Temperature Dependence of the Absorption Coefficient of Alkali Halides in the Multiphonon Regime*

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(Received 27 April 1973)

The theory of infrared absorption by an array of independent, anharmonic oscillators is discussed. When the oscillator potential is the Morse potential, the theory provides an excellent description of the temperature dependence of the absorption coefficient at 10.6 μm in NaCl and NaF reported by Harrington and Hass.

There has recently been interest in the mechanisms for absorption of infrared radiation by insulating crystals at frequencies high compared with the *Reststrahl* frequency. In the vicinity of the CO_2-laser line at 10.6 μm, and in alkali-halide crystals where the electronic band gap is very large, the principal contribution to the absorption coefficient from the bulk of the crystal comes from multiphonon processes in which five, six, or perhaps a larger number of phonons are created in the absorption process.

Quite recently, Deutsch[1] has completed a detailed experimental study of the frequency dependence of the absorption coefficient in several alkali-halide crystals at room temperature. Several groups have addressed the theory of the absorption process by models that differ significantly in physical content.[1-3] All of the theories which have been applied to the analysis of the data presume that anharmonic effects on the lattice motion may be treated by perturbation methods. One then predicts that for temperatures T large compared to the Debye temperature θ_D, the contribution to the absorption coefficient from processes which involve n phonons should vary with temperature like T^{n-1}.

A recent experimental study of the temperature dependence of the absorption coefficient α at 10.6 μm in several alkali halides has been reported by Harrington and Hass.[4] These authors find that α varies with T more slowly than T^{n-1} in the crystals examined by them. The purpose of this paper is to apply the simple theoretical model developed in our previous paper[3] to an analysis of these data.

In our previous paper, we replaced the crystal by a set of N classical, noninteracting anharmonic oscillators, where N is the number of unit cells in the crystal. Each oscillator has a reduced mass m, and a transverse effective charge q. If the crystal is illuminated by radiation with the electric field $E(t) = E_0 \cos\omega t$, then the time- and ensemble-averaged rate at which energy is absorbed by a single oscillator is given by[3]

$$\left\langle\!\!\left\langle \frac{d\mathcal{E}}{dt} \right\rangle\!\!\right\rangle = \frac{\omega\beta q^2 E_0^2}{4m^2 Z} \sum_{n=1}^{\infty} \frac{1}{n} \int_0^{\infty} dE\, e^{-\beta E} \mathcal{O}_n^2(E)\delta(\omega - n\omega(E)), \tag{1}$$

where $\beta = 1/k_B T$, Z is the partition function for a single oscillator, the period $T(E)$ of the bound orbit of energy E is written $T(E) = 2\pi/\omega(E)$, and $\mathcal{O}_n(E)$ is a measure of the amplitude of the nth harmonic in the orbit of energy E. If $p_E(t)$ gives the time dependence of the momentum in the orbit of energy E, with the origin of time chosen so that the particle is at a classical turning point at $t = 0$, then

$$\mathcal{O}_n(E) = [2/T(E)] \int_0^{T(E)} dt\, p_E(t) \sin[n\omega(E)t]. \tag{2}$$

The virtue of the model is that exact expressions for α may be obtained with it, even when the oscillator motion is very anharmonic. For the Morse potential $V(x) = D\{1 - \exp[a(x - x_0)]\}^2$ we previously obtained exact expressions for $\omega(E)$ and $\mathcal{O}_n(E)$, although we found α only when $k_B T$ was small enough for the oscillator motion to be treated as nearly harmonic. In this paper, we work with the full form of α, without this last assumption. In our earlier paper, we found

$$\omega(E) = \omega_0(1 - E/D)^{1/2}, \tag{3}$$

$$\mathcal{O}_n(E) = \frac{2\pi(2mE)^{1/2}}{\omega_0}\left(\frac{D}{E}\right)^{(n+1)/2}\left[1 - \frac{\omega(E)}{\omega_0}\right]^n, \tag{4}$$

where $\omega_0 = a(2D/m)^{1/2}$ is the frequency of the oscillatory motion, in the harmonic approximation. Equations (3) and (4) may be inserted into Eq. (1), and the integration carried out. We make one simplification in the exact result. For $k_B T \ll D$, a limit that applies to our discussions here, the partition function is well approximated by the result $Z = 2\pi k_B T/\omega_0$ obtained from the harmonic approximation.[5] In the results that follow, we use this form for Z. Then if we let $\xi = \omega/\omega_0$, and n_m is the first integer larger than ξ, we find

$$\left\langle\!\!\left\langle \frac{d\mathscr{E}}{dt} \right\rangle\!\!\right\rangle = \frac{2\pi q^2 E_0^2}{m\omega_0}\left(\frac{D}{k_B T}\right)^2 \xi^2 \sum_{n=n_m}^{\infty} \left(\frac{n-\xi}{n+\xi}\right)^n \exp\left[-\frac{D}{k_B T}\left(1-\frac{\xi^2}{n^2}\right)\right] n^{-3}. \tag{5}$$

At fixed frequency, the temperature dependence of the absorption coefficient is controlled by the single parameter $D/k_B T$, which for the case of NaCl may be obtained from our earlier work.[3] In the limit $n k_B T \ll D$, the nth term in Eq. (5) contributes to the absorption coefficient a term well approximated by the form

$$\left\langle\!\!\left\langle \frac{d\mathscr{E}}{dt} \right\rangle\!\!\right\rangle_n \cong \frac{\pi q^2 E_0^2}{4m}n!\left(\frac{k_B T}{4D}\right)^{n-1}\delta(\omega - n\omega_0). \tag{6}$$

This expression is identical to that produced by the quasiharmonic approximation utilized earlier by us.[3]

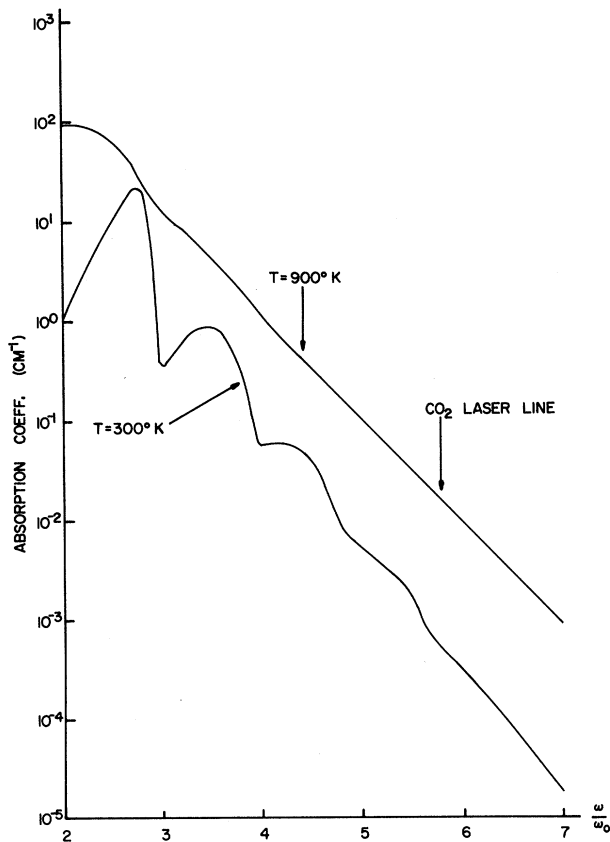In Fig. 1, we present a calculation of the fre-

FIG. 1. Frequency dependence of the absorption coefficient for a Morse-potential oscillator at $T = 300$ and 900°K, with a D chosen for NaCl.

quency dependence of the absorption coefficient for the model for $T = 300°$K and $T = 900°$K, from Eq. (5). We have used the value of D obtained for NaCl from our earlier work, and have adjusted the absolute value of α to fit the 10.6-μm data of Harrington and Hass at 900°K.

Several features of these results deserve comment. For $T = 300°$K, the $n = 3$ term in Eq. (5) produces a very sharp peak centered a bit below $\xi = 3$. This peak is quite narrow and well defined, as one would expect in the quasiharmonic approximation. For ξ near 5 or 6, the effect of anharmonicity is severe enough that α varies smoothly with frequency, displaying only gentle shoulders as a reminder of the sharp structure present in the quasiharmonic approximation. By the time $T = 900°$K, the theory produces a very smooth dependence of α with frequency.

These calculations suggest that for large values of ω/ω_0, even at room temperature, the lattice motion cannot be regarded as nearly harmonic, so the absorption coefficient cannot be calculated by perturbation-theoretic methods which treat the anharmonic terms in the crystal Hamiltonian as small. This is also clear from the data of Harrington and Hass, which we shall see are well fitted by our model, since the data show very large departures from the T^{n-1} behavior cited earlier.

It must be emphasized that at fixed T, the relative importance of the anharmonicity increases as ω/ω_0 increases. If we examine the absorption coefficient for the model near the *Reststrahl* region [the *Reststrahl* absorption is described by the term $n = 1$ in Eq. (5)], then the parameters we employ produce rather modest anharmonic effects. For example, at temperature T, the *Reststrahl* peak occurs very close to $\tilde{\omega}_0 = \omega_0(1 - k_B T/2D)$, where ω_0 is the *Reststrahl* frequency at $T = 0$. For our parameters, at room temperature $k_B T/2D \cong 0.03$ for NaCl. The half-width at half-maximum is also close to $k_B T/2D$ in magnitude, and increases linearly with T. As the parameter ω/ω_0 increases, each successive peak shifts to low-
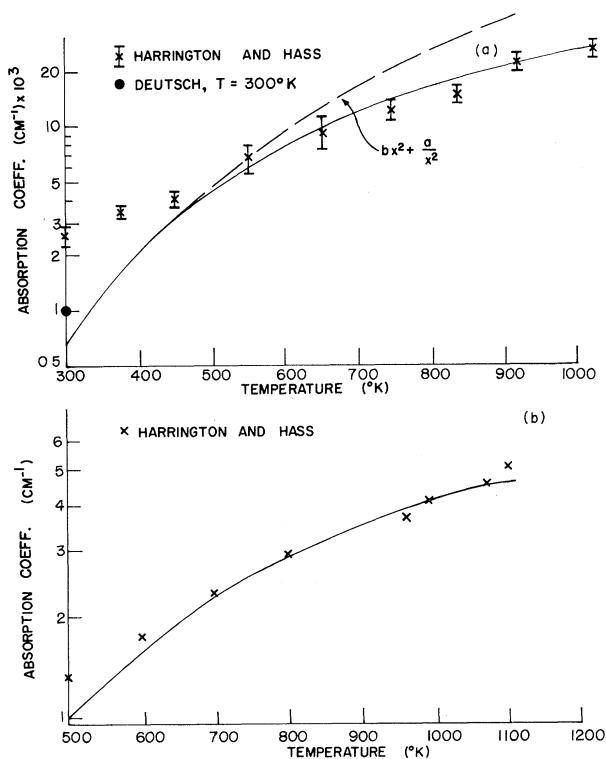
FIG. 2. Temperature dependence of the absorption coefficient at 10.6 μm in (a) NaCl and (b) NaF. The solid curve is calculated from the Morse potential and the dashed curve from $V(x) = bx^2 + a/x^2$.

er frequency by a fractional amount that increases with increasing order, and the width of each feature described by the terms in Eq. (5) increases rapidly enough so that by the time $\xi = 6$, the absorption coefficient varies smoothly with frequency at room temperature.

In Fig. 2(a), we compare the temperature dependence of the absorption coefficient at 10.6 μm obtained from our calculations with the data of Harrington and Hass. The theory has been fitted to the data at 900°K and gives a very good account of the observed temperature dependence for all but the lowest temperature. In his previous work, Deutsch has reported a value of 0.001 cm^{-1} for the absorption coefficient at room temperature, while the value reported by Harrington and Hass is larger by a factor of 2.7. Thus, near room temperature, the absorption coefficient measured by Harrington and Hass presumably contains an extrinsic contribution which is dominated by the intrinsic contribution at higher temperatures. If we accept Deutsch's value as the correct one at room temperature [see the closed circle in Fig. 2(a)], then we may fit α to within a factor of 2

over the entire temperature range.

Our model also predicts the absolute magnitude of the absorption coefficient. The rate at which energy is absorbed from the field is found by multiplying Eq. (5) by the number of molecules N (equal to the number of unit cells) in the crystal. Then upon dividing by the time-averaged energy $V\epsilon_0 E_0^2/8\pi$ stored in the field, where ϵ_0 is the high-frequency dielectric constant, and dividing by the propagation velocity $c/\epsilon_0^{1/2}$, one obtains the inverse of the length d required for the energy density in the beam to decay to $1/e$ of its initial value. This quantity is the absorption coefficient α measured in the experiments. The magnitude of α may be estimated in the multiphonon regime from dielectric-constant data[6] once D is known, since $\epsilon_s - \epsilon_0 = 4\pi n q^2/m$ for ionic crystals. For NaCl, the theory predicts that at $T = 900$°K the absorption length should be 0.011 cm^{-1} at 10.6 μm, while the data show it to be 0.020 cm^{-1}. Our model thus gives an absolute value for α in good accord with the data.

In Fig. 2(b), we compare the temperature dependence predicted for the absorption coefficient at 10.6 μm with the data on NaF. Again we obtain an excellent fit for 500°K $< T <$ 1200°K. The theory does poorly for $T <$ 500°K, presumably because $\theta_D \approx 490$°K in NaF, and our classical model is inapplicable for $T \lesssim \theta_D$. In Fig. 2(b), we have chosen $D_{\text{NaF}} = D_{\text{NaCl}}$, and adjusted the magnitude of the absorption length to fit the data at 700°K. For NaF, $\xi \cong 3.96$ at 10.6 μm. The value selected for D predicts the coefficient of linear thermal expansion for the crystal to be 38×10^{-6}°K^{-1} when $T > \theta_D$, if we use our earlier procedure to make this estimate.[3] This value is in excellent accord with the measured value of the thermal-expansion coefficient.[7] From the dielectric-constant data, the theory predicts the absorption length to be 1.2 cm^{-1} at 900°K, while the measured value is 3.4 cm^{-1}. Thus, while the absolute value for α in NaF agrees less well with the data than in the case of NaCl, the theory gives reasonable semiquantitative agreement.

One can inquire about sensitivity of these results to the details of the potential. To test this, the dashed curve in Fig. 2(a) gives the dependence on T for α at $6\omega_0$ for the potential $bx^2 + a/x^2$ examined previously,[3] with the fit to the room-temperature data carried out as in our earlier paper. This potential also provides a reasonable fit to the data, so the detailed form of the potential does not seem to be critical.

Thus our model gives a good account of the

dependence of α on T in alkali halides through the use of only a single parameter whose value may be checked through use of data on the thermal expansion coefficient. Quite recently, Sparks and Sham[8] have extended their earlier work[2] to account for the variation of α with T. Their starting Hamiltonian is more complete than ours since it includes phonon dispersion, but they calculate α by a perturbation method which introduces higher-order anharmonic effects phenomenologically only through a temperature dependence of the phonon frequencies. The two theories agree in the one important regard that in the multiphonon regime large deviations from the T^{n-1} law come from large anharmonic corrections to the perturbation-theory result for α.

We are indebted to Dr. J. A. Harrington for sending us his data in advance of publication, and for useful discussions. We are also grateful to Dr. M. Sparks for many useful conversations.

[1]T. F. Deutsch, to be published. See also F. A. Horrigan and T. F. Deutsch, Raytheon Corp., Waltham, Mass., Quarterly Technical Report No. 2, April 1972 (unpublished).

[2]M. Sparks and L. J. Sham, Solid State Commun. 11, 1451 (1972), and to be published; T. C. McGill, R. W. Hellwarth, M. Mangir, and H. V. Winston, to be published; B. Bendow, S. C. Ying, and S. P. Yukon, to be published.

[3]D. L. Mills and A. A. Maradudin, Phys. Rev. B 8, 1617 (1973).

[4]J. A. Harrington and M. Hass, second preceding Letter [Phys. Rev. Lett. 31, 710 (1973)].

[5]For $k_B T \ll D$, one has the asymptotic form $Z = 2\pi k_B T / \omega_0(1 + k_B T/2D + \cdots)$, where $k_B T/2D < 0.1$ for values of T needed here.

[6]See C. Kittel, Introduction to Solid State Physics (Wiley, New York, 1971), 4th ed., p. 190.

[7]American Institute of Physics Handbook, edited by E. Gray (McGraw Hill, New York, 1972), p. 4-139.

[8]M. Sparks and L. J. Sham, preceding Letter [Phys. Rev. Lett. 31, 714 (1973)].

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Observation of Nuclear Structure Dependence of the Phase of the (d, d') Form Factor*

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Interference between Coulomb and nuclear excitations for inelastic deuteron scattering has been observed for a number of nuclei. Most data are in qualitative, although not quantitative, agreement with collective-model distorted-wave Born-approximation predictions of constructive Coulomb-nuclear interference; excitation functions for the first 2^+ states of $N = 82$ nuclei, however, show destructive interference not predicted by the collective model.

There has recently been considerable interest[1-13] in the study of interference between Coulomb and nuclear processes for inelastic scattering. The most striking result of these studies has been the remarkable success of the collective model[14] in the distorted-wave Born-approximation (DWBA) description of the data; Coulomb-nuclear interference for α particles,[1-4] ^{3}He,[5-8] and more recently for heavy ions[10-12] is well described provided that an adequate number of partial waves is included.

In order to examine the validity of the collective model for deuterons, excitation functions at back angles have been measured for inelastic deuteron scattering from ^{54,56}Fe, ^{60}Ni, ^{114}Cd, ^{138}Ba, ^{144,150,152}Sm, and ^{192}Os. Data were obtained at back angles so that the maximum Coulomb-nuclear interference will occur near the middle of the energy range of the FN tandem accelerator. Scattered deuterons were observed using a position-sensitive proportional counter[15] on the image surface of an Enge split-pole spectrograph. Results for low-lying 2^+ and 3^- states of ^{138}Ba and ^{144,150}Sm are presented here; the other results will be published elsewhere.

Optical-model parameters used in the analysis