinate

$$\mathbf{w}=(\mathbf{u}_+-\mathbf{u}_-)(MN)^{1/2}\,,$$

where M is the reduced mass and N the number of cells per unit volume. If the electric field $E=E_0e^{i\omega t}$ is of a frequency ω well below the lattice dispersion frequency ω_0, the ionic motion is frequency independent:

$$\mathbf{w}=\left(\frac{\epsilon_0-\epsilon_\infty}{4\pi}\right)^{1/2}\frac{\mathbf{E}}{\omega_0}\,. \tag{4}$$

Here ϵ_0 and ϵ_∞ are the low- and high-frequency dielectric constants, respectively.

The total ionic displacement is partially thermal and partially caused by the external electric field

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$$\mathbf{u}_i^{(\mathrm{total})}=\mathbf{u}_i^{(\mathrm{thermal})}+K_i\mathbf{w}\,,$$

where K_i is a constant depending only on the indices i of u. Our procedure here is now to treat the w's in the same manner as the usual normal modes. Thus the expansion (3) of the third-order potential energy will now also contain some terms in $\mathbf{w}$. Since the wave vector associated with $\mathbf{w}$ is practically zero the interaction Hamiltonian between the infrared wave and the two phonons (of momenta $\mathbf{q}_1$ and $\mathbf{q}_2$) takes the form

$$H'=\sum_{1,2} B(1,2,0)Q_1Q_2w\delta(\mathbf{q}_1+\mathbf{q}_2)\,.$$

The constant $B(1,2,0)$ is similar to $A(1,2,3)$, depending on the wave vector and branch of the phonons involved. As there is too little known about it we follow the usual practice of taking it outside the summation, as a constant B. Introducing w from (4) the perturbation H' becomes

$$H'=\left(\frac{\epsilon_0-\epsilon_\infty}{4\pi}\right)^{1/2}\frac{E_0e^{i\omega t}}{\omega_0}B\sum_{1,2} Q_1Q_2\delta(\mathbf{q}_1+\mathbf{q}_2)\,.$$

This time-dependent perturbation can cause transitions, for example from a state "1" with one phonon to a state "2" with a phonon of the same wave vector, but of higher energy. The energy difference $\hbar\omega$ is supplied by the absorbed photon as indicated in Fig. 1. Also the reverse transition ("2" → "1") is possible leading to the emission of a photon. It is already plausible that the net rate at which photons are absorbed by transitions between two such phonon states should depend on the difference of their populations (n_1-n_2).

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[11] B. Szigeti, Proc. Roy. Soc. (London) **A204**, 51 (1950); **A252**, 217 (1959); **A258**, 377 (1960); **A261**, 274 (1961).

[12] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), Eqs. (9.9) and (9.16).

The transition rate from an initial state $|1\rangle$ to a final state $\langle 2|$ due to the perturbation H' is given by the standard expression

$$R=\frac{2\pi}{\hbar}|\langle 2|H'|1\rangle|^2\delta(E_2-E_1-\hbar\omega).$$

To obtain the matrix elements, creation and destruction operators can be introduced for the lattice displacements and the resulting net transition rate becomes

$$R=\frac{(\epsilon_0-\epsilon_\infty)E_0^2B^2}{8\omega_0^2}\sum\frac{(n_1-n_2)}{\omega_1\omega_2}\delta(\omega_2-\omega_1-\omega).$$

The absorption per cm, α, is defined by $(dI/I)=-\alpha d$ with

$$I=\text{intensity}=c(\epsilon_0)^{1/2}E_0^2/4\pi,$$
$$c=\text{velocity of light.}$$

If the beam has a cross section A, the rate at which energy is dissipated in the volume Ad is

$$R\times Ad\times\hbar\omega=dI\times A.$$

Thus, the coefficient of absorption for very low frequencies ($\omega\ll\omega_0$) becomes

$$\alpha=\frac{\pi}{2}(\epsilon_0-\epsilon_\infty)\frac{\hbar\omega B^2}{\epsilon_0^{1/2}c\omega_0^2}\sum_{1,2}\frac{(n_1-n_2)}{\omega_1\omega_2}\times\delta(\omega_2-\omega_1-\omega)\ [\text{cm}^{-1}].\qquad(5)$$

The result is not very different from that derived in another way by Szigeti,[11] who also considered the coupling by second-order moments.

The temperature dependence of the absorption is according to (5) only determined by the difference in occupation numbers n_1-n_2 between states of energy $\hbar\omega_1$ and $\hbar\omega_2$. Restricting ourselves to this one pair of states first, the occupation number in each state is

$$n_i=(e^x-1)^{-1}\quad x=\hbar\omega_i/kT.$$

At low frequencies when $\omega=\omega_2-\omega_1\ll\omega_1$, one finds

$$n_1-n_2=\left(\frac{\partial n_i}{\partial\omega_i}\right)\omega=\frac{dn_i}{dx}\left(\frac{\partial x}{\partial\omega_i}\right)\times\omega$$
$$=\frac{xe^x}{(e^x-1)^2}\frac{\omega}{\omega_1}=f_2(x)\frac{\omega}{\omega_1}\sim\alpha(T),$$

where $f_2(x)$ represents the only temperature-dependent part of the absorption and is plotted $(k/\hbar\omega_1)T$ in Fig. 8. It is evident that the absorption becomes linear in T in the high-temperature limit, starting already at about $T\geqq\hbar\omega_1/k$, i.e., roughly 150°K for many alkali halides. The fact that the measured absorption is the sum of many different transitions does not affect the general validity of this conclusion, since at high temperatures all different contributions become linear in T.

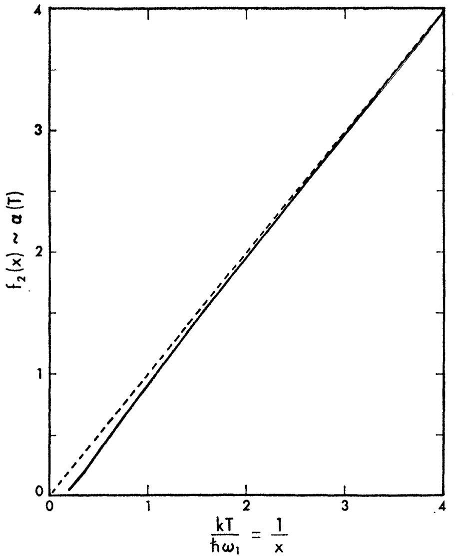

FIG. 8. Plot of $f_2(x)$ versus $(1/x)$ which represents a normalized curve of the absorption versus temperature for the 2-phonon process. The dashed line is linear in T, for comparison.

The frequency dependence of this 2-phonon absorption has been described in detail by Bilz, Genzel and Happ[2,13] in terms of a frequency-dependent damping constant. We like to mention here only that at long wavelengths and for a constant density of transitions per unit frequency interval the absorption (5) would increase as ω^2. For frequencies below a cut-off frequency ω_c, as described more fully in Sec. IV, the absorption should rapidly disappear altogether.

B. Three-Phonon Process

If we also include terms of the fourth order of the displacements in the lattice, potential-energy processes become possible in which the photon can exchange energy with three phonons.[3] Let us briefly outline this absorption process: the interaction Hamiltonian for such a 3-phonon process is, with the same notation as in III A:

$$H''=w\sum_{1,2,3}D(1,2,3,0)Q_1Q_2Q_3\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)$$

where $D(1,2,3,0)$ depends on fourth-order elastic constants. As processes leading to the absorption or emission of a photon let us, for example, consider the two pairs of diagrams in Fig. 9. The net transition rate is obtained after subtraction of the emission from the absorption process. Leaving out constants, the net

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[13] H. Bilz, L. Genzel and H. Happ, Z. Physik **160**, 535 (1960). See also: D. A. Kleinmann, Phys. Rev. **118**, 118 (1960).

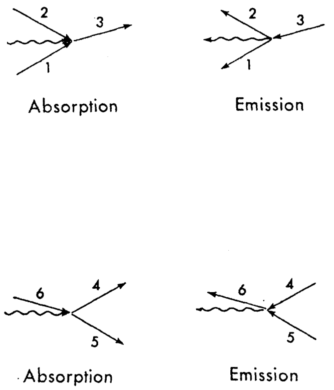

FIG. 9. 3-phonon processes leading to the absorption or emission of a photon (wavy arrow).

absorption coefficient becomes

$$\alpha\hat{=}\sum_{1,2,3}\frac{\omega}{\omega_1\omega_2\omega_3}[n_1n_2(n_3+1)-n_3(n_1+1)(n_2+1)]$$

$$+\sum_{4,5,6}\frac{\omega}{\omega_4\omega_5\omega_6}[n_6(n_5+1)(n_4+1)-n_4n_5(n_6+1)],$$

or

$$\alpha\hat{=}\sum\frac{\omega}{\omega_1\omega_2\omega_3}[n_1n_2-n_1n_3-n_2n_3-n_3]$$

$$+\sum\frac{\omega}{\omega_4\omega_5\omega_6}[n_5n_6+n_4n_6-n_4n_5+n_6].$$

The summation is again taken over all transitions conserving energy

$$\omega_3-\omega_2-\omega_1=\omega\,,\quad \omega_6+\omega=\omega_4+\omega_5\,,$$

and momentum.

At high temperatures when $kT/\hbar\omega_i>1$ and $n_i=kT/\hbar\omega_i$ the absorption from the term $[n_1n_2-n_1n_3-n_2n_3]$ becomes

$$\alpha\hat{=}\left[\frac{kT}{\hbar}\right]^2\sum\frac{\omega(\omega_3-\omega_2-\omega_1)}{(\omega_1\omega_2\omega_3)^2}=\left[\frac{kT}{\hbar}\right]^2\sum\frac{\omega^2}{(\omega_1\omega_2\omega_3)^2}.$$

The term $[n_5n_6+n_4n_6-n_4n_5]$ similarly leads to a quadratic temperature dependence. The terms n_6 and $-n_3$, which would lead to a contribution linear in T, partially cancel, and in any case become negligible at sufficiently high temperatures. But even if the cancellation is not complete, the major contribution from 3-phonon difference processes will have a quadratic temperature dependence.

If the density of transitions per unit frequency interval is constant, the absorption will—as for the 2-phonon process—increase with the square of the frequency.

At first one might consider this higher order process as less important than the 2-phonon process described earlier. But the magnitude of the 3-phonon process may not be negligible for the following reason: For 2-phonon processes the momentum conservation allows only "vertical" transitions, whereas 3-phonon processes can occur in a much greater variety and number without violating the momentum conservation. Thus, the conservation rules are less restrictive here and 3-phonon processes may contribute noticeably to the absorption. If the interpretation of our experiments is correct, the 3- and 2-phonon contributions to the absorption can, in fact, be of the same order of magnitude.

IV. DISCUSSION

A. Dependence of the Absorption on Temperature and Frequency

In Sec. III A we have seen that the temperature dependence expected from two-phonon difference processes in the far infrared should become linear in T at high temperatures. This high-temperature limit started at a temperature which corresponds to about the frequency of zone-boundary phonons. As is evident from Figs. 2–7 this is not the case in praxis: We find it necessary to add a contribution quadratic in T in order to account for the experimental observations. In some cases the temperature dependence is almost purely quadratic. This quadratic contribution agrees with our expectations for a 3-phonon difference process as explained in III B.

If two- and three-phonon contributions are both present, the total absorption should approach, at high temperatures,

$$\alpha=AT+BT^2\,,$$

where A and B are constants. This expression has already been used in II for the analysis of the data. The plot of (α/T) should approach a horizontal line for pure two-phonon absorption ($B=0$), and a straight line with slope B which extrapolates to zero for the 3-phonon process along ($A=0$). As an arbitrary example, in Fig. 10 a two- and three-phonon contribution are added such that the 3-phonon absorption α_3 is one-third of the total at room temperature. The total absorption α is normalized to 1 at 300°K. In order to draw the correct temperature dependence below room temperature, assumptions had to be made about the average phonon

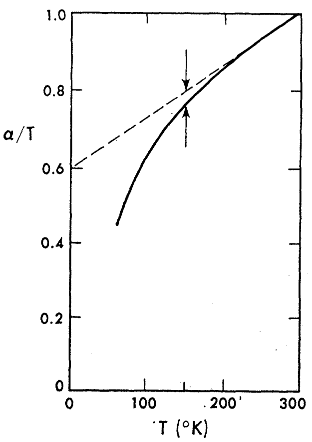

FIG. 10. Theoretical (α/T) curve for sum of 2- and 3-phonon absorption such that $\alpha_3=\alpha/3$ at 300°K. At a temperature of $T\approx(\hbar\omega_1/k)\approx150$°K, the curve deviates by about 5% from the broken line extrapolated from higher temperatures. α_3 is the contribution from 3-phonon processes only.

energies ($\hbar\omega_1$, $\hbar\omega_2$ in III), for which we choose 150°K in Fig. 10. As can be seen the effective average phonon energy corresponds to a temperature at which the (α/T) curve differs from the broken line by about 5%. This is, of course, a very rough estimate but good enough to see whether the phonons involved are located hear the zone boundary, or if they are acoustic phonons of very low momentum. This will be discussed last in this section (IV C).

In Figs. 4–7, the full curves represent our experimental values for (α/T), again normalized to 1.0 at 300°K. The dashed lines show the high temperature limit and give a good impression about the relative strength of the linear and quadratic contributions. For several crystals it is evident that the linear (2-phonon) and quadratic (3-phonon) contributions are of the same order of magnitude. In some cases, however, the dashed lines extrapolate to zero ($A=0$) indicating that the absorption is caused by three-phonon processes only (see for example: KBr at 900 μ, NaI at both 500 and 320 μ).

KI at 500 μ (see Fig. 5) appears to show an exceptional temperature dependence even steeper than T^2 above 250°K. The reason for this behavior is not clear but it may indicate the presence of even higher order processes than the two- and three-phonon processes considered here. This is in line with the fact that KI is the crystal with the lowest Debye temperature which we have studied. Certainly there is no trace of a linear contribution.

The increasing relative importance of the quadratic contribution at the longer wavelengths is a most interesting result. Previously this had only been reported for NaCl at very long wavelengths by Dötsch and Happ,[5] whose data at their longest wavelength of 3 mm are also included in Fig. 7.

Let us now turn to the frequency dependence of the absorption. We will see that beyond a certain "cutoff wavelength" the linear contribution seems to disappear leaving only the quadratic term.

The room-temperature absorption of KBr between 300 μ and 2 mm has been measured by Genzel, Happ, and Weber.[9] Their results are reproduced in Fig. 11, where the extinction coefficient $\kappa=\alpha\lambda/4\pi$ is plotted versus wavelength λ. Also included are our results on KI, KBr, and LiF as well as the data on LiF by Genzel, Klier, and Seger.[14] It is instructive to indicate on the same diagram the wavelength region where the absorption is a purely quadratic function of the temperature and where it contains both a linear and a quadratic contribution. In the pure-quadratic region we have represented the absorption by a single curve, while the simultaneous presence of a linear and quadratic term is shown by a double line. As is evident, the linear contribution is only noticeable for each crystal at wavelengths shorter than a certain wavelength λ_c which we will call here the cutoff wavelength. This cutoff wavelength lies for LiF probably at a wavelength of less than 200 μ, for KI around 350 μ, for KBr at somewhat longer wavelengths, and for NaCl (not shown here), around 2 mm. Since the linear contribution does not appear very suddenly for wavelengths shorter than λ_c, the definition of this cutoff wavelength is only meant to indicate the spectral range in which the linear contribution becomes noticeable. As expected, this onset of the linear contribution leads to a steep frequency dependence of the absorption for KI, KBr, and NaCl in the region of their respective cutoff wavelengths, where the absorption varies with wavelength more rapidly than $(1/\lambda)^2$. A variation as $(1/\lambda)^2$ seems to be representative for wavelengths far from the cutoff region.

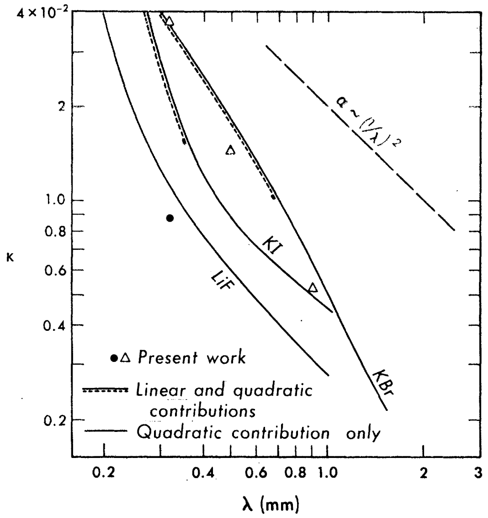

FIG. 11. Extinction versus wavelength at 300°K. (LiF data from Genzel, Klier, and Seger (Ref. 14); KBr data from Genzel, Happ, and Weber (Ref. 6); KI data are from present work.)

It is also possible for the absorption measured at long wavelengths $\lambda>\lambda_c$ to arise from the long-wavelength-tail of transitions of much higher frequency between two states which are lifetime broadened. For a transition between broadened states (linewidth $\Delta\nu$) the absorption at a frequency ν takes the form[15]

$$\alpha=K(T)\frac{\nu^2\Delta\nu}{(\nu-\nu_i)^2+(\Delta\nu)^2},$$

in which $K(T)$ is a constant, which represents the population difference and is proportional to T (see III A); $h\nu_i$ is the separation of the states and $\Delta\nu$ the linewidth, which for the simplest case of broadening by 3-phonon collisions increases linearly with temperature. At very long wavelengths ($\nu\ll\nu_i$) the absorption in the long-wavelength tail of such a transition between two

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[14] L. Genzel and M. Klier, Z. Physik **144**, 25 (1956); G. Seger and L. Genzel, *ibid.* **169**, 66 (1962).

[15] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), p. 343.

broadened phonon states becomes

$$\alpha(\nu \ll \nu_i) = K(T)\nu^2 \Delta\nu / \nu_i^2 .$$

If all the N transition frequencies ν_i are uniformly distributed over a frequency interval $\delta\nu$ around ν_0, there would be consequently $n = N\Delta\nu/\delta\nu$ transitions within the single linewidth $\Delta\nu$. Now we can estimate the relative strength of the absorption measured in the long-wavelength tail of all N transitions, relative to that measured at the frequency ν_0:

$$\frac{\alpha(\nu \ll \nu_0)}{\alpha(\nu_0)} = \frac{N(\nu^2\Delta\nu/\nu_0^2)}{n(\nu_0^2/\Delta\nu)} = \left(\frac{\nu}{\nu_0}\right)^2 \left(\frac{\Delta\nu}{\nu_0}\right) \left(\frac{\delta\nu}{\nu_0}\right) \ll 1 .$$

This ratio is very much smaller then unity because each of the 3 factors is smaller then unity by definition. We conclude therefore that this contribution cannot account for the strong absorption observed at wavelengths longer than the cutoff wavelength λ_c.

Within a region of strong two-phonon absorption ($\lambda \leqq \lambda_c$) the results should be independent of phonon lifetimes, because the integrated absorption of many transitions, which is always measured, should be independent of the lifetime, until the linewidth approaches the transition frequency,[15] i.e., $\omega\tau = 1$. In our experiments the frequency ω is probably still high enough to neglect lifetime effects as can be seen by the following estimate. Phonon broadening has been observed in neutron-scattering experiments.[16] For the case of the acoustic branches in KBr at 400°K the broadening was a few percent. For a branch of 100 cm^{-1} a broadening of 10% would correspond to a lifetime of 3×10^{-12} sec. Lifetime and relaxation effects might become important only for $\omega\tau \leqq 1$ corresponding in this case to a wavelength longer than 6 mm. Experiments on CsI at very low frequency and high temperatures may perhaps show a behavior representative for the case $\omega\tau < 1$.

B. Comparison with the Phonon Dispersion Curve

One might expect a major part of the absorption to arise from transitions involving phonons with frequencies near maxima in the density of states. These points are usually at the zone boundary in the principle symmetry directions.

In Fig. 13 dispersion curves are shown for KBr, NaI, and NaCl. The curves for NaI and KBr represent experimental data, using neutron diffraction, by Woods, Brockhouse, Cowley, and Cochran.[16] The curves for NaCl were drawn according to unpublished calculations by Karo made available to us.

For NaI the transverse and longitudinal acoustic branches are separated by about 20 cm^{-1} (500 μ) at the zone boundary in the [100] and [111] directions, while the other branches are separated more widely.

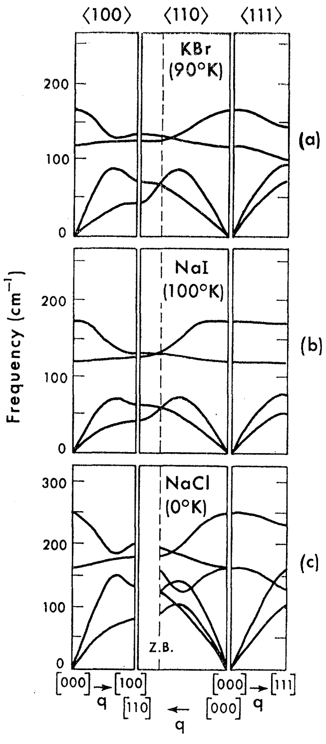

FIG. 12. Phonon dispersion curves for KBr, NaI and NaCl: (a) and (b) Experimental data after Woods *et al.* (Ref. 16). (c) Calculated curves provided by A. M. Karo (private communication).

We studied the absorption in NaI at 500 μ specifically to look for a strong 2-phonon contribution in this salt, for which the dispersion diagram is relatively simple. But at room temperature the absorption is only half as strong as for NaCl, in spite of the lower reststrahl frequency for NaI. More important, there is no trace of a two-phonon contribution, linear in T, as evident from Fig. 6.

There was the additional possibility in NaI of a transition at about 1 mm between the transverse and longitudinal optical branches (see Fig. 12(b)] But again no linear contribution was observable at 900 μ, nor at 320 μ where additional measurements were performed.

When similar experiments were repeated on a crystal of KI the absorption was, at 500 μ, even lower than in NaI. But more important, it is clear from Fig. 5 that again no linear two-phonon component appears at 500 μ. However, at 320 μ a strong linear term has become apparent in the same figure. The dispersion curves calculated by Karo and Hardy for KI show the separation of the branches at the same boundary to be about

	[100]	[111]
ta → la:	21 cm^{-1}	14 cm^{-1}
la → to:	55 cm^{-1}	15 cm^{-1}
ta → to:	77 cm^{-1}	30 cm^{-1}

(t = transverse, l = longitudinal; a = acoustic, o = optic).

Therefore, as in NaI, we expected a strong two-phonon absorption at about 500 μ representing the ta → la [100] transitions. But again, this was not observed. Besides, some absorption from the other ta → la and la → to transitions should also have appeared at 500 μ,

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[16] A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, Phys. Rev. **131**, 1025 (1963).

contrary to the observations. As Fig. 5 shows, the cutoff wavelength rather seems to lie around 350 μ corresponding to the ta → to transition in the [111] direction.

The situation is much the same in KBr where the separations of the branches at the zone boundary are [see Fig. 12(a)]

	[100]	[111]
ta → la:	30 cm^{-1}	20 cm^{-1}
la → to:	54 cm^{-1}	11 cm^{-1}
ta → to:	84 cm^{-1}	31 cm^{-1}

Here the transition involving the la- and to-[111] phonons should be seen around 900 μ, whereas only a quadratic temperature dependence is observed.

From all these observations it seems to be fair to draw the interesting conclusion that absorption by two phonon processes does not occur for transitions between *longitudinal and transverse* phonons. However, when the frequency is close to or above the smallest difference between the *transverse acoustic and transverse optic* branches the absorption shows a strong two-phonon contribution. For NaCl and KCl these branches are very close to the [111] direction: of the order of 10 cm^{-1} corresponding to $\lambda_c = 1$ mm. The analogous separations in the [111] directions for the other salts are

KI	29.7 cm^{-1}	347 μ
KBr	30.8 cm^{-1}	325 μ
NaI	64.6 cm^{-1}	155 μ

These separations probably determine the spectral range where the "cutoff" occurs. The zone edge in the [111] direction may not, of course, be the point where the transverse acoustic and transverse optical branches are closest. See, for example, Fig. 12(c) where the transverse branches split in the [110] direction and one acoustic and one optical branch come quite close together.

The possibility of similar difference processes involving two longitudinal phonons may or may not exist. Since this separation is usually large compared to the wavelengths we have used, our experiments cannot decide the matter.

Generalizing these observations, it appears that *two-phonon difference processes can only occur between branches of the same polarization.*

C. The Relative Importance of Low-Wave-Vector versus Zone-Boundary Phonons

From the plots of (α/T) versus T, it is possible (see Fig. 10) to make some estimate of the average frequency for the two-phonon processes. For example, for NaCl at 320, 500, and 1020 μ, the average phonon frequency ω_1 can be derived from Fig. 7 to be somewhere around 160°K (111 cm^{-1}). This agrees with typical frequencies at the zone boundary as seen in Fig. 12(c). If the absorption were dominated by vertical transitions involving low-wave-vector acoustic phonons, the average phonon frequency ω_1 would be much lower and should decrease with the frequency of the incident radiation. For example, from the dispersion curves in Fig. 13(c), or from ultrasonic velocity data, one can estimate the average phonon frequencies for transitions between two acoustical branches of different polarization. For NaCl and an incident radiation of 20 cm^{-1} (500 μ) the average phonon frequency turns out to be about 30 cm^{-1}, corresponding to about 45°K. Only below this temperature should the absorption deviate noticeably from a linear temperature dependence. But, as pointed out, the deviation from linearity occurs in NaCl at 160°K (by 5%) which is also representative for the other crystals. Thus it is evident that transitions involving low-wave-vector acoustic phonons do not contribute significantly do the absorption.

Considering the low density of states for acoustic phonons, this may at first not seem too surprising. However, according to Eq. (5) the absorption varies with ω_1, ω_2 as

$$\alpha \cong \sum \frac{(n_1 - n_2)}{\omega_1 \omega_2};$$

and since at high temperatures $(n_1 - n_2) \cong 1/\omega_1\omega_2$ (see part III A) this becomes

$$\alpha \cong \Omega / (\omega_1 \omega_2)^2,$$

where Ω is a measure for the density of states. Because of the factor $(\omega_1\omega_2)^2$ in the denominator, which compensates the low density of states for acoustic phonons, we conclude that acoustic phonons might be expected to contribute to the far-infrared absorption.

The failure to observe such low wave-vector acoustic transitions rather seems to be a consequence again of the "selection rule" mentioned above, which rules out transitions between branches of different polarization, i.e., between any acoustic branches.

We have been informed that group-theoretical selection rules for 2-phonon processes have been worked out for rocksalt-type crystals by Burstein, Johnson, and London.[17]

ACKNOWLEDGMENTS

We are indebted to Dr. Karo for making available to us his calculations on phonon dispersion curves prior to publication. Discussions with Dr. Ferrell, Dr. Hopfield and Dr. Worlock were greatly appreciated. L. Palmer gave us much useful advice.

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[17] E. Burstein, F. A. Johnson, and R. London (to be published).