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Effect of Quartic Anharmonicity on the Infrared Absorption of Alkali Halide Crystals

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A classical theory is given for the influence of quartic anharmonicity terms on the infrared lattice vibration spectra of ionic crystals. It is found that quartic anharmonicity introduces terms in the damping constant which are proportional to the square of the absolute temperature. A frequency renormalization is found to be necessary in order to make the simple classical theory go through for quartic terms.

I. INTRODUCTION

RECENT measurements of the infrared reflection spectrum of single crystals of sodium chloride show that the damping constant associated with the fundamental lattice vibration absorption is roughly proportional to T^2 at high temperatures.[1] Theoretical calculations of the damping constant have hitherto assumed that only cubic anharmonic interactions between the normal vibrational modes are responsible for the damping. Born and Blackman,[2] Blackman,[3] Maradudin and Wallis,[4] and Neuberger and Hatcher[5] have carried out classical calculations based on the cubic anharmonic terms and have found that the damping constant is proportional to the first power of the absolute temperature. A quantum-mechanical calculation has been given by Born and Huang,[6] and has been elaborated by Maradudin and Wallis.[7] The quantum-mechanical damping constants which arise from cubic anharmonic terms turn out to be proportional to T^3 in the high-temperature limit. None of the theoretical results is in satisfactory agreement with the experimental data. Furthermore, the Born-Huang result appears to violate the correspondence principle.

In this paper we extend the classical treatment of Blackman to include the effects of quartic anharmonicity. It is hoped that this work will shed some light on problems which arise in the quantum treatment of this problem. It is found that quartic terms in the potential do indeed yield a contribution to the damping constant which is proportional to T^2, and which adds to the cubic contribution (proportional to T) given by Blackman. A combination of cubic and quintic anharmonicity terms would also give a T^2 dependence; however, we shall not consider this contribution here.

Generalizing the Blackman treatment to quartic terms is not completely straightforward because the quartic terms contribute to frequency-shift effects in first order. This first-order shift is itself easily handled, but the second-order transition effects must be calculated using the shifted frequencies if serious problems are to be avoided.

We shall limit most of our discussion to the one-dimensional model studied by Born and Blackman[2] and more fully by Blackman,[3] although it is clear that the results we have stated above generalize to three dimensions. Blackman was able to obtain closed form expressions for the cubic contribution to the damping constant in one dimension. Unfortunately, this does not appear to be possible for the quartic contribution. We limit ourselves to a qualitative study and one limiting case.

The infrared spectra of alkali halides show subsidiary peaks in addition to the fundamental or reststrahlen absorption. The origin of these peaks is an interesting problem. (See reference 5.) For the linear chain model the quartic terms produce singularities in the absorption constant as do the cubic forces. However, it appears that this is a one-dimensional effect and does not give any real evidence for the existence of subsidiary peaks in the optical constants for a three-dimensional model. This conclusion follows from the general arguments used by Van Hove[8] to determine the singularities of the frequency distribution of a lattice of given dimension.

II. THE LINEAR DIATOMIC CHAIN

We assume that we have a linear chain of atoms of two different types; one type with mass M_2 and charge $+e$ occupies the even sites, and the other of mass M_1 and charge $-e$ occupies the odd sites. We shall assume that only the forces between adjacent atoms are important, and these include quadratic, cubic, and quartic terms. The chain is bathed in a uniform external radia-

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tion field with the electric field

$$E=E_0e^{i\omega t}. \tag{1}$$

The Hamiltonian of this sytem is

$$\begin{aligned}\mathcal{H}=&\tfrac{1}{2}\sum_n(M_2\dot{u}_{2n}^2+M_1\dot{u}_{2n+1}^2)\\&+\frac{\alpha}{2}\sum_n[(\mu_{2n+1}-u_{2n})^2+(u_{2n}-u_{2n-1})^2]\\&+\frac{\beta}{3!}\sum_n[(u_{2n+1}-u_{2n})^3-(u_{2n-1}-u_{2n})^3]\\&+\frac{\epsilon}{4!}\sum_n[(u_{2n+1}-u_{2n})^4+(u_{2n}-u_{2n-1})^4]\\&+eE\sum_n(u_{2n}-u_{2n+1}).\end{aligned} \tag{2}$$

This Hamiltonian neglects the long-range Coulomb forces between the ions which are physically very important. Nevertheless, we expect that the conclusions of this paper will remain much the same for a model including these forces, although the frequency spectrum of the lattice and the form of the cubic and quartic coupling between the normal modes will be quite different. In particular, the temperature dependence of the damping due to the cubic and quartic terms will not change.

Following Blackman,[3] but with a slight change in notation, the normal coordinates are given by

$$\begin{aligned}u_{2n}&=\frac{1}{(NM_2)^{\frac{1}{2}}}\sum_{k\sigma}e^{(2\pi ik/N)n}\xi_{k\sigma}\cos\theta_{k\sigma},\\u_{2n+1}&=\frac{-1}{(NM_1)^{\frac{1}{2}}}\sum_{k\sigma}e^{(\pi ik/N)(2n+1)}\xi_{k\sigma}\sin\theta_{k\sigma}.\end{aligned} \tag{3}$$

The index σ takes on the values 1 and 2 labeling two roots θ_{k1} and θ_{k2} of the equation

$$\tan 2\theta=2(M_1M_2)^{\frac{1}{2}}(M_1-M_2)^{-1}\cos(\pi k/N). \tag{4}$$

The first root θ_{k1} is assumed to lie in the interval $-\pi/4<\theta_{k1}\leq\pi/4$, and θ_{k2} is defined by $\theta_{k2}=\theta_{k1}-\pi/2$. (The variable ξ_{k1} is Blackman's ξ_k, ξ_{k2} is his η_k.) As stated, this transformation does not lead to the same definition of the normal modes if k is replaced by $k+N$. Since we shall require this property for later considerations, we shall choose $\theta_{k2}=\theta_{k1}+\pi/2$ when k is an odd number of N's away from the fundamental zone $0\leq k<N$. The quantity A_{k2} defined below is zero at the points of transition, so there is no discontinuity. Performing the transformation, we find

$$\begin{aligned}&u_{2n}-u_{2n+1}=N^{-\frac{1}{2}}\textstyle\sum_{k\sigma}e^{(2\pi ikn/N)}A_{k\sigma}\xi_{k\sigma},\\&A_{k\sigma}=M_2^{-\frac{1}{2}}\cos\theta_{k\sigma}+M_1^{-\frac{1}{2}}\sin\theta_{k\sigma}e^{(\pi ik/N)},\\&A_{-k\sigma}=A_{k\sigma}^*,\quad \xi_{-k\sigma}=\xi_{k\sigma}^*,\\&\mathcal{H}=\mathcal{H}_0+\mathcal{H}_A+\mathcal{H}_E,\\&\mathcal{H}_0=\textstyle\sum_{k\sigma}\frac{1}{2}\{|\dot{\xi}_{k\sigma}|^2+\omega_{k\sigma}^2|\xi_{k\sigma}|^2\},\\&\omega_{k\sigma}^2=(\alpha/M_1M_1)\{M_1+M_2+(M_1-M_2)\sec 2\theta_{k\sigma}\},\\&\mathcal{H}_A=\frac{1}{3!}\sum_{k_1k_2k_3}\sum_{\sigma_1\sigma_2\sigma_3}V_{k_1\sigma_1k_2\sigma_2k_3\sigma_3}\xi_{k_1\sigma_1}\xi_{k_2\sigma_2}\xi_{k_3\sigma_3}\\&\qquad+\frac{1}{4!}\sum_{k_1k_2k_3k_4}\sum_{\sigma_1\sigma_2\sigma_3\sigma_4}V_{k_1\sigma_1k_2\sigma_2k_3\sigma_3k_4\sigma_4}\xi_{k_1\sigma_1}\xi_{k_2\sigma_2}\xi_{k_3\sigma_3}\xi_{k_4\sigma_4},\\&\mathcal{H}_E=eEN^{\frac{1}{2}}A_{01}\xi_{01},\\&V_{k_1\sigma_1k_2\sigma_2k_3\sigma_3}=\frac{\beta}{N^{\frac{1}{2}}}(A_{k_1\sigma_1}^*A_{k_2\sigma_2}^*A_{k_3\sigma_3}^*-A_{k_1\sigma_1}A_{k_2\sigma_2}A_{k_3\sigma_3})\\&\qquad\times\Delta(k_1+k_2+k_3),\\&V_{k_1\sigma_1k_2\sigma_2k_3\sigma_3k_4\sigma_4}\\&\quad=\frac{\epsilon}{N}(A_{k_1\sigma_1}^*A_{k_2\sigma_2}^*A_{k_3\sigma_3}^*A_{k_4\sigma_4}^*+A_{k_1\sigma_1}A_{k_2\sigma_2}A_{k_3\sigma_3}A_{k_4\sigma_4})\\&\qquad\times\Delta(k_1+k_2+k_3+k_4),\end{aligned} \tag{5}$$

where

$$\begin{aligned}&\Delta(k)=1,\quad k=0\ (\mathrm{mod}\ N),\\&\Delta(k)=0,\quad \text{otherwise.}\end{aligned} \tag{6}$$

Since this transformation diagonalizes the harmonic potential energy, we have the useful relations

$$A_{k\sigma_1}A_{-k\sigma_2}+A_{k\sigma_2}A_{-k\sigma_1}=0,\quad \sigma_1\neq\sigma_2 \tag{7}$$

and

$$|A_{k\sigma}|^2=\omega_{k\sigma}^2/(2\alpha). \tag{8}$$

We shall now modify the Hamiltonian expression by adding a new set of terms to H_0 and subtracting these same terms from H_A.

$$\begin{aligned}\mathcal{H}_0'&\equiv\mathcal{H}_0+\tfrac{1}{2}\sum_{k\sigma}\mathcal{A}_{k\sigma}\xi_{k\sigma}\xi_{-k\sigma},\\\mathcal{H}_A'&\equiv\mathcal{H}_A-\tfrac{1}{2}\sum_{k\sigma}\mathcal{A}_{k\sigma}\xi_{k\sigma}\xi_{-k\sigma}.\end{aligned} \tag{9}$$

For the time being the constants $\mathcal{A}_{k\sigma}$ are arbitrary positive numbers; they will be chosen later to make certain contributions to the perturbation expansion vanish. This trick is much akin to the renormalization used in field theory. The frequencies associated with H_0' are given by

$$\Omega_{k\sigma}^2=\omega_{k\sigma}^2+\mathcal{A}_{k\sigma}. \tag{10}$$

We now perform a canonical transformation to the new variables

$$\begin{aligned}C_{k\sigma}&=\frac{1}{2}\left(\xi_{k\sigma}+\frac{1}{i\Omega_{k\sigma}}\dot{\xi}_{k\sigma}\right)e^{-i\Omega_{k\sigma}t},\\C_{k\,-\sigma}&=\frac{1}{2}\left(\xi_{k\sigma}-\frac{1}{i\Omega_{k\sigma}}\dot{\xi}_{k\sigma}\right)e^{+i\Omega_{k\sigma}t}.\end{aligned} \tag{11}$$

This is accomplished by the transformation function

$$F=\sum_{k\sigma} i\Omega_{k\sigma}[2\xi_{k\sigma}C_{-k\sigma}e^{i\Omega_{k\sigma}t}-C_{k\sigma}C_{-k\sigma}e^{2i\Omega_{k\sigma}t}-\tfrac{1}{2}\xi_{k\sigma}\xi_{-k\sigma}]. \quad (12)$$

The momentum conjugate to the coordinate $C_{k\sigma}$ is $-2i\Omega_{k\sigma}C_{-k\,-\sigma}$. Consequently, if we make the definitions

$$\Omega_{k\,-\sigma}=-\Omega_{k\sigma},\quad A_{k\,-\sigma}=A_{k\sigma}, \quad (13)$$

both equations of motion will have the same form.[9]

$$\dot{C}_{k\sigma}=\frac{i}{2\Omega_{k\sigma}}\frac{\partial\mathcal{H}}{\partial C_{-k\,-\sigma}},\quad \dot{C}_{-k\,-\sigma}=\frac{i}{2\Omega_{-k\,-\sigma}}\frac{\partial\mathcal{H}}{\partial C_{k\sigma}}. \quad (14)$$

In terms of the new variables, the Hamiltonian is

$$\mathcal{H}_0'=0,$$

$$\mathcal{H}_E=eN^{\frac{1}{2}}E_0\sum A_{0\sigma}C_{0\sigma}\exp[i(\omega+\Omega_{0\sigma})t],$$

$$\mathcal{H}_A'=\frac{1}{3!}\sum V_{k_1\sigma_1k_2\sigma_2k_3\sigma_3}C_{k_1\sigma_1}C_{k_2\sigma_2}C_{k_3\sigma_3}\times\exp[i(\Omega_{k_1\sigma_1}+\Omega_{k_2\sigma_2}+\Omega_{k_3\sigma_3})t]$$
$$+\frac{1}{4!}\sum V_{k_1\sigma_1k_2\sigma_2k_3\sigma_3k_4\sigma_4}C_{k_1\sigma_1}C_{k_2\sigma_2}C_{k_3\sigma_3}C_{k_4\sigma_4}\times\exp[i(\Omega_{k_1\sigma_1}+\Omega_{k_2\sigma_2}+\Omega_{k_3\sigma_3}+\Omega_{k_4\sigma_4})t]$$
$$-\tfrac{1}{2}\sum \mathfrak{A}_{k\sigma}C_{k\sigma}(C_{-k\,-\sigma}+C_{-k\sigma}e^{2i\Omega_{k\sigma}t}). \quad (15)$$

The sums occurring here run over both positive and negative values of sigma. The equations of motion have the form

$$\dot{C}_{k\sigma}(t)=W_{k\sigma}(t),$$

$$W_{k\sigma}(t)=\frac{i}{2\Omega_{k\sigma}}\{-\delta_{k0}eN^{\frac{1}{2}}E_0A_{0\sigma}\exp[i(\omega-\Omega_{0\sigma})t]+\tfrac{1}{2}\sum V_{-k-\sigma\,k_1\sigma_1\,k-k_1\sigma_2}C_{k_1\sigma_1}(t)C_{k-k_1\sigma_2}(t)\exp[i(\Omega_{k_1\sigma_1}+\Omega_{k-k_1\sigma_2}-\Omega_{k\sigma})t]$$
$$+\tfrac{1}{3}!\sum V_{-k-\sigma\,k_1\sigma_1\,k_2\sigma_2\,k-k_1-k_2\sigma_3}C_{k_1\sigma_1}(t)C_{k_2\sigma_2}(t)C_{k-k_1-k_2\sigma_3}(t)\exp[i(-\Omega_{k\sigma}+\Omega_{k_1\sigma_1}+\Omega_{k_2\sigma_2}+\Omega_{k-k_1-k_2\sigma_3})t]$$
$$-\mathfrak{A}_{k\sigma}\{C_{k\sigma}(t)+C_{k\,-\sigma}(t)\exp(-2i\Omega_{k\sigma}t)\}\}. \quad (16)$$

We have used here the fact that, since the cubic expression is periodic in k_2 with period N, umklapp processes are treated properly if we eliminate the Δ function simply by placing $k_2=k-k_1$. In those cases where $k-k_1$ falls outside the first Brillouin zone, the expression will have the same value at this outside point as it has at the corresponding point in the first zone. The same argument also allows us to eliminate k_3 from the quartic terms.

The indefinite integral of this equation is

$$C_{k\sigma}(t)=C_{k\sigma}(0)+\int_0^t W_{k\sigma}(t_1)dt_1. \quad (17)$$

We are particularly interested in calculating $C_{0\sigma}$ because the polarization of the lattice is

$$P=eN^{\frac{1}{2}}\textstyle\sum_\sigma A_{0\sigma}C_{0\sigma}(t)e^{i\Omega_{0\sigma}t}. \quad (18)$$

In the harmonic lattice, $C_{0\sigma}$ behaves like an undamped harmonic oscillator closely coupled to the external field:

$$C_{0\sigma}=\eta_\sigma\exp[i(\omega-\Omega_{0\sigma})t],\quad \sigma=\pm1. \quad (19)$$

This same form will be assumed for the anharmonic lattice with the constant coefficient η_σ determined by the equation of motion. This procedure is justified by the fact that it is possible to find a consistent solution in this form. We shall see that obtaining this solution requires changing the unperturbed frequencies from $\omega_{k\sigma}$ to $\Omega_{k\sigma}$.

We solve Eq. (16) with $k=0$ putting in Eq. (19) for $C_{0\sigma}$ and substituting the expression given by Eq. (17) for the other $C_{k\sigma}$'s in the right-hand side. We obtain the $C_{k\sigma}$'s in the right-hand side of Eq. (17), except for $C_{0\sigma}$'s, by again substituting in the expression given by Eq. (17). Repeating this process indefinitely gives a type of iteration expansion. We will only study the first- and second-order terms of this expansion.

Each expression in the expansion contains a number of $C_{k\sigma}(0)$'s as factors. We shall assume that these quantities have the same statistical distribution that they would have in a harmonic lattice at this temperature. This implies that the $C_{k\sigma}(0)$'s for the various normal modes are independent of each other except for the relation $C_{k\sigma}(0)^*=C_{-k\,-\sigma}(0)$ and have random phases so that

$$\langle C_{k\sigma}(0)\rangle=0. \quad (20)$$

After the averaging is carried out, most of the terms in the sums over k and σ which occur in each expression of the perturbation expansion give a zero contribution. Only those terms survive in which each $C_{k\sigma}(0)$ is matched somewhere else in the expression by $C_{-k\,-\sigma}(0)$. The average of such a pair is

$$\langle C_{k\sigma}(0)C_{-k\,-\sigma}(0)\rangle=kT/2\Omega_{k\sigma}^2. \quad (21)$$

[9] Blackman's expressions appear to be missing the factor of 2 in the denominator as well as a minus sign. There are a number of other misprints in this paper. The formulas of Neuberger and Hatcher (reference 5), who review the Born and Blackman theory in a three-dimensional formalism, appear to agree with ours.

To keep track of the many combinations which arise in carrying out the iteration and pairing together the $C_{k\sigma}(0)$'s in the various possible ways, it is most convenient to draw diagrams. We shall represent the first-order cubic term,

$$\frac{i}{4\Omega_{0\sigma}}\int_0^t dt_1 \sum_{k_1\sigma_1} V_{0\sigma\; k_1\sigma_1\; -k_1\; -\sigma_1} \times C_{k_1\sigma_1}(0)C_{-k_1-\sigma_1}(0)e^{-i\Omega_{0\sigma}t_1}, \quad (22)$$

by the diagram denoted by 1 in Fig. 1. The dashed line is meant to indicate that the two $C_{k\sigma}(0)$'s are chosen so that their phases cancel. This type of term can only give a contribution to $C_{0\sigma}(t)$. By looking at the coefficient $V_{0\sigma\; k\sigma\; -k\; -\sigma}$, we find that this term is zero. The first-order quartic term for $C_{k\sigma}(t)$,

$$\frac{i}{4\Omega_{k\sigma}}\sum_{k_1\sigma_1} V_{-k\; -\sigma, k_1\sigma_1, -k_1\; -\sigma_1, k\sigma} \times \int_0^t dt_1\, C_{k_1\sigma_1}(0)C_{-k_1\; -\sigma_1}(0)C_{k\sigma}(0), \quad (23)$$

is represented by 7 in Fig. 1. The phase of $C_{k\sigma}(0)$ on the right-hand side is "balanced" by a similar phase in the left-hand side. This is expressed by drawing the corresponding dashed line up along the arrow.

Note that this quartic term contains a combinatorial factor of 3, since such a term is produced by choosing any one of 3 sets of indices to be k, and letting the other two be equal and opposite in sign. Similar factors arise in other terms.

The counterterm which we have introduced gives the first-order contribution

$$\mathfrak{A}_{k\sigma}C_{k\sigma}(0), \quad (24)$$

which will be represented by 8 in Fig. 1. We shall choose $\mathfrak{A}_{k\sigma}$ so that the contribution from the part of a diagram given by 1 in Fig. 2 is equal and opposite to the contribution of the part labeled 2 in Fig. 2. By this we mean that we want the following expression to be zero:

$$\int_0^t dt_1 \tfrac{1}{2}\sum_{k_1\sigma_1} V_{-k\; -\sigma\; k_1\sigma_1\; -k_1-\sigma_1\; k\sigma}C_{k_1\sigma_1}(0)C_{-k_1-\sigma_1}(0) \times[f_{k\sigma}(t)+f_{k\; -\sigma}(t)e^{-2i\Omega_{k\sigma}t}]$$

$$-\int_0^t dt_1\, \mathfrak{A}_{k\sigma}[f_{k\sigma}(t)+f_{k\; -\sigma}(t)e^{-2i\Omega_{k\sigma}t}]=0. \quad (25)$$

Note that this contains the whole contribution from the diagram fragment labeled 2 because

$$V_{-k\; -\sigma\; k_1\sigma_1\; -k_1-\sigma_1\; k\sigma_2}=0 \quad \text{unless} \quad |\sigma_2|=|\sigma|, \quad (26)$$

which follows from Eq. (7). The quantities $f_{k\sigma}(t)$ in this formula can be arbitrary functions; in practice they will be given by expressions in the iteration expansion.

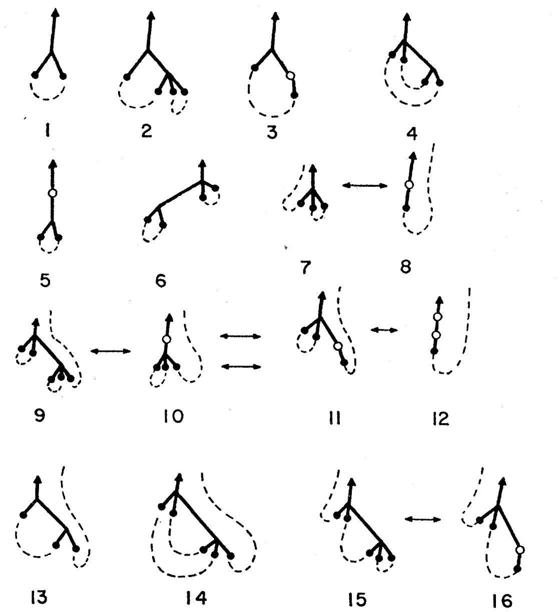

FIG. 1. Diagrams arising in the first and second orders of perturbation theory. Only 13 and 14 contribute to the final formulas.

The formula defines $\mathfrak{A}_{k\sigma}$ as

$$\mathfrak{A}_{k\sigma}\equiv\tfrac{1}{2}\sum_{k_1\sigma_1} V_{-k\; -\sigma\; k_1\sigma_1\; -k_1-\sigma_1\; k\sigma}|C_{k_1\sigma_1}(0)|^2. \quad (27)$$

In particular, with this definition, the first-order counterterm cancels the linear quartic contribution. Notice that this expression for the linear quartic contribution would introduce a first-order approximation for $C_{k\sigma}(t)$ *which is linear in t.* This behavior is not permissible in a theory which treats the system in the steady state. Such contributions do appear unless we eliminate them by introducing $\Omega_{k\sigma}$. This procedure removes all such terms from every order of the expansion and appears to be the best way of taking their effect into account. All the diagrams which arise in first and second order are shown in Fig. 1. Diagrams 1 through 6 are all zero. This can be shown by changing each index k to $-k$ and noting that the cubic anharmonicity has the property that

$$V_{-k_1\sigma_1\; -k_2\sigma_2\; -k_3\sigma_3}=-V_{k_1\sigma_1k_2\sigma_2k_3\sigma_3}, \quad (28)$$

so that each of these diagrams is equal to its own

FIG. 2. The two diagram parts which lead to a linear t dependence. The part labeled 1 is adjusted to be equal and opposite to the part labeled 2.

negative. The diagrams with double arrows between them yield terms which are equal in magnitude but opposite in sign, and therefore cancel each other. The two diagrams separated by 2 double arrows are equal, so they could be interchanged in the canceling procedure if desired. It is clear that as a result of this type of cancellation, we may drop all diagrams which contain parts of the type shown as 1 and 2 in Fig. 2, because any diagram containing one of these elements can equally well be drawn with the other. Two such terms always lie side by side in the expansion, canceling each other out.

The only two terms which must actually be considered in second order are those corresponding to diagrams 13 and 14 in Fig. 1. Thus to second order in the potential the expression for $\dot{C}_{0\sigma}(t)$ is

$$\begin{aligned}\dot{C}_{0\sigma}(t)=&\, i\eta_\sigma(\omega-\Omega_{0\sigma})\exp[i(\omega-\Omega_{0\sigma})t]=-ieN^{\frac{1}{2}}A_{0\sigma}E_0(2\Omega_{0\sigma})^{-1}\exp[i(\omega-\Omega_{0\sigma})t]\\ &-\sum_{k_1\sigma_1\sigma_2\sigma_3}\frac{|V_{0\,-\sigma\;k_1\sigma_1\;-k_1\sigma_2}|^2}{4\Omega_{0\sigma}\Omega_{k_1\sigma_1}}|C_{-k_1\sigma_2}(0)|^2\exp[i(-\Omega_{0\sigma}+\Omega_{k\sigma_1}+\Omega_{-k_1\sigma_2})t]\int_0^t dt_1\exp[i(\omega+\Omega_{k_1-\sigma_2}+\Omega_{-k_1-\sigma_1})t_1]\eta_{\sigma_3}\\ &-\sum\frac{|V_{0\,-\sigma\;k_1\sigma_1\;k_2\sigma_2\;-k_1-k_2\sigma_3}|^2}{8\Omega_{0\sigma}\Omega_{-k_1-k_2\sigma_3}}|C_{k_1\sigma_1}(0)|^2|C_{k_2\sigma_2}(0)|^2\eta_{\sigma_4}\int_0^t dt_1\exp[i(\omega+\Omega_{-k_1-\sigma_1}+\Omega_{-k_2-\sigma_2}+\Omega_{k_1+k_2-\sigma_3})t_1]\\ &\times\exp[-i(\Omega_{0\sigma}+\Omega_{-k_1-\sigma_1}+\Omega_{-k_2-\sigma_2}+\Omega_{k_1+k_2-\sigma_3})t].\end{aligned}\tag{29}$$

Hence the coupled equations we obtain for η_σ are

$$(\omega-\Omega_{0\sigma}-\gamma_\sigma)\eta_\sigma-\gamma_\sigma\eta_{-\sigma}=-eN^{\frac{1}{2}}A_{0\sigma}E_0/2\Omega_{0\sigma},\tag{30}$$

with γ_σ given by

$$\begin{aligned}\gamma_\sigma=&\sum\frac{1}{4\Omega_{0\sigma}\Omega_{k_1\sigma_1}}|V_{0\,-\sigma\;k_1\sigma_1\;-k_1\sigma_2}|^2|C_{k_1-\sigma_2}(0)|^2\frac{1-\exp[-i(\omega+\Omega_{-k\,-\sigma_1}+\Omega_{k_1-\sigma_2})t]}{\omega+\Omega_{-k_1-\sigma_2}+\Omega_{k_1-\sigma_2}}\\ &+\sum\frac{1}{8\Omega_{0\sigma}\Omega_{-k\,-k_2\sigma_3}}|V_{0\,-\sigma\;k_1\sigma_1\;k_2\sigma_2\;-k_1-k_2\sigma_3}|^2|C_{k_1\sigma_1}(0)|^2\\ &\times|C_{k_2\sigma_2}(0)|^2\frac{1-\exp[-i(\omega+\Omega_{-k_1-\sigma_1}+\Omega_{-k_2-\sigma_2}+\Omega_{k_1+k_2-\sigma_3})t]}{\omega+\Omega_{-k_1-\sigma_1}+\Omega_{-k_2-\sigma_2}+\Omega_{k_1+k_2-\sigma_3}}.\end{aligned}\tag{31}$$

The complex dielectric constant ϵ, which is the square of the complex index of refraction $n=n_r+ik$ is related to γ_σ by

$$\epsilon=(n_r+ik)^2=\epsilon_0-2\pi e^2N\omega_{01}^2\alpha^{-1}\times(\omega^2-\Omega_{01}^2-2\Omega_{01}\gamma_1)^{-1}.\tag{32}$$

The optical constants are determined by separating the real and imaginary parts of the equation and solving for n_r and k.

The first term in Eq. (31) is the cubic term studied by Blackman, but with the frequency $\omega_{k\sigma}$ appearing in his formula replaced by $\Omega_{k\sigma}$. The second term is the quartic contribution. The real part of γ_σ which we call $\Delta\omega_\sigma$ gives an additional frequency shift effect, and the imaginary part Γ_σ gives a damping constant, both of which are frequency dependent.

For each of the $|C_{k\sigma}(0)|^2$ factors we substitute its high-temperature thermal average as given by H_0'.

$$|C_{k\sigma}(0)|^2=kT/2\Omega_{k\sigma}^2.\tag{21'}$$

Using Eq. (8) we find that the thermal average of $\mathcal{A}_{k\sigma}$ is given by

$$\mathcal{A}_{k\sigma}=\frac{\epsilon kT}{8\alpha^2N}\sum_{k_1\sigma_1}\frac{\omega_{k\sigma}^2\omega_{k_1\sigma_1}^2}{\Omega_{k_1\sigma_1}^2},\tag{33}$$

putting $\mathcal{A}_{k\sigma}=b_{k\sigma}\omega_{k\sigma}^2$,

$$b_{k\sigma}=\frac{kT\epsilon}{8\alpha^2N}\sum_{k_1\sigma_1}\frac{1}{1+b_{k_1\sigma_1}}.\tag{34}$$

If $b_k=b$, a constant, we find

$$b=\frac{kT\epsilon}{2\alpha^2}\frac{1}{1+b},\quad\text{or}\quad b=\tfrac{1}{2}[-1+(1+2kT\epsilon/\alpha^2)^{\frac{1}{2}}].\tag{35}$$

Choosing the positive root of this equation for b gives us a consistent definition of $\mathcal{A}_{k\sigma}$.

The expressions given in Eq. (31) for the cubic and quartic contributions to γ_σ are not symmetric in the dummy summation indices, but can be made symmetric by adding together the various forms obtained by interchanging the labeling. Performing this process, introducing thermal averages for the $C_{k\sigma}(0)$'s, and simplifying, we obtain for the cubic term

$$\begin{aligned}\gamma_\sigma^{(3)}=&\frac{\omega_{0\sigma}\beta^2kT}{32N\alpha^3(1+b)^{\frac{5}{2}}}\sum_{k\sigma_1\sigma_2,}\sum_{|\sigma_1|\neq|\sigma_2|}\frac{\Omega_{k\,-\sigma_2}+\Omega_{-k\,-\sigma_1}}{\omega+\Omega_{k\sigma_2}+\Omega_{-k\sigma_1}}\\ &\times\{1-\exp[-i(\omega+\Omega_{k\sigma_1}+\Omega_{k\sigma_2})t]\},\end{aligned}\tag{36}$$

and for the quartic term

$$\gamma_\sigma^{(4)}=\frac{\omega_{0\sigma}\epsilon^2(kT)^2}{24N^2(2\alpha)^4(1+b)^{7/2}}\sum_{k_1k_2,\sigma_1\sigma_2\sigma_3}\frac{\omega_T\cos^2\vartheta_T}{\omega-\omega_T}\times\{1-\exp[-i(\omega-\omega_T)t]\},\quad(37)$$

where

$$\begin{aligned}\omega_T&=\Omega_{k_1\sigma_1}+\Omega_{k_2\sigma_2}+\Omega_{-k_1-k_2\sigma_3},\\ \vartheta_T&=\vartheta_{k_1\sigma_1}+\vartheta_{k_2\sigma_2}+\vartheta_{-k_1-k_2\sigma_3},\end{aligned}\quad(38)$$

with $\vartheta_{k\sigma}$ defined by

$$A_{k\sigma}=\frac{|\omega_{k\sigma}|}{(2\alpha)^{\frac{1}{2}}}\exp[i\vartheta_{k\sigma}].\quad(39)$$

It is understood in these expressions that we take the limit as t approaches infinity so that γ_σ is a constant independent of t. It can be shown that this can be done by giving ω a small negative imaginary part, $-i\kappa$, carrying out the time limit explicitly, and letting κ approach zero later in the calculation. Hence, we may write

$$\begin{aligned}\gamma_\sigma^{(3)}&=\frac{\omega_{0\sigma}\beta^2kT}{32\alpha^3(1+b)^{\frac{5}{2}}}\frac{1}{N}\times\sum_{k\sigma_1\sigma_2,|\sigma_1|\neq|\sigma_2|}\left[-1+\frac{\omega}{\omega+\Omega_{k\sigma_1}+\Omega_{-k\sigma_2}-i\kappa}\right],\\ \gamma_\sigma^{(4)}&=\frac{\omega_{0\sigma}\epsilon^2(kT)^2}{24(2\alpha)^4(1+b)^{7/2}}\{I+J\},\\ I&=-\frac{1}{N^2}\sum_{k_1k_2\sigma_1\sigma_2\sigma_3}\cos^2\vartheta_T,\\ J&=\frac{\omega}{N^2}\sum_{k_1k_2,\sigma_1\sigma_2\sigma_3}\frac{\cos^2\vartheta_T}{\omega-\omega_T-i\kappa}.\end{aligned}\quad(40)$$

For a macroscopic system, the sums over k in these expressions become integrals.

The cubic term gives[10]

$$\gamma_\sigma^{(3)}=-\frac{\omega_{0\sigma}\beta^2kT}{4\alpha^3(1+b)^{\frac{5}{2}}}+\frac{\omega_{0\sigma}\beta^2kT}{4\alpha^3(1+b)^{\frac{5}{2}}}\times\frac{\omega^2 i}{[(\omega_a^2-\omega^2)(\omega^2-\omega_b^2)]^{\frac{1}{2}}},\quad(41)$$

$$\omega_a^2=2\alpha(1+b)(M_1^{-\frac{1}{2}}+M_2^{-\frac{1}{2}})^2,$$
$$\omega_b^2=2\alpha(1+b)(M_1^{-\frac{1}{2}}-M_2^{-\frac{1}{2}})^2.$$

The sign of the square root is to be taken the same as that of ω. When ω is outside the interval of absorption, the second term is real, and the square root should be chosen with a positive sign above the region of absorption ($\omega^2>\omega_b^2$), and negative below it.

[10] Blackman calculated the imaginary part of this term but obtained a different answer. It appears that he made an error in his change of variable of integration.

It can be shown [see Eq. (44)] that the frequency dependence of the contribution to Γ_σ from this term is $\omega\rho_T(\omega)$, where $\rho_T(\omega)$ is the density of allowed transition frequencies having the value ω. The quartic contribution is more difficult to interpret because $\cos^2\vartheta_T$ is an extremely complicated function of k_1 and k_2. In general, we may expect $\cos^2\vartheta_T$ to have an average value of about $\frac{1}{2}$ on each curve of constant ω_T in the k_1, k_2 space. Since $\cos^2\vartheta_T$ varies from 0 to 1, this approximation can only fail seriously if some selection rule forces $\cos^2\vartheta_T=0$ for the whole curve at certain frequencies. We shall encounter this phenomenon later for special choices of the masses, but this does not appear to occur generally. When this approximation can be made, the quartic contribution to Γ_σ is proportional to $\omega\rho_T^{(4)}(\omega)$, where $\rho_T^{(4)}(\omega)$ is the density of allowed transition frequencies, ω_T having the value of ω. The quantity I in Eq. (40) gives only a constant frequency shift, therefore we will only discuss the effects arising from the J term.

For a macroscopic system each sum over values of k can be replaced by an integral. Because of the symmetry in the k's and σ's, many of the integrals which occur in the sums over branches in Eq. (40) are equal to each other. Hence, the expression may be reduced to a smaller number of unequal integrals.

First, we define $w_0(\varphi)$ by

$$\begin{aligned}w_0(\varphi)&=\Omega_2(\varphi),\quad 0\leq\varphi<\pi,\quad \varphi=\pi k/N\\ &=-\Omega_2(\varphi),\quad \pi\leq\varphi<2\pi\end{aligned}\quad(42)$$

$w_0(\varphi)$ is periodic with period 2π.

Although $\Omega_2(\varphi)$ must be periodic with the period π in the development of the theory in order that umklapp processes are taken into account properly, $w_0(\varphi)$ may be used to simplify the answer. In this way we may treat positive and negative acoustic frequencies together, effectively decreasing the number of branches from 4 to 3, and the number of integrals from 64 to 27. These can be expressed in terms of six integrals:

$$J=J^+(\omega-i\kappa)-J^+(-\omega+i\kappa),$$

$$\begin{aligned}J^+(x)=&\frac{1}{\pi^2}\int_0^{2\pi}d\varphi_1\int_0^{2\pi}d\varphi_2\frac{\cos^2\vartheta_T}{x+w_0+w_0+w_0}\\ &+\frac{1}{\pi^2}\int_0^{\pi}d\varphi_1\int_0^{\pi}d\varphi_2\frac{\cos^2\vartheta_T}{x+\Omega_1+\Omega_1+\Omega_1}\\ &+\frac{3}{\pi^2}\left[\int_0^{2\pi}d\varphi_1\int_0^{\pi}d\varphi_2\frac{\cos^2\vartheta_T}{x+w_0+\Omega_1+\Omega_1}\right.\\ &+\int_0^{2\pi}d\varphi_1\int_0^{2\pi}d\varphi_2\frac{\cos^2\vartheta_T}{x+w_0+w_0+\Omega_1}\\ &+\int_0^{\pi}d\varphi_1\int_0^{\pi}d\varphi_2\frac{\cos^2\vartheta_T}{x+\Omega_1+\Omega_{-1}+\Omega_1}\\ &\left.+\int_0^{2\pi}d\varphi_1\int_0^{\pi}d\varphi_2\frac{\cos^2\vartheta_T}{x+w_0+\Omega_{-1}+\Omega_1}\right].\end{aligned}\quad(43)$$

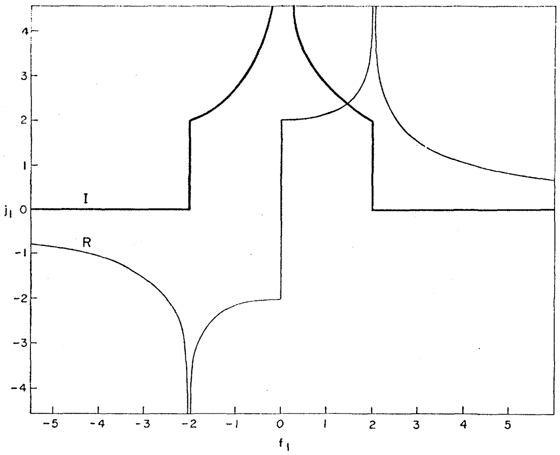

FIG. 3. Variation of Bj_1 with frequency, $f_1=(C+\omega)/B$. The imaginary part indicated by I is a measure of the absorption. The real part R gives a frequency shift.

The transformations which reduce the expression to this form are given in the Appendix.

Again, if $\cos^2\vartheta_T$ may be approximated by $\frac{1}{2}$, the imaginary part of each of these integrals becomes proportional to a density of combinations of states. It is possible to utilize the procedures developed by Van Hove[8] for the usual density of states of a crystal to deduce some of the qualitative behavior of the imaginary parts of these integrals. The denominator of any one of these integrals is in the form

$$x-\omega_T(k_1k_2)\pm i\kappa.$$

Since

$$\lim_{\kappa\to 0+}\frac{1}{x-\omega_T\pm i\kappa}=P\left(\frac{1}{x-\omega_T}\right)\mp i\pi\delta(x-\omega_T),$$

and

$$\int\delta\{x-\omega_T(k_1k_2)\}dk_1dk_2\equiv\rho_T(x), \tag{44}$$

we have that the imaginary part of each integral is proportional to a density of states. Van Hove has shown that the critical points of $\omega_T(k_1,k_2)$ represented as a surface over the (k_1,k_2) plane will give rise to singularities in the density of states. Using his arguments, we may expect each of these integrals to have at least one logarithmic singularity and two jump discontinuities, the first two jump discontinuities being located at the ends of the corresponding interval of absorption.

It is not difficult to find the exact locations and contributions of the critical points of the integral in which all three frequencies are acoustic. The critical points are determined by the equations

$$\begin{gathered}\partial w_0(\varphi_1)/\partial\varphi_1=\partial w_0(\varphi_2)/\partial\varphi_2=\partial w_0(\varphi_3)/\partial\varphi_3,\\ \varphi_1+\varphi_2+\varphi_3\equiv 0 \pmod{2\pi}.\end{gathered} \tag{45}$$

Since for this branch a given value of $\partial w_0/\partial\varphi$ is taken on only at the points φ and $2\pi-\varphi$, these equations can be solved easily to yield the three points

$$\begin{aligned}&1.\quad \varphi_1=\varphi_2=\varphi_3=2\pi/3,\\ &2.\quad \varphi_1=\varphi_2=\varphi_3=4\pi/3,\\ &3.\quad \varphi_1=\varphi_2=\varphi_3=0.\end{aligned} \tag{46}$$

The general theory of Van Hove[8] leads us to expect at least four critical points: one maximum, one minimum, and two saddle points. The first point proves to be a maximum, the second a minimum, and the origin is a multiple saddle point combining the two expected from the theory. The maximum and minimum do give jump singularities at the two ends of the absorption region, but the saddle point gives no singular contribution. The logarithmic singularity is absent in this case.

We shall now carry through a complete evaluation of J in the case when $M_2\ll M_1$, obtaining the behavior and effect of the real part as well as the imaginary part. The general case of arbitrary masses appears to be much too difficult even with $\cos^2\vartheta_T$ set equal to $\frac{1}{2}$, because of the complicated dependence of the frequencies on k. When the two masses are equal, the frequencies and $\cos^2\vartheta_T$ both have simple form, but complete evaluation in terms of standard functions still is not possible.

As M_2/M_1 becomes small, the acoustic and optic frequencies approach the limiting forms

$$\begin{aligned}w_0(\varphi)&\sim B\sin\varphi, & B&=[2\alpha(1+b)/M_1]^{\frac{1}{2}},\\ \Omega_1(\varphi)&\sim C, & C&=[2\alpha(1+b)/M_2]^{\frac{1}{2}},\end{aligned} \tag{47}$$

and the phase angles approach

$$\vartheta(\varphi)_{\pm 2}\sim\pi/2,\quad \vartheta(\varphi)_{\pm 1}\sim 0. \tag{48}$$

Consequently, $\cos^2\vartheta_T=0$ for each of the integrals which contains the acoustic branch an odd number of times. The quantity $J^+(x)$ reduces to

$$\begin{aligned}J^+(x)&=3j_1+3j_2+j_3,\\ j_1&=\frac{1}{\pi^2}\int_0^{2\pi}d\varphi_1\int_0^{2\pi}d\varphi_2\\ &\qquad\times\frac{1}{x+w_0(\varphi_1)+w_0(\varphi_2)+\Omega_1(\varphi_1+\varphi_2)},\\ j_2&=\frac{1}{\pi^2}\int_0^{\pi}d\varphi_1\int_0^{\pi}d\varphi_2\\ &\qquad\times\frac{1}{x+\Omega_1(\varphi_1)+\Omega_{-1}(\varphi_2)+\Omega_1(\varphi_1+\varphi_2)},\\ j_3&=\frac{1}{\pi^2}\int_0^{\pi}d\varphi_1\int_0^{\pi}d\varphi_2\\ &\qquad\times\frac{1}{x+\Omega_1(\varphi_1)+\Omega_1(\varphi_2)+\Omega_1(\varphi_1+\varphi_2)}.\end{aligned} \tag{49}$$

Evaluating the first integral, we obtain

$$
\begin{aligned}
j_1&=(8/\pi B f_1)K(4/f_1^2),\quad f_1>2,\\
j_1&=(4/\pi B)\{K(f_1^2/4)+iK([4-f_1^2]/4)\},\quad 0<f_1<2,\\
j_1&=(4/\pi B)\{-K(f_1^2/4)+iK([4-f_1^2]/4)\},\\
&\qquad\qquad -2<f_1<0, \qquad (50)\\
j_1&=-(8/\pi B f_1)K(4/f_1^2),\quad f<-2,
\end{aligned}
$$

where

$$f_1=(C+\omega)/B,$$

and K is the complete elliptic integral of the first kind, defined by

$$K(m)=\int_0^{\pi/2}(1-m\sin^2 u)^{-\frac{1}{2}}du. \qquad (51)$$

In this approximation the other two integrals give a δ-function absorption at the frequency of the optical branch and a δ-function absorption at a frequency three times as large. This absorption can be given a finite spread if we improve the approximation of the shape of the optical branch by including the next term in the expansion for the optical frequency. This improved approximation is

$$
\begin{aligned}
&\Omega_1(\varphi)\sim C'+D\cos 2\varphi,\\
&C'=[2\alpha(1+b)/M_2]^{\frac{1}{2}}[1+M_2/4M_1], \qquad (52)\\
&D=[\alpha M_2(1+b)/2]^{\frac{1}{2}}/2M_1,
\end{aligned}
$$

which gives for the second integral

$$j_2=-\frac{2}{\pi D[U+(U^2+V^2)^{\frac{1}{2}}]}K\left(1-\left[\frac{(U^2+V^2)^{\frac{1}{2}}-U}{(U^2+V^2)^{\frac{1}{2}}+U}\right]^2\right),\quad f_2<-\tfrac{1}{2}$$

$$j_2=\frac{2}{\pi D A^{\frac{1}{2}}}\left\{-2K\left(\frac{B}{A}\right)+iK\left(\frac{A-B}{A}\right)\right\},\quad -\tfrac{1}{2}<f_2<0$$

$$j_2=\frac{2}{\pi D(B-A)^{\frac{1}{2}}}\left\{K\left(\frac{B}{B-A}\right)+iK\left(\frac{A}{A-B}\right)\right\},\quad 0<f_2<4$$

$$j_2=\frac{2}{\pi D B^{\frac{1}{2}}}K\left(\frac{B-A}{B}\right),\quad 4<f_2$$

where

$$
\begin{aligned}
f_2&=(\omega+C+D)/D,\\
A&=2f_2+2-f_2^2+2(2f_2+1)^{\frac{1}{2}},\\
B&=2f_2+2-f_2^2-2(2f_2+1)^{\frac{1}{2}},
\end{aligned}
$$

and with U and V defined by

$$(U\pm Vi)^2=(2f_2+2-f_2^2)\pm 2(-2f_2-1)^{\frac{1}{2}}i. \qquad (53)$$

The integral j_3 is obtained from the above formulas by a substitution.

$$j_3=-[j_2(-f_3)]^*,\quad f_3=(\omega+3C-D)/D. \qquad (54)$$

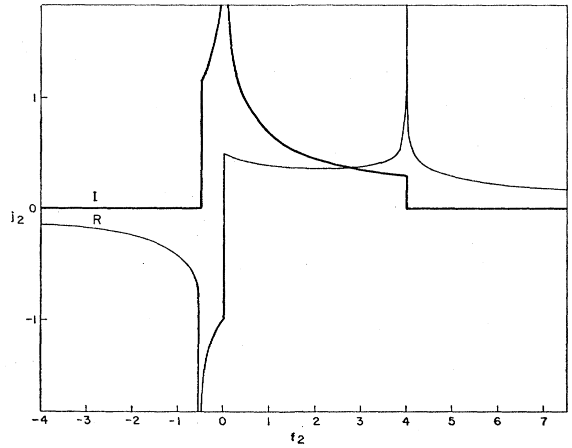

FIG. 4. Variation of Dj_2 with frequency, $f_2=(\omega+C+D)/D$. The imaginary part indicated by I is a measure of the absorption. The real part R gives a frequency shift.

We graph the behavior of j_1, j_2, and j_3 in Figs. 3, 4, and 5, giving both the imaginary part I, which is a measure of the absorption, and the real part R, which is a "small" frequency shift. Since the mass of the light atom is much less than that of the heavy atom, the frequencies of absorption from these three contributions will not overlap. To obtain $-J^+(-\omega+i\kappa)$ from the sum of the three j's, we must put in $-\omega$ for ω and change the signs of all the real parts. Adding together $J^+(\omega-i\kappa)$ and $-J^+(-\omega+i\kappa)$, we obtain the same absorption at positive and negative frequencies, but the real part has opposite sign for negative frequencies. The real part in any one of the regions of absorption will arise mainly from the same integral giving the absorption so that the R curve and I curve in each of the figures give essentially the real part and imaginary part of J in this region.

The frequency shift given by the real part makes a finite jump where the imaginary part becomes loga-

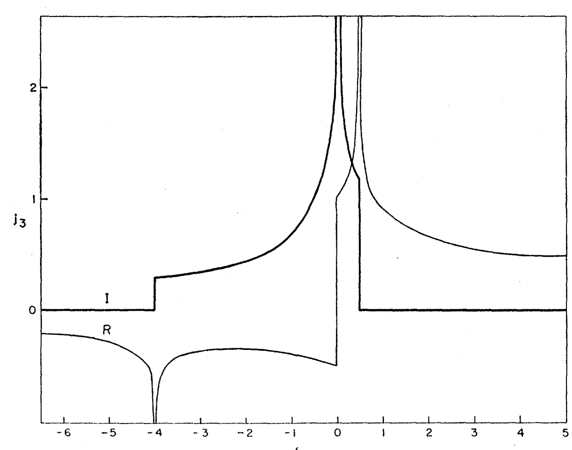

FIG. 5. Variation of Dj_3 with frequency, $f_3=(\omega+3C-D)/D$. The imaginary part indicated by I is a measure of the absorption. The real part R gives a frequency shift.

rithmically infinite. The effect of this behavior is to spread the point of infinite absorption over a finite spread of frequencies, and perhaps reduce it to a finite maximum. In the reverse situation, when the imaginary part makes a finite jump and the real part, which is otherwise small, becomes logarithmically infinite, the net effect is not so clear, but is probably to round out the corners of the jump. In three dimensions this singular behavior does not occur (see below).

III. THREE-DIMENSIONAL LATTICES

It is quite clear that the quartic contribution in the three-dimensional problem can be obtained by these same methods and would certainly yield a T^2 dependence for the damping constant. The relatively good agreement between this theoretical result and the experimental infrared data[1] for sodium chloride at high temperatures is evidence for the importance of the quartic anharmonic terms.

However, a number of the simplifying features of the one-dimensional problem do not carry over to three dimensions. In the general problem, shifting the frequencies to take into account the first-order quartic effect requires a more general set of quadratic counterterms since Eq. (7) no longer can be used. The result is that the optical and acoustic branches will be mixed together in obtaining the new frequencies $\Omega_{k\sigma}$. This could cause additional weak maxima due to failure of selection rules true for the unperturbed problem.

We should also point out that we cannot be sure that the absorption is as much a direct display of the density of transition frequencies as in the one-dimensional problem since we made express use of Eq. (8) and other special relations to reduce the frequency dependence of Eq. (31) to Eq. (36) and Eq. (37).

In any case the density of transition frequencies of a three-dimensional lattice does not have the singularities obtained in the one-dimensional model. The transition frequency ω_T for the cubic terms in three dimensions depends upon the three components of k, and the arguments of Van Hove show that in this case the critical points give rise to discontinuities in the first derivative of the density of frequencies rather than in the density function itself. The density of frequencies relevant to the quartic terms is determined from a transition frequency which depends on six k components, so that the singular behavior arising from the critical points lies in even higher derivatives of $\rho_T(\omega)$. On the other hand, we may expect that subsidiary maxima in the absorption arise from areas of the $\omega_T(k,k)$ surface which are relatively flat so that many (k,k) points give transition frequencies of nearly the same value. The critical points should occur near such flat areas if these areas exist, and a subsidiary peak should be very likely when the transition frequencies of two or more of the critical points happen to be near each other.

APPENDIX

We readily establish the relations

$$\begin{aligned} w_0(\varphi+\pi)&=-w_0(\varphi),\\ w_0(\pi-\varphi)&=w_0(\varphi),\\ \Omega(\pi-\varphi)&=\Omega(\varphi), \end{aligned} \tag{A1}$$

using the definition of $w_0(\varphi)$ and a symmetry of the frequency functions.

We shall consider in detail only the subset of terms for which all three of the σ's refer to the acoustic branch, the other integrals are handled similarly. The set of terms to be considered can be written as

$$J_{AAA}=\frac{1}{4\pi^2}\int_0^{2\pi}d\varphi_1\int_0^{2\pi}d\varphi_2 \times\sum_{\pm}\frac{\cos^2\vartheta_T}{\omega\pm\Omega_{(2)}(\varphi_1)\pm\Omega_{(2)}(\varphi_2)\pm\Omega_{(2)}(\varphi_1+\varphi_2)-i\kappa}, \tag{A2}$$

where the sum is over all combinations of plus and minus signs. The range of integration has been extended to two periods in each of the integration variables, and the effect of this change has been balanced out by dividing the result by 4. It is immediately clear that this expression is equal to

$$J_{AAA}=\frac{1}{4\pi^2}\int_0^{2\pi}d\varphi_1\int_0^{2\pi}d\varphi_2 \times\sum_{\pm}\frac{\cos^2\vartheta_T}{\omega\pm w_0(\varphi_1)\pm w_0(\varphi_2)\pm w_0(\varphi_1+\varphi_2)-i\kappa} \tag{A3}$$

because we sum over all choices of the $+$ and $-$ signs anyway. The potential and thus $\cos^2\vartheta_T$ is independent of the signs of the branch indices and, therefore, is unaffected by the transformations we are considering.

We can now show that all eight integrals obtained by choosing different combinations of the signs in Eq. (A3) are equal. Since each term in the integrand is periodic with a period of 2π in the integration variables, we are free to translate either variable by a constant and still integrate between the same limits. Making the change $\varphi_2'=\varphi_2+\pi$, we note that

$$\int_0^{2\pi}d\varphi_2\sum_{\pm}\frac{\cos^2\vartheta_T}{\omega\pm w_0(\varphi_1)+w_0(\varphi_2)\pm w_0(\varphi_1+\varphi_2)-i\kappa} =\int_0^{2\pi}d\varphi_2\sum_{\pm}\frac{\cos^2\vartheta_T}{\omega\pm w_0(\varphi_1)-w_0(\varphi_2)\mp w_0(\varphi_1+\varphi_2)-i\kappa}. \tag{A4}$$

This shows that we need only consider the plus sign in front of $w_0(\varphi_2)$ and include the contributions from the terms with the negative sign by multiplying the result by 2. By applying the same transformation to φ_1 in this new expression, we find that we may also limit

consideration to one of the signs in front of $w_0(\varphi_1)$ and multiply this result by 2. Finally, the transformation

$$\varphi_1'=\pi-\varphi_1,\quad \varphi_2'=\pi-\varphi_2,$$
$$w_0(\varphi_1+\varphi_2)=w_0(2\pi-\varphi_1'-\varphi_2')=w_0(\pi+[\pi-\varphi_1'-\varphi_2'])$$
$$=-w_0(\pi-\varphi_1-\varphi_2)=-w_0(\varphi_1+\varphi_2) \tag{A5}$$

shows that the terms with the two different signs in front of $w_0(\varphi_1+\varphi_2)$ give the same contribution. We may write the result as

$$J_{AAA}=\frac{2}{\pi^2}\int_0^{2\pi}d\varphi_1\int_0^{2\pi}d\varphi_2 \times\frac{\cos^2\vartheta_T}{\omega+w_0(\varphi_1)+w_0(\varphi_2)+w_0(\varphi_1+\varphi_2)-i\kappa}. \tag{A6}$$

The integrals containing three optic frequencies obviously need not be transformed. The remaining integrals which we have not considered separate into two groups, those containing a single acoustic frequency and two optic frequencies, and those containing two acoustic frequencies and one optic. Each of these groups can be handled by the same technique.

The original frequency denominators have the symmetrical form

$$\omega-\Omega_{\sigma_1}(\varphi_1)-\Omega_{\sigma_2}(\varphi_2)-\Omega_{\sigma_3}(\varphi_3)-i\kappa, \tag{A7}$$

with the condition

$$\varphi_1+\varphi_2+\varphi_3=0. \tag{A8}$$

Consequently, the terms which differ only in the arrangement of acoustic and optic frequencies in the denominator yield the same contribution. We may divide the integrals into three sets:

$$\begin{array}{rl} \text{set I,} & \sigma_1=\sigma_2=\sigma_3; \\ \text{set II,} & \sigma_1=\sigma_2\neq\sigma_3,\quad \sigma_1\neq\sigma_2=\sigma_3,\quad \sigma_1=\sigma_3\neq\sigma_2; \\ \text{set III,} & \sigma_1\neq\sigma_2\neq\sigma_3. \end{array} \tag{A9}$$

Set I contains three unequal integrals, set II contains six unequal integrals, each repeated three times, and set III contains one integral which is repeated six times.

Another symmetry enables us to reduce the number of integrals to be studied still further. We notice in the original expression that $-J(-\omega+i\kappa)$ has the same form as $J(\omega-i\kappa)$ with the signs of each of the $\Omega_{k\sigma}$ reversed. If we define J^+ to be similar to the original expression but with a definite one of the frequencies always chosen positive, then we may generate the entire expression by the formula

$$J=J(\omega-i\kappa)=J^+(\omega-i\kappa)-J^+(-\omega+i\kappa). \tag{A10}$$

This same procedure may be adapted to the modified expressions obtained by introducing $w_0(\varphi)$, the main difference being that we introduce the contribution of Eq. (A6) into J^+, omitting the factor of 2 which appears in Eq. (A6). We obtain for J^+ the expression given in Eq. (43).