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TEMPERATURE EFFECTS
IN TWO-PHONON SPECTRA

1981

I. INTRODUCTION

The two-phonon crystal spectra are the object of numerous experimental (refs.[1-4], and many others as well) and theoretical investigations (refs.[5-9], etc.). In those works the researchers' attention is first and foremost directed to the changes of the spectrum caused by anharmonicity in the region of the summation of frequencies of the two phonons. The temperature influence in this case is examined as a secondary factor only (see, e.g., refs.[4,7]). It is not difficult however to foresee that the temperature excitation of the optical phonons can be the reason for two important qualitative effects:

1. At zero temperature the anharmonic interaction is carried out between two virtual quasiparticles. At finite temperatures the interaction between the phonon modes increases, the anharmonic interaction of the really existing temperature excited phonons being added. This leads to removing the discrete biphonon levels from the summation two-particle bands $\omega_1(k) + \omega_2(K-k)$.

2. At different from zero temperatures, processes of creating one phonon and of annihilating a real phonon from another mode are possible. The spectrum in the region of the frequency differences of the two phonons is renormalized by anharmonicity and besides the ever existing two-particle bands $\omega_1(k) - \omega_2(K+k)$, it can contain discrete levels of one-particle states (difference biphonons).

The assumptions of the temperature variation of the phonon spectrum are used at the analysis of the experimental data[10,11] Those papers report on the observations of the polariton spectrum peculiarities in the region of difference tones. An equation for the two-phonon spectrum at nonzero temperatures is deduced in ref. [7]. In that paper, however, the provoked by anharmonicity qualitative variations of the spectrum in the difference region are not analysed.

In the present work the dielectric permittivity in the regions of summation and difference of frequencies of two phonons (connected by quartic anharmonicity) is calculated by the method of the temperature Green functions. The necessity of calculating the dielectric permittivity is provoked by the strong influence which its peculiarities exert on the polariton spectrum in these regions.

II. DIELECTRIC PERMITTIVITY IN THE REGION OF THE SUMMATION AND DIFFERENCE TONES

Let the spectrum of an ideal crystal contain two phonon modes of nondegenerate vibrations. We shall denote by b_k^+, b_k, $\omega_1(k)$ and respectively by c_k^+, c_k, $\omega_2(k)$ the creation and annihilation operators and the dispersion law of the two modes (we shall consider that $\omega_2(k) > \omega_1(k)$). Let's suppose that the anharmonic cubic terms are annulled (for symmetry reasons), and that the anharmonic quartic terms are essential. The crystal Hamiltonian assumes the following shape:

$$
\hat{H} = \sum_k h\,\omega_1(k)\,b_k^+ b_k + \sum_k h\omega_2(k)\,c_k^+ c_k +
$$

$$
+ \frac{A}{N} \sum_{K,k_1,k_2} (b_{k_1} + b_{-k_1}^+)(b_{-K-k_1} + b_{K+k_1}^+)(c_{k_2} + c_{-k_2}^+)(c_{K-k_2} + c_{-K+k_2}^+)
$$

(1)

(A – anharmonicity constant, N – number of elementary cells in the crystal).

At calculating the tensor of the transversal dielectric permittivity we shall use the following formula (refs [12,13])

$$
\epsilon_{ij}(\omega,K) = (1 - \frac{4\pi}{\omega^2 V} \ll \sum_\alpha \frac{e_\alpha^2}{m_\alpha} \gg)\delta_{ij} - \frac{4\pi}{\omega^2 V h} \ll \hat{J}_i(K,t)\hat{J}_j(-K,t') \gg_\omega , \quad (2)
$$

where V is the crystal volume, e_α and m_α are correspondingly the charge and mass of the particles α (electron or nucleus) and the last expression stands for the Fourier-transform in respect to the time of the retarded temperature Green function:

$$
G(K,t-t') = -i\theta(t-t') \ll \hat{J}_i(K,t)\hat{J}_j(-K,t) \gg . \quad (3)
$$

The operator $\hat{J}$ in a dipole approximation is expressed by the following sum of the operators $\hat{J}_{\mu_n}$ of the impulses of all the charges in the crystal [12] (see also ref [14])

$$
\hat{J}_i(K) = \sum_{n,\mu_n} \frac{e_{\mu_n}}{m_{\mu_n}} \hat{J}_{\mu_n}^{(i)} e^{-iK\cdot n} \quad (4)
$$

(μ_n includes all charged particles in the point n of the lattice). We use the relation between the matrix elements of the impulse operator and the electric dipole moment $p^{(2)}(K,k)$, to express operator (4) in the regions we are interested in $\omega_2(k_1) \pm \omega_1(k_2)$

$$\hat{J}_i(K) = i \sum_k \omega_1(k) p_i^{(2)}(K,k)(b_{-k}^+ - b_k)(c_{-K+k}^+ + c_{K-k}) + $$

$$+ i\sum_k \omega_2(K-k) p_i^{(2)}(K,k)(b_{-k}^+ + b_k)(c_{-K+k}^+ - c_{K-k}). \tag{5}$$

The matrix element $p^{(2)}(K,k)$ expresses the electrooptical anharmonicity [14], and is usually several times smaller in size or by an order smaller than the matrix element $p^{(1)}$ for the transition from a ground state $|0>$ into a state with a dipole-active phonon. Further we shall consider that the quantity $p^{(2)}(K,k) \equiv p^{(2)}$ depends slightly on the wave vectors K, k. Such a supposition is fulfilled, e.g., in the case of the intramolecular vibrations in a molecular crystal with one molecule in the elementary cell.

Having in mind equations (2), (3) and (5), the calculation of the dielectric permittivity is reduced to finding the Fourier-transform of the Green functions of the following type:

$$G^{(1)}(k_1,k,t) = -i\theta(t) << (b_{-k_1}^+(t) - b_{k_1}(t))(c_{-K+k_1}^+(t) + c_{K-k_1}(t)),$$

$$(b_{-k}^+(0) - b_k(0))(c_{K+k}^+(0) + c_{-K-k}(0)) >> \tag{6}$$

as well as of the functions $G^{(2)}$, $G^{(3)}$, $G^{(4)}$ with other combinations of operators in the moments t and $t=0$ (see (3) and (6)).

The calculation is done by the standard methods with time differentiation and with a following splitting of the chain of equations for the Green functions. Let's limit to the first order terms by the constant of anharmonicity. At the calculations we shall use correlations of the type:

$$<<b_{k_1}^+(t) b_{k_2}(t) b_{k_3}(t) b_{k_4}(t)[b_{-k}^+(0) - b_k(0)][c_{K+k}^+(0) + c_{-K-k}(0)]>> \approx \tag{7}$$

$$\approx <<b_{k_1}^+(t)b_{k_2}(t)>> \cdot <<b_{k_3}(t)b_{k_4}(t)[b_{-k}^+(0) - b_k(0)][c_{K+k}^+(0) + c_{-K-k}(0)]>>.$$

The first correlator we express by the occupation numbers $n^b(k)$, $n^c(k)$ for the two phonon modes ($n^b(k) = [\exp(\hbar\omega_1(k)/kT) - 1]^{-1}$)

$$<<b_{k_1}^+(t) b_{k_2}(t)>> \approx \delta_{k_1 k_2} n^b(k_1). \tag{8}$$

We introduce the symbols:

3

$$T_1(K,\omega) = \frac{1}{N} \sum_k \frac{[n^b(k) + n^c(K-k)+1] \cdot [\omega_1(k) + \omega_2(K-k)]}{\omega^2 - [\omega_1^2(k) + \omega_2(K-k)]^2}, \tag{9a}$$

$$T_2(K,\omega) = \frac{1}{N} \sum_k \frac{[n^c(K+k) - n^b(k)] \cdot [\omega_1(k) - \omega_2(K+k)]}{\omega^2 - [\omega_1(k) - \omega_2(K+k)]^2}. \tag{9b}$$

For the dielectric permittivity we get the expression:

$$\frac{1}{\epsilon_{ij}} (\omega,K) = \delta_{ij} - \frac{8\pi p_i^{(2)} p_i^{(2)}}{v h} \left[\frac{T_1(K,\omega) + T_2(K,\omega)}{\Delta_0(K,\omega)} - \frac{2 A R(K,\omega,T)}{\Delta_0^2(K,\omega)} \right] \tag{10}$$

(the addend $\ll \sum_a e_a^2/m_a \gg$ is eliminated by using sum rules, similar to those deduced in ref.[12], ch. II). The poles of the Green functions and respectively the resonances of $\epsilon_{ij}^+(\omega,K)$ we find from the equation:

$$\Delta_0(K,\omega) \equiv 1 - 4 A h^{-1} [T_1(K,\omega) + T_2(K,\omega)] = 0. \tag{11}$$

The function $R(K,\omega,T)$ has the following form:

$$R(K,\omega,T) = \frac{\omega^2}{N^2 h} \sum_{k_1} \left[\frac{1}{\omega^2 - [\omega_1^2(k_1) + \omega_2(K-k_1)]^2} - \frac{1}{\omega^2 - [\omega_1(k_1) - \omega_2(K+k_1)]^2} \right]$$

$$\times \sum_{k_2} \left\{ \frac{[2n^b(k_2)+1] \cdot [2n^c(K-k_2)+1]+1}{\omega^2 - [\omega_1(k_2) + \omega_2(K-k_2)]^2} + \frac{[2n^b(k_2)+1] \cdot [2n^c(K+k_2)+1] - 1}{\omega^2 - [\omega_1(k_2) - \omega_2(K+k_2)]^2} \right\}. \tag{12}$$

III. PECULIARITIES OF THE TWO-PHONON SPECTRUM

1. At zero temperature ($n^c = n^b \equiv 0$) only a two-particle band $\omega_1(k) + \omega_2(K-k)$ appears in the spectrum (see (11)). At greater values of the anharmonicity constant A, a biphonon level splits from this band because of the addend 1 in the numerator of the sum (9a). (This level corresponds to the bound movement of the two phonons in the crystal). At temperatures different from zero, the positive value $n^b(k) + n^c(K-k)$ is added to the addend 1, owing to which the effective anharmonicity constant grows. At narrow phonon bands [$\Delta\omega_1/\omega_1, \Delta\omega_2/\omega_2 \ll 1$; $\Delta\omega_1, \Delta\omega_2$ – width of the bands] and at high temperatures ($kT \gg h\omega_1, h\omega_2$) this "constant" is a linear function of temperature:

$$A^+ = A(1 + n_{av}^b + n_{av}^c) \approx A \left[1 + \frac{kT}{h} \left(\frac{1}{\omega_1^{av}} + \frac{1}{\omega_2^{av}} \right) \right]. \tag{13}$$

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With the growth of temperature, the biphonon level moves away from the two-particle band $\omega_1(k) + \omega_2(K-k)$, and the distance will increase linearly with temperature when the anharmonicity is strong, $A^+ \gg \hbar(\Delta\omega_1 + \Delta\omega_2)$.

2. At zero temperature the quantity $T_2(K,\omega) \equiv 0$, and therefore in the linear by anharmonicity A approximation the latter won't influence the band $\omega_2(K+k) - \omega_1(k)$ (see equation (11)). At nonzero temperatures anharmonicity manifests also in the difference tones with the effective "constant"

$$A^- = A(n_{av}^b - n_{av}^c) \approx A\frac{kT}{\hbar}(\frac{1}{\omega_1^{av}} - \frac{1}{\omega_2^{av}}). \qquad (14)$$

The more different the frequencies ω_1 and ω_2 of the two vibrations, the more visible the anharmonicity effects are. At considerable values of the quantity A^-, a discrete level of a difference biphonon splits from the two-particle band $\omega_2(K+k) - \omega_1(k)$. Its dependence on the temperature T will be stronger than at the summation biphonon (compare (13) and (15)).

3. Simultaneously with the appearance of discrete levels inside each band $\omega_2(k_1) \pm \omega_1(k_2)$, quasibound, decaying states come into being. These states are solutions of the equation for the two-phonon spectrum (11) as well, and their position will change in a complex manner with the change of temperature. The quasibound states will manifest as peculiarities of the density of the states, sometimes too strong, not coinciding with the Van Höve critical points.

IV. PECULIARITIES OF THE DIELECTRIC PERMITTIVITY

At the analysis of the dielectric permittivity we shall first discuss the role of the first term in the brackets in formula (10). With the increase of temperature the absolute values of the quantities $T_1(K,\omega)$ and $T_2(K,\omega)$ grow (see (9)). Beside the discussed in the above passage temperature dependence of the summation and difference biphonon levels, this leads to increasing of the resonance part of the refractive index and the absorption coefficient for the summation and difference regions with temperature. In the vicinity of the discrete biphonon levels the frequency dependence of $\varepsilon^\perp(\omega,K)$ has a character analogous to the region of the fundamental tones of the vibrations (Lorentz's curce with a width equal to the sum of the widths of the two phonon levels $\omega_1(k), \omega_2(k)$).

In the two-particle bands $\omega_2(k_1)\pm\omega_1(k_2)$ the dielectric permittivity has (shows) peculiarities caused by the quasibound levels (see the end of the above section) and by the Van Höve critical points. As far as the quantities n^b and n^c depend monotonously on the phonon frequencies, the character of the ϵ (ω,K) change near the Van Höve critical points remains the same as at zero temperatures (see. ref. [15]).

The second term in (10) $2AR(K,\omega,T)\Delta_0^{-2}(K,\omega)$ is proportional to the anharmonicity constant A, and hence, it is with a smaller order than the first term. The presence of an anharmonicity term in Hamiltonian (1) is the reason for appearing of polarization in the crystal to the difference region. Therefore the band $\omega_2(k_1)-\omega_1(k_2)$ will manifest in the dielectric permittivity at $T=0$ as well. In the present paper, however, it is shown that the action of anharmonicity at nonzero temperatures may cause the splitting of a difference biphonon discrete level from the band $\omega_2(k_1)-\omega_1(k_2)$.

A particularly simple expression for the dielectric permittivity can be obtained in the high temperature region, if the condition $h\omega_1 \ll kT \ll h\omega_2$ is fulfilled (i.e., the vibrations of the mode only are excited by temperature: $n^b \approx kT/h\omega_1 \gg 1 \gg n^c$). It is easy to show that the expression for ϵ (ω,K) assumes the following shape:

$$\epsilon_{ij}(\omega,K) = \delta_{ij} - \frac{4\pi p_i^{(2)} \cdot p_j^{(2)}}{v\hbar} - \frac{kT}{\hbar\omega_1^{av}} \frac{S_1(K,\omega)+S_2(K,\omega)}{1 - 2A\frac{kT}{\hbar\omega_1^{av}}[S_1(K,\omega)+S_2(K,\omega)]} \quad (15)$$

$$[S_\ell(K,\omega) = \int \frac{g_\ell(K,\omega_\ell')d\omega_\ell'}{\omega-\omega_\ell'} - i\pi g_\ell(\omega)],$$

$g_\ell(\omega)$ is the density of the states in the harmonic two-particle bands $\omega_2(k_1)\pm\omega_1(k_2)$ in the summation $(\ell=1)$ and in the difference $(\ell=2)$ regions.

In both frequency regions the temperature excitation and the anharmonicity condition two effects: 1. increase of the general contribution in the dielectric permittivity $kT/h\omega_1$ times (the absorption coefficient grows respectively); 2. growth of the anharmonicity constant by the same factor. The distance of the summation/difference biphonon levels from the summation/difference two-particle bands grows approximately in the same manner.

V. CONCLUSION

The investigations in the present work show that the joint influence of temperature (at $kT \gtrsim \hbar\omega_{ph}$) and of anharmonicity of the two-phonon spectra can prove too strong. The two-particle bands will be influenced relatively weaker as far as their position in the spectrum and their structure are determined in harmonic approximation. But temperature will strongly influence the position of the levels of the anharmonic bound states (the biphonons). We can consider as a qualitatively new result the possibility for existing of bound (one-particle) bands in the region of the frequency difference of vibrations. The temperature dependence of the biphonon levels will cause a strong temperature dependence of the polariton spectrum. In the spectrum of the normal electromagnetic waves in the crystal a gap will appear[9] above the biphonon levels (both in the summation and difference regions). With the growth of temperatire the gap's position in the spectrum will change, and its width will grow as well (see formula (15)).

Naturally, the investigations of the phonon and polariton spectra at high temperatures will be hampered by the strong excitation of the low-frequency acoustic modes. In order to observe the predicted temperature effects, there should be chosen optical phonon modes with narrow phonon bands in crystals with strong anharmonicity. In this case, the biphonon levels will be sufficiently removed from the two-particle bands and the inevitable at higher temperatures background of acoustic phonons won't be an obstacle for observing the temperature changes of the phonon and polariton spectra in the two-phonon band.

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