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Lattice Absorption in Finite Crystals

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Certain size and shape effects in the infrared lattice absorption spectra of crystals of finite size have been predicted theoretically by Rosenstock using a simple nearest-neighbor model in the harmonic approximation with free end boundary conditions. Atoms of equal mass, but of opposite sign, were assumed to lie on adjacent sites. In the present investigations, these results were extended to consider the case where the adjacent atoms are of unequal mass. In the case of the one-dimensional chain, this inequality can introduce surface modes and critical points at the zone boundary. Absorption of radiation propagating along the chain can occur because of interaction with the transverse vibrations over the entire range of permitted lattice frequencies and that of the surface mode. However, the amount of energy absorbed (neglecting beam-attenuation effects) can be shown to be directly proportional to the chain length in the frequency region of the long-wavelength optical branch modes, but is independent of chain length elsewhere. In the three-dimensional case, the absorption for the cases of adjacent atoms of equal mass and that for adjacent atoms of unequal mass are expected to be similar, and calculations have been carried out only for the former situation. Subsidiary absorption bands in the frequency region associated with some, but not all, critical points can occur, and this can be readily explained in terms of the atomic amplitudes. A size dependence of the absorption corresponding to the one-dimensional chain can be expected. The question of infrared absorption in one-dimensional chains whose length can be either smaller or larger than the wavelength of the interacting radiation has been considered from a simple point of view. In this approach, the nature of the modes interacting with the radiation can be regarded as different for large crystals and small crystals. However, the total absorption in the fundamental frequency region is directly proportional to the chain length, regardless of the ratio of chain length to the wavelength of interacting radiation. The possibility of experimental observation of these various effects is discussed.

I. INTRODUCTION

IN crystals containing N atoms, there are $3N$-3 vibrational modes, all of which may be infrared and Raman active. However, very strong infrared absorption can result from only relatively few modes in the fundamental or "reststrahl" frequency region. In addition to the strong absorption associated with the fundamentals, there can be a small amount of infrared absorption associated with a large number of other modes even within the harmonic approximation. This behavior was demonstrated in an article by Rosenstock[1] (designated as I) for a monatomic lattice with Hooke's law forces between nearest neighbors and free end boundary conditions. Atoms of opposite sign and equal mass were assumed to be located adjacent to each other along the chain with the Coulomb forces between them ignored in the dynamical problem. With the aid of this model it was possible to obtain relatively simple expressions for the lattice absorption. Furthermore, it was found that the dependence of the absorption on the length of the chain depended on the frequency range under consideration. The absorption was shown to be proportional to the chain length in the fundamental region as expected, but was not proportional to the chain length in the other frequency regions. These results were rederived in more detail and extended to two- and three-dimensional crystals in a subsequent article[2] (designated as II). In the multidimensional case small subsidiary absorption bands were found associated with certain critical frequencies. A corresponding size dependence was also deduced in the multidimensional case.

Using this same type of simple model, Wallis[3,4] showed that in diatomic lattices, surface modes can occur whose frequencies and atomic amplitudes can be calculated. It was suggested that lattice absorption associated with these surface modes could occur, although specific expressions were not given.

In the present article, some aspects associated with the infrared lattice absorption of finite crystals treated in articles I and II are discussed further. The absorption associated with a one-dimensional diatomic chain with nearest-neighbor interactions is treated, as this is the simplest situation in which critical points at the zone boundary and surface modes can occur. Expressions for the bulk mode absorption as well as an expression for the surface mode absorption (due to Wallis) are given. The size dependence of the absorption noted in I and II has been examined from a somewhat different point of view. It can be shown that the absorption in a one-dimensional chain away from the fundamental frequency (designated as nonfundamental) region is essentially independent of the length of the chain. Calculations of the lattice absorption of a three-dimensional crystal have been carried out along the lines indicated in II for a specific case. The subsidiary absorption bands have been associated with the appropriate critical frequencies and their origin can be understood by a consideration of the atomic amplitudes. The possibility of experimental observation of these effects is noted.

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[1] H. B. Rosenstock, J. Chem. Phys. **23**, 2415 (1955).

[2] H. B. Rosenstock, J. Chem. Phys. **27**, 1194 (1957).

[3] R. F. Wallis, Phys. Rev. **105**, 540 (1957).

[4] R. F. Wallis, Phys. Rev. **116**, 302 (1959).

Finally the general question of photon-phonon interactions in one-dimensional chains has been considered from a simple point of view neglecting retardation. In the usual treatment of photon interactions, strong (i.e., fundamental) interaction is said to occur when the photon frequency and wavelength are of the order of the optical branch phonon frequency and wavelength. It is appropriate to apply this condition only when the chain length is much longer than the absorbing wavelength of the fundamental optical modes. When the chain length is much smaller than this absorbing wavelength, the condition stated above is not appropriate to the problem as the maximum phonon wavelength is then of the order of the chain length and thus much smaller than the absorbing wavelength. In such cases, the usual "dipole" approximation for atomic and molecular problems is employed. The connection between these two limiting cases of large and small chains has not been discussed previously to the best of our knowledge. The treatment given here provides an expression for the absorption for chains of any length and gives some insight into the nature of the absorbing modes in finite crystals.

II. THE ONE-DIMENSIONAL DIATOMIC CHAIN

It is assumed that a one-dimensional chain can be described by an assembly of coupled harmonic oscillators. Consider a system of point atoms arranged on a line in which different charges may lie on the various atoms. If radiation propagates along the chain, only those normal modes in which the displacements of the atoms are perpendicular to the chain will contribute to the absorption. Application of the usual semiclassical time-dependent perturbation theory leads to an expression for $\kappa_n(N)$, the absorption[5] associated with the nth normal mode of frequency ω_n for a chain of N atoms, given by

$$\kappa_n(N)=\frac{C\omega_n}{\pi}\int_0^{2\pi}|\tau_n(N)|^2 d\Delta, \tag{2.1}$$

in which C contains only fundamental constants. The term $\tau_n(N)$ involves the sum

$$\tau_n(N)=\sum_{j=1}^{N} e(j)u_n(j)\eta(j,\Delta). \tag{2.2}$$

Here $e(j)$ is the charge on the jth atom, $u_n(j)$ is the displacement of the jth atom in the nth normal mode, and $\eta(j,\Delta)$ represents the spatial dependence of the vector potential arising from an electromagnetic wave propagating along the chain and having a phase shift Δ with respect to the first atom so that

$$\eta(j,\Delta)=\sin(k'x_j+\Delta). \tag{2.3}$$

The coordinate x_j represents the position along the chain of the jth atom and k' is the photon wave which is related to the number frequency ω_n and photon wavelength $\lambda_{n'}$ by $k'=\omega_n/c=2\pi/\lambda_{n'}$. For chains which are short compared to the wavelength $\lambda_{n'}$ the term $k'x_j=2\pi x_j/\lambda_{n'}$ can be considered small for all values of j so that expression (2.1) can be reduced to

$$\kappa_n(N)=C\omega_n|\textstyle\sum_j e(j)u_n(j)|^2, \quad k'x_j\to 0. \tag{2.4}$$

This small crystal approximation will be employed in this and the following section and a consideration of the more general situation will be postponed until Sec. IV.

The spectrum of a system of harmonically coupled oscillators will then consist of sharp lines at the various frequencies ω_n. For systems containing a large number of particles, the frequencies will usually lie close together, enabling an absorption spectrum to be deduced by forming a histogram as is done for density-of-states calculations. However, it will be seen that these lattice absorption histograms have an unusual behavior in that doubling the number of atoms in the chain can double the lattice absorption in some frequency regions, but leave it unchanged in other regions.

In order to evaluate the absorption for a specific case, consider a one-dimensional lattice of N atoms of mass M_1 and N atoms of mass M_2 with $M_2>M_1$. These atoms are assumed to be arranged in an alternating array spaced a distance a apart so that the end atoms have different masses. The light atoms are located on the odd-number lattice sites $2j-1$, $2j+1$, $\cdots$ and heavy atoms on the even-numbered sites $2j$, $2j+2$, $\cdots$. The nearest-neighbor Hooke's law force constant for displacements perpendicular to the chain is denoted by β. The dispersion relation for such a system has been found by Wallis[3] using free end boundary conditions to be[6]

$$\omega_n^2=\frac{\beta}{\bar{M}}\pm\frac{\beta}{\bar{M}}\left(1-\frac{4\bar{M}^2}{M_1M_2}\sin^2 k_n a\right)^{1/2}, \tag{2.5}$$

in which the characteristic values of the phonon wave number k_n are given by

$$k_n=n\pi/2Na, \quad n=1,2,3,\cdots,N-1, \tag{2.6}$$

where $\bar{M}$ is the reduced mass $M_1M_2/(M_1+M_2)$. The fundamental frequency $\omega_0=(2\beta/\bar{M})^{1/2}$ is defined for the limiting case $k_na=0$, although this is not a normal mode of the system. For a total number of $2N$ atoms,

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[5] The term "absorption" in this context refers to the fractional energy of the incident beam absorbed by the sample, assuming that attenuation effects of the beam in traversing the sample are small. This quantity is not to be confused with the absorption coefficient appearing in Lambert's law relating transmission and thickness.

The absorption $\kappa_n(N)$ can be shown to be temperature-independent for an assembly of harmonic oscillators [see Ref. 2, Eq. (26)]. A phase factor Δ, not present in Ref. 2, has been introduced here.

[6] Equation (2.5) is given in the reduced zone scheme and is equivalent to Eq. (6.1) of Wallis (Ref. 3) in the extended zone scheme with a change in notation.

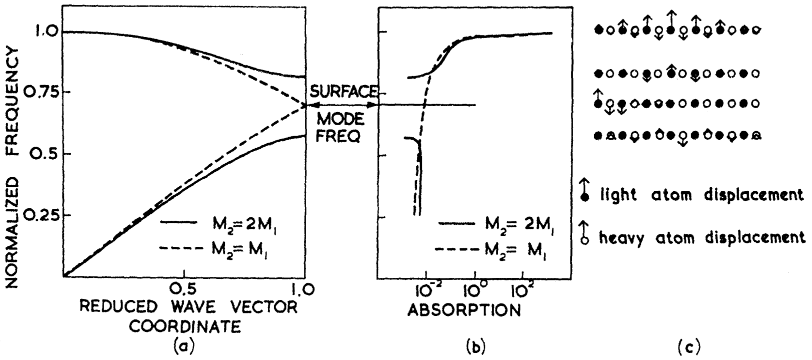

FIG. 1. (a) Dispersion curves for the one-dimensional diatomic chain with nearest-neighbor interactions and free end boundary conditions. (b) Relative lattice absorption of a one-dimensional diatomic chain 2000 ion pairs long. (c) Atomic displacements in various frequency regions for the one-dimensional diatomic chain with $2M_1=M_2$. The bulk mode displacements are typical of atoms on different locations on a chain of many ion pairs. The surface mode displacements are typical of the atoms near the surface.

the number of permitted modes (excluding pure translation) in one transverse dimension is $2N-1$ of which $2N-2$ of these are accounted for by the condition (2.6). An additional solution is provided by the surface mode at the frequency ω_s given by[3]

$$\omega_s^2=\beta/\bar{M} \tag{2.7}$$

and this lies in the gap between the optical and acoustical branches. The dispersion curves are illustrated in Fig. 1(a).

The form of the normal mode vibrations corresponding to various values of k_n is of interest in calculating the lattice absorption. By proceeding in this way indicated in Refs. 2 and 3, the following expressions for the displacements $u_n(2j)$ and $u_n(2j-1)$ can be obtained:

$$u_n(2j-1)=c_b[\sin 2(j-1)k_na-(1-M_2\omega_n^2/\beta)\sin 2jk_na], \tag{2.8a}$$

$$u_n(2j)=c_b[-\sin 2(j-1)k_na+(1-M_1\omega_n^2/\beta)\sin 2jk_na]. \tag{2.8b}$$

The constant c_b is given by

$$c_b=\bar{M}^{3/2}/M_1M_2(N\bar{M}\omega_n^2/\beta)^{1/2}(\bar{M}\omega_n^2/\beta-1). \tag{2.9}$$

The corresponding expressions for the surface mode amplitudes given by Wallis[3] are

$$u_s(2j-1)=c_s(-1)^{j-1}(M_1/M_2)^{j-1}, \tag{2.10a}$$

$$u_s(2j)=c_s(-1)^{j}(M_1/M_2)^{j}, \tag{2.10b}$$

$$c_s=\{[M_1M_2/(M_2-M_1)][1-(M_1/M_2)^{2N}]\}^{-1/2}.$$

The form of the displacement amplitudes is illustrated in Fig. 1(c) for certain modes. Use of free rather than clamped boundary conditions results in the end atoms always having a small but finite amplitude.

The lattice absorption can be calculated in the following way. Assume that atoms of opposite charge $\pm e$ are located on alternate sites with the Coulomb interaction neglected in the dynamical problem. The absorption for the case of the small crystal approximation in (2.4) becomes

$$\kappa_n(N)=C\omega_n|\textstyle\sum_j[eu_n(2j-1)-eu_n(2j)]|^2. \tag{2.11}$$

With the aid of the amplitude expressions (2.8a) and (2.8b), the absorption $\kappa_n(N)$ can be reduced to[7]

$$\begin{aligned}\kappa_n(N)&=C\omega_n\left(\frac{e^2}{\bar{M}N}\right)\left(\frac{\cos k_na}{\sin k_na}\right)^2\left[\frac{\bar{M}\omega_n^2/\beta}{(\bar{M}\omega_n^2/\beta)-1}\right] && \text{for } n \text{ odd}\\ \kappa_n(N)&\approx 0 && \text{for } n \text{ even.}\end{aligned} \tag{2.12}$$

In the limiting case of $M_1=M_2$ all of the terms for n even will be rigorously zero by symmetry considerations. When $M_1\neq M_2$, these modes become permitted, but their intensity will be considerably less than that of the adjacent odd modes.

Calculations of the absorption for a chain of 2000 atoms have been carried out using Eq. (2.12). The results are shown in Fig. 1(b). Although a curve is shown, this is actually an intensity histogram in which the frequency range has been divided into 100 equal increments. As a result, any sharp maxima will tend to smooth out and the sharpness of the curve depends upon the width of the frequency interval chosen. This spectrum shows strong absorption in the region of the fundamental and weak absorption elsewhere. The absorption in the region of the zone-boundary frequencies show minima even though there are maxima in the density of states. This arises because the absorption associated with the individual modes near the boundary ($k\rightarrow\pi/2a$) decreases faster than the density of modes in this region.

The corresponding expression for the surface mode absorption is given by[7]

$$\kappa_s(N)=C\omega_se^2c_s^2[1-(-1)^N(M_1/M_2)^N]^2. \tag{2.13}$$

This results in a weak absorption at the surface mode frequency ω_s. For the usual situation in which $N\gg1$, the intensity associated with this mode is independent of N. The atomic motions corresponding to this surface mode are illustrated in Fig. 1(c), and the absorption relative to the bulk mode absorption is shown in Fig. 1(b).

If calculations are carried out for chains of different lengths, the expression for the absorption as a function

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[7] Numerically equivalent expressions for (2.8) and (2.12) have been obtained independently by R. F. Wallis (private communication).

of length depends on the frequency range under consideration. In computing the absorption, the frequency range of interest is divided up into a large number of intervals (but still much less than N) of width $\Delta\omega$. The absorption in each interval is given by

$$\sum_{\Delta\omega}\kappa_n(N)\,, \tag{2.14}$$

in which the values of $\kappa_n(\omega)$ are summed for all modes whose frequency lies between ω and $\omega+\Delta\omega$. It will be shown that

$$\sum_{\Delta\omega}\kappa_n(N)\propto N\,;\quad \omega<\omega_0<\omega+\Delta\omega\,, \tag{2.15}$$

provided the fundamental frequency ω_0 lies within the interval ω and $\omega+\Delta\omega$.[8] Furthermore, for nonfundamental frequency intervals (except the ones which include the zone-boundary frequencies), it will be shown that

$$\sum_{\Delta\omega}\kappa_n(N)=F(\omega,\Delta\omega)\,;\quad \omega+\Delta\omega<\omega_0 \tag{2.16}$$

in which $F(\omega,\Delta\omega)$ is only a function of the frequency ω and the frequency width $\Delta\omega$ and does not depend upon the length of the chain N. Explicit values of $\kappa_n(N)$ can be obtained from the absorption expression (2.12). In the fundamental region, the factor k_na is much less than $\frac{1}{2}\pi$ so that (2.12) can be expressed as

$$\kappa_n(N)=C\omega_n\left(\frac{2e^2}{\bar{M}N}\right)\frac{1}{(k_na)^2}=\frac{8C\omega_nNe^2}{\bar{M}\pi^2n^2}\,,\quad k_na\ll\tfrac{1}{2}\pi\,. \tag{2.17}$$

The first term, where $n=1$, is much larger than any of the others and this occurs at a frequency extremely close to the fundamental frequency ω_0. Consequently, any sum of the form (2.14) which includes this first term will be nearly proportional to N. Because of the flatness of the dispersion curve for $k_na\ll\frac{1}{2}\pi$, the next closest frequency interval will involve terms in which the index n is large so that $\kappa_n\approx\kappa_{n+2}$. As a result, sums in the other frequency regions can be represented as the product of an average value of $\kappa_n(N)$ in the frequency interval and the number of states $\rho(N,\omega,\Delta\omega)$ in the interval so that

$$\sum_{\Delta\omega}\kappa_n(N)=\langle\kappa_n(N)\rangle\rho(N,\omega,\Delta\omega)\,. \tag{2.18}$$

The function $\kappa_n(N)$ can always be regarded as a function of ω_n since the index n and the frequency ω_n are related through the dispersion relation (2.5) giving

$$\kappa_n(N)=(C/N)f(\omega_n)\,, \tag{2.19}$$

in which all terms in (2.12) which are functions of ω_n and k_na are considered to be functions of the frequency ω_n. The number of states in the interval $\Delta\omega$ is directly proportional to N so that

$$\rho(N,\omega,\Delta\omega)=Ng(\omega,\Delta\omega)\,.$$

Consequently the product $\langle\kappa_n(N)\rangle\rho(N,\omega,\Delta\omega)$ is given by

$$\begin{aligned}\langle\kappa_n(N)\rangle\rho(N,\omega,\Delta\omega)&\\ &=(C/N)f(\omega)Ng(\omega,\Delta\omega)=Cf(\omega)g(\omega,\Delta\omega)\\ &=F(\omega,\Delta\omega)\,,\end{aligned} \tag{2.20}$$

which indicates that the resulting absorption in the nonfundamental frequency range is a function only of the frequency and the width of the frequency interval under consideration and does not depend upon the length of the chain.

III. THE THREE-DIMENSIONAL CRYSTAL

The case of the three-dimensional crystal represents a closer approach to reality. Preliminary calculations of the lattice absorption for the case of NaCl-type cubic lattice with nearest-neighbor interactions (neighboring atoms were assumed to have equal mass in the dynamical problem and opposite charges in calculating the absorption) have been carried out by Rosenstock.[2] In order to obtain a more general solution, the case of the diatomic crystal in which adjacent atoms have unequal mass was treated and the expression for the phonon dispersion has been obtained. Owing to the added complexity of the problem, an expression for the lattice absorption has not been derived. However, arguments will be advanced on the basis of the phonon dispersion curves which suggest that the principal features of the lattice absorption of the equal mass case will be nearly the same as for the unequal mass situation in contrast to the situation in one dimension. The surface mode absorption has not been calculated, but such absorption is expected corresponding to the modes discussed by Wallis.[4]

The dispersion relation for the three-dimensional NaCl-type diatomic crystal can be deduced by an extension of the approach used by Rosenstock[2] for the monatomic crystal. The results of such a procedure give an expression of the form

$$\omega_{lmn}{}^2=\frac{\alpha}{M}(1+2\sigma)\left\{1\pm\left[1-\frac{4\bar{M}^2}{M_1M_2}\times\left(1-\frac{f^2(k_1a,k_2a,k_3a)}{(1+2\sigma)^2}\right)\right]^{1/2}\right\} \tag{3.1}$$

for the eigenfrequencies of a cubic-shaped crystal containing N^3-ion pairs where the macroscopic cube edges are parallel to the crystallographic unit cell and where $f(k_1a,k_2a,k_3a)=\cos k_1a+\sigma(\cos k_2a+\cos k_3a)$. The phase factors k_1a, k_2a, and k_3a extend from $0<ka<\pi$. Here a is the nearest-neighbor distance and k_1, k_2, and k_3 represent propagation vector components along the cube edges. The parameter σ is equal to β/α, where α

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[8] This condition is somewhat stronger in that ω_0 should not be close to the edge of an interval.

and β are the force constants for parallel and perpendicular displacements of nearest-neighbor atoms.

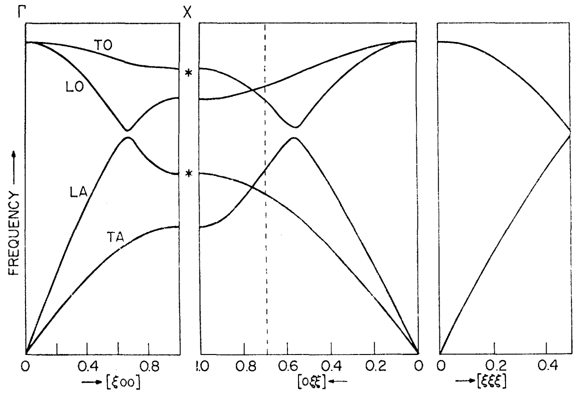

FIG. 2. Dispersion curves in the three principal symmetry directions for the diatomic crystal with nearest-neighbor interactions and free end boundary conditions with nearly equal masses $M_1 \approx M_2$ and force constant ratio $\sigma = \beta/\alpha = \frac{1}{4}$. The strongest subsidiary absorption maxima are expected to occur in the X-point frequency region denoted by an asterisk.

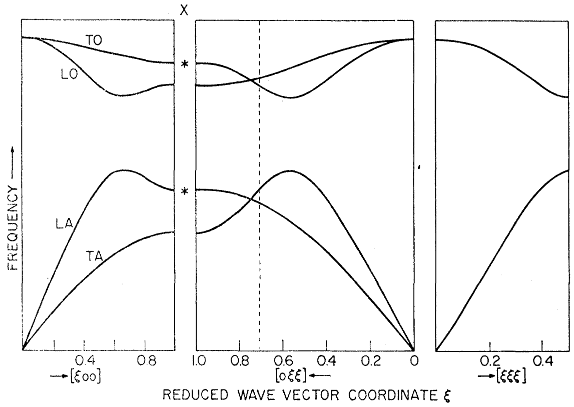

FIG. 3. Dispersion curves in the three principal symmetry directions for the diatomic crystal with nearest-neighbor interactions and free end boundary conditions with unequal masses $2M_1 = M_2$ and force constant ratio $\sigma = \beta/\alpha = \frac{1}{4}$. The strongest subsidiary absorption maxima are expected to occur in the X-point frequency region denoted by an asterisk.

The dispersion relation represented by Eq. (3.1) is shown in graphical form[9] in Figs. 2 and 3 corresponding to the cases of $M_2/M_1 \approx 1$ and $M_2/M_1 = 2.0$. It can be seen from Figs. 2 and 3 that the zone-boundary frequencies are not markedly changed by varying the mass M_2/M_1 nor do there appear to be any zone-boundary degeneracies which are split as in the one-dimensional case.[10] The principal difference is the splitting of a degeneracy part way through the zone. Consequently, it is not unreasonable to expect that any subsidiary lattice absorption bands appearing for the case $M_1 \approx M_2$ will not be markedly changed for $M_1 \neq M_2$. Furthermore, it is probably the case that any new absorption bands which would arise or increase in intensity for $M_1 \neq M_2$ would still be much less intense than those which absorb regardless of the ratio M_2/M_1. These arguments are employed to justify use of the simple expressions for the case of $M_1 = M_2$. For the case of $M_1 = M_2$, the lattice can be regarded as simple cubic rather than face-centered cubic and the following expression (applicable only to simple cubic) can be employed[11]:

$$\kappa_{lmn}(N) = C'\omega_{lmn}\left(\frac{e}{M}\right)^2 \frac{8M}{N^3}\left(\frac{1}{\cos(l\pi/2N)} \times \frac{1}{\cos(m\pi/2N)}\,\frac{1}{\cos(n\pi/2N)}\right)^2; \quad l, m, n = 1, 3, 5, \cdots, N-1 \qquad (3.2)$$

for light propagating along the edge of a cubic-shaped crystal having N atoms on a side. The lattice absorption spectrum has been calculated using (3.2) for a cubic-shaped crystal having 100 atoms on a side, and the results are shown in Fig. 4. It can be seen that there are two subsidiary absorption maxima at frequencies which are the same as those for the $X(LA)$ and $X(TO)$

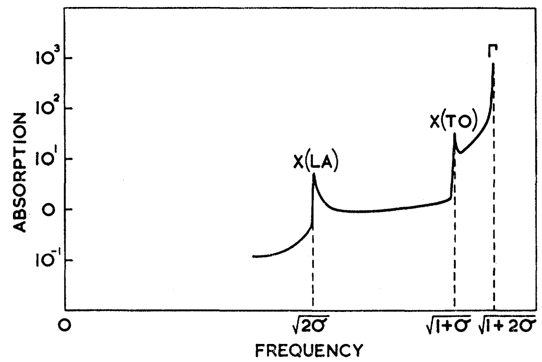

FIG. 4. Relative lattice absorption of a crystal with 100 atoms on a side and equal masses of all atoms. The corresponding dispersion curve is very close to that given in Fig. 2. Much weaker absorption maxima than those indicated occur near other zone-boundary frequencies, but these do not show up with the scale used.

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[9] One peculiarity of this model is that there is an unrealistic lack of coupling between the displacements in the x direction and those in the y and z directions (see Ref. 4, Sec. II). Thus each set of permitted values of k_1, k_2, k_3 corresponds to three modes in which the atom motions are always along either the x, y, or z directions. Furthermore, the model does not possess rotational invariance.

The deduction of the dispersion curves in Figs. 2 and 3 from Eq. (3.1) can be carried out in the following way. The dispersion curves in the [00ξ] direction represent solutions of Eq. (3.1) setting $k_1a = 0 \rightarrow \pi$ and $k_2a = k_3a \approx 0$, for the longitudinal modes. The transverse modes, which are twice as numerous, are obtained by setting $k_1a = k_3a \approx 0$, $k_2a = 0 \rightarrow \pi$ and $k_1a = k_2a = \pi/N \approx 0$, $k_3a = 0 \rightarrow \pi$. The terms "transverse" and "longitudinal" for this model refer to the number of solutions, rather than the relation between the atomic motions and direction of propagation of a phonon.

[10] This is probably a consequence of the particular lattice chosen rather than a general result.

[11] Reference 2, Eq. (61) with $ka \rightarrow 0$.

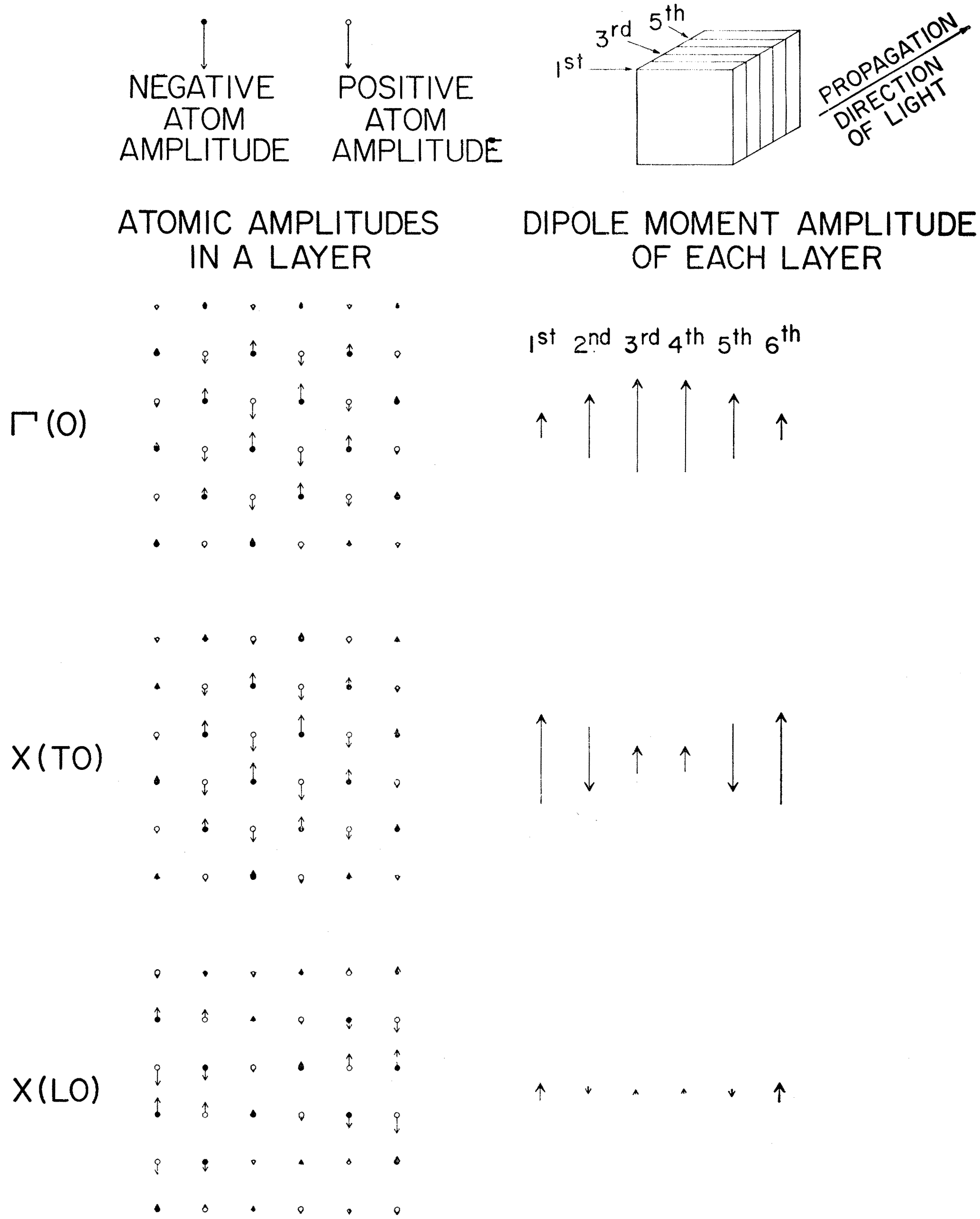

FIG. 5. Amplitude and dipole moment diagrams for representative modes in various regions of the zone for an NaCl-type lattice with $M_1 \approx M_2$ and the dispersion curves given in Fig. 2. The left-hand side gives the atomic amplitudes for a sheet of atoms perpendicular to the direction of propagation of the radiation. The right-hand side gives the relative dipole moment of each sheet of atoms constituting the crystal.

points in the Brillouin zone for a face-centered cubic lattice with $M_1 \approx M_2$. (Here LA and TO stand for longitudinal acoustic and transverse optic, respectively.) Some subsidiary absorption bands also appear corresponding to other zone-boundary critical frequencies but their intensity is substantially less and cannot be shown in Fig. 4. Since the model employed is sufficiently simple, it is possible to explain the intensity in the various critical-point regions from a consideration of the atomic amplitudes, which can be readily calculated from the three-dimensional equivalent of Eq. (37) of article II.

These atomic amplitudes are shown in Fig. 5. The highest frequency mode in the fundamental region designated as Γ corresponds to the usual out-of-phase motion of adjacent atoms. On the other hand, the motion of the X(TO) mode and also of the X(LA) mode can best be described as that of layers in which each layer has a large dipole moment, but the moments of adjacent layers nearly, but not quite cancel. The large density of states at these frequencies results in a subsidiary absorption band. On the other hand, in the region of the other critical frequencies, the absorption associated with the individual modes is much lower. The reason for this is illustrated for the X(LO) case where it can be seen that the motions are such that there is no sheet of atoms with a large moment. At best there are only lines of atoms which have large moments and adjacent lines tend to cancel.

The dependence of the absorption on size of the three-dimensional crystal is somewhat more complicated than the one-dimensional case. However, in the case of slab-shaped crystals in which the radiation propagates in a direction normal to the large face, the problem becomes essentially a one-dimensional one and most of the results found in Sec. II can be applied. By proceeding along the same general lines, it can be established that the absorption in the nonfundamental frequency region is independent of the thickness of the slab. This result holds for all frequency intervals including those occurring at zone-boundary frequencies (which were excluded in the one-dimensional case).[12] The situation for crystals of other shapes is more complicated. However, it has been shown for crystals of a few simple geometric shapes that the absorption away from the fundamental can be considered proportional to the surface area and this result is probably true in general.

The occurrence of nonfundamental absorption discussed here is very similar to one-phonon impurity-induced absorption which has been observed in ionic crystals. In both cases, the translational symmetry of the lattice is broken down by either impurities or the surface. The intensity of the impurity-induced absorption is proportional to the impurity content.[13] In a similar way, the intensity of the finite-size nonfundamental absorption discussed here would be expected to be proportional to the surface area.

IV. ABSORPTION IN SMALL AND LARGE CRYSTALS

In previous sections it has been assumed that the size of the sample is small compared to the wavelength of the absorbing radiation. In this approximation, the largest absorption is associated with the mode $n=1$ and it has been shown that the absorption in the fundamental frequency region is directly proportional to the chain length. When the chain is comparable in size with the absorbing wavelength the mode having the largest absorption is no longer $n=1$ but a mode whose wavelength is closest to the wavelength of the absorbing radiation. In fact the exact value of the index n in any particular case will depend upon the chain length. In such a situation it is not immediately obvious that the absorption in the fundamental frequency region is directly proportional to chain length with the same proportionality constant as in the small crystal approximation. However, it will be shown in this section that the total absorption in the fundamental frequency region, which is summed over all absorbing modes in this region, is directly proportional to the chain length for chains of any ratio of chain length to absorbing wavelength.

The general expression for the absorption is given by Eq. (2.1) which involves the atomic amplitudes. The optical branch amplitudes in the long wavelength (fundamental) frequency region are given to a very good approximation by

$$u_n(2j-1)=(2\bar{M}/N)^{1/2}(\sin 2jk_na)/M_1,\qquad k_na\ll\tfrac{1}{2}\pi;\quad (4.1a)$$

$$u_n(2j)=-(2\bar{M}/N)^{1/2}(\sin 2jk_na)/M_2,\qquad k_na\ll\tfrac{1}{2}\pi,\quad (4.1b)$$

which are obtained by series expansion of (2.8a) and (2.8b) for $k_na\ll\frac{1}{2}\pi$. The absorption expression (2.1) then becomes

$$\kappa_n(N)=C\omega_n(2e^2/N\bar{M}\pi)\times\int|\textstyle\sum_j\sin(2jk_na)\sin(2jk'a+\Delta)|^2d\Delta\quad (4.2)$$

$$=C\omega_n(2e^2/N\bar{M}\pi)\times\Big[\int|\textstyle\sum_j\sin(jn\pi/N)\sin(jn'\pi/N)\cos\Delta|^2d\Delta+\int|\sum_j\sin(jn\pi/N)\cos(jn'\pi/N)\sin\Delta|^2d\Delta\Big],\quad (4.3)$$

in which the cross term containing the product $\sin\Delta\times\cos\Delta$ vanishes on integration. The substitutions $k_na=n\pi/2Na$ and $k'a=\omega_n/c=n'\pi/2Na$ have been made where n' is some number which may be either integral or nonintegral in the range $0<n'\ll N$. In order to evaluate the sum in (4.3) it is convenient to replace the sum over the variable j by an integral in the variable j. This can be done since it has been assumed that N is large. The expression for $\kappa_n(N)$ then reduces to

$$\kappa_n(N)=\frac{2C\omega_ne^2N}{\bar{M}\pi^2}\left|\frac{n}{n^2-n'^2}\right|^2\{\sin^2n'\pi+[1-(-1)^n\cos n'\pi]^2\}\quad (4.4)$$

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[12] In the one-dimensional chain, the absorption $\kappa_n(N)$ decreases sharply near the zone-boundary frequencies, and this is associated with an atomic motion in which the amplitude of one type of atom is very small. In the three-dimensional case, the amplitudes associated with both types of atoms are comparable in magnitude near zone-boundary frequencies and there is no sharp drop off in $\kappa_n(N)$ as the zone-boundary frequency is approached.

[13] A. J. Sievers, A. A. Maradudin, and S. S. Jaswal, Phys. Rev. **138**, A272 (1965).

for the more difficult case where n' is assumed nonintegral. In deriving (4.4), it is helpful to remember that all terms containing $\sin n\pi$ can be set equal to zero since the phonon index n is always an integer. The expression (4.4) has a maximum value for $n \approx n' \ll N$ except for the case when $n' \ll 1$. The latter case arises when the chain length $2Na$ is much smaller than the photon wavelength $\lambda_{n'}$. In this case the largest value of $\kappa_n(N)$ is for the smallest phonon index $n=1$. The phonons of interest for both large and small chains will be those in the range $n=1$ to $n=$ integer $\ll N$. All modes for these phonon indices have practically the same frequency which can be set equal to the fundamental frequency ω_0. In any frequency interval which includes ω_0, the above modes can be summed to give the total absorption in the interval. Since the absorption of the individual modes drops off sharply for n not of the order of n', the sum over a finite number of modes can be replaced to a good approximation by a sum extending to infinity giving

$$\sum_{n=1}^{\infty} \kappa_n(N) = (2C\omega_0 e^2 N/\bar{M}\pi^2) S(n'), \qquad (4.5)$$

where

$$S(n') = \sum_{n=1}^{\infty} \left| \frac{n}{n^2 - n'^2} \right|^2 \times \{\sin^2 n'\pi + [1 - (-1)^n \cos n'\pi]^2\}. \qquad (4.6)$$

The sum $S(n')$ can be shown to be independent of n' and equal to $\frac{1}{2}\pi^2$. This result, which was demonstrated by John Slater of the University of Reading, is outlined in Appendix A. It follows that the absorption in a frequency interval $\Delta\omega$ which includes the fundamental frequency ω_0 is given by

$$\sum\nolimits_{\Delta\omega} \kappa_n(N) = C\omega_0 e^2 N/\bar{M}, \quad \omega < \omega_0 < \omega + \Delta\omega. \qquad (4.7)$$

Expression (4.7) has the same dependence on N for both small crystals and large crystals.[14]

Some physical insight into the absorption process can be obtained by considering two limiting approximations. In the small crystal case, the chain length $2Na$ is small compared to the photon wavelength $\lambda_{n'}$ so that $n' = 4Na/\lambda_{n'}$ tends to zero. In the limiting case the absorption (4.4) becomes equal to the previously derived expression (2.17) and is proportional to $1/n^2$. The result (4.7) can also be obtained by summing the small crystal expression (2.17). This sum will consist of a large first term ($n=1$) which contributes over 80% of the final result. The remaining odd terms contribute less than 20%. A different distribution of intensity among the various modes occurs in the large crystal approximation. The special case of a chain whose length is some large integral number of half-wavelengths of the radiation can be calculated directly from (4.3) as $n' = 2Na/\frac{1}{2}\lambda$ is an integral number. In such a case, the first term on the right-hand side of (4.3) contributes 50% of the absorption and this term is finite only for $n = n'$ or where the photon and phonon wavelengths are equal. The other half of the absorption arises when $|n - n'| = 1, 3, 5, \cdots$. The distribution of intensity among the various modes in the small and large crystal limiting cases is more easily represented in the dispersion curve shown in Fig. 6. Here the percent absorption associated with various modes in the small and large crystal approximations is shown.

V. SUMMARY AND EXPERIMENTAL CONSEQUENCES

The lattice vibration spectrum and resulting infrared absorption spectrum have been calculated for a crystal model involving nearest-neighbor forces only with free-end boundary conditions. The following features of the absorption are predicted on the basis of this model: (1) Absorption of incident radiation is expected to occur over the entire range of permitted lattice frequencies and at the frequencies of some surface modes. The most intense absorption would occur in the frequency region of the long-wavelength optical branch modes (designated as the fundamental frequency region). Much weaker absorption could occur in the frequency region of other modes (designated as the nonfundamental frequency region). There may be some structure in the nonfundamental absorption associated with certain critical frequencies in the lattice vibration spectrum. (2) In the fundamental frequency region, the amount of energy absorbed by a sample would be expected to be proportional to the volume of material in the beam (neglecting attenuation effects on the beam within the sample). On the other hand, in the nonfundamental frequency region, the amount of energy absorbed would be proportional to the surface area of the material. This behavior is analogous to impurity-induced one-phonon absorption in which the surface layer is regarded as the impurity. In the case of a slab-shaped crystal, this would imply that the transmittance of radiation normally incident on a slab would be independent of thickness in the nonfundamental frequency region.

These predictions of the infrared absorption spectrum have been made using a mathematically simple, but in many ways physically unrealistic model. This has the advantage in that these effects can be readily interpreted in terms of the atomic amplitudes. However, the question arises as to whether these predictions would also hold for more realistic models. The two principal factors which have been neglected are: (1) retardation and (2) Coulomb forces between atoms. Retardation effects are of principal importance in considering the long-wavelength optical branch modes where there is a

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[14] A different conclusion was reached in article II, and this was due in part to the fact that a sum was not taken over all relevant modes and the phase factor was neglected. The correct expressions for the small-crystal case were obtained, but not for the large-crystal case.

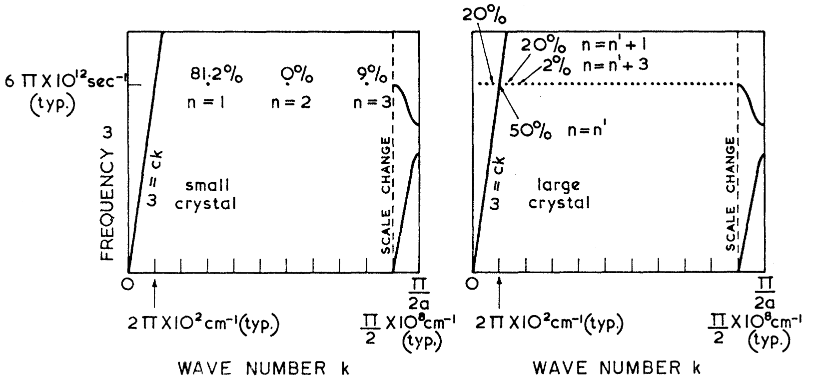

FIG. 6. Dispersion curves for two finite one-dimensional chains. The wave number scale has been greatly expanded in the region of small k so that points rather than lines are used. The left-hand side is for the shorter chain (chain length $2Na=\frac{1}{6}\lambda$ where λ is the absorbing wavelength of the radiation). The right-hand side is for the longer chain ($2Na=2\lambda$). If the short chain ($2Na\ll\lambda$) approximation were to be fulfilled, then the percent absorption associated with various modes would be given by the numbers indicated. If the long chain ($2Na\gg\lambda$) approximation were to be fulfilled with the chain length $2Na$ being some large integral multiple of the absorbing half-wavelength, then the percent absorption associated with various modes would be given by the numbers indicated. The solid line labeled $\omega=ck$ represents the dispersion curve of the photons.

strong coupling between the photon and phonon systems. The main prediction given about these modes is that the amount of incident energy which would be absorbed is proportional to the volume of the sample. This appears to be a reasonable prediction and would also follow from a macroscopic phenomenological treatment of the dielectric polarization. Admittedly, it would require a more extensive treatment to justify this result from a lattice dynamical point of view. Retardation effects can be ignored in dealing with modes whose frequencies lie in the nonfundamental frequency region where the phonon-photon interaction is much weaker. The neglect of Coulomb forces, however, can alter the results over the entire frequency range. Changes both in the dispersion curves and in the absorption associated with individual modes can occur when Coulomb forces are included. Absorption over the entire range of permitted lattice frequencies is still expected regardless of model. The intensity of such absorption could be considerably different from that for the case calculated where only nearest-neighbor interactions are involved. Nevertheless, it is still of considerable interest to estimate the magnitude of the nonfundamental absorption using the nearest-neighbor model in order to determine whether further experimental and theoretical studies are warranted. This can be done in the following way.

The absorption calculations for a cubic-shaped crystal with 100 atoms on a side are shown in Fig. 4. By inspection of this curve, it can be seen that the ratio of fundamental to nonfundamental frequency absorption is roughly about 100. That is, the fundamental absorption can be considered as proportional to the number of atoms along the direction of propagation with the nonfundamental absorption proportional to unity. For the alkali halides and many other ionic crystals, the fundamental can be observed with a thin film about 2000 Å or 400 ion pairs thick. Thus, if it were possible to intercept the beam with 400 layers of this thickness, then the nonfundamental absorption might become observable. Assuming that the layers are 2000 Å thick, radiation would then have to traverse about 0.08 mm of material. Slabs of alkali halides of this thickness are opaque at room temperature in the nonfundamental frequency region because of difference bands arising from higher order anharmonic processes. At low temperatures, the intensity of these difference bands is markedly reduced so that these materials are transparent in thicknesses of several millimeters.[15] As a result the experiment described above becomes feasible, although there can be considerable experimental difficulties in passing the radiation through a large number of layers. It may be possible to achieve this by some multiple-pass technique. A cruder way of accomplishing the same effect is by use of finely powdered samples in order to achieve a large surface-to-volume ratio. In fact, it has been claimed that the absorption of finely powdered crystals shows increased absorption in the nonfundamental frequency region compared to bulk crystals of the same material.[15] While such results are in accord with the calculations given here, the observed result may be due to other factors such as impurities and endogenous imperfections such as vacancies and dislocations. Purification of materials can usually be carried out sufficiently well so that impurity-induced one-phonon absorption cannot be observed in thicknesses of several millimeters. However, the contributions due to endogenous imperfections are somewhat more difficult to separate out than those contributions due to finite size effects.

As noted earlier, the estimate of the size absorption has been carried out with the aid of a very simple model. If a realistic model were used, the intensities could be considerably different. Another way of estimating the

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[15] A. Hadni, G. Morlot, X. Gerbaux, D. Chanal, F. Brehat, and P. Strimer, Compt. Rend. 260, 4973 (1965).

intensity can be made by noting the similarity between the size absorption and impurity-induced one-phonon absorption. The impurity-induced absorption can be observed with impurity concentration in the range of 10^{19} impurities/cc.[13] Regarding the surface atomic layer as analogous to the impurity situation, then the calculated effective "impurity" concentration of a slab 2000-Å thick is also in the range of 10^{19} atoms/cc. This suggests that the size absorption discussed here should be observable with a sufficient number of layers.

It would be desirable to calculate the size effect using a realistic model. However, the lattice dynamics of finite crystals with long-range Coulomb forces is quite complicated. A promising approach of the long-wavelength optical modes of a finite crystal has been given recently by Kliewer and Fuchs.[16] One consequence of the inclusion of long-range Coulomb forces is a separation of the long-wavelength transverse and longitudinal optical modes. A related effect is the following: In models involving only short-range interactions, the dispersion curves for long wavelengths are flat. That is, all of the long-wavelength modes have practically the same frequency. When long-range Coulomb forces are allowed and the crystal size is small compared to the absorbing wavelength, it has been suggested that the longest wavelength modes do not all have the same frequency.[17] As a result there may be a marked size and shape dependence in the fundamental frequency region in addition to the other effects discussed here.

In conclusion, the results of this present investigation indicate that the lattice absorption of a finite crystal can be quite complicated even within the framework of the harmonic approximation. A number of effects have been predicted, and these might be experimentally observable under suitable conditions.

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APPENDIX A

It is desired to show that the sum $S(n')$ defined by

$$S(n')=\sum_{n=1}^{\infty}\left|\frac{n}{n^2-n'^2}\right|^2\{\sin^2 n'\pi+[1-(-1)^n\cos n'\pi]^2\}\qquad\text{(A1)}$$

is in fact a constant independent of n' whose value is $\frac{1}{2}\pi^2$. Let

$$S'(n')=\sum_{n=1}^{\infty}\left|\frac{n}{n^2-n'^2}\right|^2.\qquad\text{(A2)}$$

Then

$$S(n')=2S'(n')-2\cos n'\pi\sum_{n=1}^{\infty}(-1)^n\left|\frac{n}{n^2-n'^2}\right|^2\qquad\text{(A3)}$$

$$=2S'(n')-2\cos n'\pi\times\left(\sum_{n\text{ even}}\left|\frac{n}{n^2-n'^2}\right|^2-\sum_{n\text{ odd}}\left|\frac{n}{n^2-n'^2}\right|^2\right),\qquad\text{(A4)}$$

in which the sums are taken over even or odd integral values of n. Since

$$S'(n')=\sum_{n\text{ even}}\left|\frac{n}{n^2-n'^2}\right|^2+\sum_{n\text{ odd}}\left|\frac{n}{n^2-n'^2}\right|^2$$

and

$$\sum_{n\text{ even}}\left|\frac{n}{n^2-n'^2}\right|^2=\sum_{n=1}^{\infty}\left|\frac{2n}{(2n)^2-n'^2}\right|^2=\tfrac{1}{4}\sum_{n=1}^{\infty}\left|\frac{n}{n^2-(\frac{1}{2}n')^2}\right|^2=\tfrac{1}{4}S'(\tfrac{1}{2}n'),$$

Eq. (A4) can be written as

$$S(n')=2(1+\cos n'\pi)S'(n')-(\cos n'\pi)S'(\tfrac{1}{2}n').\qquad\text{(A5)}$$

In order to evaluate $S'(n')$, consider the identity[18]

$$\frac{\pi\sin n'x}{2\sin n'\pi}=\frac{\sin x}{1-n'^2}-\frac{2\sin 2x}{2^2-n'^2}+\frac{3\sin 3x}{3^2-n'^2}\cdots=\sum_{n=1}^{\infty}\frac{(-1)^{n+1}n\sin n\pi}{n^2-n'^2}.\qquad\text{(A6)}$$

On squaring both sides and integrating over a range of x from $-\pi$ to $+\pi$, all cross terms on the right-hand side of (A6) vanish except for those of the form

$$\left|\frac{n}{n^2-n'^2}\right|^2\int_{-\pi}^{\pi}\sin^2 nx\,dx=\left|\frac{n}{n^2-n'^2}\right|^2\pi.\qquad\text{(A7)}$$

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[16] R. Fuchs and K. L. Kliewer, Phys. Rev. **140**, A2076 (1965); K. L. Kliewer and R. Fuchs, *ibid.* **150**, 573 (1966).

[17] M. Hass, Phys. Rev. Letters **13**, 429 (1964); A. A. Maradudin and G. H. Weiss, Phys. Rev. **123**, 1968 (1961); J. Grindlay, Can. J. Phys. **43**, 1604 (1965); R. Englman and R. Ruppin, Phys. Rev. Letters **16**, 898 (1966).

[18] R. Courant, *Differential and Integral Calculus* (Blackie and Sons, Ltd., London, 1937), 2nd ed., Vol. I, p. 445.

As a result, it is possible to write

$$\frac{\pi^2}{4\sin^2 n'\pi}\int_{-\pi}^{\pi}\sin^2 n'x\,dx=\sum_{n=1}^{\infty}\pi\left|\frac{n}{n^2-n'^2}\right|^2=\pi S'(n') \quad \text{(A8)}$$

and

$$\frac{\pi^2}{4\sin^2 n'\pi}\left(1-\frac{\sin 2n'\pi}{2n'\pi}\right)=S'(n'). \quad \text{(A9)}$$

On inserting expressions for $S'(n')$ and $S'(\frac{1}{2}n')$ from (A9) into Eq. (A5) the desired sum $S(n')$ becomes a complicated trigonometric function of $2n'\pi$, $n'\pi$, and $n'\pi/2$. With the aid of standard trigometric identities, it is possible to reduce this and to show that

$$S(n')=\tfrac{1}{2}\pi^2. \quad \text{(A10)}$$

This particular treatment holds for any nonintegral value of n', where n' may approach an integral value arbitrarily closely.

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Electric Field Effects on the Dielectric Constant of Solids*

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Calculations of the imaginary part of the dielectric constant of an anisotropic solid in the region of a critical point are used to obtain the real part of the dielectric constant through Kramers-Kronig relations. Changes in the real and imaginary parts of the dielectric constant are expressed in closed form for all four types of critical points. Description of these changes can be made with only two functions. The effect of the finite extent of a band is investigated, and it is shown that previous calculations of the change in the imaginary part of the dielectric constant, based on bands of infinite extent, are valid as long as transitions are restricted to regions near the critical point. Closed-form expressions for the Lorentzian broadening of the changes in the dielectric constants are given in terms of Airy functions of complex argument.

I. INTRODUCTION

WITH the evaluation of certain integrals involving Airy functions, it has been possible to obtain the change in the imaginary part of the dielectric constant or optical absorption caused by the application of an arbitrarily oriented electric field near critical points in solids.[1] The same methods can be applied to evaluate the change in the real part of the dielectric constant near critical points, which formerly had been obtained only by numerical integration about the fundamental absorption threshold[2–4] and about the M_1 critical point in the special case of the field parallel to the negative-mass symmetry axis.[2] It is the purpose of this paper to evaluate the dielectric-constant changes caused by an electric field in closed form for an arbitrarily oriented electric field in an anisotropic solid near all four types of critical points, and to investigate the effects of the finite extent of the energy bands on both the real and imaginary parts of the dielectric constant in the presence of an electric field. The weak-field effective-mass approximation will be used throughout.

Rapid changes in the dielectric constant occur at Van Hove singularities in an energy band, where the gradient of the relative energy, $\nabla_{\mathbf{k}}(E_c-E_v)$, vanishes at some value of $\mathbf{k}$.[5,6] Such singularities are of four types, depending on the band curvature or the signs of the reduced masses in the effective-mass approximation. Assuming quadratic energy surfaces, we take the mass of a conduction-band electron along the axes of symmetry as m_{ex}, m_{ey}, and m_{ez}, and the hole masses along the same axes as m_{hx}, m_{hy}, and m_{hz}. Defining the reduced mass m_i for each coordinate $i=x$, y, and z as

$$m_i=\frac{m_{ei}m_{hi}}{m_{ei}+m_{hi}}, \quad (1)$$

the four different critical points may be defined by the reduced-mass signs[6]:

M_0: m_x, m_y, m_z positive (ellipsoid);

M_1: m_x, m_y positive, m_z negative (saddle point);

M_2: m_x, m_y negative, m_z positive (saddle point);

M_3: m_x, m_y, m_z negative (ellipsoid).

For the two saddle-point singularities M_1 and M_2, the mass of odd sign is conventionally taken as m_z.

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