

BIPHONONS, FERMI RESONANCE, AND POLARITON EFFECTS IN THE THEORY OF
RAMAN SCATTERING OF LIGHT IN CRYSTALS

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A theory of Raman scattering of light (RSL) of the second order by optical phonons is developed for the case when oscillation anharmonicity and Fermi resonance with a polariton lead to a significant change in the crystal oscillation spectrum in the overtone frequency region. The RSL cross section in this case is found to be a nonanalytic function of the anharmonicity constants and hence phonon-phonon interaction cannot be analyzed within the framework of small-perturbation theory. The dependence of the RSL intensity on the photon energy and the scattering angle is analyzed. It is shown that polariton effects are very important at small scattering angles, particularly when Fermi resonance with a polariton occurs. The shape of the RSL spectrum involving biphonon excitation is considered. The role of resonant states is also considered. It is shown that owing to Fermi resonance with polaritons some of these states in the RSL spectrum should be manifest only at small scattering angles.

1. INTRODUCTION

THE use of lasers in optical experimentation has led to a vigorous development of research on the properties of elementary excitations in crystals. One of the main research methods has been Raman scattering of light (RSL). During the last few years, the RSL phenomenon has been observed not only on optical phonons, which were already investigated earlier with the aid of RSL, but also on polaritons, plasmo-phonons, magnons, etc. (see, for example,^[1]). It is important that the modern RSL method makes it possible to obtain sufficiently exact and complete information also on those RSL processes which are accompanied by simultaneous production or annihilation of several quasiparticles (in the simplest case—two). In these processes there should appear to some degree or another a "residual" interaction between the quasi-particles, which need not necessarily be regarded as weak. As applied to magnons, for example, owing to the possible formation of bimagnons, this circumstance was pointed out already long ago^[2,3]. In recent years it was shown both theoretically^[4] and experimentally^[5] that in antiferromagnets the magnon-magnon interaction influences in a radical manner also the form of the spectrum of RSL on magnons.

Analogous effects of interaction between quasiparticles may also turn out to be important for phonons. In particular, as shown in^[6-8], effects of phonon-phonon interaction can lead to significant changes in the spectra of optical phonons (in particular, to the appearance of their bound states (biphonons)). This circumstance makes it urgent to construct a theory of RSL on phonons in which the anharmonicity of the lattice vibrations is considered in a form admitting of a consistent allowance for the bound states of the phonons.

The present paper is devoted to a theory of this type. We confine ourselves here to a discussion of the RSL processes in which the change of the photon energy corresponds to simultaneous production of only two optical phonons (i.e., at $\omega - \omega' \approx 2\Omega_1$, where ω and

ω' are the frequencies of the incident and scattered light, and Ω_1 is the frequency of the optical oscillation). In addition, we shall assume that the frequencies ω and ω' lie sufficiently far from the lines of the intrinsic absorption of the crystal, so that we shall be able to disregard certain complications of the theory that arise when resonant RSL is considered (see^[9,12]). At the same time, we take into consideration the possibility of Fermi resonance, i.e., we assume that the spectral region under consideration includes, in addition to the overtone, also the fundamental frequency $\Omega_2 \approx 2\Omega_1$ of some other oscillation. One or both of the oscillations participating in the Fermi resonance can, generally speaking, be dipole-active. Therefore oscillations of this type are accompanied by the occurrence of a macroscopic electric field, and when a theory of RSL by these oscillations is constructed it is also necessary to take into consideration the retarded interaction. This interaction can lead to significant changes in the form of the spectrum in the region of long wavelengths not only for the fundamental frequencies (see, for example,^[10]) but also, as shown in^[8], for frequencies lying in the overtone region. Therefore in the subsequent calculations of the RSL probability we shall take into consideration also the retarded interaction. Such an approach makes it possible to take into account, within the framework of a unified analysis, a large number of effects due both to the anharmonicity in the phonon system and to the retarded interaction between the charges. In particular, in Sec. 4 we consider a situation analogous to that obtaining in the experimental study^[11], in which the phenomenon of RSL by overtones was first observed under conditions of Fermi resonance with a polariton.

2. DERIVATION OF FORMULA FOR THE RSL CROSS SECTION IN THE PRESENCE OF FERMI RESONANCE

As is well known (see, for example,^[10], Sec. 49), to obtain the perturbation operator \hat{H}_1 that leads to the RSL processes on phonons, we can use the relation

$$\hat{H}_i = -\frac{1}{2} \sum_n \delta \hat{P}(n) E(n), \quad (1)$$

where the operator $\delta \hat{P}(n)$ is determined by the change of the contribution of the electrons to the polarizability of the molecule n ($n \equiv n, \alpha$), occurring when the nuclei are displaced from their equilibrium positions, and $E(n)$ is the intensity of the macroscopic electric field at the point r_n ¹⁾.

In the harmonic approximation, the displacements of the nuclei can be represented in the form of a linear expansion in normal coordinates. Since we are interested here in RSL processes proceeding with excitation of two phonons Ω_1 , we retain in the series expansion of the operator $\delta \hat{P}$ in the displacements of the nuclei those terms which are quadratic in the normal coordinates corresponding to the phonons Ω_1 . However, under Fermi-resonance conditions, it is necessary to retain in addition to these quadratic terms also the terms that are linear in the normal coordinates and correspond to phonons with frequencies $\Omega_2 \approx 2\Omega_1$. In addition, since we propose to consider also polariton effects, it is necessary to take into account the fact that the macroscopic field accompanying the dipole-active oscillations also influences the electronic-polarizability tensor of the crystal (the electro-optic effect).

Taking these considerations into account, we represent the expression for $\delta \hat{P}$ in the following form:

$$\begin{aligned} \delta \hat{P}_i(n) = & \sum_{i,j} a_{ij,ii}^\alpha U_n^{(B)} U_n^{(C)} E_j(n) \\ & + \sum_{i,j} b_{ij,i}^\alpha U_n^{(C)} E_j(n) + \sum_{i,j} c_{ij,i}^\alpha E_i^p(n) E_j(n). \end{aligned} \quad (2)$$

Here a^α and b^α are tensors of fourth and third rank, respectively, which determine the changes of the polarizability of the molecule α as a result of the displacement of its atoms; the operators $U_n^{(B)}$ and $U_n^{(C)}$ correspond to the displacements of the nuclei in the molecule n under the influence of normal oscillations with frequencies Ω_1 and Ω_2 (B and C oscillations, $\Omega_2^C \approx 2\Omega_1^B$); c^α is the electro-optic tensor, which determines the change of the electric dipole moment of the molecule due to the dependence of the electronic-polarizability tensor on the "external" macroscopic electric field E^p , which occurs when a low-frequency polariton propagates in the crystal. Since the frequencies ω and ω' lie in the transparency region of the crystal, the tensors a^α , b^α and c^α are symmetrical with respect to permutation of the indices i and j .

The B and C oscillations may also turn out to be dipole-active. Therefore, generally speaking, it is necessary to take into account the possible interaction of the macroscopic electric field with both the C and B phonons. However, the electric field excited by two B-phonons in either the bound or in the free state is small, owing to the smallness of the oscillator strength of the transition to the state at the overtone frequency.

¹⁾We consider here a molecular crystal (n is an integer-number lattice vector, $\alpha = 1, 2, \dots, \sigma$ is the number of the molecule in the unit cell, and $r_n = n + r_\alpha$ is the radius vector determining the equilibrium position of its center of gravity). However, the results obtained below can be used for dielectrics of any nature (see Sec. 4).

Since we are interested in RSL precisely in the region of the overtone frequencies, we shall henceforth neglect the direct interaction of the macroscopic electric field with the B-phonons. On the other hand, allowance for the interaction of the macroscopic electric field with the C-phonons leads to the formation of polaritons.

That part \hat{H}_p^C of the crystal Hamiltonian which describes the C-phonons, the transverse photons, and the interaction between them, can be diagonalized exactly in the harmonic approximation by changing over to the polariton representation (see^[12]). In this representation

$$\hat{H}_p^c = \sum_{\mathbf{K}, \rho} \mathcal{E}_\rho(\mathbf{K}) \xi_\rho^+(\mathbf{K}) \xi_\rho(\mathbf{K}), \quad (3)$$

where $\mathcal{E}_\rho(\mathbf{K})$ is the energy of the polariton of the ρ -branch with wave vector \mathbf{K} , and $\xi_\rho^+(\mathbf{K})$ and $\xi_\rho(\mathbf{K})$ are Bose operators for the creation and annihilation of the $\rho\mathbf{K}$ polariton. Therefore, in the approximation under consideration, the total Hamiltonian \hat{H} of the crystal takes the form

$$\hat{H} = H_p^c + \hat{H}_B + H_{BC}, \quad (4)$$

and contains, besides the operator \hat{H}_p^C , also the operator \hat{H}_B which describes the system of the B-phonons that interact with one another, and also the operator \hat{H}_{BC} , which describes the interaction between the B and C phonons. In accordance with^[6,8], these parts of the total Hamiltonian are of the form²⁾

$$\hat{H}_B = \sum_n \hbar \Omega B_n^+ B_n + \sum_{n,n'} V_{nn'}^{(B)} B_n^+ B_{n'} - A \sum_n (B_n^+)^2 B_n^2 \quad (5)$$

$$\hat{H}_{BC} = \Gamma \sum_n [C_n (B_n^+)^2 + B_n^2 C_n^+]. \quad (6)$$

In these expressions, B_n^+ , B_n , and C_n^+ , C_n are the operators for the creation and annihilation in the n -th molecule of the B- and C-quanta of the oscillations, respectively. The constant A in (5) determines that part of the anharmonicity in the B-phonon system which does not lead to a mixing of the B-oscillations with other oscillations; at the same time, the quantity Γ in (6) is the anharmonicity constant and determines the intensity of the BC interaction. In accordance with^[12], the operators C^+ and C can be expressed in terms of the polariton creation and annihilation operators. The corresponding relation is

$$\begin{aligned} C_n = & \frac{1}{\sqrt{N}} \sum_{\mathbf{k}, \mu} u_{\alpha\mu}(\mathbf{k}) e^{i\mathbf{k}n} C_\mu(\mathbf{k}), \quad n \equiv n, \alpha, \\ C_\mu(\mathbf{k}) = & \sum_\rho \{u_{\mu\mathbf{k}}(\rho) \xi_\rho(\mathbf{k}) + v_{-\mathbf{k}\mu}^*(\rho) \xi_\rho^+(-\mathbf{k})\}. \end{aligned} \quad (7)$$

Here $C_\mu(\mathbf{k})$ is the operator for the annihilation of a C-phonon in a crystal with wave vector \mathbf{k} in the μ -th branch of the spectrum, while $u_{\alpha\mu}(\mathbf{k})$, $u_{\mu\mathbf{k}}(\rho)$, and $v_{\mathbf{k}\mu}(\rho)$ are the coefficients of the linear transformations into phonons and polaritons, respectively (for more details see^[12], Chapters 2 and 3).

If we change over in the complete Hamiltonian from the operators C_n^+ and C_n to the operators ξ^+ and ξ ,

²⁾The use of expressions (5) and (6) implies smallness of the phonon-band widths and of the anharmonicity constants compared with the energy of the phonons under consideration.

then the operator H turns out to be expressed only in terms of the operators ξ , ξ^+ and B , B^+ . We express in terms of ξ , ξ^+ , B , and B^+ also the operator of the interaction between the crystal and the high-frequency electro-magnetic field. To this end we note that in the harmonic approximation, the displacement operators $U_n^{(B)}$ and $U_n^{(C)}$ in (2) are given by

$$\begin{aligned} U_n^{(B)} &= U_n^{(B)} (B_n + B_n^+) \equiv U_n^{(B)} B_n, \\ U_n^{(C)} &= U_n^{(C)} (C_n + C_n^+) \equiv U_n^{(C)} C_n. \end{aligned} \quad (8)$$

In this relation eU_n are the matrix elements of the dipole-moment operator of the isolated molecule, and correspond to a transition from the ground state to the state with one B- or C-phonon, respectively, and e is the effective charge. Substituting (8) in (2), we obtain in this relation terms that are quadratic in the operators B and B^+ . It is clear that terms of the same type arise if we retain in (2) also the terms that are linear in $U_n^{(B)}$, but write relation (8) with allowance for the anharmonic terms. It is easy to verify, however, that this refinement is unnecessary, since it leads only to an inessential redefinition of the tensors a , b , and c (see (2)), which in the present paper are not calculated but are assumed known.

The electric-field intensity operator is expressed in terms of the Bose operators of the polaritons (see^[12], Ch. 3) as follows:

$$\hat{E}(r) = \sum_{\rho k} S_\rho(\mathbf{K}) \xi_\rho(\mathbf{K}) e^{i\mathbf{K}r} + \text{h.c.} \quad (9)$$

where $S_\rho(\mathbf{K})$ is the amplitude of the electric-field intensity in the polariton $\rho\mathbf{K}$. Therefore, if we retain in the operator of the interaction between the crystal and the high-frequency electromagnetic field only that part which describes the Raman scattering of the polariton (ρa , \mathbf{k}_a , $\mathcal{E} = \hbar\omega$) which results in the polariton (ρb , \mathbf{k}_b , $\mathcal{E} = \hbar\omega'$), then we obtain for the perturbation operator

$$\begin{aligned} \hat{H}_1 &= - \sum_n F^\alpha(\mathbf{K}) e^{i\mathbf{K}n} \hat{B}_n^\alpha \xi_{\rho_a}^+(k_a) \xi_{\rho_b}^+(k_b) \\ &- \sqrt{N} \sum_p D_p(\mathbf{K}) \xi_{\rho_a}^+(\mathbf{K}) \xi_{\rho_b}^+(k_a) \xi_{\rho_b}^+(k_b) + \text{h.c.} \end{aligned} \quad (10)$$

where $\rho\mathbf{K}$ corresponds to the low-frequency polariton and where we have introduced the notation

$$\begin{aligned} F^\alpha(\mathbf{K}) &= \sum_{i,j,l} a_{ij,l} U_\alpha^{(B)} U_\alpha^{(B)} S_{\rho_a}^i(k_a) S_{\rho_b}^{*j}(k_b), \\ D_p(\mathbf{K}) &= \sum_{\alpha,i,j} [b_{ij,i} U_\alpha^{(C)} d_\alpha^\rho(\mathbf{K}) + \sqrt{N} c_{ij,i} S_{\rho_a}^i(\mathbf{K}) S_{\rho_b}^{*j}(k_a) S_{\rho_b}^{*j}(k_b)], \\ d_\alpha^\rho(\mathbf{K}) &= \sum_\mu [u_{\alpha\mu}(\mathbf{K}) u_{\mathbf{K}\mu}(\rho) + u_{\alpha\mu}^*(-\mathbf{K}) v_{\mathbf{K}\mu}(\rho)], \\ &\quad \mathbf{K} = \mathbf{k}_a - \mathbf{k}_b. \end{aligned} \quad (11)$$

We now use the Van-Hove method^[13] to calculate the RSL cross section, assuming the crystal temperature to be zero. In this case we obtain for the RSL differential cross section per unit crystal length, per unit solid angle O' , and per unit frequency interval ω' , in first order of perturbation theory, the relation

$$\frac{d^2\sigma}{dO' d\omega'} = M_{ab} \sum_{\nu\nu'} A_\nu^* A_{\nu'} a_{\nu\nu'}(E), \quad (12)$$

where the index $\nu(\nu')$ runs through the values $\nu = n \equiv (n, \alpha)$ and $\nu = \rho$, and where we use the notation

$$\begin{aligned} A_n &= F^\alpha(\mathbf{K}) e^{i\mathbf{K}n}, \quad A_\rho = \sqrt{ND_\rho}(\mathbf{K}), \quad E = \hbar(\omega - \omega'), \\ M_{ab} &= V^2 k_a^2 / (2\pi)^3 \hbar^2 v_a v_b, \\ a_{\nu\nu'}(E) &= \int_{-\infty}^{+\infty} e^{-iE t/\hbar} \langle 0 | a_{\nu'}(0) a_\nu^\dagger(t) | 0 \rangle dt, \end{aligned} \quad (12a)$$

with

$$a_\nu(t) = B_n^\nu(t) \text{ for } \nu = n, \quad a_\nu(t) = \xi_\rho(\mathbf{K}, t) \text{ for } \nu = \rho.$$

In formulas (12a), V is the volume of the crystal, v denotes the group velocity of the polariton, and the operators B , ξ , and ξ^+ are taken in the Heisenberg representation.

Thus, it follows from (12) that to determine the cross section it is necessary to find the Fourier components of the four correlation functions $a(E)$ in (12). It is more convenient, however, to calculate the Fourier components of the four retarded Green's functions:

$$\Phi_{\nu\nu'}(t) = 1/2 i \theta(t) a_{\nu\nu'} \langle 0 | a_{\nu'}(0) a_\nu^\dagger(t) | 0 \rangle, \quad (13)$$

where the coefficient $\alpha_{\nu\nu'} = 2$ if both or one of the indices ν or ν' is equal to ρ , and $\alpha_{\nu\nu'} = 1$ in all other cases. In (13), $\theta(t) = 1$ when $t > 0$, and $\theta(t) = 0$ when $t < 0$. The Fourier components of the correlation functions $a_{\nu\nu'}$ in (12) are expressed in terms of the corresponding Fourier components of the functions (13), as is well known (see, for example,^[14]), in the following manner:

$$a(E) = \frac{1}{i} [\Phi(E - i\delta) - \Phi(E + i\delta)]_{\delta \rightarrow +0}. \quad (14)$$

For the retarded Green's functions (13) it is possible to obtain, with the aid of a standard procedure consisting of differentiating these functions with respect to the time and using the complete Hamiltonian (4), a system of equations that is closed and linear in this case in spite of allowance for the anharmonicity. Its solution is simplified by changing over to the four-momentum representation. It can be shown that in this representation the Green's functions (13) are given by

$$\begin{aligned} \Phi_{\alpha\beta}(E, \mathbf{K}) &= \sum_\nu \Delta_{\alpha\nu}^{-1}(E, \mathbf{K}) \Phi_{\nu\beta}^{(0)}(E, \mathbf{K}), \\ \Phi_{\alpha, \mathbf{K}\rho}(E, \mathbf{k}') &= \frac{2\Gamma}{E - \mathcal{E}_\rho(\mathbf{K})} \frac{\delta_{\mathbf{k}', -\mathbf{K}}}{\sqrt{N}} \sum_\nu \Phi_{\alpha\nu}(-\mathbf{K}, E) q_\nu^*(\mathbf{K}\rho), \\ \Phi_{\mathbf{K}\rho, \alpha}(E, \mathbf{k}') &= \frac{2\Gamma}{E - \mathcal{E}_\rho(\mathbf{K})} \frac{\delta_{\mathbf{k}', \mathbf{K}}}{\sqrt{N}} \sum_\nu q_\nu(\mathbf{K}\rho) \Phi_{\nu\alpha}(\mathbf{K}, E), \\ \Phi_{\mathbf{K}\rho_1, \mathbf{K}\rho_2}(E) &= \delta_{\mathbf{K}\rho_1, \mathbf{K}\rho_2} \left[\frac{\delta_{\rho_1\rho_2}}{E - \mathcal{E}_{\rho_1}(\mathbf{K}_1)} \right. \\ &\left. + \frac{2\Gamma^2/N}{[E - \mathcal{E}_{\rho_1}(\mathbf{K}_1)][E - \mathcal{E}_{\rho_2}(\mathbf{K}_1)]} \sum_{\nu\nu'} \Phi_{\nu\nu'}(E, \mathbf{K}_1) q_\nu(\mathbf{K}_1\rho_1) q_{\nu'}^*(\mathbf{K}_1\rho_2) \right]. \end{aligned} \quad (15)$$

Here $\Phi_{\alpha\beta}^{(0)}(E, \mathbf{K})$ is the Green's function without allowance for the anharmonicity. It is expressed in terms of the energies and wave functions of the individual phonons obtained in the harmonic approximation, and has the following form:

$$\Phi_{\alpha\beta}^{(0)}(E, \mathbf{K}) = \sum_{\mu_1\mu_2} \frac{u_{\alpha\mu_1}(\mathbf{k}_1) u_{\alpha\mu_2}(\mathbf{k}_2) u_{\beta\mu_1}(\mathbf{k}_1) u_{\beta\mu_2}(\mathbf{k}_2)}{E - E_{\mu_1}(\mathbf{k}_1) - E_{\mu_2}(\mathbf{k}_2)}, \quad (16)$$

where

$$\mathbf{k}_1 = 1/2(\mathbf{K} + \mathbf{k}), \quad \mathbf{k}_2 = 1/2(\mathbf{K} - \mathbf{k}).$$

In addition, we have used in (15) the notation

$$\Delta_{\alpha\beta}(E, \mathbf{K}) = \delta_{\alpha\beta} + \frac{2A}{N} \Phi_{\alpha\beta}^{(0)}(E, \mathbf{K}) - \frac{2\Gamma^2}{N} \sum_{\gamma} Q_{\alpha\gamma}(-\mathbf{K}) \Phi_{\alpha\gamma}^{(0)}(E, \mathbf{K}),$$

$$Q_{\alpha\beta}(\mathbf{K}) = \sum_{\rho} \frac{q_{\alpha}(\mathbf{K}\rho) q_{\beta}(\mathbf{K}\rho)}{E - \mathcal{E}_{\rho}(\mathbf{K})}, \quad q_{\alpha}(\mathbf{K}\rho) = \sum_{\mu} u_{\alpha\mu}(\mathbf{K}) u_{\mu\rho}(\rho). \quad (17)$$

Relations (15)–(17) determine completely all the Green's functions needed for the calculation of the RSL. Their use in general form, however, is cumbersome. We therefore confine ourselves below to a detailed analysis of only some of the most important cases.

3. CROSS SECTION OF SECOND-ORDER RAMAN SCATTERING FROM PHONONS WITH ALLOWANCE FOR ANHARMONICITY

In this section we consider RSL from phonons with allowance for anharmonicity, assuming, however, that the crystal and its constituent molecules have an inversion center. In this case $\Gamma = 0$ and Fermi resonance with the dipole C-oscillation is impossible. The polariton effects for B-phonons also become insignificant. According to (12), the cross section for RSL from B-phonons at $\Gamma = 0$ is given by the relation

$$\frac{d^2\sigma}{d\Omega' d\omega'} = M_{ab} \sum_{\alpha\beta} F^{\alpha\beta}(\mathbf{K}) F^{\beta\alpha}(\mathbf{K}) a_{\beta\alpha}(E, \mathbf{K}). \quad (18)$$

At the same time, we get from (15) that, for example, for a crystal with one molecule per unit cell (see also (16)), at $\Gamma = 0$,

$$\Phi_{11}(E, \mathbf{K}) = \Phi_{11}^{(0)}(E, \mathbf{K}) \left[1 + \frac{2A}{N} \Phi_{11}^{(0)}(E, \mathbf{K}) \right]^{-1}, \quad (19)$$

$$\Phi_{11}^{(0)}(E, \mathbf{K}) = N\mathcal{G}(E, \mathbf{K}), \quad \mathcal{G}(E, \mathbf{K}) = \int \frac{g(\epsilon, \mathbf{K}) d\epsilon}{E - \epsilon}, \quad (20)$$

where $g(\epsilon, \mathbf{K})$ is the density of states of two free phonons with a summary momentum equal to \mathbf{K} . It follows from this relation (see also (14) that

$$a(E, \mathbf{K}) = 2\pi g(E, \mathbf{K}) N \{ [1 + 2A\mathcal{G}(E, \mathbf{K})]^2 + 4\pi^2 A^2 g^2(E, \mathbf{K}) \}^{-1}. \quad (21)$$

The integral in (21) is taken in the sense of the principal value.

If the energy E lies outside the energy band of the two free B-phonons with specified momentum \mathbf{K} , then $g(E, \mathbf{K}) \rightarrow 0$ in (21). This yields for the spectral density

$$\frac{1}{N} a(E, \mathbf{K}) = \frac{\pi}{A} \delta(1 + 2A\mathcal{G}(E, \mathbf{K}))$$

$$= \frac{\pi}{2A^2} \delta(E - E_0(\mathbf{K})) \left[\int \frac{g(\epsilon, \mathbf{K}) d\epsilon}{(E - \epsilon)^2} \right]^{-1}, \quad (22)$$

where $E_0(\mathbf{K})$ is the solution of the equation

$$1 + 2A\mathcal{G}(E, \mathbf{K}) = 0. \quad (23)$$

This equation, as shown in^[6], determines the energy of the bound state of two phonons with summary momentum equal to \mathbf{K} . Thus, if the energy E lies outside the energy band of the two free B phonons, then RSL occurs only when the energy E is equal to the biphonon

energy. On the other hand, if the energy E falls in the energy band of the free phonons, then the anharmonicity can be particularly significant only at values of E corresponding to a small density of states $g(E, \mathbf{K})$ and satisfying at the same time Eq. (23).

The situation arising here is quite analogous to that obtaining in the theory of resonant local oscillations produced in the vicinity of an impurity^[15]. Namely, in the case considered by us the presence of a quasibound resonant state of two phonons can lead in the RSL spectrum to the appearance of additional peaks, the positions of which are not connected with the singularities of the function $g(E, \mathbf{K})$, and the widths of which are the smaller the smaller the density of states $g(E, \mathbf{K})$ in the region of the resonant-state energy. In perfect analogy, we can obtain with the aid of the system (21) the values of $a_{\alpha\beta}(E, \mathbf{K})$ for crystals with more than one molecule per unit cell. The results obtained thereby are qualitatively similar, in the main, to those obtained for crystals with $\sigma = 1$.

In connection with the statements made in the present section, we note that the formula obtained above for the RSL cross section at $\sigma = 1$ (one molecule per unit cell), and also the formulas given below (see Sec. 4), are not only valid for molecular crystals, but also describe the dependence of the cross section of second-order RSL from non-degenerate optical phonons for any type of dielectric, provided the bandwidth and the anharmonicity A for the indicated phonons are small compared with the phonon energy. For these phonons, the oscillations of the atoms inside the unit cell are similar to the intramolecular vibrations in molecular crystals, since the relative smallness of the phonon bandwidth is evidence of weakness of the interaction between vibrations of atoms situated in different unit cells. For the same reason, the formulas for RSL at $\sigma > 1$ can be used for an analysis of the RSL in non-molecular crystals from such optical phonons with narrow energy bands, which correspond to a degenerate oscillation inside the unit cell.

4. RSL CROSS SECTION IN THE PRESENCE OF FERMI RESONANCE

In this section we determine the cross section of RSL in a crystal with one molecule per unit cell in the presence of Fermi resonance between the overtone and the dipole-active C-oscillation. Of course, the Fermi resonance, generally speaking, is possible also with dipole-inactive C-oscillations, and only such a situation is possible in crystals with an inversion center. Since the transition to the dipole-inactive C oscillations corresponds to elimination of polariton effects from the general relations, such a limiting case can likewise be easily considered.

It follows from (12) that the RSL cross section at $\sigma = 1$ is determined by the relation

$$\frac{d^2\sigma}{d\Omega' d\omega'} = J_1(E) + J_2(E) + J_3(E), \quad E = \hbar(\omega - \omega'), \quad (24)$$

where

$$J_1(E) = M_{cb} |F(\mathbf{K})|^2 f_{11}(E, \mathbf{K}), \quad (25)$$

$$J_2(E) = M_{ab} N \sum_{\rho_1, \rho_2} D_{\rho_1}(\mathbf{K}) D_{\rho_2}(\mathbf{K}) f_{\rho_1 \rho_2}(E, \mathbf{K}), \quad (26)$$

$$J_3(E) = M_{00} \sqrt{N} \sum_{\nu} [F(\mathbf{K}) D_{\rho}^*(\mathbf{K}) f_{\mathbf{K}\rho,1}(E, -\mathbf{K}) + F^*(\mathbf{K}) D_{\rho}(\mathbf{K}) f_{1,\mathbf{K}\rho}(E, \mathbf{K})], \quad (27)$$

and where the spectral densities f are connected with the functions Φ by relation (14).

In the absence of Fermi resonance (i.e., when $\Gamma = 0$), the quantity $J_1(E)$ goes over into the RSL cross section considered in Sec. 3, while $J_2(E)$ goes over into the cross section for RSL from C-polaritons (see, for example, [16]), whereas $J_3(E)$ vanishes. On the other hand, if $\Gamma \neq 0$, then in the region of the Fermi resonance (i.e., at $E \approx \mathcal{E}_{\rho}(\mathbf{K}) \sim 2\hbar\Omega_1$), all three terms in (24) make contributions of equal order of magnitude. In this region of the spectrum, when calculating the RSL cross section, we can confine ourselves to allowance for only that C-polariton branch of $\mathcal{E}_{\rho}(\mathbf{K})$ which intersects the overtone-frequency region.

In this case (see also (17))

$$Q(\mathbf{K}) = \frac{|u_c(\mathbf{K}\rho)|^2}{E - \mathcal{E}_{\rho}(\mathbf{K})}, \quad q(\mathbf{K}\rho) = u_c(\mathbf{K}\rho),$$

where $u_c(\mathbf{K}\rho)$ is a coefficient determining the fraction of the mechanical energy in the C-polariton $\mathbf{K}\rho$. Using (15) and (14), we find the spectral densities contained in (25)–(27):

$$f_{11}(E, \mathbf{K}) = \frac{2\pi N g(E, \mathbf{K})}{\Delta^2(E, \mathbf{K}) + 4\pi^2 g^2(E, \mathbf{K}) [A'(E, \mathbf{K})]^2}, \quad (28)$$

where

$$\begin{aligned} \Delta(E, \mathbf{K}) &= 1 + 2A'(E, \mathbf{K}) \mathcal{Z}(E, \mathbf{K}), \\ A'(E) &= A - \frac{\Gamma^2 |u_c(\mathbf{K}\rho)|^2}{E - \mathcal{E}_{\rho}(\mathbf{K})}, \end{aligned} \quad (28a)$$

$$f_{1,\mathbf{K}\rho}(E, \mathbf{K}) = f_{\mathbf{K}\rho,1}(E, -\mathbf{K}) = \frac{2\Gamma u_c(\mathbf{K}\rho) \sqrt{N}}{E - \mathcal{E}_{\rho}(\mathbf{K})} f_{11}(E, \mathbf{K}), \quad (29)$$

$$f_{\mathbf{K}\rho, \mathbf{K}\rho}(E) = \frac{2\pi g(E, \mathbf{K})}{E - \mathcal{E}_{\rho}(\mathbf{K})} \frac{2A\Delta(E, \mathbf{K}) - 2A'(E, \mathbf{K}) [1 + 2A\mathcal{Z}(E, \mathbf{K})]}{\Delta^2(E, \mathbf{K}) + 4\pi^2 g^2(E, \mathbf{K}) [A'(E, \mathbf{K})]^2}. \quad (30)$$

These relations ($\mathcal{Z}(E, \mathbf{K})$ are taken in the sense of the principal value), together with the relations (25)–(27), determine completely the RSL cross section under the conditions of Fermi resonance. Let us consider in greater detail the dependence of this cross section on E and \mathbf{K} .

We assume first that the energy E lies outside the energy band of the two free B-phonons. In this case $g(E, \mathbf{K}) \rightarrow 0$, so that

$$\begin{aligned} f_{11}(E, \mathbf{K}) &= \frac{\pi}{A'(E, \mathbf{K})} \delta(1 + 2A'(E, \mathbf{K}) \mathcal{Z}(E, \mathbf{K})), \\ f_{\mathbf{K}\rho, \mathbf{K}\rho}(E) &= \frac{2\pi \Gamma^2 |u_c(\mathbf{K}\rho)|^2}{[E - \mathcal{E}_{\rho}(\mathbf{K})]^2} \frac{\delta(1 + 2A'(E, \mathbf{K}) \mathcal{Z}(E, \mathbf{K}))}{A'(E)}. \end{aligned}$$

Consequently, in this case RSL is possible only when the energy $E = \hbar(\omega - \omega')$ is equal to the polariton energy, which in turn is determined from the equation (see also [81])

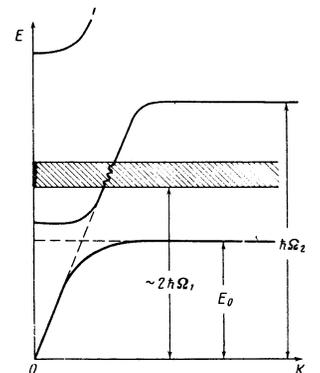
$$1 + 2 \left[A - \frac{\Gamma^2 |u_c(\mathbf{K}\rho)|^2}{E - \mathcal{E}_{\rho}(\mathbf{K})} \right] \mathcal{Z}(E, \mathbf{K}) = 0. \quad (31)$$

As shown in [81], Eq. (31), which determines the spectrum of the polaritons in the energy region of the overtone under the Fermi-resonance conditions, leads to a relation $E = E(\mathbf{K})$ which differs noticeably from

$E = \mathcal{E}_{\rho}(\mathbf{K})$. This difference is particularly large in the case when bound states of B-phonons are produced under the influence of the anharmonicity. At the same time, a gap is produced in the polariton spectrum $E = E(\mathbf{K})$ (see the figure), with a width that is directly proportional to the fraction of the mechanical energy in the C-polariton at the frequency of the Fermi resonance between the biphonon and the C-polariton ($\mathcal{E}_{\rho}(\mathbf{K}) = E_0(\mathbf{K})$, where $E_0(\mathbf{K})$ is the energy of the biphonon without allowance for the Fermi resonance; this energy satisfies the equation $1 + 2AG(E, \mathbf{K}) = 0$ (see also [61]).

If with increasing scattering angle (i.e., with increasing $|\mathbf{K}|$) we "move" along that branch of $E = E(\mathbf{K})$ which goes over at large $|\mathbf{K}|$ into $E_0(\mathbf{K})$, then the ratio $f_{\mathbf{K}\rho, \mathbf{K}\rho}(E)/f_{11}(E)$ decreases like $[E(\mathbf{K}) - \mathcal{E}_{\rho}(\mathbf{K})]^{-1}$. The ratio $f_{\mathbf{K}\rho, 1}(E)/f_{11}(E)$ decreases analogously. This means that for this branch, at large $|\mathbf{K}|$, the RSL cross section goes over into the cross section considered in Sec. 3. On the other hand, if we "move" with increasing $|\mathbf{K}|$ along that branch of $E(\mathbf{K})$ which goes over into $\mathcal{E}_{\rho}(\mathbf{K})$, then the RSL cross section goes over into the cross section of RSL by a C-polariton, obtained without allowance for the Fermi resonance. Of course, the character of the transition to the indicated asymptotic forms depends on the values of Γ and A , on the width of the B-phonon band, on the values of the tensors a , b , and c in (2), etc., and should be considered separately in each concrete case.

We now proceed to consider the RSL cross section for energies $E = \hbar(\omega - \omega')$ that fall in the energy band of two free B-phonons. In this case, as seen from (30), the RSL cross section can also depend strongly on the presence of anharmonicity. The main difference between the present situation and that considered in Sec. 3 is that in the presence of Fermi resonance with the polariton the resonant-state spectrum determined from the relation $\Delta(E, \mathbf{K}) = 0$ depends essentially on the value of \mathbf{K} . This dependence is due to the strong dependence of the C-polariton energy $\mathcal{E}_{\rho}(\mathbf{K})$, which enters in the expression for the function $A'(E, \mathbf{K})$ (see (30)), on $|\mathbf{K}|$. The most interesting from the point of view of observing this dependence (see also [81]) is the region of small $|\mathbf{K}|$, at which the ρ branch of the C-polariton spectrum intersects the energy band of the two free B-phonons. For these values of $|\mathbf{K}|$, the density of states $g(E, \mathbf{K})$ is already practically independent of \mathbf{K} , so that all possible effects can be due only to the dependence of $A'(E, \mathbf{K})$ on \mathbf{K} . Their experimental study, and incidentally also further investiga-



Dependence of the polariton energy on the wave vector in the Fermi-resonance region. E_0 —biphonon energy; the shaded energy band corresponds to the free motion of two B-phonons.

tions of the spectrum of polaritons in the Fermi-resonance region (see^[11]), are quite promising.

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