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Temperature Dependence of Multiphonon Absorption*

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The temperature dependence of multiphonon absorption in NaF, NaCl, and KCl was studied from room temperature to near the melting point at a wavelength of 10.6 μm. A large discrepancy was noted between the experimental results and those predicted using the usual expressions based upon temperature-dependent Bose-Einstein population factors and temperature-independent transition matrix elements.

In this Letter, experimental measurements of the temperature dependence of the multiphonon lattice absorption in NaF, NaCl, and KCl are presented, which differ markedly from those expected by application of the usual simple expressions based upon consideration of phonons as bosons. This suggests that there are some inadequacies in the approach which have not been evident in previous measurements. In earlier work,[1,2] the simple expressions based upon Bose-Einstein population factors have appeared to be satisfactory to explain the temperature dependence of multiphonon absorption. However, practically all of the previous investigations in this area have involved lower-order processes at lower temperatures. The present work is primarily concerned with higher-order processes at higher temperatures in which the temperature dependence is expected to be much greater.

The usual expressions for the temperature dependence of multiphonon processes can be written in terms of the energies of the various phonons participating in the process. For higher-order processes this can be quite complicated, but Sparks and Sham[3] pointed out that a T^{n-1} law would be expected to hold (if some average phonon frequency is assumed) in the high-temperature limit, where n is the number of phonons participating in the process. Similar results were obtained by Rosenstock,[4] who employed a Debye spectrum for the crystal, and by Hardy and Agrawal,[5] using an Einstein oscillator-type model. Under this latter approach,[5] the contribution to the multiphonon absorption coefficient β at high temperatures will be dominated by the contribution

$$(\bar{n}+1)^n - (\bar{n})^n, \tag{1}$$

where $\bar{n}$ is the usual Bose-Einstein population factor

$$\bar{n} = [\exp(\hbar\bar{\omega}/kT) - 1]^{-1}, \tag{2}$$

and the transition matrix elements are assumed to be essentially temperature independent. After rearrangement, the coefficient β can be expressed as a function of temperature giving

$$\beta \propto \frac{1 - \exp(-n\hbar\bar{\omega}/kT)}{[1 - \exp(-n\hbar\bar{\omega}/kT)]^n}. \tag{3}$$

In the limit where $kT \gg \hbar\bar{\omega}$, it can be seen that the temperature dependence of β will be given by

$$\beta \propto n(kT/\hbar\bar{\omega})^{n-1} \tag{4}$$

so that β is proportional to T^{n-1}. Consequently, if measurements are carried out at a frequency high compared to a single-phonon frequency, then the resulting multiphonon absorption would be expected to exhibit a very large temperature dependence at high temperatures. Any failure to exhibit a temperature dependence predicted by Eq. (4) could most likely be attributed to the failure of the assumption that the transition matrix element is temperature independent.

In order to test the applicability of Eq. (4), careful measurements of the absorption coefficient at 10.6 μm from 300 K to within 50 K of the melting point were obtained in single-crystal NaF, NaCl, and KCl. In the cases of NaCl and KCl, the absorption coefficients were small and were measured by calorimetric methods using a CO_2 laser source.[6] In the case of NaF, simple transmission measurements with a laser and power meter were adequate. All measurements were carried out inside a stabilized oven on samples whose surfaces were first mechanically, then chemically, polished.

The experimental results for these compounds are shown in Figs. 1, 2, and 3, along with the temperature dependence predicted by Eq. (3) in which the parameters were selected in a way which will be discussed shortly. It can be seen that in the cases of NaF and NaCl, the experimentally determined temperature dependence differs markedly from that given by Eq. (3). In the case of KCl, the absorption coefficient and its temperature dependence have been observed to vary markedly from sample to sample. In most cases, the temperature dependence below 600 K is essentially independent of temperature or even decreases with temperature. In the high-temperature limit for one of our purer samples (obtained from Hughes Research Laboratories), the temperature dependence does increase more sharply at high temperatures, as would be expected for intrinsic behavior.

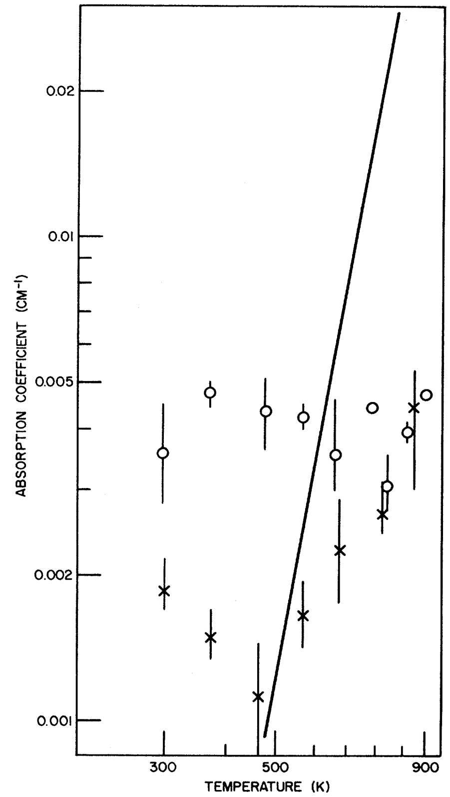

FIG. 1. Temperature dependence of absorption coefficient for KCl. Open circles, data from Harshaw KCl; crosses, data from KCl sample obtained from Hughes Research Laboratories, Malibu; solid line, temperature dependence calculated from Eq. (3).

These results might be interpreted in the following way. In the cases of NaF and NaCl, the absorption is expected to be largely intrinsic, based upon a semiempirical extrapolation of the frequency dependence of the absorption.[7] In the case of KCl, the observed absorption coefficient in all known samples is well above the extrapolated absorption coefficient[7] of about 8×10^{-5} cm^{-1} at 10.6 μm and thus is probably largely extrinsic in origin at room temperature. These extrinsic contributions could arise from impurities, surfaces, or some other imperfections. It has been predicted that the temperature dependence of the absorption associated with impurities will be less than that for the intrinsic case.[4,5] This appears to be the case for KCl, although there are some quantitative discrepancies. In the case of the Hughes KCl crystal where the absorption decreases with temperature in the low-temperature re-

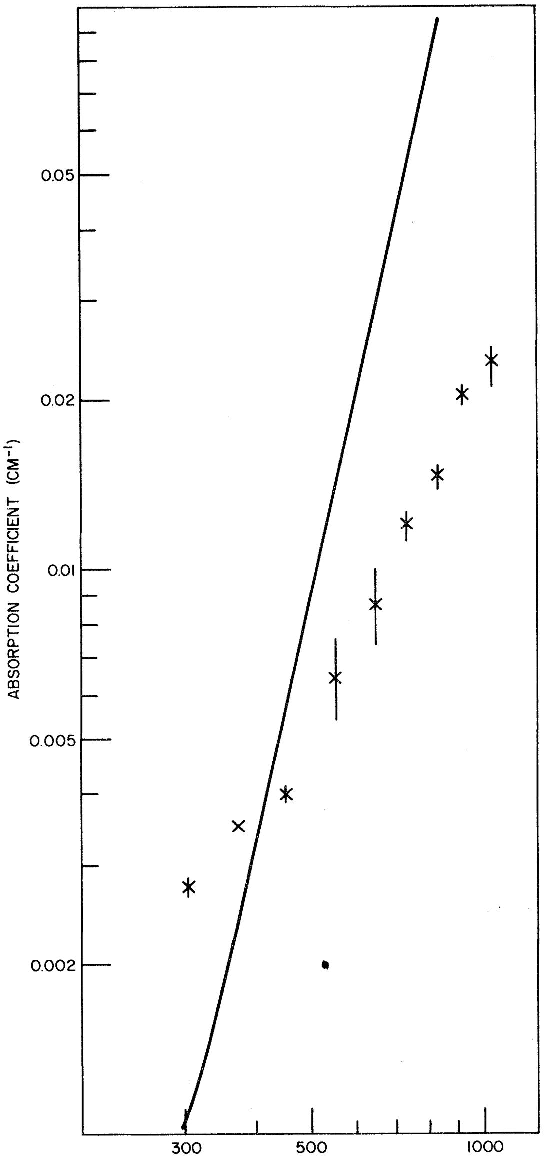

FIG. 2. Temperature dependence of absorption coefficient for NaCl. Solid line, temperature dependence calculated from Eq. (3).

gion, it is believed that this is associated with some absorbing imperfection centers which are being annealed out. In the high-temperature region above 500 K where the absorption increased markedly with temperature, it is not clear if this can be attributed to extrinsic or intrinsic processes.

It can be seen from Figs. 1, 2, and 3 that a plot of the logarithm of the absorption coefficient as a function of the logarithm of the temperature yields nearly a straight line, implying a power-law dependence of the form given by Eq. (4). The experimentally determined exponential factors are listed in Table I along with the values expected using a mean single-phonon frequency $\bar{\omega}$. For simplicity, $\bar{\omega}$ was selected as the frequency closest to the transverse optic mode, so that $n\bar{\omega} = 943$ cm^{-1} (10.6 μm), with n integral. The values are shown in Table I. Even though the way in which $\bar{\omega}$ and n have been chosen here is slightly different from that used by others,[3-5] this difference will not lead to any significant changes. In the case of NaF, the theoretical curves were adjusted in scale to fit the experimental value at room temperature. Since the absorption levels are suf-

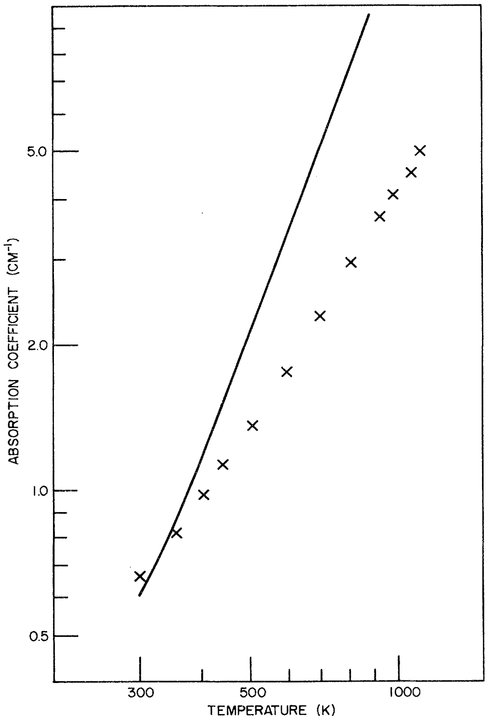

FIG. 3. Temperature dependence of absorption coefficient for NaF. Solid line, temperature dependence calculated from Eq. (3).

TABLE I. Comparison of theoretical and experimental exponential temperature factors for multiphonon absorption at 10.6 μm.

Crystal	$\bar{\omega}$ (cm^{-1})	n Theoretical	n Experimental
KCl	134.7	7	2.8[a]
NaCl	157.2	6	3.3
NaF	235.7	4	2.6

[a] Possibly limited by extrinsic processes.

ficiently high to be ascribed to intrinsic behavior, this procedure is justified. For KCl and NaCl, the observed room-temperature values are believed to be higher than intrinsic. Here, the curves were normalized to a room-temperature value predicted by extrapolating measurements of the absorption coefficients in the intrinsic region to 10.6 μm. It has been noted that the intrinsic absorption is exponential on the high-frequency side of the *Reststrahl* band for many materials.[7] While an extrapolation to higher frequencies cannot be rigorously justified, it appears reasonable, and a dependence which is nearly exponential can be deduced from theoretical considerations.[3] As a result, the scale for our theoretical curves is not arbitrarily chosen.

The large discrepancy between the experiment and predictions from the Bose-Einstein population factors seems quite remarkable. We are not aware of such discrepancies being reported elsewhere, although a similar analysis to that presented here has not been given. Some studies of the multiphonon absorption of alkali halides in the high-temperature region have been reported by Barker.[8] While a comparison of the type given here was not made, inspection of his curves suggests that the temperature dependence could not be satisfied with a simple expression of the form in Eq. (3).

While the agreement between the experiment and theory reported here might be improved somewhat by consideration of lower-order processes involving only high-energy phonons, good agreement would still not be obtained. This suggests that some other explanation be sought. The theory of higher-order multiphonon absorption has been addressed by a number of investigators.[3-5,9] These treatments have not been carried sufficiently far to yield temperature-dependence predictions adequate to explain the present experimental results. As a direct result of this discrepancy, the theoretical treatments have very recently been extended by Sparks and Sham,[10] Maradudin and Mills,[11] and McGill[12] and can now provide good agreement with experiment. In the quantum-mechanical treatment of Sparks and Sham[10] a perturbation calculation, employing a Born-Meyer potential, is used to calculate the n-phonon absorption coefficient. Phonon dispersion is included through the use of the central-limit theorem. McGill[12] makes use of a quantum-mechanical molecular (Einstein) model with a Morse potential, while Maradudin and Mills[11] treat a similar model classically. All of the investigators have been able to fit the data reasonably well and thus are able to show that, in the high-temperature limit, the absorption decreases at a rate less than that given by the T^{n-1} law.

The analysis of Maradudin and Mills indicates that the T^{n-1} law holds only when the multiphonon transitions lie in the quasiharmonic region. Since alkali halides are known to have a relatively large thermal-expansion coefficient, a large temperature coefficient of the lattice frequencies is expected. One implication of this is that the anharmonic nature of the potential must be treated more carefully, especially at high temperatures. In the Maradudin-Mills approach this can be accounted for in a simple way, and their analysis also suggests that a temperature dependence of both the lattice frequencies and the linewidth are important. On the other hand, in the treatments of McGill and of Sparks and Sham, only the temperature dependence of the lattice frequencies is included and the linewidth has been assumed to be independent of temperature. As a result, it is not completely settled as to what the dominant contributions to the high-temperature multiphonon absorption in alkali halides can be attributed.

In conclusion, it is believed that these studies of the multiphonon absorption have revealed a serious shortcoming in the usual approach employed to calculate the temperature dependence of multiphonon absorption. In addition, they provide a way of distinguishing intrinsic and extrinsic absorption in highly transparent materials, as well as providing a tool for studying imperfection-induced absorption.

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Temperature Dependence of Multiphonon Infrared Absorption*

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Measurements of Harrington and Hass and of Barker indicate that the temperature dependence of the infrared absorption coefficient β in the n-phonon region is considerably weaker than $\beta \sim T^{n-1}$, which had been predicted for the high-temperature limit of multiphonon absorption. This discrepancy is resolved by taking into account the temperature dependence of the phonon frequencies and the lattice constant. The agreement between the experimental and theoretical results with no adjustable parameters is good. A new evaluation of the multiphonon sums yields $\beta \sim \exp(-\omega\tau)$ directly, rather than as a sum on n.

The nearly exponential frequency dependence[1] of infrared absorption in the region of low absorption has been explained recently by a simple multiphonon-absorption theory[2-5] and by independent-molecule models.[6] The frequency and temperature dependence of the optical absorption coefficient β are of fundamental interest, and both should be useful in identifying intrinsic absorption and in distinguishing between intrinsic and extrinsic absorption.[7,3,4] Harrington and Hass[8] have shown that the temperature dependence of β is considerably weaker than the expected dependence[2-4]

$$\beta \sim [1-\exp(-\omega/\omega_T)][1-\exp(-\omega/n\omega_T)]^{-n} \cong T^{n-1}$$

for n-phonon absorption. The approximate equality is the high-temperature limit, ω is the laser frequency, and $\omega_T \equiv k_B T/\hbar$. Re-examination of earlier data[9] reveals similar discrepancies, which constitute the most serious problem in the recent developments in the theory of multiphonon absorption.

These discrepancies are explained by including the temperature dependence of the phonon frequencies ω_Q and lattice constant in our previous theory. A simple estimate indicated previously that the resulting deviations would be quite large.[10] The previous expression[2-4,10] for β is

$$\beta = f(\omega)\omega^{-4} \sum_{n=2}^{\infty} (\Lambda_n{}^2 v^n/n!) \sum_{Q_1} \cdots \sum_{Q_n} \delta(\omega - \sum_{j=1}^{n} \omega_{Q_j}) \prod_{l=1}^{n} \sigma_{Q_l}, \tag{1}$$

where $f(\omega) = \text{const}[1-\exp(-\omega/\omega_T)]$, $v = \hbar/2\rho_K{}^2 m$, $\sigma_{Q_l} = W_{Q_l}(n_{Q_l}+1)/N\omega_{Q_l}$, W_{Q_l} is of order unity for large ω_{Q_l} and is very small for small ω_{Q_l}, n_{Q_l} are phonon occupation numbers, the Q's denote wave vectors and branches, m is the reduced mass, ρ_K is the Born-Meyer repulsive-potential parameter (units cm), $2N$ is the number of ions in the crystal, and the higher-order terms in the perturbation expansion give rise to the vertex-correction factors[4,10] $\Lambda_n = 1 + A_n\xi + O(\xi^2)$, where $A_4 = 1.94$, $A_5 = 3.92$, $A_6 = 7.15$, and $\xi = 9B_0 a_0/$