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TEMPERATURE DEPENDENCE OF THE LINE WIDTH OF RESONANCE ABSORPTION BY THE LATTICE OF IONIC CRYSTALS

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A quantum theory of the line width of resonance absorption by ionic crystal lattices is developed, taking into account third and fourth order anharmonic terms. An analysis of the vibrational spectra of diatomic ionic crystals indicates that the contribution of fourth-order anharmonic terms may be comparable to that of third-order terms.

1. INTRODUCTION

THE method recently proposed by Heilmann[1] for determining the optical constants associated with lattice vibrations in ionic crystals has made possible the determination of the temperature dependence of the line width of resonance absorption. It has been found for LiF at high temperatures $T > \Theta$ (Θ is the Debye temperature) the line width is $\Gamma \sim T^2$,[1] whereas for NaCl the exponent of the temperature is close to $^3/_2$.[2]

This raises the problem of the theoretical interpretation of the temperature dependence of Γ and its difference in these crystals. Born and Blackman[3] developed a classical theory for the line width, taking account of third-order anharmonicity, and obtained the result $\Gamma \sim T$. Jepsen and Wallis[4] showed that fourth-order anharmonicity gives, in the classical case, $\Gamma \sim T^2$. However, there has been no satisfactory interpretation of experiment, since the conditions have not been made clear under which anharmonicity of the fourth order can be comparable to that of third order.

A quantum theory of line width for third-order anharmonicity has been developed in several papers[5-7] and has led to a result that gives $\Gamma \sim T$ in the high-temperature classical limit. The purpose of this paper is to develop a quantum theory taking into account both third-order and fourth-order anharmonicity and discuss the conditions under which one or the other mechanism of line broadening predominates.

2. CONNECTION BETWEEN ELECTRICAL CONDUCTIVITY AND PHONON GREEN FUNCTIONS

Let us consider an ionic crystal in the field of an electromagnetic wave $\mathbf{E} = \mathbf{E}^0 e^{i(\mathbf{kx}-\omega t)}$, $\mathbf{E}^0 = i\omega c^{-1}\mathbf{A}^0$, where $\mathbf{A}^0$ is the amplitude of the vector potential (the scalar potential can be taken as zero). In the presence of the perturbation

$$\mathcal{H}^t_{int} = -c^{-1}\int d\mathbf{x} J_\mu(\mathbf{x})\, A_\mu(\mathbf{x}t) \tag{1}$$

the departure of the distribution function for lattice vibrations from equilibrium[8] has the form

$$F(t) = -\frac{i}{\hbar}\int_{-\infty}^{0} d\tau\, [\mathcal{H}^{t+\tau}_{int}(\tau),\, F_0]. \tag{2}$$

Here

$$\mathcal{H}^{t+\tau}_{int}(\tau) = \exp\{iH\tau/\hbar\}\, \mathcal{H}^{t+\tau}_{int} \exp\{-iH\tau/\hbar\},$$

F_0 is the equilibrium distribution function, H is the total Hamiltonian of the system, and the square brackets indicate the commutator.

The Fourier component of the current

$$J_\nu(\mathbf{k}) = V^{-1}\int d\mathbf{x}\, e^{-i\mathbf{kx}} J_\nu(\mathbf{x}) \tag{3}$$

has the mean value

$$\langle J_\nu(\mathbf{k})\rangle = \mathrm{Sp}\,\{F(t)\, J_\nu(\mathbf{k})\}$$
$$= E^0_\mu e^{-i\omega t}\frac{V}{\hbar\omega}\int_{-\infty}^{0} d\tau\, e^{-i\omega\tau}\, \mathrm{Sp}\,\{F_0\, [J_\nu(\mathbf{k}, 0),\, J_\mu(-\mathbf{k}, \tau)]\}, \tag{4}$$

where V is the volume of the crystal.

The density of current associated with the movement of ions,

$$\mathbf{J}(\mathbf{x}) = \sum_{ls} e_s \mathbf{v}_{ls}\delta(\mathbf{x} - \mathbf{r}_l). \tag{5}$$

Here l is the number of the unit cell and s the number of the ion in the cell; e_s is the effective charge of the s-th ion, $\mathbf{v}_{ls}$ is the velocity of the ion, and $\mathbf{r}_l$ is the equilibrium coordinate of the ion (for long-wave vibrations the quantities $\mathbf{r}_{ls}$ can be considered as independent of s). In Eq. (5) we retain only the linear term of the expansion of ionic current in the displacements; higher terms of this expansion lead to continuous absorption associated with moments of higher orders.

Transforming to the normal coordinates of the lattice vibrations, we set

$$\mathbf{v}_{ls} = \dot{\mathbf{x}}_{ls} = -\left(\frac{v_0}{V}\right)^{1/2} \sum_{\mathbf{q}j} (\hbar/2M\omega_{j\mathbf{q}})^{1/2} i\omega_{j\mathbf{q}} Q_{j\mathbf{q}} \xi_{sj}(\mathbf{q})\, e^{i\mathbf{q}\mathbf{r}_l}. \quad (6)$$

Here $\mathbf{x}_{ls}$ is the displacement of the ion from its equilibrium position; v_0 and M are the volume and mass of the unit cell; $\omega_{j\mathbf{q}}$ is the frequency of the lattice vibration branch j with wave vector **q**; $Q_{j\mathbf{q}}$ is the normal coordinate; $\xi_{sj}(\mathbf{q})$ is a complex polarization vector satisfying the condition $\xi_{sj}(\mathbf{q}) = \xi^*_{sj}(-\mathbf{q})$.

Substituting Eq. (6) into Eq. (4) and keeping in mind that $\langle J_\nu \rangle = \sigma_{\nu\mu} E_\mu$, we obtain

$$\sigma_{\nu\mu} = -\frac{i\hbar}{\omega} \sum_{jj'} B^{\nu\mu}_{jj'} D_{jj'}(\omega). \quad (7)$$

Here

$$B^{\nu\mu}_{jj'} = \frac{1}{2Mv_0} (\omega_{j0}\omega_{j'0})^{1/2} \sum_{ss'} e_s e_{s'} \xi^\nu_{sj} \xi^\mu_{s'j'} \quad (8)$$

is the aggregate of lattice constants that form tensors with the dimensionality and order of magnitude of ω_0^3; the quantity

$$D_{jj'}(\omega) = \frac{1}{i\hbar} \int_{-\infty}^{0} d\tau\, e^{-i\omega\tau}\, \mathrm{Sp}\,\{F_0 [Q_{j0}, Q_{j'0}(\tau)]\} \quad (9)$$

is the Fourier transform of the retarded Green's function of the phonons. In Eqs. (8) and (9) the frequencies ω_{j0}, the polarizations $\xi_{sj}(0)$, and the normal coordinates Q_{j0} are taken for $\mathbf{k} = 0$, since in our case $\mathbf{k}\cdot\mathbf{a} \ll 1$ (**a** is the lattice parameter).

It can be shown[9] that the Lehman expansion over the states of the exact Hamiltonian H for (9) is the same as the Lehman expansion of the quantity

$$D_{jj'}(\omega_\nu) = \int_0^\beta d\lambda\, e^{i\omega_\nu \hbar\lambda}\, \mathrm{Sp}\,\{F_0 T_\lambda Q_{j0} Q_{j'0}(\lambda)\}, \quad (10)$$

if ω_ν is replaced in the latter expansion by $-i\omega$, thus achieving analytic continuation. Here $\omega_\nu = 2\pi\nu/\hbar\beta$, where ν runs over integral values and $\beta = T^{-1}$.

We introduce in the usual way the phonon creation and annihilation operators: $Q_{j\mathbf{k}} = b_{j\mathbf{k}} + b^+_{j-\mathbf{k}}$. Then it is easy to show that in the absence of interaction between the phonons Eq. (10) coincides with the temperature Green functions of free phonons[9] and after analytic continuation it is found to equal

$$D^0_{jj'}(\omega) = \hbar^{-1}\{(\omega + \omega_{j0} + i\delta)^{-1} - (\omega - \omega_{j0} + i\delta)^{-1}\}\,\delta_{jj'}. \quad (11)$$

The real part of the conductivity, which determines the absorption, is

$$\mathrm{Re}\,\sigma_{\nu\mu} = \frac{\pi}{\omega} \sum_j B^{\nu\mu}_j\, \delta(\omega - \omega_{j0}). \quad (12)$$

Thus we have obtained resonance absorption at a frequency equal to the limiting frequency of optical vibrations. To find the width of this resonance peak, it is necessary to consider the phonon interactions. This leads to renormalization of the phonon Green's function (11).

3. LINE WIDTH OF RESONANCE ABSORPTION

For our estimates, three- and four-phonon interactions can be written in the form

$$H_3 = E_3 \frac{V}{v_0} \left(\frac{\hbar}{2Ma^2} \frac{v_0}{V}\right)^{3/2} \sum (\omega_{j\mathbf{q}} \omega_{j_1\mathbf{q}_1} \omega_{j_2\mathbf{q}_2})^{-1/2} \times (b_{j\mathbf{q}} + b^+_{j-\mathbf{q}})(b_{j_1\mathbf{q}_1} + b^+_{j_1-\mathbf{q}_1})(b_{j_2\mathbf{q}_2} + b^+_{j_2-\mathbf{q}_2}), \quad (13)$$

$$H_4 = E_4 \frac{V}{v_0} \left(\frac{\hbar}{2Ma^2} \frac{v_0}{V}\right)^{2} \sum (\omega_{j\mathbf{q}} \omega_{j_1\mathbf{q}_1} \omega_{j_2\mathbf{q}_2} \omega_{j_3\mathbf{q}_3})^{-1/2} \times (b_{j\mathbf{q}} + b^+_{j-\mathbf{q}})(b_{j_1\mathbf{q}_1} + b^+_{j_1-\mathbf{q}_1})(b_{j_2\mathbf{q}_2} + b^+_{j_2-\mathbf{q}_2})(b_{j_3\mathbf{q}_3} + b^+_{j_3-\mathbf{q}_3}). \quad (14)$$

The summation is carried out in H_3 over $j\mathbf{q}$, $j_1\mathbf{q}_1$, and $j_2\mathbf{q}_2$ with the condition that $\mathbf{q} + \mathbf{q}_1 + \mathbf{q}_2 = \mathbf{K}$, and in H_4 over $j\mathbf{q}$, $j_1\mathbf{q}_1$, $j_2\mathbf{q}_2$, and $j_3\mathbf{q}_3$, with the condition $\mathbf{q} + \mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 = \mathbf{K}$. Here **K** is the reciprocal lattice vector; E_3 and E_4 are characteristic energies on the atomic scale.

As Born and Kun Huang have shown,[10] the interaction of five phonons is comparable in order of magnitude to the departure from the adiabatic approximation. It cannot be handled in the framework of adiabatic theory, and in those cases in which it is significant, a special investigation is required.

In the presence of phonon interaction we can write for $D_{jj_1}(\omega_\nu)$ Dyson's equation[9]

$$D_{jj_1} = D^0_j \delta_{jj_1} + \sum_{j_2} D^0_j \Pi_{jj_2} D_{j_2 j_1}, \quad (15)$$

where Π_{jj_2} is the polarization operator.

In each approximation of perturbation theory, the diagrams corresponding to the diagonal terms $\Pi_{jj} \equiv \Pi_j$ contain resonance denominators in the highest power. The most important diagrams near resonance consist of a geometrical progression with the denominators of $\Pi_j D^0_j$. Summing the progression and fulfilling analytical continuity, we obtain

$$D_{jj'}(\omega) = \frac{D^0_j}{1 - \Pi_j D^0_j} = -\frac{1}{i\hbar(\omega - \omega_{j0}) + \Pi_j}, \quad (16)$$

and

$$\operatorname{Re}\sigma_{\nu\mu} = \frac{\hbar}{\omega}\sum_j B_j^{\nu\mu}\frac{\operatorname{Im}\Pi_j}{\hbar^2(\omega-\omega_{j0})^2+(\operatorname{Im}\Pi_j)^2}. \tag{17}$$

Here ω_{j0} represents the lattice vibration frequency renormalized to the magnitude of $\operatorname{Re}\Pi_j$; $\operatorname{Im}\Pi_j \equiv \Gamma_j$ gives the line width of this resonance absorption.

For a three-phonon interaction, Π_j is determined by the diagram shown in Fig. 1. Carrying out the calculation according to the known rules,[9] we obtain

$$\begin{aligned}\Gamma_j^3 \equiv \operatorname{Im}\Pi_j^3\,(\omega_{j0}) &= E_3^2\left(\frac{\hbar}{2Ma^2}\right)^3\frac{v_0}{8\pi^2\hbar}\sum_{j_1j_2}\int d^3\mathbf{q}\,(\omega_{j0}\omega_{j_1\mathbf{q}}\omega_{j_2\mathbf{q}})^{-1}\\ &\times\{[(N_{j_1}+1)(N_{j_2}+1)-N_{j_1}N_{j_2}]\,\delta\,(\omega_{j0}-\omega_{j_1\mathbf{q}_1}-\omega_{j_2\mathbf{q}})\\ &+2\,[(N_{j_2}+1)\,N_{j_1}-N_{j_2}\,(N_{j_1}+1)]\,\delta\,(\omega_{j0}+\omega_{j_1\mathbf{q}}-\omega_{j_2\mathbf{q}})\}.\end{aligned} \tag{18}$$

Here $N_j(\mathbf{q})$ is the equilibrium number of phonons. At high temperatures $T \gg \Theta$, $N_j(\mathbf{q}) \approx T/\hbar\omega_{j\mathbf{q}}$ and the line width varies linearly with temperature.[4-6] In the case of fourth-order anharmonicity, the diagram in Fig. 2 gives a contribution to $\operatorname{Im}\Pi_j$. The result of the calculation is

$$\begin{aligned}\Gamma_j^4 &\equiv \operatorname{Im}\Pi_j^4(\omega_{j0})\\ &= E_4^2\left(\frac{\hbar}{2Ma^2}\right)^4\frac{v_0^2}{64\pi^5\hbar}\sum_{j_1j_2j_3}\int d^3\mathbf{q}_1 d^3\mathbf{q}_2\,(\omega_{j0}\omega_{j_1\mathbf{q}_1}\omega_{j_2\mathbf{q}_2}\omega_{j_3(\mathbf{q}_1+\mathbf{q}_2)})^{-1}\\ &\times\{[(N_{j_1}+1)(N_{j_2}+1)(N_{j_3}+1)\\ &-N_{j_1}N_{j_2}N_{j_3}]\,\delta\,(\omega_{j0}-\omega_{j_1\mathbf{q}_1}-\omega_{j_2\mathbf{q}_2}\\ &-\omega_{j_3(\mathbf{q}_1+\mathbf{q}_2)})+3\,[(N_{j_1}+1)(N_{j_2}+1)\,N_{j_3}\\ &-N_{j_1}N_{j_2}\,(N_{j_3}+1)]\,[\delta\,(\omega_{j0}-\omega_{j_1\mathbf{q}_1}-\omega_{j_2\mathbf{q}_2}+\omega_{j_3(\mathbf{q}_1+\mathbf{q}_2)})\\ &-\delta\,(\omega_{j0}+\omega_{j_1\mathbf{q}_1}+\omega_{j_2\mathbf{q}_2}-\omega_{j_3(\mathbf{q}_1+\mathbf{q}_2)})]\}.\end{aligned} \tag{19}$$

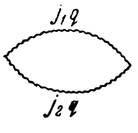

FIG. 1

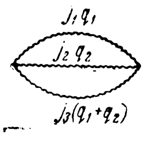

FIG. 2

In the high-temperature limit $\Gamma^4 \sim T^2$, in agreement with the classical calculation.[4]

4. DISCUSSION OF RESULTS

In order to explain the observed temperature dependence of the line width it is necessary to compare the contributions of Γ^3 and Γ^4. In the high-temperature limit the order of magnitude of Γ^3 and Γ^4 can be determined from Eqs. (18) and (19) by the expressions

$$\Gamma^3/\hbar\widetilde{\omega} \approx C^3\,(E_3/\hbar\widetilde{\omega})^2\,(\hbar/M\widetilde{\omega}a^2)^3\,T/\hbar\widetilde{\omega}, \tag{20}$$

$$\Gamma^4/\hbar\widetilde{\omega} \approx C^4\,(E_4/\hbar\widetilde{\omega})^2\,(\hbar/M\widetilde{\omega}a^2)^4\,(T/\hbar\widetilde{\omega})^2, \tag{21}$$

and their ratio can be written in the form

$$\Gamma^4/\Gamma^3 \approx (C^4/C^3)\,(\hbar/M\widetilde{\omega}a^2)\,(T/\hbar\widetilde{\omega}). \tag{22}$$

Here $\widetilde{\omega}$ is a kind of effective frequency that depends on the integration interval specified by the conservation laws in (18) and (19). C^3 and C^4 are numerical factors that take into account the number of combinations of the branches of the vibrational spectrum of the lattice and the effective volumes in the momentum space of the phonons over which the conservation laws are satisfied. A quantitative estimate of these factors requires a calculation using the entire vibrational spectrum of the crystal. We shall not do this, but limit ourselves to approximate semi-quantitative considerations, which will demonstrate the comparability of Γ^3 and Γ^4, even though they are determined by different approximations of the interaction.

It is obvious that C^4 is always larger than C^3, since Γ^4 contains a much larger number of combinations of branches of the lattice spectrum and a larger volume of integration in the momentum space of the phonons. We reduce the ratio of C^4 to C^3 if we consider only the first circumstance. However, it turns out that even this is sufficient to show that Γ^4 and Γ^3 are comparable.

For anharmonicity of the $(n+1)$-st order the conservation laws appearing in $\Gamma^{(n+1)}(\omega_0)$ can be written as: $\omega_0 = \pm\omega_1 \pm \omega_2 \ldots \pm \omega_n$, where the frequencies $\omega_1 \ldots \omega_n$ can belong to different branches of the vibrational spectrum. For diatomic crystals the number of branches equals six and hence the total number of combinations of these branches and the signs $(\pm)$ in the conservation laws is

$$C^{n+1} = (2^n-1)\,6^n \approx 12^n, \tag{23}$$

and the ratio $C^{n+1}/C^n \approx 12$. If for an estimate we take the square of the relative amplitude of the lattice vibrations $\hbar/M\widetilde{\omega}a^2 \sim 10^{-3}$, then $\Gamma^{n+1}/\Gamma^n \sim 10^{-2}T/\hbar\widetilde{\omega}$. From this it is seen that anharmonicities of high orders must make a small contribution to the line width, in agreement with the adiabatic approximation.

This estimate, however, turns out to be inapplicable to the comparison of anharmonicities of fourth and third orders. Actually conservation laws reduce the "statistical weight" C^3 of anharmonic terms of the third order to a greater degree than the "statistical weight" of anharmonic terms of the fourth order and the "statistical weights" of higher order anharmonicities.

We shall make a very rough estimate of C^3 and C^4 for LiF and NaCl crystals. According to Eq. (23) the total number of combinations in Γ^3 is 108. The data calculated from the vibrational spectra of these crystals[11-13] show that the following three-phonon processes are possible: three processes in which a resonant optical phonon is converted into a longitudinal optical phonon by incorporating an acoustical phonon, and ten processes in which the resonant phonon is decomposed into two acoustical phonons. Thus, only 10 of the 108 possibilities exist.

A similar, but more tedious consideration of four-phonon processes shows that approximately 800 out 1512 combinations exist. Hence the ratio $(C^4/C^3)_{\min} \approx 80$. Then the ratio $\Gamma^4/\Gamma^3 \sim 10^{-1}\, T/\hbar\omega$. Using the experimental values of $T/\hbar\omega \sim 5$–6, we obtain $\Gamma^4/\Gamma^3 \sim 0.5$–$0.6$. It is obvious that though our estimates are rough, it makes sense to speak of the comparability of Γ^4 and Γ^3.

However, this treatment does not make it possible for us to understand quantitatively the difference in the temperature dependences of the line width for LiF and NaCl crystals. Therefore we limit ourselves to the formulation of some qualitative considerations that will permit an understanding of the observed dependences.

It is known[10] that the greater the difference in mass of the atoms in its unit cell, the greater the separation between the branches of the vibrational spectrum. But, the greater this separation, the more difficult is it to satisfy the conservation laws which enter into Γ^3 and Γ^4. Since Γ^3 is determined by a smaller number of parameters (branches and phonon momenta) than Γ^4, it is more sensitive to changes in separation between branches. Consequently the reduction of Γ^3 compared to Γ^4 should be more sharply expressed in that crystal having a larger separation between branches.

Let us consider the crystals of LiF and NaCl. The separation between branches is larger in the first than in the second.[11-13] Thus, the anharmonic terms of fourth order should play a greater role in LiF than in NaCl. Correspondingly, the temperature dependence of the line width is closer to T^2. In NaCl, on the other hand, the third-order terms play a larger role, and the temperature dependence of the width is slower than T^2. This is just what is observed in experiment.[1,2]

If these considerations are valid, then in KCl, where the masses of the atoms in the unit cell are almost the same and consequently the branches of the spectrum are separated even less than in NaCl,[12] the temperature dependence of the line width should be still closer to being a linear one. On the other hand, in crystals with strongly differing atomic masses the role of third-order anharmonic terms should be entirely insignificant.

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