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Infrared absorption due to multiphonon processes in the transparent regime of solids*

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We have considered the problem of residual absorption in the transparent regime of a solid. In particular, the frequency dependence of absorption coefficient due to higher-order multiphonon processes in alkali halides has been treated. Joint phonon density of states up to sixth-order processes have been obtained using a breathing-shell model of lattice dynamics. Calculated values of absorption coefficient of NaCl and KCl agree with the observation of exponential frequency dependence in the transparent regime.

I. INTRODUCTION

The phenomenon of infrared absorption in solids has attracted renewed interest since the advent of high-power infrared lasers such as the CO_2 laser. Materials suitable for optical components in such devices, particularly as windows, are the immediate objects of interest. Materials with small percentage absorption are suitable for low-power devices. For high-power lasers it is just not enough to have small percentage absorption, instead it is the total-power absorption which should be small. For large total-power absorption, components of such devices will experience excessive heating with possible deterioration of their performance. The absorption processes that limit the transparency of a solid are either due to lattice vibrations, as in ionic solids, or due to electronic processes. For most materials a sufficiently wide spectral window exists between these two limits, where the material is transparent. However, this transparent regime displays residual absorption. This absorption may be either due to multiphonon processes or due to various defects and impurities in the material. Because of the anharmonic nature of the crystal potential, the incident photon may interact with more than one phonon giving rise to the multiphonon absorption. This process is operative both for ionic and homopolar solids, even though there is no intrinsic one-phonon absorption in the latter case.

To continue with the example of a CO_2 laser which primarily emits in the region of 10.6 μm (943 cm^{-1}), alkali halide crystals seem to be reasonably suitable as window materials. The residual absorption in this transparent regime for the alkali halides is caused mainly by impurity effects and multiphonon processes. Impurity-induced absorption has been investigated in detail by several workers[1] and will not be treated here. Multiphonon processes have been studied in relatively simple solids like inert-gas solids,[2] alkali halides,[3] diamond,[4] etc. In these investigations the main emphasis has been on the study of lifetime and self-energy shifts of the lattice modes. Also the treatments have generally been restricted to two- and three-phonon processes. The two- and three-phonon processes usually produce a structure in the absorption, particularly in the high-frequency side of the one-phonon absorption band (reststrahlen region) of ionic solids,[5] and the absorption coefficient is still so substantial that the crystal can hardly be considered transparent.

An operational definition of the range of transparency may be the frequency region in which the absorption coefficient is roughly between 10^1 to 10^{-4} cm^{-1}. This is the region in which approximately four- to eight-phonon processes are operative. For example, the frequency of the photon emitted by a CO_2 laser (943 cm^{-1}) is about four to eight times the long-wavelength longitudinal-optic phonon frequency (the frequency maximum of the one-phonon density of states) of most of the alkali halides,[6] making them suitable candidates for windows for this particular laser. In this paper we consider the problem of absorption due to higher-order multiphonon processes in alkali halides.

Recently infrared absorption in ionic solids has been measured by several workers.[7,8] It has been observed that the absorption coefficient in the transparent regime varies exponentially with frequency. Several attempts have been made to explain this exponential behavior.[9,10] Our treatment differs from these in that we start from the definition of the absorption coefficient and relate it to higher-order phonon density of states through first-principles calculations.

In what follows, we present a treatment based on a phenomenological approach to understand this exponential dependence of absorption coefficient on frequency. In Sec. II we establish a relation connecting the absorption coefficient with the higher-order-phonon density-of-states functions. In Sec. III a method is presented to calculate these density-of-states functions. To do this, we take into account only the summation processes, i.e., the processes in which all phonons participating in the absorption process are created. Processes in which some phonons are created and some phonons are annihilated in the interaction are not considered. Section IV deals with the calculation of the oscillator strengths for different processes. Finally, the results of the calculations of the absorption coefficient for NaCl and KCl are presented along with the experimental results in Sec. V.

II. ABSORPTION COEFFICIENT

In ionic crystals, the long-wavelength transverse-optic-phonon (TO) mode has a finite polarization associated with it, i.e., when the dipole moment due to the displacement of all particles in the crystal is added together, it yields a finite value. For all the other modes, such a sum vanishes. Consequently, only the TO mode interacts with the infrared photon of suitable frequency in these crystals giving rise to the reststrahlen phenomenon. For a crystal such as diamond or silicon, no such dispersion exists. In a harmonic crystal, there is no coupling between different modes of the crystal, therefore such a crystal shows absorption only at the TO-mode frequency. In a real crystal, however, due to anharmonicity, different crystal modes can couple together and interact with an infrared photon at a frequency other than the TO-mode frequency, provided the wave vector and the energy are conserved.

Absorption of radiation is specified by the absorption coefficient α. Amplitude of a wave at a particular point in the medium is related to the amplitude at another point separated by a distance x in the medium by the relation

$$A(x) = A_0 e^{-\alpha x/2} \; . \qquad (1)$$

In the above relation A_0 is the amplitude of the wave at the former point. Intensity of radiation, which is related to the square of the amplitude, is given by

$$I(x) = I_0 e^{-\alpha x} \; . \qquad (2)$$

The quantity α is related to the real and the imaginary parts, ϵ' and ϵ'' of the dielectric constant ϵ by the expression

$$\alpha = 2(\epsilon'^2 + \epsilon''^2)^{1/4} \left(\frac{1}{2} - \frac{\epsilon'}{2(\epsilon'^2 + \epsilon''^2)^{1/2}} \right)^{1/2} \frac{\omega}{c} \, , \qquad (3)$$

where, ω is the photon frequency and c is the velocity of light. For the case where $\epsilon' \gg \epsilon''$, i.e., in the transparent region, this expression reduces to

$$\alpha = \epsilon'' \omega / c \epsilon'^{1/2} . \qquad (3')$$

For an ionic crystal, ϵ' and ϵ'' are given by the phenomenological expressions[11]

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)[1 - (\omega/\omega_0)^2]}{[1 - (\omega/\omega_0)^2]^2 + (\gamma_0 \omega / \omega_0^2)^2} \qquad (4)$$

and

$$\epsilon'' = \frac{-(\epsilon_0 - \epsilon_\infty)(\gamma_0 \omega/\omega_0^2)}{[1 - (\omega/\omega_0)^2]^2 + (\gamma_0 \omega/\omega_0^2)^2} \; . \qquad (5)$$

In the above expression, ω_0 is the long-wavelength TO mode frequency, γ_0 is the damping constant, and ϵ_∞ and ϵ_0 are the high- and low-frequency dielectric constants.

In the phenomenological expression, the absorption of radiation is explained in terms of damping. The fundamental phonon absorbs energy from the infrared photon because of the polarization present at the frequency of the transverse-optic mode. Subsequently, this energy decays to other modes of the solid. The damping constant γ_0 depends upon the rate of decay of the fundamental mode energy to the different combinations of the normal modes.

In general, a frequency dependent, γ_0, can explain the absorption of infrared energy in ionic crystals in the vicinity of the reststrahlen region. In addition to this one-phonon process considered above, there will be contributions to the dispersion due to multiphonon processes. Because of the anharmonicity in the crystal, the polarization $\vec{P}$ is no more a linear function of particle displacements, but it also contains higher-order terms. Thus,

$$\vec{P} = e\vec{X} + k_2 \cdot \vec{X}_1 \vec{X}_2 + k_3 \cdot \vec{X}_1 \vec{X}_2 \vec{X}_3 + \cdots \, , \qquad (6)$$

where k_i's are the suitable constants and $\vec{X}_i$'s are the particle displacements. Hence, the polarization is present, not only at the TO-mode frequency but at other frequencies as well (which are combinations of different mode frequencies of the crystal). For example, if two modes, with the same wave vector but belonging to the different branches with frequencies $\omega(\vec{k}, j_1)$ and $\omega(\vec{k}, j_2)$, combine, they will give rise to a polarization which has a zero wave vector and frequency $\omega(\vec{k}, j_1) \pm \omega(\vec{k}, j_2)$. Such a polarization can interact with electromagnetic waves with suitable frequency (and which have a very small wave vector). This gives rise to additional sources of absorption. At the frequencies which are combinations of those frequencies where the phonon density of states is very high (i.e., at the critical points), one observes singular rise in the absorption.[6] The positions of such peaks can be located from the joint density of states for two- or three-phonon process.

Now that the polarization is present at more than one frequency, the dielectric constant can be expressed as the following function:

$$\epsilon = \epsilon_\infty + \frac{A_0}{[1 - (\omega/\omega_0)^2] + i(\gamma_0 \omega/\omega_0^2)}$$

$$+\sum_i \frac{A_i}{[1-(\omega/\omega_i)^2]+i(\gamma_i\omega/\omega_i^2)} \quad . \qquad (7)$$

In the above expression, the subscript 0 stands for the fundamental oscillator and the subscript i stands for the various subsidiary oscillators. When expressed in terms of the joint density of states $\rho_j(\omega)$, we get

$$\epsilon=\epsilon_\infty+\frac{A_0}{[1-(\omega/\omega_0)^2]+i(\gamma_0\omega/\omega_0^2)}$$

$$+\sum_j \int \frac{A_j(\omega_i)\rho_j(\omega_i)}{[1-(\omega/\omega_i)^2]+i\gamma_j(\omega_i)\omega/\omega_i^2}\, d\omega_i \quad . \qquad (8)$$

The first term in the above expression is the high-frequency dielectric constant, the second term gives the contribution due to the fundamental process and the following terms give the contribution due to the higher-order processes. $\rho_j(\omega_i)$ denotes the number of multiphonon oscillators with frequency ω_i due to a j-phonon process. This expression for the dielectric constant will be used for the calculation of its real and imaginary parts, and finally the absorption coefficient. If we neglect the damping for the higher-order processes, the expression for the dielectric constant reduces to a simpler form. In the limit of damping constants γ_i's going to zero, Eq. (8) reduces to

$$\epsilon=\epsilon_\infty+\frac{A_0}{[1-(\omega/\omega_0)^2]+i\ \gamma_0\omega/\omega_0^2}$$

$$+\sum_j \int A_j(\omega_i)\,\rho_j(\omega_i)$$

$$\times\left(\frac{\omega_i^2}{\omega_i^2-\omega^2}\,\Bigg|_{\mathcal{P}} -\pi i\delta(\omega^2-\omega_i^2)\,\omega_i^2\right) d\omega_i \quad . \qquad (9)$$

The first term in the large parentheses gives the contribution to the real part of the dielectric constant. The symbol $\mathcal{P}$ denotes the principal part. The second term gives contribution to the imaginary part of the dielectric constant. Separating the real and the imaginary parts of the dielectric constants, we get for the imaginary part,

$$\epsilon''=\frac{-A_0(\gamma_0\omega/\omega_0^2)}{[1-(\omega/\omega_0)^2]^2+(\gamma_0\omega/\omega_0^2)^2}$$

$$-\sum_j \int A_j(\omega_i)\rho_j(\omega_i)\,\pi\delta(\omega^2-\omega_i^2)\,\omega_i^2\, d\omega_i \quad . \qquad (10)$$

The functions $\delta(\omega^2-\omega_i^2)$ are related to the functions $\delta(\omega-\omega_i)$ by the relation

$$\delta(\omega^2-\omega_i^2)=\delta(\omega-\omega_i)/2\omega_i \quad . \qquad (11)$$

Consequently, the expression for ϵ'' reduces to

$$\epsilon''=\frac{-A_0(\gamma_0\omega/\omega_0^2)}{[1-(\omega/\omega_0)^2]^2+(\gamma_0\omega/\omega_0^2)^2}$$

$$-\sum_j \int A_j(\omega_i)\rho_j(\omega_i)\,\tfrac{1}{2}\pi\delta(\omega-\omega_i)\omega_i\, d\omega_i$$

$$=\frac{-A_0(\gamma_0\omega/\omega_0^2)}{[1-(\omega/\omega_0)^2]^2+(\gamma_0\omega/\omega_0^2)^2} -\sum_j A_j(\omega)\rho_j(\omega)\tfrac{1}{2}\pi\omega \quad . \qquad (10')$$

The expression for the absorption coefficient in terms of the imaginary part of the dielectric constant is already given [Eq. (3′)].

III. PHONON DENSITY OF STATES

If the phonon density-of-states functions are known, one can estimate the absorption coefficient of the solid. To obtain the one-phonon and higher-order-phonon density-of-states functions, one needs a suitable lattice dynamical model. A criterion for the suitability of the lattice-dynamical model is that it should not have too many model parameters, determination of which would need detailed data from inelastic neutron scattering experiments (which are not available for many crystals). Moreover, the model should predict with a reasonable accuracy, not only the phonon dispersion relation, but other physical properties as well. The breathing-shell model of lattice dynamics is a satisfactory model for this purpose. The breathing-shell model,[12] with only one ion polarizable, has six model parameters, namely, two first- and one second-neighbor short-range force constants, the effective ionic charge, the shell charge on the anions, and the shell-core force constant for the anions. These parameters can be determined with the help of three elastic constants C_{11}, C_{12}, C_{44}, the long-wavelength transverse-optic phonon frequency ω_{TO}, and the high- and the low-frequency dielectric constants ϵ_∞ and ϵ_0. Accurate experimental values of these are available for most of the alkali halides. This model accurately predicts the dispersion relations along with other physical properties such as heat capacity, thermal expansion, Debye-Waller factor, etc. By solving the lattice dynamics for all the possible wave vectors in the first Brillouin zone, one can obtain the one-phonon density-of-states function. From these, higher-order density-of-states functions are obtained by the following procedure.

When a number of crystal modes interact to create a combination mode, energy and momentum have to be conserved. From the energy-conservation rule, one gets

$$\omega'(\vec{k})=\omega(\vec{k}_1 j_1)+\omega(\vec{k}_2 j_2)+\ldots+\omega(\vec{k}_n j_n) \qquad (12)$$

and

$$\omega''(\vec{k})=\left|\,\omega(\vec{k}_i j_i)\pm\omega(\vec{k}_2 j_2)\pm\ldots\pm\omega(\vec{k}_n j_n)\right| . \qquad (13)$$

In Eq. (13) any combination of positive and negative signs may be used as appropriate. $\omega'(\vec{k})$ and

$\omega''(\vec{k})$ are the frequencies of two possible combinational modes with wave vector $\vec{k}$. The $\omega(\vec{k}_i j_i)$'s are the crystal-mode frequencies belonging to the branch j_i with wave vector $\vec{k}_i$. In the first process, i.e., the summation process, n crystal phonons are annihilated (created) to create (annihilate) a combination phonon. In the second process, i.e., difference process, some crystal phonons are created and some crystal phonons are annihilated to create (annihilate) a combination mode. The momentum-conservation rule in both cases is given by

$$\vec{k}=\vec{k}_1+\vec{k}_2+\ldots+\vec{k}_n\ . \tag{14}$$

Both summation and difference processes are present simultaneously.

In general, for a given infrared photon, the process which involves only creation of phonons will be of the lowest order, i.e., will involve a smaller number of phonons than in the processes in which some phonons are created and some are annihilated; the latter will be of higher order. Contribution to the absorption goes down with the order of the process. For example, the ratio between the contributions from the $(n+m)$th-order and the nth-order process is approximately given by $(\Delta r/r_0)^{2m}$, where Δr is the amplitude of thermal vibration of the particles and r_0 is the separation between the nearest atoms.[13] $\Delta r/r_0$ is a very small fraction even up to the melting point of the solid. Thus for a given photon energy the summation processes will predominate over the difference processes. In the present work we thus consider only the summation processes. Moreover, by neglecting the difference processes, the calculation of density-of-states functions simplifies to a very large extent. Of these combination modes, only the mode with wave vector $\vec{k}\sim 0$, interact with the infrared photons, because the infrared photons have a very small wave vector. Accordingly, for the multiphonon absorption, only the combination modes with the zero wave vector are of interest to us. Consequently the wave-vector conservation rule reduces to

$$\vec{k}_1+\vec{k}_2+\ldots+\vec{k}_n=0\ . \tag{15}$$

A. Two-phonon density of states

In order to obtain the two-phonon density of states, one needs two modes belonging to the same wave vector. (In fact we need two modes with wave vector $\vec{k}$ and $-\vec{k}$. Since mode frequencies are even functions of wave vector, $\vec{k}$ and $-\vec{k}$ have the same frequencies.) The two-phonon density-of-states function is obtained by selecting a wave vector in the Brillouin zone and obtaining possible combinations of all the modes belonging to it, taking two at a time (keeping in mind selection rules, such as no two modes having the same wave vector and belonging to the same branch can combine to create or annihilate a combination mode in a crystal having inversion symmetry) and calculating the corresponding summation frequencies. For the fundamental density of states, a mesh of 512 wave vectors is selected in the first Brillouin zone. This gives a total of 3072 mode frequencies for a diatomic crystal. The above procedure gives rise to about 15 000 infrared-active combination mode frequencies for 512 points in the Brillouin zone. The two-phonon density of states thus calculated is given for NaCl in Fig. 1 along with the one-phonon density of states.

B. Three-phonon density of states

For the three-phonon process, the wave-vector conservation rule specifies that

$$\vec{k}_1+\vec{k}_2+\vec{k}_3=0 \quad\text{or}\quad 2\pi\vec{\tau}\ , \tag{16}$$

where $\vec{\tau}$ is a reciprocal-lattice vector. The first step in the calculation of the density-of-states function is to obtain all possible groups of wave vectors taken three at a time which would satisfy the above relation. It is obvious that the number of groups to satisfy the above relation is N^2, if we have a mesh of N wave vectors in the first Brillouin zone. Next, one selects a group of wave vectors at a time and obtains the different possible combination modes to obtain the three-phonon density-of-states function. For these calculations a mesh of 64 wave vectors was selected in the first Brillouin zone. Such a mesh gives rise to about 900 000 frequencies for the three-phonon density-of-states function. A finer mesh, say of 512 points will give rise to a much larger number of combination modes and an enormous amount of computation will be needed to obtain all the possible frequencies.

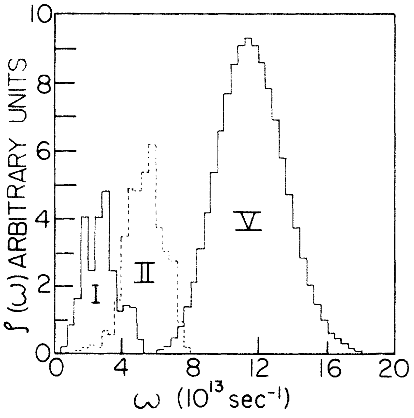

FIG. 1. One-phonon (I), two-phonon (II) and five-phonon (V) density-of-states functions for NaCl.

C. Four-phonon and higher-order density-of-states functions

It is clear that as the order (n) increases it becomes increasingly difficult to obtain the corresponding density-of-states function obeying all the selection rules. At the same time the wave-vector selection rule itself becomes less and less restrictive. If, for example, we select a mesh of 512 points in the first Brillouin zone, we will get $(512)^3$ possible groups of wave vectors which satisfy the wave-vector conservation rule for the fourth-order process. Each such group will give rise to about 1300 combination modes which amounts to a total of about 17×10^8 modes for the four-phonon density-of-states function. This involves an enormous amount of computation. At the same time as n increases, the combined density-of-states function, thus obtained, resembles more and more a normal distribution function. Therefore, higher-order density-of-states functions do not show any structure. And hence, a much simpler and approximate procedure is followed. From three-phonon onwards the density-of-states function is calculated simply from the following relation:

$$\rho_n(\omega)=\int_{\omega_1=0}^{\omega}\int_{\omega_2=0}^{\omega=\omega_1}\cdots\int_{\omega_{n-1}=0}^{\omega-\omega_1-\omega_2\cdots\omega_{n-2}}\rho(\omega_1)\rho(\omega_2)\cdots$$

$$\times\rho(\omega_{n-1})\rho(\omega-\omega_1-\omega_2\cdots\omega_{n-1})\,d\omega_1\,d\omega_2\cdots d\omega_{n-1}\,. \tag{17}$$

In the above relation $\rho_n(\omega)$ is the n-phonon density-of-states function and $\rho(\omega)$ is the one-phonon density-of-states function. Phonon density of states are calculated for NaCl and KCl from one-phonon to six-phonon processes. Results for some of these for NaCl are presented in Fig. 1.

IV. OSCILLATOR STRENGTH

After phonon density-of-states functions for higher-order processes are obtained, the task remains to obtain the quantities A_j's. We assume these functions to be independent of frequency. These depend on the corresponding derivatives of the crystal potential energy. Crystal potential energy for NaCl type of crystals contains a Coulomb part and a non-Coulomb part. The Coulomb part of the potential function is a relatively slowly varying function of r as compared to the non-Coulomb part.

At a finite temperature, the atoms in the solid have a finite amplitude of vibration. The potential energy of the crystal can be schematically expressed as a Taylor-series expansion in terms of the particle displacements:

$$\Phi=\Phi_0+\sum\frac{\partial\Phi}{\Phi r}\,\Delta r+\frac{1}{2!}\sum\frac{\partial^2\Phi}{\partial r^2}\,\Delta r^2+\frac{1}{3!}\sum\frac{\partial^3\Phi}{\partial r^3}\,\Delta r^3$$

$$+\cdots+\frac{1}{n!}\sum\frac{\partial^n\Phi}{\partial r^n}\,\Delta r^n+\cdots$$

$$=\Phi_0+\sum\frac{\partial\Phi}{\partial r}\,\Delta r+\frac{1}{2!}\sum r_0^2\frac{\partial^2\Phi}{\partial r^2}\left(\frac{\Delta r}{r_0}\right)^2$$

$$+\frac{1}{3!}\sum r_0^3\,\frac{\partial^3\Phi}{\partial r^3}\left(\frac{\Delta r}{r_0}\right)^3+\cdots$$

$$+\frac{1}{n!}\sum r_0^n\frac{\partial^n\Phi}{\partial r^n}\left(\frac{\Delta r}{r_0}\right)^n+\cdots\,. \tag{18}$$

The first term in the above expression is inconsequential. Under the equilibrium condition the second term vanishes. The third term is the harmonic term. This expression can further be simplified to

$$\Phi=\Phi_0+\left[\frac{r_0^2}{2!}\sum\frac{\partial^2\Phi}{\partial r_0^2}\left(\frac{\Delta r}{r_0}\right)^2\right]$$

$$\times\left[1+\frac{2!\,r_0}{3!}\left(\sum\frac{\partial^3\Phi}{\partial r^3}\Big/\sum\frac{\partial^2\Phi}{\partial r^2}\right)\left(\frac{\Delta r}{r_0}\right)\right.$$

$$+\frac{2!\,r_0^2}{4!}\left(\sum\frac{\partial^4\Phi}{\partial r^4}\Big/\sum\frac{\partial^2\Phi}{\partial r^2}\right)\left(\frac{\Delta r}{r_0}\right)^2$$

$$\left.+\cdots+\frac{2!\,r_0^{n-2}}{n!}\left(\sum\frac{\partial^n\Phi}{\partial r^0}\Big/\sum\frac{\partial^2\Phi}{\partial r^2}\right)\left(\frac{\Delta r}{r_0}\right)^{n-2}+\cdots\right]. \tag{19}$$

The first term in the large square bracket denotes the harmonic part. Other terms constitute the anharmonic part. These are usually treated as a perturbation. Rigorous analysis[3] shows that the oscillator strength $A_i(\omega)$ involves terms of the type

$$\left[\frac{\partial^n\Phi}{\partial r^n}\left(\frac{\Delta r}{r_0}\right)^n\right]^2\,.$$

Usually A_i's are not only functions of ω but they are also functions of wave vectors of the modes participating in the interaction. Accurate estimation of these requires immense amount of calculation. To reduce the numerical work, we make certain simplifying assumptions which are not in contradiction with the rigorous theory. Firstly, in the absence of reliable experimental data for the higher derivatives of the potential function, we assume a Born-Mayer-type potential function,

$$\Phi=-A/r+Be^{-r/\rho}\,, \tag{20}$$

where A, B, and ρ are the constants of the potential function. In the calculation of the anharmonicity the contribution due to the Coulomb part of the potential function is neglected (see Appendix A). Average particle displacements needed in the above expression can be obtained by solving the secular equation for all possible wave-vector values in the first Brillouin zone, and calculating the Debye-

Waller factors. Instead we follow the following approximate procedure.

The mean-square displacement $\langle \Delta r^2 \rangle$ of atoms in a solid due to all possible modes, is given by

$$\langle \Delta r^2 \rangle = \frac{1}{N} \int_{\omega=0}^{\omega_{\max}} g(\omega)\, d\omega \left(\frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} + \frac{\hbar\omega}{2} \right) \frac{1}{m\omega^2}\,, \tag{21}$$

where $g(\omega)$ is one-phonon density-of-states function, $\omega_{\max}$ is the maximum frequency, m is the atomic mass, and N is the total number of modes. If we assume a Debye-type frequency distribution for $g(\omega)$, Eq. (21) is modified to

$$\langle \Delta r^2 \rangle = \frac{1}{N} \int \frac{3N\omega^2}{\omega_{\max}^3} \left(\frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} + \frac{\hbar\omega}{2} \right) \frac{1}{m\omega^2}\, d\omega\,. \tag{22}$$

For solids like alkali halides, we use an average atomic mass. In order to simplify the calculations, we further assume that the energy of each mode is kT. Hence, we obtain

$$\langle \Delta r^2 \rangle = 3kT/\omega_{\max}^2\, m\,. \tag{23}$$

We are interested in the ratio $\langle \Delta r^2 \rangle / r_0^2$ for which we obtain

$$\langle \Delta r^2 \rangle / r_0^2 = 3kT/\omega_{\max}^2\, m r_0^2\,. \tag{24}$$

Again assuming Debye-type distribution, $\omega_{\max}$ can be obtained by the following approximate relation (Appendix B):

$$\frac{\omega_{\max}^2}{\pi^2/r_0^2} = \frac{B}{\rho} = \frac{2Br_0^3}{(m_+ + m_-)}\,. \tag{25}$$

In this expression B is the isothermal bulk modulus, and m_+ and m_- are the masses of the alkali and the halogen ions, respectively. After simplification we obtain

$$\tfrac{1}{2}(m_+ + m_-)\, \omega_{\max}^2\, r_0^2 = B\pi^2 r_0^3 \tag{26}$$

or

$$m\omega_{\max}^2 r_0^2 = B\pi^2 r_0^3\,, \tag{27}$$

where m is the average mass of the atoms as mentioned earlier. Substituting this relation in the expression for $\Delta r^2/r_0^2$ we obtain

$$\langle \Delta r^2 \rangle / r_0^2 = 3kT/B\pi^2 r_0^3\,. \tag{28}$$

As mentioned earlier, A_i's in general are functions of frequency. We feel that the dependence of A_i on its order is much more significant than its dependence on frequency. In the present calculation we assume A_i's to be independent of frequency. These are then assumed to be proportional to

$$A_{i+1}\, \alpha \left[r_0^i \frac{\partial^{i+2}\Phi}{\partial r^{i+2}} \left(\frac{\Delta r}{r_0} \right)^i \Big/ \frac{\partial^2 \Phi}{\partial r^2} \right]^2 = \left(\frac{r_0}{\rho} \right)^{2i} \left(\frac{3kT}{B\pi^2 r_0^3} \right)^i\,. \tag{29}$$

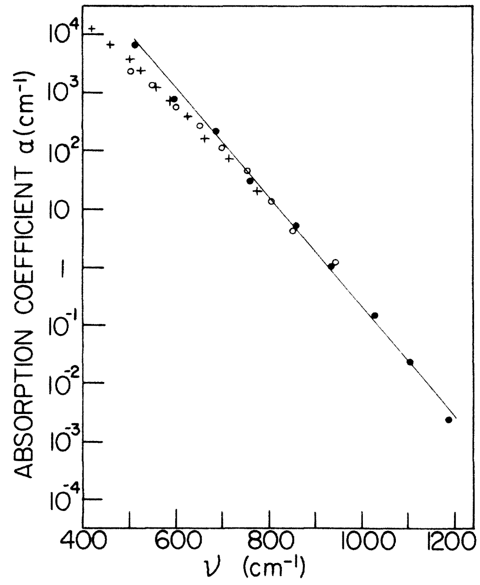

FIG. 2. Frequency dependence of absorption coefficient for NaCl. Solid circles give the results of the calculation. Crosses and empty circles are experimental data from Refs. 8 and 14, respectively. Solid line is a linear fit to the calculation.

V. RESULTS

Substituting for A_i in the imaginary part of the dielectric constant, we obtain

$$\epsilon'' = -\frac{-A_0(\gamma_0\omega/\omega_0^2)}{[1-(\omega/\omega_0)^2]^2 + (\gamma_0\omega/\omega_0^2)^2} - \sum_{j>1} \pi \left(\frac{r_0}{\rho} \right)^{2(j-1)} \left(\frac{3kT}{B\pi^2 r_0^3} \right)^{(j-1)} \chi\rho_j(\omega) \tfrac{1}{2}\omega\,. \tag{30}$$

In the region where $\epsilon' \gg \epsilon''$, the absorption coefficient α is already given by Eq. (3′). From this relation, one next obtains the frequency dependence of the absorption coefficient α in the three- and higher-phonon region, as

$$\alpha \sim \sum_{j>2} \pi\rho_j(\omega)\omega^2 \left(\frac{r_0}{\rho} \right)^{2(j-1)} \left(\frac{3kT}{B\pi^2 r_0^3} \right)^{(j-1)}\,. \tag{31}$$

In this region the real part of the dielectric constant becomes a very slowly varying function of ω. When plotted on a semilog scale, we get a linear dependence of α on ω. Results of the calculation for NaCl and KCl are presented in Figs. 2 and 3. Also plotted in the figures are the experimentally[8, 14] observed frequency dependence of α. Agreement with the experiment is excellent. We wish to emphasize here that the object of the present calculation is not to obtain an absolute magnitude of α but to obtain frequency dependence of α which can give some insight into the possible mechanisms for infrared absorption in this region. One may extend

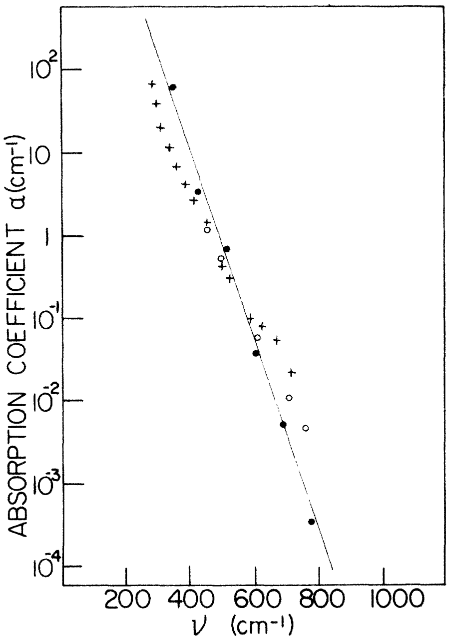

FIG. 3. Frequency dependence of absorption coefficient for KCl. Legend same as in Fig. 2.

the calculation, if so desired, to include contributions from higher-order density of states. In the present calculations we stop at six-phonon process because the experimentally available data on NaCl and KCl are covered by the processes up to the sixth order. For an alkali halide with heavier ions, like RbI, one may have to go to higher-order processes to cover the same spectral region. We further emphasize that this calculation, albeit approximate, is from first principles, in other words from the definition of the absorption coefficient. Density-of-states functions are calculated from the lattice dynamics. Approximations such as the Debye approximation or Born-Mayer potential are used only in the estimation of the oscillator strengths.

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APPENDIX A

Under central-force approximation the crystal potential can be expressed in the following form:

$$\Phi = -A/r + Be^{-r/\rho} . \tag{A1}$$

In the equilibrium condition, the first derivative of the crystal potential vanishes and we obtain

$$\left.\frac{\partial\Phi}{\partial r}\right|_{r_0} = \frac{A}{r_0^2} - \frac{B}{\rho} e^{-r_0/\rho} = 0 \tag{A2}$$

or

$$\frac{A}{r_0^2} = (B/\rho)\, e^{-r_0/\rho} . \tag{A3}$$

Derivative of the nth order is given by

$$\left.\frac{\partial^n\Phi}{\partial r^n}\right|_{r_0} = (-1)^n \left(-\frac{An!}{r_0^{n+1}} + \frac{B}{\rho^n} e^{-r_0/\rho}\right) \tag{A4}$$

or, after substituting for A/r_0^2,

$$\left.\frac{\partial^n\Phi}{\partial r^n}\right|_{r_0} = (-1)^n \left(-\frac{n!}{r_0^{n-1}} \frac{B}{\rho} e^{-r_0/\rho} + \frac{B}{\rho^n} e^{-r_0/\rho}\right)$$

$$= (-1)^n \frac{B}{\rho^n} e^{-r_0/\rho} \left[1 - n!\left(\frac{\rho}{r_0}\right)^{n-1}\right] . \tag{A5}$$

Since ρ/r_0 is of the order 0.1 for the alkali halides, the term $n!(\rho/r_0)^{n-1}$ becomes very small and may consequently be neglected.[15]

APPENDIX B

In the Debye approximation the mode frequency is expressed as

$$\omega^2/k^2 = C/\rho , \tag{B1}$$

where $|\vec{k}|$ is the wave vector and C is some average elastic constant. ρ is the density of the material. From this relation we obtain for ω_{max}

$$\omega_{max}^2/k_{max}^2 = C/\rho . \tag{B2}$$

For NaCl-type crystals, k_{max} is of the order π/r_0. For the average elastic constant we select the bulk modulus B.

Substituting for k_{max} and C in Eq. (B2) we obtain

$$\frac{\omega_{max}^2}{(\pi^2/r_0^2)} = \frac{B}{\rho} = \frac{B2r_0^3}{(m_+ + m_-)} . \tag{B3}$$

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