# Effects of strong anharmonicity in the spectra of optical phonons and polaritons

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This review discusses the results of theoretical and experimental studies of biphonons (phonons bound to one another) and other effects of strong anharmonicity for the spectral region of overtones and compound tones of high-frequency optical vibrations of the crystal lattice. Longitudinal-transverse splitting of a biphonon and features of the structure of its spectrum in anisotropic crystals and Fermi resonance with bulk and surface polaritons are discussed, as well as the effect of this resonance on the dispersion of polaritons. Considerable attention is paid to analyzing the experimental data (infrared and Raman spectra) in which biphonons and cardinal rearrangement of the dispersion of a polariton in the region of a Fermi resonance have been found. The influence of a Fano antiresonance and singular points of the density of states are discussed in connection with Raman spectra of polaritons.

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### **1. INTRODUCTION**

Contemporary optical methods enable one to obtain rather exact and full information, in particular, on processes involving simultaneous creation or annihilation of several' quasiparticles (two in the simplest case). These processes are of special interest, since a "residual" interaction between the quasiparticles must be manifested to some extent, and certainly can not always be considered weak.

In the case of phonons, anharmonicity acts as such a "residual" interaction that is generally not taken into account in calculating the frequencies and amplitudes of normal vibrations. In this harmonic approximation,<sup>1,2</sup> which arose at the very beginning of the development of contemporary solid-state theory, the excited states of the lattice correspond to sets of different phonon numbers of various types. For example, the energy of the excited state of a lattice with two phonons as referred to its ground-state energy is

$$\boldsymbol{E}_{\boldsymbol{l}_1\boldsymbol{l}_2}(\mathbf{k}_1, \ \mathbf{k}_2) = \hbar\Omega_{\boldsymbol{l}_1}(\mathbf{k}_1) + \hbar\Omega_{\boldsymbol{l}_2}(\mathbf{k}_2). \tag{1}$$

Here  $l_1$  and  $l_2$  are the numbers of the branches of the phonon spectrum, while  $\mathbf{k}_1$  and  $\mathbf{k}_2$  are the wave vectors of the phonons. The state being studied, in contrast to a state with one phonon, is characterized by the values of the two quasimomenta  $\hbar \mathbf{k}_1$  and  $\hbar \mathbf{k}_2$ , and thus is a two-particle state. Analogously one can write down the energy of the states of a lattice with a large number of phonons. Since the phonons  $(\mathbf{k}_1, \mathbf{l}_1)$ ,  $(\mathbf{k}_2, \mathbf{l}_2)$ , etc. do not interact with one another in multipleparticle states of this type when one neglects anharmonicity, the width of the band of any multiparticle state proves to be the sum of the widths of the energy bands of the individual phonons.

Taking into account the anharmonicity of the lattice vibrations gives rise to interaction of the phonons with one another. Whenever this interaction proves strong enough, states of mutually bound quasiparticles can be formed in addition to the multiparticle states cited above. That is, they constitute states absent in the description of the crystal in the harmonic approximation. In states of this type the quasiparticles move through the crystal as a unit and hence, just like individual phonons, are characterized by only a single value of the wave vector.

The bound state of two phonons is usually called a biphonon.<sup>3a</sup> In the course of the past ten years, a rather complete theory of biphonons has been developed. Also, as is most essential, convincing experimental proofs of their exis-

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tence in different types of crystals have been obtained.

Although biphonons as well as other, more complicated phonon complexes must be manifested in inelastic neutronscattering spectra, currently the most important experimental results have been obtained by analyzing infrared spectra as well as spectra of Raman scattering by polaritons.

As is known, Raman scattering by polaritons is allowed by the selection rules only in crystals lacking as inversion center. It is precisely in this type of crystal that a Fermi resonance with polaritons, which will be discussed below, has proved to be the physical phenomenon most sharply manifesting the features of biphonon spectra. Let us explain what we have said.

In crystals the polariton (light) branch intersects not only the region of fundamental frequencies of the lattice vibrations, but also the region of two-particle, three-particle, etc., states. Resonance with these states affects the polariton dispersion law. The result of this influence can be studied directly by observing the spectra of Raman scattering by polaritons. In this case actually a resonance occurs that is analogous to the Fermi resonance in molecules, since one of the normal waves in the crystal (polariton) resonances with states analogous to the overtones or compound tones of the intramolecular vibrations.

We recall, as is known, that resonance with the dipoleactive modes in the region of the fundamental optical lattice vibrations leads to splitting of the polariton branch. This splitting has been well studied by various methods. The essential point is that it arises even in the harmonic approximation and as a rule, it is inessential here to allow for anharmonicity.

A different situation occurs in the region of the overtones or the compound tones of the lattice vibrations, which leads to a number of qualitatively new effects. Namely, whenever the anharmonicity is rather strong and biphonons arise under its influence, a gap can be formed in the polariton spectrum at the biphonon frequency. Such a gap arises if the biphonon is sufficiently dipole-active, so that the width of the gap is larger or of the order of magnitude of the width of the polariton level. Since, by definition, the frequency of the biphonon lies outside the band of two-particles (twophonon or dissociated) states (1), the gap in the polariton spectrum must also lie in the stated spectral region. Therefore the observation of a gap under these conditions at the same time proves the formation of a biphonon, which in many studies has been used both for interpreting spectra and for estimating the anharmonicity constants (for details see below in Secs. 3 and 4).

When a polariton enters the band of two-particle states, a situation arises of the type that occurs in a Fano antiresonance: the polariton state with the given value of the wave vector  $\mathbf{Q}$  resonates with the entire continuum of two-particle states of (1) having the total wave vector  $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{Q}$ . Owing to this resonance, depending on the values of the characteristic anharmonicity constants that determine the intensity of the interaction of the polariton with the twoparticle states, various effects can occur. For example, when the anharmonicity constants are small enough, the entrance of a polariton into a band must be accompanied only by an increase in the width of its level (a new channel of its decay is opened) without a substantial effect on the dispersion of the polariton. Conversely, when the interaction of the polariton with the band of two-particle states is intense enough, the dispersion of the polariton also changes, both inside the band of two-particle states and on the approaches to it (see Sec. 4). The overall pattern of the effects that arise within the band substantially depends also on the distribution of the density of states in the band (singular points, etc). At present it would seem to constitute the most interesting aspect of study of Fermi resonance with polaritons.

Evidently a pattern analogous in many ways must occur also for surface polaritons. In connection with the development of studies on surface spectroscopy, we shall also discuss the features that arise here (Sec. 5).

Before proceeding to discuss the results obtained here, let us make some remarks on the history of the development of the studies.

First we stress that biphonons are fully analogous to the bound states of two magnons.<sup>4–6</sup> Moreover, crystalline hydrogen states of this type were studied by Van Kranendonk<sup>7,8</sup> more than twenty years ago, and shortly after this they were also observed experimentally.<sup>9</sup> In fact, Refs. 7 and 8 treated only bound states of two different quasiparticles under conditions in which the motion of one of them can be neglected in the first approximation (Van Kranendonk model). This situation did not allow use of the Van Kranendonk method for analyzing the biphonon spectrum in the compound-tone region for a number of crystals (CO<sub>2</sub>, NO<sub>2</sub>, OCS, etc.; see Ref. 10), and also for analyzing the spectrum of vibron states in molecular crystals (see the review of Ref. 11).

A generalization of the biphonon theory that allowed escaping the framework of the Van Kranendonk model has been carried out in Refs. 12–14. Subsequently a series of studies<sup>3,15–17</sup> has treated the influence of anharmonicity on the dispersion of polaritons in the spectral region of biphonons and two-particle states, while Refs. 18 and 19 have treated the contribution of biphonons to the nonlinear polarizabilities of the crystal. Questions of the theory of local and quasilocal biphonons in disordered media have been discussed in Refs. 12, 20, and 21. The influence of anharmonicity in crystals on neutron inelastic-scattering spectra has been discussed in Refs. 22 and 23.

In the presentation below we shall touch again to some extent on the results of the studies mentioned above. Yet we note now that the studies of Ref. 13 were started in connection with attempts at interpreting second-order Raman spectra in diamond. The interest in this crystal arose from the fact that Krishnan<sup>24</sup> had observed, as early as 1946, a sharp peak in the Raman spectrum of diamond at a frequncy then thought to exceed twice the maximum optical-phonon frequency ( $\Omega_0 \approx 1332.5 \pm 0.5 \text{ cm}^{-1}$ ) by about  $1.9 \pm 1.5 \text{ cm}^{-1}$ . Since the nature of this peak remained unclear, the authors of Ref. 13 advanced the hypothesis that the peak arises from the excitation of a biphonon. It was assumed that the stated phonon frequency  $\Omega_0$  corresponds to the value  $\mathbf{k} = 0$ , that optical phonons with small  $\mathbf{k}$  have a negative effective mass, and that formation of biphonons with an en-

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ergy exceeding the energy of two-particle states requires repulsion rather than attraction.

Since that time no peak in Raman spectra analogous to the peak observed by Krishnan has been observed in the series of crystals such as silicon and germanium having a structure of the diamond type and having a greater anharmonicity than diamond. This has impelled the authors of Ref. 25 to refine the calculations of the structure of the phonon bands in crystals having a diamond-type structure. It was shown by detailed calculations that the dispersion curve of the stated high-frequency phonon in diamond does not have the highest maximum at  $\mathbf{k} = 0$ , but at  $\mathbf{k} \neq 0$ . This result implied that the peak observed experimentally in Raman spectra of diamond lies in the region of the two-phonon continuum and cannot correspond to a biphonon, but most likely involves features of the density of two-particle (dissociated) states (however, see Ref. 93).

Apparently a bound state of two phonons for the overtone region was first identified in Ref. 26. In this study the absorption spectrum was measured of an HCl crystal in the region of the overtone of the fundamental vibration (i.e., at  $\omega = 2\Omega$ ,  $\Omega = 2775 \text{ cm}^{-1}$ ). Along with a broad absorption band corresponding to excitation of two free phonons (the width of this band is  $2\Delta$ , where  $\Delta$  is the width of the phonon band,  $\Delta \approx 90 \text{ cm}^{-1}$ ), an absorption peak also proved to lie in the region of lower frequencies with a maximum at  $\omega = 5313$ cm<sup>-1</sup> and a half-width  $\approx 20 \text{ cm}^{-1}$ ) (for spectra of liquid HCl see Ref. 92).

We emphasize that anharmonicity cannot be taken into account within the framework of perturbation theory in the theory of biphonons or more complicated phonon complexes, as is done, e.g., in the theory of heat conductivity, thermal expansion, etc.<sup>27,28</sup> In many crystals for the optical branches of the spectrum, the dimensionless parameter  $A / \Delta$ , which is the ratio of the anharmonicity constant A to the width  $\Delta$  of the phonon band, can be of the order of unity. It is precisely in situations of this type that strong anharmonicity gives rise to qualitatively new features in phonon spectra.

Moreover, we must consider the idea that anharmonicity in crystals, together with quantum objects formed from a small number of quasiparticles, such as biphonons, also makes possible "elementary" excitations corresponding to propagation of purely classical nonlinear waves (of the soliton type) that are solutions of the corresponding nonlinear equations of motion. In quantum language one can say that this type of excitation corresponds to bound states of a large number of quasiparticles. While this is a matter for the future, an analysis of the experimental conditions under which one might note, e.g., Raman processes involving these waves, would substantially assist the development of studying them. The energy of nonlinear "elementary" excitations must be large in comparison with the energy of one quasiparticle (phonon, polariton), so that the study of Raman scattering by nonlinear waves, at least far from structural phasetransition points accompanied by formation of a soft mode, would probably require the use of quite powerful light sources. However, under high pumping levels of crystals, the concentration of various types of quasiparticle (e.g., phonons or polaritons) can sharply increase. In this connection the highly interesting question also arises of the conditions of existence of second sound or other excitations in a system of quasiparticles not in a state of thermodynamic equilibrium, and of whether this sound can be observed by optical methods. If one is speaking, e.g., of polaritons, then the velocity of second sound in a system of them must be of the order of the velocity of light. Just like the observation of polaritons themselves, the observation of second sound would require, e.g., small-angle Raman study.

While mentioning here along with biphonons, to which this review is devoted, also the classical nonlinear waves of the silicon type and second sound in a system of quasiparticles, we have wished only to call attention to the wide possibilities opened up here and the directions of searches and analysis of the effects of strong anharmonicity of phonons, and also to the place taken in this field of solid-state theory by studies of such simple products of strong anharmonicity as biphonons.

In the following sections of this review we shall discuss the foundations of the theory of biphonons, examine the features of Fermi resonance, in particular Fermi resonance with polaritons, and also analyze the existing data obtained in studying infrared absorption and Raman spectra.

We emphasize that reviews by one of the present authors<sup>3</sup> have already been devoted to discussing the effects of strong anharmonicity in Raman spectra, so that the attention in the present article has been concentrated mainly on the results of the theory and experiment not found in Ref. 3.

### 2. THE GREEN'S-FUNCTION METHOD IN THE THEORY OF BIPHONONS: FERMI RESONANCE AND THE STRUCTURE OF THE SPECTRUM

#### a) Model Hamiltonian

One can conclude that the anharmonicity of the optical vibrations in crystals for the overtone region of the spectrum of intramolecular vibrations can be very considerable, even from purely qualitative considerations. Actually, in isolated molecules the anharmonicity energy A of the intramolecular vibrations usually amounts to a value of the order of 1-3% of the quantum energy of the fundamental vibrations  $\hbar\Omega$ . Here one takes the anharmonicity energy A to mean the quantity  $A = (2\hbar\Omega - E_2)/2$ , where  $E_2$  is the energy of the excited state having the quantum number n = 2. For example, when  $\Omega = 1000 \text{ cm}^{-1}$ , the energy A usually proves to be of the order of 10-30  $\text{cm}^{-1}$ . At the same time, as is implied, e.g., from measuring second-order Raman spectra (see Ref. 29), the intermolecular interaction energy in crystals, which determines the width of the phonon energy band  $\Delta$  for the stated region of frequencies  $\Omega$  also can be of the order of magnitude of tens of reciprocal centimeters. Therefore the dimensionless ratio  $A/\Delta$ , as was noted in the Introduction, is generally not small. This is precisely why, whenever the width of the phonon bands is of the order of A, the spectrum of optical vibrations in the overtone or compound-tone regions can have a highly complex structure. In the harmonic approximation (see Ref. 36) the Hamiltonian of the crystal describing the effect of the intermolecular interaction on the spectrum, e.g., of nondegenerate molecular vibrations, can be written as follows:

$$\hat{H}_0 = \sum_n \hbar \Omega B_n^* B_n + \sum_{n, m} V_{nm} B_n^* B_m.$$
<sup>(2)</sup>

Here  $B_n^+$  and  $B_n$  are the Bose operators for creation and annihilation of a quantum of intramolecular vibrations with the energy  $\hbar\Omega$  in the molecule *n*, and  $V_{nm}$  is the matrix element of the interaction energy of the molecules *n* and *m* corresponding to transfer of one quantum of energy from molecule *m* to molecule *n*. If several molecules are contained in the unit cell of the crystal, then the index *n* is composite,  $n \equiv (\mathbf{n}, \alpha)$ , where **n** is the integral lattice vector, and  $\alpha$  is the number of the molecule in the unit cell:  $\alpha = 1, 2, ...$ 

To take intramolecular anharmonicity into account, one must add the following operator to the Hamiltonian of (2):

$$\hat{H}_{A} = -A \sum (B_{n}^{*})^{2} B_{n}^{2}.$$
(3)

Thus the complete Hamiltonian is<sup>1)</sup>

$$\hat{H}' = \hat{H}_0 + \hat{H}_A. \tag{4}$$

We have chosen the operator of (3) in such a way that the correct values of the energy of a crystal with two vibrational quanta are obtained in the absence of an intermolecular interaction.

When we take many intramolecular vibrations into account, the Hamiltonian has the form

$$\hat{H}' = \sum_{nj} \hbar \Omega B_n^{+j} B_n^{j} + \sum_{\substack{m, n \ j < j'}} V_{nm}^{jj'} B_n^{+j} B_m^{j'} - \sum_{\substack{n, i < j' \ n < j'}} A(jj') B_n^{+j} B_n^{+j'} B_n^{j} B_n^{j'}.$$
(4')

This Hamiltonian must be used in discussing the spectra of crystals containing molecules with degenerate or close-lying frequencies.

At the same time, strictly speaking, one can use the operator (4) or (4') for studying the state of a crystal with two vibrational quanta only in cases in which the intramolecular anharmonicity of the form of (3) is fundamental, while the component of the anharmonicity involving the existence of an intermolecular interaction can be omitted.<sup>2)</sup> We also emphasize that intermolecular anharmonicity can prove important, even in the limit of large A, in calculating the width of biphonon bands. In this case one must include the following term in the Hamiltonian  $\hat{H}'$ :

$$\hat{H}_{\rm T} = \frac{1}{2} \sum_{n,m} W_{nm} \, (B_n^{+})^2 \, B_m^2. \tag{5}$$

This leads to the joint/transfer of two vibrational quanta from molecule *m* to molecule *n* and vise versa  $(n \neq m)$ . Of course, this transfer of two vibrational quanta is allowed also when one uses the Hamiltonian of (4). However, in this approximation the corresponding matrix element differs from zero only in second-order perturbation theory in the intermolecular interaction  $V_{nm}$ . As we can easily convince ourselves, this matrix element equals  $V_{nm}^2$ , so that the terms containing  $V_{nm}$  could be omitted under the condition that

$$\frac{V_{nm}^2}{4} \gg |W_{nm}|. \tag{6}$$

Even if this inequality is satisfied for small  $|\mathbf{n} - \mathbf{m}|$ , it generally can break down for large  $|\mathbf{n} - \mathbf{m}|$ , since the dipole-active

overtones have  $|W_{nm}| \sim |\mathbf{n} - \mathbf{m}|^{-3}$ , whereas the quantity  $V_{nm}^2$  can decline with increasing  $|\mathbf{n} - \mathbf{m}|$  as  $|\mathbf{n} - \mathbf{m}|^{-6}$  or faster. For the dipole-active overtones it is also important to allow for the operator of (5), because this operator corresponds to Coulomb long-range action. For example, in cubic crystals it leads to longitudinal-transverse splitting of biphonons. Fortunately, inclusion of the operator of (5) in the complete Hamiltonian (see also Refs. 31 and 32) only insubstantially modifies the schema of the calculation, as will be illustrated below.<sup>3)</sup>

If the anharmonicity is so large that the inverse relationship holds instead of (6), then specifically the terms containing  $W_{nm}$  make the fundamental contribution to the width of the biphonon energy band. In this case the biphonon energy is

$$E_{l}(\mathbf{k}) = 2\hbar\Omega - 2A + \sum_{m} W_{nm} e^{i\mathbf{k} \cdot (\mathbf{m} - \mathbf{n})} + O\left(\frac{\Delta^{2}}{A}\right)$$
(7)

This relationship is exact in the limit of large A. The quantities  $W_{nm}$  that figure here, and which determine the matrix element for transfer of two quanta from molecule n to molecule m, must be found by taking the intramolecular anharmonicity into account. In order to stress this situation, we shall write the corresponding matrix elements in the form  $W_{nm}^{A}$ . In line with what we have said, in the following analysis of the biphonon states we shall use a more general Hamiltonian than (4) in the form

$$\hat{H} = \hat{H}_{0} + \hat{H}_{A} + \hat{H}_{T}.$$
 (8)

In deriving this Hamiltonian we have started with the model of a molecular crystal. Actually its field of applicability also covers nonmolecular crystals, provided only that one is speaking of optical phonons whose band width is far smaller than the phonon frequency. In these regions of the spectrum the vibrations inside the unit cell resemble molecular vibrations in molecular crystals, since the relatively small phonon band width indicates weakness of interaction of the vibration of atoms lying in different unit cells.

#### b) Fermi resonance in crystals

One can find the energy of the biphonons, in particular, by using the Green's function method. Within the framework of the model being discussed, this method proves highly productive, This is because, despite allowing for anharmonicity, all the Green's functions needed for calculating the dielectric permittivity of the crystal, its nonlinear polarizabilities, the density of states, the Raman cross-sections, and other physical properties can be found exactly without using perturbation theory. Below we shall illustrate what we have said by going to a model even more general than that discussed above. Namely, we shall seek the Green's functions in the presence of Fermi resonance in the crystal.

In Fermi resonance in an isolated molecule, the frequency of one of the molecular vibrations proves to be close to the frequency of an overtone (or a compound tone) of some other vibration. In the case, e.g., of nondegenerate vibrations, resonance arises here of the two excited states of the molecule. Owing to the anharmonicity of the intramolecular vibrations, this leads to characteristic doublets of com-

parable intensity in absorption spectra or Raman spectra or even in the other types of spectra (depending on the symmetry of the molecule and the type of vibrations). If degenerate vibrations also participate in the Fermi resonance, the number of lines in these spectra can be large.<sup>37</sup> In going from an isolated molecule to a crystal, branches of optical phonons arise in the region of the fundamental vibrations of the molecule owing to the translational symmetry and under the influence of the intermolecular interaction. In the overtone and compound-tone region, bands of multiparticle states arise, and if the anharmonicity is strong enough, also bands of states of mutually bound quasiparticles, (e.g., biphonons). Therefore, in a Fermi resonance generally a large number of excited states of the crystal resonate with one another, so that the spectra that arise here are substantially complicated.

In order to analyze them, and in particular, to study the effect of Fermi resonance on biphonon spectra, we must generalize somewhat the Hamiltonian of (8).

We shall assume that the conditions for Fermi resonance are fulfilled even in the free molecule. That is, for the sake of simplicity, there are two nondegenerate vibrations Band C with the frequencies  $\Omega_1$  and  $\Omega_2$ , for which, e.g., we have  $2\Omega_1 \approx \Omega_2$ . In this case, when we take the intramolecular cubic anharmonicity into account (with the constant  $\Gamma$ ), we must add to the Hamiltonian of (8) the sum of two terms:

$$\hat{H}_{0}(\mathbf{C}) + \hat{H}_{\mathbf{F}}(\mathbf{B}, \mathbf{C}),$$
  
(C) -  $\sum \hbar O C^{\dagger}C + \sum Y V^{(2)} C^{\dagger}C$  (9)

$$\hat{H}_{0}(C) = \sum_{n} \hbar \Omega_{2} C_{n}^{*} C_{n} + \sum' V_{nm}^{(2)} C_{n}^{*} C_{m}, \qquad (9)$$

$$\hat{H}_{n}(P_{n}, C) = P_{n} \sum_{n} V_{n}^{(2)} C_{n}^{*} C_{n}^{*} C_{m}, \qquad (10)$$

$$\hat{H}_{\mathbf{F}}$$
 (B, C) =  $\Gamma \sum_{n} [(B_{n}^{+})^{2}C_{n} + C_{n}^{+}(B_{n})^{2}].$  (10)

Here the operator  $\hat{H}_F$  gives rise to the interaction of the B and C vibrations (B and C phonons), and the operators  $C_n$ and  $C_n^+$  (Bose operators for creation and annihilation of a quantum of intramolecular vibrations with the energy  $\hbar\Omega_2$ ) also figure alongside the Bose operators  $B_n$  and  $B_n^+$ . The anharmonicity constant  $\Gamma$  differs from zero only for pairs B and C of intramolecular vibrations for which the matrix element  $\langle 2B|\pi|1C\rangle \equiv \pi_{21}$  differs from zero. Here  $\pi$  is the potential energy of the intramolecular vibrations with allowance for anharmonicity, whereas  $|1C\rangle \equiv C^+|0\rangle$  and  $|2B\rangle$  $\equiv (B^+)^2 |0\rangle$ . Here  $|0\rangle$  is the ground state of the molecule. Since the quantity  $\pi$  is fully symmetric with respect to all symmetry elements of the molecule, the condition  $\pi_{21} \neq 0$ imposes evident restrictions on the symmetry of the B and C vibrations being treated. It is also evident that the anharmonicity term of (10) for  $\Gamma \neq 0$  is the fundamental term in the region of crystal energies  $E \approx 2\hbar\Omega_1 \approx \hbar\Omega_2$ , while the addition of another type of anharmonic term, e.g., terms of the form  $C^+C^2$  + h.c. (Hermitian conjugate), etc., leads only to small corrections. Thus, the complete Hamiltonian H acquires the form

$$\hat{H} = \hat{H}_0(B) + \hat{H}_0(C) + \hat{H}_A(B) + \hat{H}_T(B) + \hat{H}_F(B, C).$$
(11)

For simplicity we shall assume that the unit cell of the crystal contains one molecule, and transform to the momentum representation for the operators B and C:

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$$B_{n} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} B_{\mathbf{k}} e^{i\mathbf{k}\mathbf{n}},$$
$$C_{n} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}\mathbf{n}}.$$

In this representation the Hamiltonian of (11) has the form

$$\begin{split} \hat{H} &= \sum_{\mathbf{k}} \left[ \epsilon_{1} \left( \mathbf{k} \right) B_{\mathbf{k}}^{\dagger} B_{\mathbf{k}} + \epsilon_{2} \left( \mathbf{k} \right) C_{\mathbf{k}}^{\dagger} C_{\mathbf{k}} \right] \\ &- \frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}} \widetilde{A} \left( \mathbf{k} + \mathbf{k}' \right) B_{\mathbf{k}}^{\dagger} B_{\mathbf{k}'}^{\dagger} B_{\mathbf{q}} B_{\mathbf{k} + \mathbf{k}' - \mathbf{q}} \\ &+ \frac{\Gamma}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{k}'} \left( B_{\mathbf{k}}^{\dagger} B_{\mathbf{k}'}^{\dagger} C_{\mathbf{k} + \mathbf{k}'} + \mathbf{h.c.} \right), \end{split}$$

where we have

$$\widetilde{A}(\mathbf{k}) = A - \frac{1}{2} W^{A}(\mathbf{k}).$$

If we introduce the operator

$$\hat{T}(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{q} B_{\frac{\mathbf{k}'}{2} - q} B_{\frac{\mathbf{k}}{2} + q}, \qquad (12)$$

then we can write the Hamiltonian  $\hat{H}$  in a more compact form:

$$\begin{split} \hat{H} &= \sum_{\mathbf{k}} \left\{ \varepsilon_1 \left( \mathbf{k} \right) B_{\mathbf{k}}^* B_{\mathbf{k}} + \varepsilon_2 \left( \mathbf{k} \right) C_{\mathbf{k}}^* C_{\mathbf{k}} - \widetilde{A} \left( \mathbf{k} \right) T^+ \left( \mathbf{k} \right) T \left( \mathbf{k} \right) \right. \\ &+ \Gamma \left[ T^+ \left( \mathbf{k} \right) C_{\mathbf{k}} + C_{\mathbf{k}}^* T \left( \mathbf{k} \right) \right] \right\}. \end{split}$$

Assuming the temperature of the crystal to be zero, we shall seek the retarded Green's function

$$G_{\mathbf{k}}^{(1)}(t) = -i\theta(t) \langle 0 | C_{\mathbf{k}}(t) C_{\mathbf{k}}^{\dagger}(0) | 0 \rangle.$$
(12')

Here we have  $\theta(t) = 1$  for t > 0, and  $\theta(t) = 0$  for t < 0, while we also have the functions

$$\begin{aligned} G_{\mathbf{k}}^{(3)}\left(t\right) &= -i\theta\left(t\right)\left\langle 0 \mid T\left(\mathbf{k}, t\right)C_{\mathbf{k}}^{*}\left(0\right) \mid 0\right\rangle,\\ G_{\mathbf{k}, q}^{(3)}\left(t\right) &= -i\theta\left(t\right)\left\langle 0 \mid B_{\frac{\mathbf{k}}{2} + q}\left(t\right)B_{\frac{\mathbf{k}}{2} - q}\left(t\right)C_{\mathbf{k}}^{+}\left(0\right) \mid 0\right\rangle. \end{aligned}$$

Evidently we have

$$\frac{1}{\sqrt{N}} \sum_{\mathbf{q}} G_{\mathbf{k},\mathbf{q}}^{(3)}(t) = G_{\mathbf{k}}^{(2)}(t).$$

Employing the usual method (for details see Ref. 3b), we can easily convince ourselves that the Green's function is

$$G_{\mathbf{k}}^{(1)}(\omega) = \frac{\hbar \left[1 + 2\widetilde{A}\left(\mathbf{k}\right) R\left(E, \mathbf{k}\right)\right]}{\left[E - \varepsilon_{2}\left(\mathbf{k}\right)\right] \Delta\left(E, \mathbf{k}\right)},$$
(13)

Here we have  $R(E,\mathbf{k}) = 2 \int [\rho_0(\varepsilon,\mathbf{k})/(E-\varepsilon)] d\varepsilon \ (\rho_0(\varepsilon,\mathbf{k}))$ is the density of two-particle states for  $A = \Gamma = 0$ , and

$$\Delta (E, \mathbf{k}) = 1 + 2 \left[ \widetilde{A} (\mathbf{k}) - \frac{\Gamma^2}{E - \varepsilon_f (\mathbf{k})} \right] R (E, \mathbf{k}), \quad (13')$$

$$G_{\mathbf{k}}^{(2)}(\omega) = \frac{2\hbar\Gamma R\left(E,\,\mathbf{k}\right)}{\left[E - \varepsilon_{2}\left(\mathbf{k}\right)\right]\Delta\left(E,\,\mathbf{k}\right)}.$$
 (14)

To calculate the Raman cross-section and the cross-sections of nonlinear optical processes, we must know also a series of other Green's functions in addition to the functions  $G_k^{(1)}$ , and  $G_k^{(2)}$ , in particular, the two-particle Green's function  $G_{k,q,q'}^{(4)}(t)$ , as defined by the relationship

$$G_{\mathbf{k},\mathbf{q},\mathbf{q}'}^{(4)}(t) = i\theta(t) \langle 0 | B_{\frac{\mathbf{k}}{2}+\mathbf{q}}(t) B_{\frac{\mathbf{k}}{2}-\mathbf{q}}(t) B_{\frac{\mathbf{k}}{2}+\mathbf{q}'}(0) B_{\frac{\mathbf{k}}{2}-\mathbf{q}'}(0) | 0 \rangle.$$

One can show that

$$\begin{aligned} G_{\mathbf{k},\mathbf{q},\mathbf{q}'}^{(4)}\left(\omega\right) &= -\frac{2}{\sqrt{N}} \frac{\widetilde{A}\left(\mathbf{k}\right) G_{\mathbf{k}\mathbf{q}}^{(5)}\left(\omega\right) - \Gamma G_{\mathbf{k},\mathbf{q}'}^{(6)}\left(\omega\right)}{E - \varepsilon_{1}\left(\frac{\mathbf{k}}{2} + \mathbf{q}\right) - \varepsilon_{1}\left(\frac{\mathbf{k}}{2} - \mathbf{q}\right)} \\ &+ \frac{\hbar \left(\delta_{\mathbf{q}+\mathbf{q}'} + \delta_{\mathbf{q}+\mathbf{q}'}\right)}{E - \varepsilon_{1}\left(\frac{\mathbf{k}}{2} + \mathbf{q}\right) - \varepsilon_{2}\left(\frac{\mathbf{k}}{2} - \mathbf{q}\right)} \,. \end{aligned}$$

Here  $G_{\mathbf{k},\mathbf{q}}^{(5)}(\omega)$  is the Fourier component of the Green's function  $G_{\mathbf{k},\mathbf{q}}^{(5)}(t)$ , while

$$G_{\mathbf{k},\,\mathbf{q}'}^{(5)}\left(t\right) = -i\theta\left(t\right)\left\langle 0 \mid T\left(\mathbf{k},\,t\right)B_{\frac{\mathbf{k}}{2}-\mathbf{q}'}^{*}\left(0\right)B_{\frac{\mathbf{k}}{2}+\mathbf{q}'}^{*}\left(0\right)\mid 0\right\rangle.$$

The latter is defined by the relationship

 $G_{\mathbf{k},\mathbf{q}'}^{(5)}(\omega)$ 

$$=\frac{2\hbar}{\sqrt{N}\left[E-\varepsilon_{1}\left(\frac{\mathbf{k}}{2}+\mathbf{q}'\right)-\varepsilon_{1}\left(\frac{\mathbf{k}}{2}-\mathbf{q}'\right)\right]}\frac{1}{\Delta\left(E,\mathbf{k}'\right)},\quad(16)$$

whereas

$$G_{\mathbf{k},\mathbf{q}'}^{(6)}(\omega) = \frac{\Gamma}{E - \varepsilon_2(\mathbf{k})} G_{\mathbf{k},\mathbf{q}'}^{(5)}(\omega)$$
(17)

is the Fourier component of the Green's function

$$G_{\mathbf{k}, \mathbf{q}'}^{(\theta)}(t) = -i\theta(t) \langle 0 | C_{\mathbf{k}}(t) B_{\frac{\mathbf{k}}{2}}^{+} - \mathbf{q}'(0) B_{\frac{\mathbf{k}}{2}}^{+} - \mathbf{q}'(0) | 0 \rangle.$$

The expressions given above imply that taking the anharmonicity in the system of the phonons into account, which is characterized by the anharmonicity constants Aand  $\Gamma$  in the framework of the model being discussed, with poles of the form of (1), leads directly to appearance in the Green's functions of a new type of poles defined by the relationship

$$\Delta (\mathbf{k}, \ \mathbf{\omega}) = 0 \ . \tag{18}$$

This equation allows one to calculate the energy of the biphonons allowing for the Fermi resonance of the two-particle states of the B phonons with the band of C phonons. The relationship (18) implies that the anharmonicity constants are as though renormalized when one takes account of the Fermi resonance:



FIG 1. The function  $\Phi_1(E)$ . Here  $\varepsilon_2(\mathbf{k})$  is the energy of a C phonon, and  $\tilde{\varepsilon}_2 = \varepsilon_2 + (\Gamma^2/\widetilde{A})$ .

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$$\widetilde{A}(\mathbf{k}) \rightarrow \widetilde{A}(\mathbf{k}) - \frac{\Gamma^2}{E - \epsilon_2(\mathbf{k})}, \quad E = \hbar \omega.$$

The new anharmonicity "constant" becomes a function of the energy E, while its effective value in the energy region under discussion proves to depend substantially on the position of the energy of a C phonon with respect to the band of two-particle states. Therefore, generally a Fermi resonance strongly affects the conditions for formation of biphonons and the positions of the levels. Let us explain what we have said by turning to Eq. (18).<sup>4)</sup> We can conveniently rewrite this equation, which determines the value of the biphonon energy  $E = E' + i\gamma$ , in the form

$$\Phi_1(E) = \Phi_2(E). \tag{19}$$

Here we have

1 40

$$\Phi_{1}(E) = -1 + \frac{\Gamma^{2}/\widetilde{A}(\mathbf{k})}{\widetilde{\epsilon}_{2}(\mathbf{k}) - E}, \quad \widetilde{\epsilon}_{2} = \epsilon_{2} + \frac{\Gamma^{2}}{\widetilde{A}}, \quad (20)$$

$$\Phi_{2}(E) = 2\widetilde{A}(\mathbf{k}) \oint \frac{\rho_{0}(\varepsilon, \mathbf{k})}{E-\varepsilon} d\varepsilon + 2\pi i \widetilde{A}(\mathbf{k}) \rho_{0}(E, \mathbf{k}).$$
(21)

### c) Biphonons and quasibiphonons

The graph of the function  $\Phi_1(E)$  for the case  $\tilde{A} > 0$  is schematically shown in Fig. 1 (here we have taken into account the fact that  $\Gamma^2/\tilde{A}\varepsilon_2(\mathbf{k}) < 1$ ). In this same diagram, the dotted line indicates the value of the function  $\Phi_1(E)$  upon neglecting the Fermi resonance (i.e., when  $\Gamma = 0$ : in this case we have  $\Phi_1(E) = -1$ ). Figure 2 shows for the same case  $\tilde{A} > 0$  the variation of Re  $\Phi_2(E)$  without account taken of damping. Within the framework of the model being discussed, the damping of biphonon states can involve the decay into two free phonons. Evidently, this type of quasistationary (resonance) states—quasibiphonons—can have a physical meaning only in the region of small  $\rho_0(E,\mathbf{k})$ , where their width is  $\gamma < \operatorname{Re} E = E'$ .

The function  $\operatorname{Re}\Phi_2(E)$  in three-dimensional crystals is everywhere bounded. In particular, for states with small **k**, we have the functions  $\rho(\varepsilon, \mathbf{k}) \approx \rho(\varepsilon, 0)$ . In the neighborhood of the edge of  $\tilde{\varepsilon}(\varepsilon = \varepsilon_{\min} \text{ or } \varepsilon = \varepsilon_{\max})$ , the bands of twoparticle states are  $\rho_0(\varepsilon, 0) = \rho_0 \sqrt{|\tilde{\varepsilon} - \varepsilon|}$ . Therefore, as *E* approaches  $\bar{\varepsilon}$  outside the band of two-particle states, the function  $\Phi_2(E) = \operatorname{Re} \Phi_2(E)$ , while remaining finite, has an



FIG. 2. The function Re  $\Phi_2(E)$  (solid lines). The dotted line corresponds to the function  $\Phi_1(E) = -1$ . The open circle corresponds to a biphonon, and the solid circle to a quasibiphonon.

infinite derivative (see Fig. 2). Figure 2 also shows the function  $\Phi_1 = -1$  for  $\Gamma = 0$ . This diagram implies that, whenever the value of  $\Phi_2(E)$  for  $E \rightarrow \varepsilon_{\min}$  approaches a quantity smaller than unity (i.e.,  $|\Phi_2(\varepsilon_{\min})| < 1$ ), a bound state of two phonons arises, or a biphonon. Along with the biphonon state, which has an energy  $E_2 < \varepsilon_{\min}$  (open circle in Fig. 2), a quasibiphonon is also formed (solid circle in Fig. 2) with the energy  $E_{qb}$ , lying inside the band of two-particle states. If the anharmonicity is not too strong, so that the quantity  $|\Phi_2(\varepsilon_{\min})|$  does not exceed unity by too much, the quasibiphonon lies in a region of low density of two-particle states. Its width proves to be small in comparison with the band, while a maximum arises in the density of states upon allowing for anharmonicity that is not associated with Van Hove points.

Actually, the density of states having the total wave vector  $\mathbf{q} + \mathbf{q}' = \mathbf{k}$  is determined by the relationship

$$\rho(E, \mathbf{k}) = -\frac{1}{2\pi N} \sum_{\mathbf{q}} (1 + \delta_{\mathbf{q}0}) \operatorname{Im} G_{\mathbf{k}, \mathbf{q}, \mathbf{q}}^{(+)}(E + i\gamma),$$
  

$$\gamma \rightarrow +0.$$
(22)

For noninteracting phonons (i.e., when  $\bar{A} = \Gamma = 0$ ), we have

$$\rho(E, \mathbf{k}) \equiv \rho_0(E, \mathbf{k})$$
  
=  $\frac{1}{2N} \sum_{\mathbf{q}} (1 + \delta_{\mathbf{q}0}) \delta \left[ E - \varepsilon_1 \left( \frac{\mathbf{k}}{2} + \mathbf{q} \right) - \varepsilon_1 \left( \frac{\mathbf{k}}{2} - \mathbf{q} \right) \right].$ 

If  $\tilde{A} \neq 0$ , but  $\Gamma = 0$  (no Fermi resonance), the function  $G_{k,q,q}^+(E)$  is determined by the relationship

$$G_{\mathbf{k},\mathbf{q},\mathbf{q}}^{+}(E) = \left[E - \varepsilon_{1}\left(\frac{\mathbf{k}}{2} + \mathbf{q}\right) - \varepsilon_{1}\left(\frac{\mathbf{k}}{2} - \mathbf{q}\right)\right]^{-1} - \frac{4\widetilde{A}\left(\mathbf{k}\right)\Delta^{-1}\left(E,\mathbf{k}\right)}{N\left[E - \varepsilon_{1}\left(\frac{\mathbf{k}}{2} + \mathbf{q}\right) - \varepsilon_{1}\left(\frac{\mathbf{k}}{2} - \mathbf{q}\right)\right]^{2}},$$

so that

$$= \rho_0(E, \mathbf{k}) + \frac{16\widetilde{A}^2(\mathbf{k}) D(E, \mathbf{k}) \rho_0(E, \mathbf{k})}{[1 + 2\widetilde{A}(\mathbf{k}) R'(E, \mathbf{k})]^2 + 16\pi^2 \widetilde{A}^2(\mathbf{k}) \rho_0^2(E, \mathbf{k})}.$$
 (23)

Here we have

 $\rho(E, \mathbf{k})$ 

$$R'(E, \mathbf{k}) \equiv \operatorname{Re} R(E, \mathbf{k}) = 2 \oint \frac{\rho_0(\varepsilon, \mathbf{k}) d\varepsilon}{E - \varepsilon},$$
$$D(E, \mathbf{k}) = \oint \frac{\rho_0(\varepsilon, \mathbf{k}) d\varepsilon}{(E - \varepsilon)^2}.$$
(23a)

In the region of the energy E where  $\rho_0(E,\mathbf{k}) = 0$ , i.e., outside the band of two-particle states, Eq. (23) reduces to the following:

$$\rho (E, \mathbf{k}) = 4D (E, \mathbf{k}) | \widetilde{A} (\mathbf{k}) | \delta [1 + 2\widetilde{A} (\mathbf{k}) R (E, \mathbf{k})],$$
(23b)

or

 $\rho(E, \mathbf{k}) = \delta(E - E_{\mathbf{b}}).$ 

Here the biphonon energy  $E_{\rm b}$  is a root of the equation

$$\mathbf{1} + 4\widetilde{A} (\mathbf{k}) \oint \frac{\rho_0 (\boldsymbol{\varepsilon}, \, \mathbf{k}') \, \mathrm{d}\boldsymbol{\varepsilon}}{\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}} = 0.$$
 (24)

Inside the band of two-particle states in the energy region

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FIG. 3. The functions  $\Phi_1$  (*E*) and  $\Phi_2$  (*E*) in the presence of Fermi resonance. Here  $\varepsilon_{\min}$  and  $\varepsilon_{\max}$  are the boundaries of the band of two-particle dissociated states. The lower left open circle corresponds to a biphonon, and the right-hand circle to a quasibiphonon.

 $E \simeq E_{\rm qb}$ , where  $E_{\rm qb}$  is a root of the equation

$$1+4\widetilde{A}(\mathbf{k})\,\oint \frac{\rho_0\left(\boldsymbol{\varepsilon},\ \mathbf{k}\right)\,\mathrm{d}\boldsymbol{\varepsilon}}{\boldsymbol{\varepsilon}-\boldsymbol{\varepsilon}}=0,$$

we can write the relationship (23) in the form

$$\rho(E, \mathbf{k}) = \rho_0(E, \mathbf{k}) + \frac{1}{\pi} \frac{\gamma}{(E - E_{\rm qb})^2 + \gamma^2}.$$
 (25)

Here  $\gamma = \pi \rho_0 (E_{qb}, \mathbf{k}) / D(E_{qb}, \mathbf{k})$  is the half-width of the quasibiphonon level. The presented expression for  $\gamma$  implies that this half-width can be rather small only when the quasibiphonon level lies in a region of low densities of levels of two-particle states  $\rho_0 (E_{qb}, \mathbf{k})$ .

Now let us proceed to discuss the case with a Fermi resonance  $(\tilde{A} \neq 0 \text{ and } \Gamma \neq 0)$ .

In this case the position and number of the roots of Eq. (19) depend substantially on the relationship between the quantities  $\tilde{A}$  and  $\Gamma$ , and on the position of the energy  $\varepsilon_2(\mathbf{k})$  with respect to the band of two-particle states. To illustrate what we have said, Figs. 3–5 show the graphs of  $\Phi_1(E)$  and  $\Phi_2(E)$  and indicate the roots of Eq. (19) in three limiting cases.

Figure 3 corresponds to the case in which both the energy  $\varepsilon_2(\mathbf{k})$  of a C phonon and the energy  $\tilde{\varepsilon}(\mathbf{k}) = \varepsilon_2(\mathbf{k}) + [\Gamma^2 / \tilde{A}(\mathbf{k})]$  lie outside the band of two-particle states and are far enough from the energy  $\varepsilon_{\min}$  at its bottom. In this case the number of solutions of Eq. (18) lying outside the band of two-particle states is two. One of them (the lower one) is genetically associated with the C-phonon state, and transforms into it as the energy of a C phonon becomes farther removed from the band of two-particle states.

In the case depicted in Fig. 4, the energy  $\tilde{\varepsilon}_2(\mathbf{k})$  lies in the



FIG. 4. The same as in Fig. 3, but with  $\varepsilon_{\min} < \tilde{\varepsilon}_2 < \varepsilon_{\max}$ .



FIG. 5. The same as in Fig. 3, but with  $\tilde{\varepsilon}_2 > \varepsilon_{\text{max}}$ .

band of two-particle states, while we have  $\tilde{A} \approx \Gamma$ . For the energy region  $E < \varepsilon_{\min}$ , Eq. (19) has only a single solution, and a quasibiphonon state is not formed.

If the energy of a C phonon lies above the band of twoparticle states and the width  $\Delta$  of this band is large in comparison with  $\Gamma$ , a situation can occur that corresponds to Fig. 5. In this case the solutions of Eq. (19) lie on different sides of the band of two-particle states, and a quasibiphonon state can be formed.

To find the density of states in the presence of a Fermi resonance Eqs. (15)–(17) have to be used. This can be carried out analogously to what was done for the case  $\Gamma = 0$ . We shall not present the corresponding calculations here.

The dielectric permittivity in the region of two-phonon spectra is also determined by the Green's functions found above.

Taking account of the anharmonicity, which affects the density of two-particle states of (23), simultaneously gives rise both to new resonances of the light-absorption coefficient  $\kappa(E)$  with biphonons (outside the band of two-particle states) and with quasibiphonons (inside this band) (see (23a) and (23b) and also Ref. 3b). Moreover, interesting features arise in the density of states  $\rho(E,K)$ , and hence in the light-absorption coefficient  $\kappa(E)$ , at E values that correspond to the Van Hove critical points of the unperturbed (i.e., with A = 0) density of states  $\rho_0(E,K)$ .

The function  $\varkappa(E)$  is nonanalytic with respect to the anharmonicity constant  $\tilde{A}(0)$ . If the anharmonicity is not taken into account ( $\tilde{A} = 0$ ), the function  $\varkappa(E)$  is proportional to the density of states  $\rho_0(E,K)$  and has the same features. When one takes account of anharmonicity ( $\tilde{A} \neq 0$ ), the derivative of  $\varkappa(E)$  approaches  $+\infty$  on both sides near the critical points, and four cases can arise, which are presented in Fig. 6. Their existence becomes obvious when we take account of the fact that the density of states  $\rho_0(E,K)$  is continuous in three-dimensional crystals, while its derivative shows a discontinuity at the analytic singular points. Thus, for example, at the minimum  $E \approx E_{\min}$  we have

$$\rho_0(E, 0) = a = \text{const}, \ E < E_{\min},$$

 $\rho_0(E, 0) = a + b\sqrt{E^2 - E_{\min}^2}, \quad E > E_{\min}, \quad a, b > 0.$ At these critical points the function R'(E,0) (see (23a)) remains continuous, but its derivative increases without bound on the side of the singularity where the density of states  $\rho_0(E,0)$  is constant (e.g., in the region  $E \approx E_{\min}$ , we have  $dR'/dE \rightarrow -\infty$  as  $E \rightarrow E_{\min}$ ,  $E < E_{\min}$ ; for more details see Ref. 16).



FIG. 6. Singularities of the absorption coefficient at the Van Hove critical points with anharmonicity taken into account.

The features of the dielectric permittivity arising from anharmonicity can be manifested not only in the absorption spectra, but generally can also give rise to features in the polariton spectrum of the crystal.

#### 3. EXPERIMENTAL STUDIES OF BIPHONONS

#### a) Infrared absorption spectra

As we have already stressed, many crystals have exhibited biphonons both in infrared absorption spectra and in Raman spectra.

In speaking of infrared absorption spectra, along with the study of Ron and Hornig,<sup>26</sup> which has already been discussed in the Introduction (in this regard see also the theoretical studies of Refs. 94, 95), let us also mention the studies of Dows and Schettino<sup>41</sup> and Schettino and Salvi.<sup>42</sup>

In Ref. 41 the spectrum of a CO<sub>2</sub> crystal was studied in the frequency region corresponding to the compound tone of the intramolecular vibrations  $v_1$  and  $v_3$  ( $v_1 + v_2 \approx 3720$  cm<sup>-1</sup>).

Reference 42 was concerned with measuring the infrared spectra of crystals of  $N_2O$  and OCS. The  $CO_2$  and  $N_2O$  molecules are linear, do not possess permanent dipole moments, and form a simple cubic lattice upon crystallization with four molecules per unit cell oriented along the tetrahedral axes. The OCS molecule is also linear, but forms a crystal of the trigonal system with one molecule per unit cell.

Since the CO<sub>2</sub> molecule is symmetric, its stretching vibration  $v_3$  is infrared-inactive and practically shows no dispersion. Therefore the Van Kranendonk model can be used in interpreting the experiment for the region of the compound frequency  $v_1 + v_3$ , as was actually taken into account in Ref. 10.

Figure 7 shows the transmission measured<sup>41</sup> for a crystal 1.8- $\mu$ m thick. The calculations performed in Ref. 10 showed that the sharp absorption peak in this case corresponds to excitation of a biphonon.

Analogous results have been obtained<sup>42</sup> for an N<sub>2</sub>O crystal in the frequency region corresponding to the compound frequency  $v_2 + v_3$ . The N<sub>2</sub>O molecule is not symmetric, and hence all its three intramolecular vibrations  $v_1$ ,  $v_2$ , and  $v_3$  are infrared-active. Its bending vibration  $v_2$  is doubly degenerate and possesses a weak dispersion throughout the Brillouin zone (less than 3 cm<sup>-1</sup>), owing to the small value of the dipole moment. Therefore, for the frequency region of

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FIG. 7. Fragment of the transmission spectrum of a  $CO_2$  crystal. The graph is taken from Ref. 10 (see also Ref. 41). The dotted lines indicate the absorption spectrum calculated in Ref. 10.

 $v_2 + v_3$ , just as for the  $v_1 + v_2$  region, one can also use the Van Kranendonk model (this has been done in Ref. 10). Figure 8 shows the transmission spectrum<sup>42</sup> of a film of N<sub>2</sub>O crystal 18- $\mu$ m thick in the  $v_2 + v_3$  band.

#### b) Raman spectra

Extensive experimental material has been obtained by studying the effects of anharmonicity in crystals by Raman scattering.

First of all we note the studies of Scott,<sup>43</sup> which were devoted to investigating the temperature-dependence of the soft mode in crystals of AlPO<sub>4</sub> and in quartz. As the temperture increases and approaches the  $\alpha$ - $\beta$  phase transition point, the frequency of the soft mode declines and enters the band of two-particle states of acoustic phonons. These studies have stimulated investigations on the theory of Fermi resonance in crystals.

A biphonon has been noted in calcite,<sup>44,45</sup> where the relatively narrow band of two-particle states  $(2v_p \sim 1424-1430 \text{ cm}^{-1})$  proved to lie close to the fundamental tone of another vibration. Two maxima were distinctly observed in the Raman spectrum: one maximum within the limits of the band (the change in frequency of the photon in Raman scattering is  $\Delta \omega_{\text{phot}} = 1425 \text{ cm}^{-1}$ ) and another maximum below the band (biphonon,  $\Delta \omega = 1412$ 



FIG. 8. Transmission spectrum in the  $v_2 + v_3$  band of an N<sub>2</sub>O crystal. The graph is taken from Ref. 10 (see Ref. 42). The dotted lines indicate the absorption spectrum calculated<sup>10</sup> for an N<sub>2</sub>O crystal 18- $\mu$ m thick.

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 $cm^{-1}$ ). Analogous maxima have also been detected in the infrared transmission spectra of the extraordinary ray in a specimen oriented at a 45° angle to the optic axis.

The anharmonicity of phonons is manifested very distinctly in the optical spectra of an NH<sub>4</sub>Cl crystal (in the lowtemperature IV phase). Hence this crystal has been the object of numerous studies<sup>46-48</sup> (Ref. 46 also studied the Raman spectra of ammonium bromide and the deuteroammonium halides). In the IV phase these crystals have a cubic structure and the  $NH_4^+$  groups interact relatively weakly with one another. The simplicity of the structure of the crystal is due also to the presence of only one structural unit per unit cell. Although the crystal is nonmolecular, the theory of vibrational excitons and biphonons developed for molecular crystals is quite suitable for the optical vibrations of the  $NH_4^+$  ion (the space-group symmetry of the crystal is  $T'_d$ ; the point-group of the crystal coincides with the local group of the  $NH_4^+$  ion  $(T_d)$ , which has no center of inversion owing to the symmetry of the ion).

The Raman spectrum of the NH<sub>4</sub>Cl crystal shows a band of two-particle states with sharply distinguished edges  $(2v_4 = 2800-2910 \text{ cm}^{-1})$ , and with an intensity peak at the lower edge of the band (see below for the interpretation of this peak). A Fermi resonance is observed in the region of  $3100 \text{ cm}^{-1}$ , where the sum of frequencies of two phonons is close to or coincident with the frequency of the fundamental tone of a dipole-active vibration. Strong hybridization occurs between the one and two-phonon states. A longitudinal biphonon was first identified and the magnitude of the longitudinal-transverse splitting was determined<sup>49,50</sup> from Raman spectra obtained by using various polarizations of the incident and scattered light.

Experimental results of no less interest have been obtained in Ref. 51, where Raman spectra were studied in a crystal of HIO<sub>3</sub>: this crystal is biaxial (point-group symmetry 222). The phonon spectrum of this crystal has been well studied, and is usually subdivided into four groups: lattice vibrations (0–220 cm<sup>-1</sup>), deformation vibrations of the IO<sub>3</sub> group (290–400 cm<sup>-1</sup>), stretching vibrations of the IO<sub>3</sub> group (600–845 cm<sup>-1</sup>), vibrations of the OH group (nonplanar deformational (twisting) (560 cm<sup>-1</sup>), planar (deformational) (1160 cm<sup>-1</sup>), and stretching (2440 cm<sup>-1</sup>)). Nevertheless, the Raman spectra in the frequency region  $\approx$  2270 cm<sup>-1</sup> (scattering angle  $\theta \approx$  90°) show a broad band at the low-frequency edge of which (i.e., at  $\omega = 2270 \text{ cm}^{-1}$ ) there is a rather narrow and intense peak. According to Ref. 52, the scattering in the frequency region 2270  $cm^{-1} < \omega < 2940$  cm<sup>-1</sup> corresponds to excitation of twoand three-particle states. Apparently the peak at  $\omega = 2270$  $cm^{-1}$  indicates the existence of a biphonon split off from the overtone band of the fundamental vibration at the frequency  $\Omega = 1160 \text{ cm}^{-1}$ . Upon cooling the crystal from T = 300 K, one observes a substantial decrease in the width of this line, and its position is somewhat shifted toward the band of twoparticle states.

Among the numerous experimental studies of biphonons, we note moreover Ref. 53 (also Ref. 45), which has shown that measurements of second-order spectra with allowance for anharmonicity in the Van Kranendonk model

allow rather complete information on the density of states in the phonon band. Especially we call attention to Ref. 75, which contains the first experimental demonstration of the possibilities of studying the homogeneous width of two-particle states by active Raman spectroscopy using picosecond pumping pulses. Reference 75 has studied the spectral region of the  $2v_2$  overtone in liquid and crystalline CS<sub>2</sub> at T = 165 and 160 K, respectively. For coherent pumping of the overtones, two picosecond pulses were used, superimposed in time with the frequencies  $\omega_s$  and  $\omega_L$ , so that  $\omega_L - \omega_S = \Omega_0$ , where  $\Omega_0$  is the overtone frequency (in the liquid  $\Omega_0 = 795 \text{ cm}^{-1}$ , while in the crystal  $\Omega_0 = 801 \text{ cm}^{-1}$  is the quasibiphonon frequency). The evolution (decay) of the excitation of the crystal caused by the picosecond pulses was studied from the dependence on the lag time of the intensity of the anti-Stokes third (probe) pulse at the overtone. It was shown that the excitation caused by the picosecond pulses of both liquid and crystalline CS2 decays exponentially. In liquid CS<sub>2</sub> the decay time  $T_2$  is  $1.8 \pm 0.15$  ps, whereas in the crystal  $T_2 = 14 \pm 3$  ps. Such a sharp decrease in the homogeneous width in the crystal as compared with the liquid state apparently indicates the existence in the liquid of decay channels of the  $2v_2$  overtone that are absent in the crystalline state (breakdown of translational symmetry, fluctuation of short-range order, etc.; see Ref. 75). This type of study as applied to polaritons in the overtone region of the spectra might yield information on the many effects discussed above, e.g., on the width of the polariton lines (see also Ref. 98).

### 4. FERMI RESONANCE WITH POLARITONS

#### a) Microscopic theory

Let us examine the effects that arise whenever the branch of C phonons corresponds to dipole-active vibrations. In the region of small  $k \sim 2\pi/\lambda$ , where  $\lambda$  is the wavelength of light having the frequency  $\omega \approx \Omega_2$ , this type of phonon interacts strongly with the transverse photons. Consequently, instead of C phonons and transverse photons, in the long-wavelength region new elementary excitations are formed—polaritons (see also Refs. 54–56, 72). In their properties (spectrum, polarization) at small k they substantially differ from photons in vacuo and from phonons.

The spectrum of polaritons can be found by using the macroscopic Maxwell equations, provided only one assumes the dielectric-permittivity tensor of the medium to be known.38 The results of the corresponding analysis, in which the point is to use the theory of lattice vibrations in the harmonic approximation, are known and have been presented in many monographs and textbooks on solid-state theory. Without going into the details, we stress here that a gap always arises in the polariton spectrum in the region of a fundamental dipole-active vibration (C phonon, exciton, etc.) (we are not taking account of spatial dispersion here). The width of this gap is proportional to the oscillator strength of the corresponding resonance. Upon taking account of many phonon branches, many gaps are formed, and this situation is also well known. At present a rather detailed theory of Raman scattering by polaritons exists, with account taken of

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many phonon bands. It enables one to calculate the Raman cross-section at different scattering angles, provided only that one knows the dielectric-permittivity tensor of the crystal and the dependence of the polarizability of the crystal on the displacements of the lattice nodes and the electric field created thereby.<sup>57</sup>

The essential point is that the mentioned gaps in the polariton spectrum differ from zero even within the framework of the linear theory, just like the corresponding interaction between a photon and a phonon. Generally they do not require allowance for anharmonicity. Therefore it is reasonable to understand a polariton Fermi resonance to mean only a situation in which the vibrations of overtones or compound tones resonate with a polariton. We shall proceed to analyze this type of rather complicated situation, which requires one to take into account multiparticle excitations of the states of the crystal. Figure 9a depicts schematically a typical polariton spectrum, while the band of two-particle states of B phonons is shown against its background. If biphonons are formed under the influence of anharmonicity, then these states also resonate with the polariton, affecting its spectrum.

Since the Raman scattering by polaritons is very intense for many crystals lacking an inversion center, whereas second-order Raman scattering (i.e., Raman scattering accompanied by the excitation of two quasiparticles) is relatively weak as a rule, the crossing of the biphonon levels and the band of two-particle states indicated in Fig. 9a by the polariton branch under the influence of anharmonicity leads in many cases to repumping of the Raman scattering intensity from the polariton to the biphonon and the two-particle states, which can be considered a characteristic marker of the phenomenon. However, we note, along with this effect,



FIG. 9. a) Polariton dispersion in a region of Fermi resonance without allowance for anharmonicity; ( $\varepsilon_2$  (0) is the energy of the fundamental vibration for K = 0;  $\varepsilon_{\min}$  and  $\varepsilon_{\max}$  are the minimum values of the energy in the band of two-particle states;  $E_b$  is the biphonon level); b) the same, but with allowance for anharmonicity.

which is of great importance in the experimental study of the states mentioned above, that a substantial alteration of the spectra of polaritons and two-particle states also occurs in the crossing region (see Fig. 9), and can be manifested in the Raman spectra. However, as we shall show below, the character of these changes depends cardinally on whether biphonons are formed in the region of overtones or compound tones. Therefore, by studying spectra of Raman scattering by polaritons under conditions of polariton Fermi resonance, one can decide experimentally on the presence of bound states of phonons (biphonons). At present extensive experimental material has been obtained in this field, and the special next section is devoted to reviewing it. Now we shall turn to the results of the previous subsection and show how Fermi resonance with polaritons can be treated within the framework of the microtheory (see also Ref. 15).

In order to take into account the interaction of phonons and photons, we should add to the Hamiltonian of (11) the Hamiltonian of the free field of transverse photons  $H_0(a)$ and the Hamiltonian of the interaction of the field of transverse photons with the phonons  $H_{int}$ .

We must include in the Hamiltonian  $H_{int}$  with allowance for anharmonicity not only the terms quadratic in the Bose operators a, B, and C, but also the cubic terms. We shall discuss the structure of these terms below. At present we emphasize that the linear transformation from the operators a, B, and C to the operators for creation and annihilation of polaritons, i.e., to the operators  $\xi_{\rho}^{+}(\mathbf{K})$  and  $\xi_{\rho}(\mathbf{K})$ , where  $\rho$  is the number of the polariton branch and **k** is the wave vector of the polariton, diagonalizes the quadratic component of the complete Hamiltonian. However, such a diagonalization of the quadratic component of the complete Hamiltonian is actually not necessary for analyzing spectra in the region of a Fermi resonance. The transformation from the operators a and C to polaritons in the spectra region being discussed is actually important, since here taking account of retardation substantially affects the structure and spectrum of the C phonons. As regards the two-particle states of the crystal corresponding to excitation of two B phonons, it can prove important to take their retardation into account only in extreme cases. Providing that we are not speaking of the edges of the band of two-particle states, the fundamental contribution to the two-particle states, even with small values of the total momentum (only these states resonate with the polariton) comes from the states  $B_{(\mathbf{k}/2)+\mathbf{q}}^{+}B_{(\mathbf{k}/2)-\mathbf{q}}^{+}|0\rangle$  with large **q**. Since it is not essential to take into account retardation for B phonons with large values of the wave vector, the meaning of the statement made above on the degree of influence of retardation on the twoparticle states of B phonons becomes clear. The extreme cases mentioned above can arise in crystals where an energy minimum or maximum corresponds to small k in the band of B phonons, the B phonon is dipole-active, and the oscillator strength corresponding to it is large enough. In these cases the edge of the band of two-particle states, respectively a minimum or maximum, is spread out by an amount of the order of the energy of the longitudinal-transverse splitting of a B phonon  $\varepsilon_{\parallel,1}$ . Then it can become important to take retardation into account if the width  $\Delta$  of the B-phonon band is small in comparison with  $\varepsilon_{\parallel,1}$ . Yet if the inequality  $\Delta \geq \varepsilon_{\parallel,1}$ holds, just as will be assumed below, it is not essential to take into account retardation of the B phonons. Bearing in mind what we have said, let us write the component of the complete Hamiltonian quadratic in the Bose operators in the form of the sum  $\hat{H}_0(B) + \hat{H}_0(\xi)$ :

$$\hat{H}_{0}\left(\xi\right) = \sum_{
ho, \mathbf{k}} \mathscr{E}_{
ho}\left(\mathbf{k}\right) \xi_{
ho}^{+}\left(\mathbf{k}\right) \xi_{
ho}\left(\mathbf{k}\right).$$

Here  $\xi_{\rho}(\mathbf{k}) = \hbar \omega_{\rho}(\mathbf{k})$  is the energy of the polariton  $(\rho, \mathbf{k})$ .

Now let us turn to the Hamiltonian  $\hat{H}_{int}$  and discuss therein the structure of the terms cubic in the operators for creation and annihilation of quasiparticles.

Evidently, in the case being discussed of a crystal with one molecule per unit cell, these terms have the form

$$\hat{H}_{int} = \sum_{n \to \infty} \sum_{\mathbf{k}} \left[ \Gamma_{\rho} \left( \mathbf{k} \right) (B_{n}^{*})^{2} \xi_{\rho} \left( \mathbf{k} \right) \frac{e^{i\mathbf{k}n}}{\sqrt{N}} + \text{ h.c. } \right].$$
(26)

To find the quantities  $\Gamma_{\rho}(\mathbf{k})$ , we must take into account the fact that the operators  $C_n$  are expressed in terms of the operators for creation and annihilation of polaritons as follows (see Ref. 55):

$$C_{n} = \frac{1}{\sqrt{n}} \sum e^{\mathbf{i}\mathbf{k}\mathbf{n}} \left[ u_{\rho}\left(\mathbf{k}\right) \xi_{\rho}\left(\mathbf{k}\right) + v_{\rho}^{*}\left(-\mathbf{k}\right) \xi_{\rho}^{+}\left(-\mathbf{k}\right) \right].$$
(27)

Here  $u_{\rho}$  and  $v_{\rho}$  are certain coefficients. Therefore, upon taking (27) into account we find that  $\Gamma_{\rho}(\mathbf{k}) = \Gamma u_0(\mathbf{k})$ . However, in addition to the operator of (26),  $H_{\text{int}}$  actually contains also an operator corresponding to the direct interaction of transverse photons with the overtones. This operator is

$$\hat{H}'' = \sum_{n, \mathbf{k}, \mathbf{\gamma}} \left[ D(\mathbf{k}, \mathbf{\gamma}) (B_n^+)^2 a_{\mathbf{k}\mathbf{\gamma}} + \text{h.c.} \right].$$

It arises upon taking into account not only the terms linear in  $(B_n + B_n^+)$  in the dipole-moment operator of the molecule, but also the terms proportional to  $(B_n + B_n^+)^2$  (see Refs. 15 and 58). Thus the operator under discussion corresponds to taking into account the so-called electro-optic anharmonicity,<sup>29</sup> so that the constants  $\Gamma_{\rho}(\mathbf{k})$  that figure (26) are determined by the total contribution of both the mechanical and the electro-optical anharmonicity. Hence they generally depend on the two independent phenomenological constants  $\Gamma$  and D.

By comparing the Hamiltonian of (11) with the Hamiltonian

$$\hat{H} = \hat{H}_{0}(B) + \hat{H}_{0}(\xi) + \hat{H}_{\rm int}^{(3)} + \hat{H}^{\rm (L)}(B),$$

where  $\hat{H}^{(L)}(B)$  is the third term in (11), we conclude that the overall structure of the Hamiltonian has been conserved upon transforming to polaritons. This situation allows us to proceed directly to formulating the results, rather than reporting the calculations.

First of all, let us turn to analyzing the dispersion law for polaritons in the region of a Fermi resonance. To do this by analogy with (12a), let us examine the expression for the Fourier components of the Green's function

$$G_{\mathbf{k}\rho}^{(1)}(t) = -i\theta(t) \langle 0_{\mathbf{k}}^{t} | \xi_{\rho}(\mathbf{k}, t) \xi_{\rho}^{+}(\mathbf{k}, 0) | 0 \rangle_{\bullet}$$

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Taking into account only the polariton branch  $\rho$  that crosses the region of two-particle states, we find the following expression upon allowing for anharmonicity:

$$G_{\mathbf{k}\rho}^{(1)}(E) = \frac{1 + 2\widetilde{A}(\mathbf{k}) \left[R(E, \mathbf{k}) + 2\pi i \rho_{0}(E, \mathbf{k})\right]}{\widetilde{\Delta}(E, \mathbf{k}) \left[E - \mathscr{E}_{0}(\mathbf{k})\right]}.$$
 (28)

Here we have

$$\widetilde{\Delta} (E_{\mathbf{x}} \mathbf{k}) = 1 + 2B (E, \mathbf{k}) [R (E, \mathbf{k}) + 2\pi i \rho_0 (E, \mathbf{k})],$$
(29)

Henceforth we shall neglect this dependence and assume  
that the quantities 
$$R(E, \mathbf{k})$$
 and  $\rho_0(E, \mathbf{k})$  depend only on E as  
 $k \rightarrow 0$ . Consequently we obtain the following expression for

the Green's function of (28):

 $B(E, \mathbf{k}) = \widetilde{A}(\mathbf{k}) - \frac{|\Gamma_{\rho}(\mathbf{k})|^{2}}{E - \mathscr{C}_{\rho}(\mathbf{k})}$ 

$$\begin{aligned} \mathcal{F}_{\mathbf{k}\rho}^{(1)}(E,\,\mathbf{k}) &= \left\{ [\mathbf{1} + 2B\,(E,\,\mathbf{k})\,R\,(E)]^2 + [4\pi\rho_0\,(E)\,B\,(E,\,\mathbf{k})]^2 \right\}^{-1} \\ &\times \left\{ \frac{[\mathbf{1} + 2\widetilde{A}R\,(E)]\,[\mathbf{1} - 2B\,(E,\,\mathbf{k})\,R\,(E)] + 16\pi^2\rho_0\,(E)\,\widetilde{A}B\,(E,\,\mathbf{k})}{E - \varepsilon_\rho\,(\mathbf{k})} + 4\pi i\rho_0\,(E)\,\frac{|\Gamma_\rho\,(\mathbf{k})|^2}{[E - \varepsilon_\rho\,(\mathbf{k})]^2} \right\}. \end{aligned} \tag{31}$$

Outside the band of two-particle states, i.e., when  $\rho_0(E) \rightarrow 0$ , or inside this band, but with  $\rho_0(E) \lt R(E)$ , the imaginary component of the Green's function, which determines the density of polariton states, acquires the form

$$\operatorname{Im} G_{\mathbf{k}\rho}^{(1)}(E, \mathbf{k}) = \frac{|\Gamma_{\rho}(\mathbf{k})|^{2}}{[E - \mathscr{E}_{\rho}(\mathbf{k})]^{2}} \frac{\delta [1 + 2B(E, \mathbf{k}) R(E)]}{B(E, \mathbf{k})}.$$
 (32)

We can conveniently write the equation for the polariton energy 1 + 2B(E,k) R(E) = 0 in the form

$$1 + 2\widetilde{A}(\mathbf{k}) R(E) = 2 \frac{|\Gamma_{\rho}(\mathbf{k})|^{2}}{E - \mathcal{E}_{\rho}(\mathbf{k})} R(E).$$
(33)

The left-hand side of Eq. (33) can equal zero outside the region of the spectrum of two-particle states if a biphonon level exists for  $\Gamma_{\rho}(\mathbf{k}) = 0$ . If the biphonon energy in this case is  $E_{\rm b}(\mathbf{k})$ , we can write the left-hand side of Eq. (33) for  $E \approx E_{\rm b}(\mathbf{k})$  in the form  $\alpha^2(\mathbf{k})[E - E_{\rm b}(\mathbf{k})]$ , so that Eq. (33) acquires the form

$$[E - E_{\rm b}(\mathbf{k})] [E - \mathcal{E}_{\rho}(\mathbf{k})] = \frac{|\Gamma_{\rho}(\mathbf{k})|^2}{\alpha^2 (\mathbf{k}) \widetilde{A}(\mathbf{k})}.$$
 (34)

This relationship implies that, when  $\mathbf{k}_0$  has a value such that  $E_b(\mathbf{k}_0) = \mathscr{C}_\rho(\mathbf{k}_0)$ , i.e., at the crossing point of the biphonon level with the polariton, a gap is formed in its spectrum (see Fig. 9a) with the half-width

$$\delta = \left| \frac{\Gamma_{\rho}(\mathbf{k}_0)}{\alpha(\mathbf{k}_0)} \right| (\widetilde{A})^{-1/2} \cdot$$

Owing to the possible decay of a polariton into two phonons, the polariton level is broadened inside the band of two-particle states, and the very concept of a dispersion curve requires some refinement. We shall understand the dispersion law of a polariton to be the dispersion of the maximum of its density of states, i.e., the maximum of the imaginary component of the Green's function of (31). We can easily convince ourselves that the maximum of  $\operatorname{Im} G_{\mathbf{k}\rho}^{(1)}(E,\mathbf{k})$  for a fixed value of **k** corresponds to the condition

$$R(E) + 2B(E, \mathbf{k}) [R^{2}(E) + (2\pi\rho_{0}(E))^{2}] = 0.$$
 (35)

This transforms into (32) as  $\rho_0(E) \rightarrow 0$ . Thus, in the sense pointed out above, Eq. (35) is a generalization of (33). Let us write Eq. (35) in a more convenient form:

$$f_{1}(E) \equiv \frac{R(E) + 2\widetilde{A}(\mathbf{k}) \left[R^{2}(E) + 4\pi^{2}\rho_{0}^{2}(E)\right]}{2\left[R^{2}(E) + 4\pi^{2}\rho_{0}^{2}(E)\right]}$$
$$= \frac{|\Gamma_{\rho}(\mathbf{k})|^{2}}{E - \mathscr{F}_{\rho}(\mathbf{k})} \equiv f_{2}(E).$$
(35a)

Near the center of the Brillouin zone  $(\mathbf{k} \approx 0)$ , the density of states can depend on  $\mathbf{k}$  only because of the nonanalyticity of the dispersion relationship  $\varepsilon_1(\mathbf{k})$  for B phonons.

(30)

Here the left-hand side involves only the properties of B phonons, and the right-hand side involves the polariton.

We can find the dispersion of the polariton at Fermi resonance by solving Eq. (35a) for all values of the wave vector k (Figs. 10–12 show the possible situations under the condition that the lower branch of the polariton dispersion curve  $\mathscr{C}_{\rho}(\mathbf{k})$  crosses the region of frequencies of two phonons). Along with the existence of the gaps indicated above in the biphonon energy region (see Fig. 10), and in the presence of a strong enough interaction of the polariton with the two phonons (see Fig. 11), the following features can arise:

a) The band of two-particle states can contain a frequency region in which Eq. (35) has no solutions (see the cross-hatched part of the band of multiparticle states in Figs. 11 and 12). In the sense of the definition of the dispersion of a polariton that we have adopted (as the maximum of the imaginary part of the Green's function), the dispersion curve is not defined in these regions, and one can say that a "gap" arises in the polariton spectrum. However, such a "gap" differs substantially from gaps outside the band, where the imaginary part of the Green's function equals zero. For the "gaps" in the band of two-particle states, the imaginary part of the Green's function differs from zero. In the region of the "gap" this can lead to strong damping of electromagnetic waves. Consequently the polariton dispersion curve becomes "diffuse". However, it is precisely in these frequency intervals that one can observe maxima in the infrared absorption spectra (see Ref. 50).

b) In the vicinity of the analytic critical points of the density of states, both on the right and the left, the derivative of  $f_1(E)$  in Eq. (35a) always increases without limit in modulus (see the remark at the end of Sec. 4). Therefore, at the critical point itself this function always has a vertical tangent. Here the four types of singularities can occur that are indicated in Fig. 6. At the critical points of the density of states the polariton dispersion curve has horizontal tangents. The dispersion curve also has such a singularity for

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FIG. 10. a) Graphical solution of Eq. (35a) for  $k = \infty$  and in the presence of the biphonon  $E = E_b$  ( $\mathscr{G}_p$  ( $k = \infty$ ) is the polariton level for large k when unperturbed by anharmonicity; the  $\varepsilon_{cr}$  are the Van Hove critical points); b) polariton dispersion curve in the presence of Fermi resonance—case of strong anharmonicity (dotted curve—polaritons without taking interactions with two phonons into account); TP—band of twoparticle states.





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FIG. 12. The same as in Fig. 10: case of weak anharmonicity (small values of the constants A and  $\Gamma$  (k)). A gap of small width arises in the TP band below the quasibiphonon level  $E_{\rm qb}$ .

frequencies outside the band of two-particle states, but close to its boundaries (see Fig. 10–12). The various phenomena in which Fermi resonance with polaritons is manifested and in which the polariton dispersion curve is observed can be employed to study the phonon bands. Naturally, the broadening of the dispersion curve in the band of two-particle states must diminish the resolving power of these methods and hinder the discovery of singularities near critical points. Perhaps the situation that proves to be the most convenient is the one that is characterized by a relatively weak anharmonicity with low values of the constants A and  $\Gamma_{\rho}$  (k) (see Fig. 12). Here the broadening will be small, while the width of the "gap" will occupy a small fraction of the entire band.

More detailed studies of the phenomenon of Fermi resonance with polaritons with account taken of the concrete structure and symmetry of the crystals, of nonanalytic critical points, etc., will prove to be of current interest only upon future improvement of the sensitivity of the experimental methods for the region of the continuum of two-particle states.

# b) Macrotheory: transverse and iongitudinal biphonons

We have already stressed above the fact that one can also find the polariton spectrum within the framework of macroscopic electrodynamics, which requires that one should know the dielectric-permittivity tensor of the crystal. As one should expect, the results of the corresponding analysis are equivalent to the results of the microtheory. Nevertheless, we shall employ the macrotheory below as applied to cubic crystals and shall show how one justifies the possible existence of longitudinal and surface biphonons within the framework of this approach (see also Ref. 3).

We stress in this connection that the microscopic theory developed above of Fermi resonance with polaritons cannot be directly applied to cubic crystals. In this type of crystal the dipole-active transitions correspond to triply degenerate states (for the corresponding generalization of the theory, see Ref. 32), while above we have considered these transitions nondegenerate for the sake of simplicity.

It is well known that the dielectric-permittivity tensor with neglect of spatial dispersion reduces to the scalar  $\varepsilon$  ( $\omega$ ). If we take no account of attenuation we can represent this scalar in the region of the band of two-particle states as follows:

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{F_{b}\Omega_{\perp b}^{2}}{\omega^{2} - \Omega_{\perp b}^{2}} - \oint \frac{F(\omega')(\omega')^{2} d\omega'}{\omega^{2} - (\omega')^{2}}.$$
 (36)

Here  $\varepsilon_{\infty}$  is a quantity that is determined by the contribution of remote resonances, which can be considered independent of  $\omega$  in the region of the spectrum being studied. Also we have  $\Omega_{1b} = E_{b}^{\perp}(0)/\hbar$ , where  $E_{b}^{\perp}(\mathbf{k})$  is the energy of a transverse biphonon having the wave vector  $\mathbf{k}$ ,  $F_{\mathbf{k}}$  is a coefficient proportional to the oscillator strength of a biphonon, and F $(\omega')$  is a quantity proportional to the oscillator strength corresponding to the excitation of two free B phonons having the total energy  $\hbar \omega'$ . The quantity  $F(\omega')$  is also proportional to the density of energy levels having the total wave vector  $\mathbf{k} = 0$  in the band of two-particle states. Thus we have F  $(\omega') = 0$  if the frequency  $\omega'$  lies outside the band  $(F_{\min})$ ,  $E_{\rm max}$ ). The integral over the frequency in (36) is taken as the principal value, and this formula also allows for the fact that the resonances of  $\varepsilon$  ( $\omega$ ) corresponding to the frequencies of the fundamental lattice vibrations (i.e., the frequencies found in the harmonic approximation) do not lie in the frequency interval being studied.

In cubic crystals with neglect of spatial dispersion, the polaritions are strictly transverse, so that their dispersion law, i.e., the dependence of the frequency on the wave vector, can be found from the relationship

$$\varepsilon (\omega) = \frac{k^2 c^2}{\omega^2}.$$
 (37)

If we let the velocity of light approach infinity, i.e., neglect retardation, the relationship (37) acquires the form

$$\varepsilon (\omega) \to \infty.$$
 (38)

This relationship implies that the resonances of  $\varepsilon$  ( $\omega$ ) correspond to the frequencies of transverse vibrations found upon allowing only for the instantaneous Coulomb interaction. Hence, the resonance in (36) at the frequency  $\Omega_{1b}$  corresponds to taking into account the resonance at the transverse-biphonon frequency, which is reflected in the notation.

In addition to transverse polaritions, longitudinal waves can also exist in the spectral region being studied, whose frequencies satisfy the equation

$$\varepsilon(\omega) = 0.$$
 (39)

These waves are not manifested in infrared absorption spectra, but with an appropriate choice of the incident and scattered light, they can be observed in Raman spectra.

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To find the dispersion of the polaritions, one must use Eq. (37) to find the value of  $\omega$  as a function of k. We shall proceed to discuss the form of this function below. But first we shall study the features of  $\varepsilon$  ( $\omega$ ) that stem from Eq. (36). First we note that the quantity  $\varepsilon$  ( $\omega$ ) acquires the values  $+\infty$  or  $-\infty$ , depending on whether the frequency  $\omega$  approaches  $\Omega_{1b}$  from the right or the left. But if the frequency  $\omega$  lies inside the band of two-particle states, then, since the function  $F(\omega')$  is finite, the value of  $\varepsilon(\omega)$  is also finite and remains so even when the frequency  $\omega$  approaches one of the boundaries of the band of two-particle states from the outside. A singularity arises only in the derivative of  $\varepsilon$  ( $\omega$ ), since the density of states  $\rho(\omega')$  in three-dimensional crystals and hence also the quantity  $F(\omega')$  in the vicinity of either of the boundaries of the band  $\overline{\varepsilon}$  has , as was mentioned earlier, the form  $\rho(\omega') = \rho_0 \sqrt{|\hbar\omega' - \bar{\varepsilon}|}$ . This is exactly why, when  $\omega$  approaches one of the boundaries of the band of two-particle states from the outside or approaches the frequencies of the critical points of the density of states, the function  $\varepsilon$  ( $\omega$ ) remains finite, but has an infinite derivative.

In view of what we have said, we can schematically represent the  $\varepsilon$  ( $\omega$ ) relationship in the frequency region being discussed with  $\hbar\Omega_{1b} < \varepsilon_{\min}$  in the form shown in Fig. 13. The fact that a term exists in the expression (36) arising from the presence of a biphonon, as we see from Fig. 13, causes a frequency interval to arise near the frequency  $\Omega_{1b}$  in which  $\varepsilon$  ( $\omega$ ) <0. This means that the electromagnetic waves in this frequency region—bulk polaritons—are impossible (owing to (37) they would correspond to negative values of  $k^2$ ). Thus, in full accord with the results of the microtheory, this frequency region corresponds to a gap in the spectrum of bulk polaritions.

We note that the vanishing of the quantity  $\varepsilon$  ( $\omega$ ) at a certain value of the frequency  $\omega \equiv \Omega_{\parallel b}$  ( $\varepsilon(\Omega_{\parallel b}) = 0$ ,  $\Omega_{\parallel b} > \Omega_{1b}$ ) indicates that a longitudinal biphonon is also formed with the energy  $\hbar \Omega_{\parallel b}$  in the case being studied of a cubic crystal, simultaneously with the transverse biphonon, which leads to the appearance of the "gap" in the polariton spectrum. The frequency of the longitudinal biphonon in the region of small k can depend on k only weakly (see Fig. 9b).

We emphasize that the longitudinal-transverse splitting of the biphonon in the case being discussed no longer follows the well-known Lyddane-Sachs-Teller formula, which is



FIG. 13. Dependence of the dielectric permittivity on the frequency in the region of overtone frequencies.  $E_{\parallel b}$  and  $E_{\perp b}$  are respectively the longitudinal and transverse biphonon energies,  $E_{\min}$  and  $E_{\max}$  are the minimum and maximum values of the energy in the band of two-particle states.

valid for the region of an isolated frequency of a fundamental vibration. Owing to the contribution of the integral term, the low-frequency value of  $\varepsilon$  ( $\omega$ ) is determined by the relationship

$$\varepsilon (0) = \varepsilon_{\infty} + F_{b} + \bigvee F (\omega') d\omega'.$$

Thus, generally speaking, the Lyddane-Sachs-Teller relationship mentioned above  $\Omega_{\parallel}^2 = \varepsilon(0) \Omega_1^2 / \varepsilon(\infty)$  for the frequencies  $\Omega_{\parallel b}$  and  $\Omega_{1b}$  no longer holds (see also Ref. 32).

We can consider the remarks made above, which are based on using relationship (36) for  $\varepsilon$  ( $\omega$ ), to be justified only in crystals where the widths of the lines are small in comparison with the magnitude of the longitudinal-transverse biphonon splitting. We shall show in discussing the experimental data that this type of situation can actually occur.

For anisotropic crystals an analysis of the features of the dispersion in the region of two-particle states also can prove useful. In this case, in writing the phenomenological relationship of the type of (36) defining the  $\omega$ -dependence of the dielectric permittivity tensor  $\varepsilon_{ij}(\omega)$ , we must take into account the fact that the dipole-active biphonons, just like dipole-active phonons, transform for  $\mathbf{k} = 0$  according to certain representations of the crystal class. Therefore, e.g., in uniaxial crystals the dipole-active biphonons can be polarized either along the optic axis (transition frequency  $\Omega_{1b}$ ) or transverse to it (transition frequency  $\Omega_{2b}$ ), so that we have

$$\varepsilon_{ij}(\omega) = \varepsilon_{ij}^{\infty} - \frac{F_{b}^{(1)}}{\omega^{2} - \Omega_{1b}^{2}} \delta_{i3} \delta_{j3} - \frac{F_{b}^{(2)}(\delta_{i1}\delta_{j1} + \delta_{i2}\delta_{j2})}{\omega^{2} - \Omega_{2b}^{2}} - \vec{\chi} \frac{F_{ij}(\omega')(\omega')^{2} d\omega'}{\omega^{2} - (\omega')^{2}}.$$
 (40)

Here the tensor quantity  $F_{ij}(\omega')$  is zero when  $i \neq j$ , while  $F_{11}(\omega') = F_{22}(\omega')$ . We assume in writing the relationship (40) that the optic axis of the crystal lies along the z axis, while spatial dispersion and damping are not taken into account.

In closing we note that also Fermi resonance with plasmons<sup>59</sup> can exist in degenerate semiconductors, along with Fermi resonance with phonons and polaritions. In this type of crystal the spectrum of long-wavelength longitudinal vibrations reduces not, even in the region of the fundamental frequencies, to plasmons and longitudinal phonons, but to plasmophonons.<sup>60</sup>

It turns out that analogous "mixing" effects must generally occur also in cases in which the plasmon frequency is close to the frequency of an overtone or a compound tone, i.e., when the conditions are realized for Fermi resonance with the plasmon. In contrast with the situation already mentioned above, which was discussed in Ref. 60, in this case it is very essential to take anharmonicity into account. Resonance with a biphonon, if the latter is formed, leads to the appearance in the plasmon spectrum of a gap, and this effect can be most simply understood and described by starting with purely phenomenological considerations.

For the details, together with the microscopic theory of the effect, see Refs. 3b and 59. We also point out Ref. 61, in which the intensity of Raman scattering by plasmons and phonons was calculated under conditions of Fermi resonance.

The experimental detection of Fermi resonance with plasmons in a ZnSe crystal has been reported in Ref. 62.

### 5. FERMI RESONANCE WITH SURFACE POLARITONS: SURFACE BIPHONONS AND SPLITTING OF THE DISPERSION CURVE

It is well known that surface electromagnetic waves can propagate along the boundary between two media (surface polaritons), with their amplitude declining exponentially with distance from the boundary into the interior of either medium (see, e.g. Refs. 38 and 63). The dispersion curve of surface polaritons (SPs) at the boundary of isotropic media lies in the region of the gap of the spectrum of bulk polaritons that arises upon longitudinal-transverse splitting (inside this gap the dielectric permittivity of the medium acquires negative values). At the boundary with a vacuum, the dispersion law of SPs with retardation taken into account is given by the relationship

$$c^2 = \frac{\omega^2}{c^2} \frac{\varepsilon(\omega)}{\varepsilon(\omega) + 1}$$

The effects of strong anharmonicity, which are analogous to the effects in the bulk of the crystal, can lead to substantial changes in the spectrum of surface polaritons. Thus, in the region of the longitudinal-transverse splitting of biphonons  $\Omega_{1b} < \omega < \Omega_{\|b}$ , where  $\varepsilon(\omega) < 0$ , surface biphonons should also exist. One might study surface biphonons, e.g., by using the method of frustrated total internal reflection. As is well known, in contrast to the method of Raman scattering by polaritons, this method is effective independent of whether the crystal has an inversion center, and in this sense is more universal. At the same time, the experimental discovery of a surface biphonon in the frequency region lying below the band of two-particle states would indirectly indicate the existence of both transverse and longitudinal biphonons. Actually, owing to the fact that  $\varepsilon_{\infty} > 0$ , the magnitude of  $\varepsilon$  ( $\omega$ ) determined by Eq. (36) can be negative in a certain frequency region  $\omega < \varepsilon_{\min} / \hbar$  only when (36) contains a resonance term with the frequency  $\Omega_{\rm lb} < \varepsilon_{\rm min}/\hbar$ .

Now let us discuss the problem of the surface-polariton spectrum at Fermi resonance, i.e., under conditions in which the SP frequencies lie near the band of two-particle states of some kind of optical surface phonons (Fig. 14) (see Refs. 64 and 65).

One can take into account the effect of surface phonons on the spectrum of surface polaritons within certain limits within the framework of the theory of SPs with account taken of the transition layer.<sup>63,66</sup> These studies have shown that the dispersion equation of a surface polariton at the boundary of two isotropic media having the dielectric permittivities  $\varepsilon$  ( $\omega$ ) and  $\varepsilon_1$  ( $\varepsilon_1 > 0$  is constant) with allowance for the polarizability of a transition layer of thickness l < 1/k (k is the component of the wave vector of the polariton parallel to the surface) has the following form:

$$\frac{\varepsilon_1}{\kappa_1} + \frac{\varepsilon(\omega)}{\kappa} = -\gamma(\omega) l.$$
(41)

Here  $\gamma$  ( $\omega$ ) is the polarizability of the transition layer, and we have



FIG. 14. Dispersion of surface polaritons in a region of Fermi resonance without allowance for the influence of critical points. The hatched region is the band of two-particle states. The dot-dash line indicates the polariton dispersion curve without allowance for Fermi resonance.

$$\varkappa_{1} = \sqrt{k^{2} - \frac{\omega^{2}}{c^{2}}} \varepsilon_{1}, \quad \varkappa = \sqrt{k^{2} - \frac{\omega^{2}}{c^{2}}} \varepsilon(\omega).$$

If the band of two-particle states (see Fig. 14) lies within the region of variation of the frequency of surface polaritons  $(\Omega_{\perp}, \Omega_{s})$ , where  $\Omega_{s}$  is a root of the equation  $\varepsilon_{1} + \varepsilon(\omega) = 0$ , then in the absence of damping one can represent the quantity  $\gamma(\omega)$  as follows:

$$\gamma(\omega) = \frac{f_{\rm b}}{\Omega_{\rm b}^2 - \omega^2} + I(\omega), \quad I(\omega) = \oint \frac{A(\omega') g(\omega') d\omega'}{(\omega')^2 - \omega^2}.$$
(42)

In (42) the first term is determined by the contribution of surface biphonons, while the integral is determined by the contribution of the band of two-particle states of surface phonons; the quantities  $f_b$  and  $A(\omega')$  are proportional to the oscillator strengths respectively of the transition to the biphonon state and to a state of energy  $\hbar \omega'$  in the band;  $g(\omega')$  is the density of states in the band of two-particle states. In the neighborhood of the biphonon frequency  $\Omega_{\rm b}$ , the surfacepolariton spectrum is split with a separation proportional to the quantity  $\sqrt{l}$ . If it exceeds the width of the polariton line, then it can be detected experimentally. (For observations of a gap in the spectrum of surface polaritons, see, e.g., Ref. 38). Inside the band of two-particle states, the behavior of the polarizability  $\gamma(\omega)$  of the transition layer, just like the solutions of Eq. (41), depends on the density-of-states function g ( $\omega$ ). At the edge of the band of two-particle states with k = 0 in the two-dimensional case, the density of states does not depend on  $\omega$ . Therefore here the integral in (42) diverges logarithmically: in the limits as  $\omega \rightarrow 2\omega_{\min}$  and  $\omega \rightarrow 2\omega_{\rm max}$  ( $\omega_{\rm min}$  and  $\omega_{\rm max}$  are the boundaries of the surfacephonon spectrum):

$$I(\omega) \approx \frac{A(2\omega')}{2\omega\Delta} \ln \left| \frac{2\omega_{\max} - \omega}{2\omega_{\min} - \omega} \right|.$$

Here we have  $\Delta = \omega_{\max} - \omega_{\min}$ .

As an analysis of the solution of Eq. (41) shows, given this frequency-dependence of  $I(\omega)$ , frequency doublets arise (Fig. 15) near the edges of the band of two-particle states in certain intervals of the wave vector for each k. The components of the doublets approach one another with increasing k. The estimates made in Ref. 64 show that the components of the doublet should be separated by  $\approx 2-6$ cm<sup>-1</sup> for a width of the band of two-particle states  $\omega_{max}$ .



FIG. 15. The same as in Fig. 14, but with allowance for the influence of a singular point.

 $-\omega_{\min} \sim 20-40$  cm<sup>-1</sup> and with the usual values of the remaining quantities ( $\Omega_{\perp}$ , A ( $\omega$ ), etc.).

One or several singular points of the density of states must always exist inside the band of two-particle states. Since we are discussing surface phonons, i.e., two-dimensional phonons, the singularities of the functions  $g(\omega)$  in (42) differ from those in the three-dimensional case. In the two-dimensional case at the singular points  $\omega_1$ , the density of states diverges logarithmically, so that in a certain region of width  $2\omega_a$  the function  $g(\omega)$  has a nonregular component<sup>67</sup>:

$$\Delta g(\omega) = -g_0 \ln \left| \frac{\omega - \omega_1}{\omega_a} \right|$$
(43)

Here  $g_0$  is the mean value of the nonregular component. One can easily show that such a singularity leads to a discontinuity in the values of the integral  $I(\omega)$  in (42), with

$$\boldsymbol{I}\left(\boldsymbol{\omega}_{1}+0\right)-\boldsymbol{I}\left(\boldsymbol{\omega}_{1}-0\right)=-\frac{\pi^{2}}{2}A\left(2\boldsymbol{\omega}_{1}\right)\frac{g_{0}}{g_{1}}.$$

Hence the dispersion curve of a surface polariton for  $\omega \approx \omega_1$ also undergoes a discontinuity (see Fig. 15). Here the magnitude  $\delta$  of the gap that arises depends essentially on the ratio  $g_0/g_1$  ( $g_1$  is the mean value of the regular component of the density of states in the band).

Thus the study of Fermi resonance with surface polaritons enables one, in principle, not only to find the position of the surface-biphonon frequency, but also to study certain singularities of the structure of the band of surface phonons.

Apparently it has been possible by using the frustrated total internal reflection method to observe for the first time the effect of an overtone of a surface vibration on the spectrum of a surface polariton (see Ref. 68).

#### 6. THEORY OF RAMAN SCATTERING OF LIGHT BY POLARITONS AT A FERMI RESONANCE: DENSITY OF STATES AND FANO ANTIRESONANCE

In crystals lacking a center of inversion, the dipole-active phonons that form polaritons are also active in Raman spectra. Therefore Raman scattering by polaritons is widely employed for studying the dispersion of light in the infrared region of the spectrum.<sup>69–71</sup> In particular, one also observes in Raman spectra the features of the dispersion of normal electromagnetic waves, particularly in the region of Fermi resonance, that we have already discussed in the previous sections of this article. At Fermi resonance the intensity of Raman scattering is determined by: a) Scattering by a polariton-this is a firstorder process. The polariton leads to displacement of the nuclei and to simultaneous appearance in the crystal of a low-frequency macroscopic electric field. Both these factors give rise to a polarization that leads to Raman scattering. b) Two B phonons in a crystal also create an extra polarization, but scattering in an overtone is now a second-order process. Thus, Raman scattering at Fermi resonance by polaritons proves to result from the interference of the stated two contributions.

Schematically one can write the perturbation operator that leads to Raman scattering in the following form<sup>72</sup>:

$$\hat{H}_{i} = -\frac{1}{2} \sum_{n} \delta \mathscr{P}(n) \mathbf{E}(n).$$

Here the quantity  $\delta \mathscr{P}(n)$  is determined by the change in the contribution of electrons to the polarizability of molecule  $n(n=n, \alpha, \alpha = 1, 2, ..., \sigma)$ , where  $\sigma$  is the number of molecules in the unit cell) that arises upon displacement of its nuclei,  $\mathbf{E}(n)$  is the value of the field intensity at the point  $\mathbf{r}_n$ . One can expand the polarization  $\delta \mathscr{P}(n)$  in a power series in the normal coordinates  $u_n^{(b)}$  and  $u_n^{(c)}$  characterizing the motion of the nuclei in the molecule and in powers of the intensity of the low-frequency macroscopic field  $E^P(n)$  that accompanies the polarition:

$$\delta \hat{P}_{i}(n) = \sum_{j,l} a_{ij,l}^{(\alpha)} u_{n}^{(b)l} E_{f}(n) + \sum_{j,l} b_{ij,l}^{(\alpha)} u_{n}^{(c)l} E_{f}(n) + \sum_{j,l} c_{ij,l}^{(\alpha)} E_{l}^{p}(n) E_{f}(n) + \sum_{j,l,l'} d_{ij,ll'}^{(\alpha)} u_{n}^{(b)l} u_{n}^{(b)l'} E_{f}(n).$$

Here  $a^{(\alpha)}$ ,  $b^{(\alpha)}$ ,  $c^{(\alpha)}$ , and  $d^{(\alpha)}$  are certain tensors that define the change in the polarizability of the molecule  $\alpha$  caused by the displacement of its atoms. The operators  $u_n^{(b)}$  and  $u_n^{(c)}$ correspond to the partial displacements of the nuclei in the molecule *n* under the influence of the normal coordinates of the B phonons and C phonons;  $c^{(\alpha)}$  is the electro-optic tensor that defines the change in the electric-polarizability tensor under the influence of the field  $E^P(n)$ . We can represent the operators  $\hat{u}_n^{(b)}$  and  $\hat{u}_n^{(c)}$  in the following form:

$$\hat{u}_{n}^{(b)} = \frac{\mathbf{p}_{\alpha}^{(b)}}{e} (b_{n} + b_{n}^{*}) + \frac{\mathbf{p}_{\alpha}^{(2)}}{e} (b_{n} + b_{n}^{*})^{2} + \dots,$$

$$\hat{u}_{n}^{(c)} = \frac{\mathbf{p}^{(c)}}{e} (C_{n} + C_{n}^{*}) + \dots,$$

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

Here *e* is the effective charge, while  $\mathbf{p}^{(b)}$ ,  $\mathbf{p}^{(2)}$ , and  $\mathbf{p}^{(c)}$  are the matrix elements of the dipole-moment operator of the molecule,  $\xi_{\rho}^{+}$  (**k**) is the operator for creation of a polariton of the  $\rho$ th branch having the wave vector **k**, and  $S_{\rho}$  (**k**) is the amplitude of the electric field of the same polariton (see Ref. 36). One can express the operators  $C_n$  and  $C_n^{+}$  by using the linear transformation (27) in terms of the polariton operators  $\xi_{\rho}$  (**k**) and  $\xi_{\rho}^{+}$  (**k**). In the operator  $H_1$  we shall keep only the terms that lead to processes of Raman scattering of the polariton ( $\rho_a$ ,  $k_a$ ,  $\hbar\omega'$ ) to give rise to the polariton ( $\rho_b$ ,  $k_b$ ,  $\hbar\omega''$ ). Then we obtain the following expression for the perturbation operator:

$$egin{aligned} \hat{H}_{i} &= \sum\limits_{\mathbf{n}lpha} F^{(lpha)}\left(\mathbf{k}
ight) e^{i\mathbf{k}\cdot\mathbf{n}} b_{\mathbf{n}lpha}^{+\mathbf{a}} \xi_{
holpha}\left(\mathbf{k}_{a}
ight) \xi_{
hoeta}^{+}\left(\mathbf{k}_{b}
ight) \ &+ \sqrt{N}\sum\limits_{
ho} D_{
ho}\left(\mathbf{k}
ight) \xi_{
ho}^{+}\left(\mathbf{k}
ight) \xi_{
hoa}\left(\mathbf{k}_{a}
ight) \xi_{
hob}^{+}\left(\mathbf{k}_{b}
ight) + \mathrm{h.c.} \end{aligned}$$

Here  $\mathbf{k} = \mathbf{k}_a - \mathbf{k}_b$  corresponds to the wave vector of the low-frequency polariton  $\rho$  from the Fermi-resonance region, while the quantities  $F^{\alpha}$  (**k**) and  $D_{\rho}$  (**k**) are expressed in an obvious way in terms of the tensors *a*, *b*, *c*, and *d*, the vectors  $\mathbf{p}^{(b)}$ ,  $\mathbf{p}^{(c)}$ , etc.

A calculation of the Raman cross-section by the Van Hoye method has been given in Ref. 15 (see also Ref. 17). Without going into the details of the calculations, we shall write out the expression for the double differential Raman cross section per unit length of crystal per unit solid angle o''and per unit frequency interval of  $\omega''$  for crystals with one molecule per unit cell:

$$\frac{\mathrm{d}^{2}\sigma}{\mathrm{d}\sigma''\,\mathrm{d}\omega''} = M_{ab}\varkappa\left(\omega,\,\mathbf{k}\right) \left|F\left(\mathbf{k}\right) + \sum_{\rho}\frac{\Gamma_{\rho}\left(\mathbf{k}\right)\,D_{\rho}\left(\mathbf{k}\right)}{\hbar\omega - \mathscr{E}_{\rho}\left(\mathbf{k}\right)}\right|^{2}.$$
(44)

Here the quantity  $M_{ab}$  equals  $V^2 k_b^2 / [(2\pi)^3 \hbar^2 v_a v_b]$ ,  $v_a$  and  $v_b$  are the group velocities of the polaritons, and  $\varkappa (\omega, \mathbf{k})$  is the spectral density:

$$\boldsymbol{\epsilon}(\omega, \mathbf{k}) = \frac{4\pi\rho_0 (E)}{[1+2B(E, \mathbf{k}) R(E)]^2 + [4\pi\rho_0 (E) B(E, \mathbf{k})]^2}. \quad (44')$$

Also we have  $E = \hbar(\omega' - \omega'')$ ; for the rest of the notation see Sec. 6a.

The principal component of the frequency-dependence of the Raman cross section is determined by the renormalized anharmonicity of the spectral density of states  $\varkappa$  ( $\omega$ , **k**) of (44'). The maximum of the Raman cross section with respect to **k** corresponds to the value  $\mathbf{k}_0$  ( $\omega$ ), which is the solution of Eq. (35). If the value of  $\omega$  lies outside the band of two-particle states, the solution determines the wave vector **k** of the polariton at Fermi resonance, while the spectral density  $\varkappa^{(b)}$  ( $\omega$ , **k**) coincides with the  $\sigma$ -function (see (32)). In the band of two-particle states itself, the  $\mathbf{k}_0$  ( $\omega$ ) relationship determines the dispersion curve of normal electromagnetic waves in the generalized sense pointed out above. Precisely in this sense the dispersion of maxima in Raman spectra determines the dispersion curve of polaritons, even in the band of two-particle states.

Since in the presence of strong anharmonicity regions of values of frequencies  $\omega_g$  exist for which Eq. (33) has no solutions for any value of the wave vector, gaps arise in the Raman spectra. If the frequency  $\omega_g$  lies inside a gap outside the band of two-particle states, then scattered light having the frequency  $\omega'' = \omega' - \omega_g$  is absent in the Raman-scattering process.

In the band of two-particle states the spectral density of (44'), and correspondingly also Raman scattering, always differ from zero. Therefore, if the frequency  $\omega_g$  lies in the band of two-particle states, then diffuse light scattering arises without a marked maximum in k. Here the integral intensity of light scattered in all directions can prove to be considerable. For some regions of values  $\omega \approx \omega_g$ , the integral intensity sometimes proves to be so small that a trough<sup>50,70</sup> (or "gap") is clearly visible in the Raman spectrum.

The last factor in (44) expresses the interference of the

contributions to the Raman cross section of the overtone F(k) and the polariton  $D_{\rho}$  (k). The interference can lead to troughs in the intensity of the Raman spectrum for certain values of k that satisfy the relationship

$$F(\mathbf{k}) + \sum_{\rho} \frac{\Gamma_{\rho}(\mathbf{k})}{\hbar\omega_{1} - \mathscr{E}_{\rho}(\mathbf{k})} D_{\rho}(\mathbf{k}) = 0.$$

For these values of  $\mathbf{k} = \mathbf{k}_a - \mathbf{k}_b$ , the Raman intensity must be suppressed, and evidently this effect is analogous to the Fano antiresonance in atomic spectra<sup>73</sup> (the possibilities of antiresonance in spectra of Raman scattering by phonons resulting from the interaction of a discrete level and a continuum of states have been discussed earlier in Ref. 74, and in connection with Raman scattering at Fermi resonance by polaritons in Ref. 65). Evidently, this type of trough in the Raman intensity can be appreciable only in crystals in which the partial Raman intensities in the overtone  $F(\mathbf{k})$  and the polariton  $D_{\rho}$  (k) are quantities of the same order of magnitude. Studies of the form of the polariton curve  $\omega$  (k) in an antiresonance region are generally difficult. Only attentive analysis in each concrete case can show whether an observed trough in the intensity results from antiresonance, or whether it reproduces features of the spectrum of electromagnetic waves in the crystal that are determined by its spectral density (44').

# 7. EXPERIMENTAL STUDIES OF FERMI RESONANCE WITH POLARITONS

Fermi resonance with polaritons has already been studied for more than ten years. Therefore considerable experimental material exists at present on Raman scattering at small scattering angles in noncentrosymmetric crystals. In many cases it allows one to reconstruct the spectrum of normal electromagnetic waves in the overtone region (see Refs. 69–71 and below). In this regard we shall discuss the existing experiments in the light of the most recent data, both theoretical and experimental.

At first the attention of investigators was focused on the strongest effect of anharmonicity: the appearance of a bound state of phonons and correspondingly of a gap in the polariton spectrum near the two-phonon band. The first convincing proof of the existence of a gap pertained to the uniaxial crystal of lithium niobate LiNbO<sub>3</sub>.<sup>76,77</sup> In this crystal the dispersion curve for transverse polaritons is split in a region ( $\omega \approx 525$  cm<sup>-1</sup>; Fig. 16) containing no first-order vibrations



FIG. 16. Polariton dispersion curve in the biphonon region in a  $\rm LiNbO_3$  crystal.  $^{76}$ 

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(the frequency of the nearest first-order vibration is of the order of 582  $cm^{-1}$ ). Subsequently an analogous phenomenon has been observed for a large number of crystals, and the results of the corresponding experiments will be discussed below. However, we emphasize that gradually the attention of experimentalists has shifted toward studying the phenomena in the band of two-particle states itself. First of all, this interest in them was aroused by the fact that, as it has turned out, broad phonon bands are very often encountered,<sup>78,79</sup> and in these regions of the spectrum the interaction of polaritons specifically with unbound states of phonons governs both the linear and the nonlinear optical properties of crystals. The interaction of the polariton  $\rho$ , k with the band of unbound states models the situation in which the interaction occurs between the individual level  $\mathscr{C}$ (k) with a continuum of states corresponding to the same value of the wave vector k. We must bear in mind the fact that most crystals whose polariton spectra show Fermi resonance have a complicated phonon spectrum, and the bands of unbound states corresponding to different overtones or compound tones lie very close together or overlap. Therefore one often cannot observe the dispersion curve of polaritons in the vicinity of a solitary band or in the band itself, and the effects on the polariton spectrum of different bands are superimposed on one another. Nevertheless the fundamental results discussed below provide an idea of the nature of Fermi resonance with polaritons, and also of its influence on the properties of the crystals in the corresponding frequency regions.

The band of two-particle states is manifested most sharply in the polariton spectrum of the noncentrosymmetric cubic crystal of  $NH_4Cl$ . We have already spoken of the spectrum of its states at large k and have noted the relatively simple structure of its phonon spectrum.<sup>46</sup> Analysis of the first and second-order Raman spectra here enables one to establish the positions of the bands of unbound states. It has been shown from the studies performed that effects are observed in the Raman spectrum of the crystal under discussion from interaction of polaritons with the already mentioned band  $2v_4$ , which lies in the region 2800–2910 cm<sup>-1</sup>. This band is well isolated from the bands of the fundamental tones, yet at the same time it is rather intense in the Raman spectra. One sees in the spectrograms the sharply marked boundaries of this band, and intense diffuse scattering exists inside it. Nevertheless, the polariton dispersion curve in the region where it approaches the boundaries of the band, as well as its course in many regions inside the band, are rather clearly visible (see Ref. 80). The maxima of intense scattered light in certain places inside the band enable one to determine unambiguously the position of the polariton dispersion curve (Fig. 17). On the whole one observes a pattern of the Raman spectrum that qualitatively corresponds to that described in Sec. 7 with respect to the behavior of polaritons inside the band of two-particle states. Here approximately the same features of Raman scattering by polaritons are also observed inside other bands of unbound states.<sup>50</sup> In this case one could quantitatively compare theory with experiment if one knew the distribution of the density of states in the aforementioned band of two-particle states, as well as

ctailed -



FIG. 17. Section of the polariton spectrum in NH<sub>4</sub>Cl crystals.<sup>50,70</sup> The behavior of polaritons has been studied in greatest detail in the  $2v_4$  band. Note also the singularities of the polariton dispersion curve in the  $v_2 + v_4$  band.

the parameters of the crystal that govern the anharmonicity constants. In principle both can be found on the basis of model calculations or measured in independent experiments (e.g., the density of states can be measured with inelastic neutron scattering).

The manifestation of Fermi resonance in Raman spectra of a crystal of LiIO<sub>3</sub> has been reported.<sup>81,82,99</sup> High-resolution measurements<sup>82,99</sup> have made possible the detection of four breaks in the polariton dispersion curve in the region 1500–1600 cm<sup>-1</sup>. In the vicinity of each of the resonances, the course of the polariton dispersion curve is analogous to its course in LiNbO<sub>3</sub> and agrees well with the predictions of theory (see Ref. 99).

The course of the polariton dispersion curve in the bands of unbound states has also been observed in a crystal of lithium formate.<sup>78,83</sup> A change in the course of the dispersion curve is observed in two regions (2150–2450 and 2520–2570 cm<sup>-1</sup>). Here the polariton curve is broadened, but remains continuous.<sup>5)</sup> Characteristic bends of the curve are observed, whose amplitude is greater than its width. Qualitatively the polariton spectron is very similar to the spectrum due to a weak interaction between phonons and polaritons (see Fig. 12). Of course, one cannot interpret the details of the ob-

served structure of the polariton curve within the framework of a model having one band. One requires a more complex theory that allows for the simultaneous interaction of the polariton with a large number of bands. In the presence of a rich phonon spectrum and with a large number of overlapping bands of multiparticle states, it is difficult to take into account the influence of each band individually (with its critical points and singularities). A distinctive stochastic problem arises for describing the behavior of polaritons in such a spectral region: to calculate the dispersion of a polariton interacting with a large number of "random" continua with overlapping boundaries.

In an  $HIO_3$  crystal a rearrangement of the polariton spectrum is observed, both in the biphonon region and in the band of two-particle states.<sup>52</sup> One observes a gap in the region of frequencies of the bound state in the polariton branch, while in the band the Raman line is strongly broadened. The structure of the spectrum in the band becomes more distinct upon cooling the crystal, while the polariton curve even breaks inside the band.

The broadening of the polariton branch in the region of dissociated states arises from the opening of a new decay channel, and we have already mentioned this effect above. The casue is not yet evident of the breaks in the polariton branch that arise in this same region of the spectrum on lowering the temperature of the crystal. Only by future studies can we hope to elucidate which of these breaks arise from critical points of the density of two-particle states, from the formation of quasibiphonons, or from interference of the type of a Fano antiresonance.

We note that the temperature-dependence of the width of the spectral lines at Fermi resonance with polaritons (see Refs. 35 and 51) can be very strong. Its nature is as yet little studied, and the analysis here first of all hinges on the question of the temperature-dependence of the widths of the biphonon and quasibiphonon lines. Since the binding energy in a biphonon is generally small in comparison with the energy of short-wavelength acoustic phonons, it would be natural to assume that the width of the level of a biphonon is

# $\Gamma \thickapprox 2\Gamma_0 + \gamma_{\rm ,dis}$ .

Here  $\Gamma_0$  is the width of the level of an individual optical phonon, while  $\gamma_{dis}$  is the width arising from the thermally activated process of dissociation of a biphonon accompanied by its conversion into two free phonons (crudely speaking,  $\gamma_{dis} \approx \gamma_0 e^{-u/kT}$  when  $u \gg kT$ , where U is the binding energy in the biphonon). For a quasibiphonon ( $E = E_{qb}$ ), one could write an analogous expression for  $\Gamma$ , but with  $\gamma_{dis} \sim \rho_0(E_{qb})$ ,  $\rho_0(E)$  is the density of two-particle states for  $E = E_{qb}$ . In both cases, i.e., for the biphonon and the quasibiphonon, we have  $\Gamma > \Gamma_0$ . This is precisely the situation that must be subjected to experimental analysis. A breakdown of the stated inequality might mean that anharmonicity substantially changes also the relaxation processes responsible for the decay of individual high-frequency optical phonons.

Since in uniaxial crystals the frequency  $\omega \rho$  (k) of the extraordinary polaritons (see, e.g., Refs. 69 and 70) depends strongly on the direction of the wave vector k, changes in the direction of the wave vector of the incident light with respect

to the optic axis, and hence, changes in the wave vector **k** of the polariton being created, enable one to vary the relative position of the energy of the polariton and the energy band of two-particle states. Here the conditions of Fermi resonance are varied. In particular, as was shown in Ref. 79, upon gradually changing the direction of the wave vector **k** of the polariton and shifting it from the extraordinary to the ordinary ray, one can observe a change in the polariton-twophonon interaction from the change in the form of the dispersion curve. The dispersion curve initially broadens, then bends appear in it and increase in amplitude, while the dispersion curve breaks as k approaches the direction of the optic axis. The latter indicates in this case a sharp increase in the anharmonicity constant. Reference 79 has explained such a strong influence of Fermi resonance by the large anharmonicity of hydrogen bonds, which makes possible a considerable polariton-two-phonon interaction.

A break in the polariton curve in the band of two-particle states in the CdS crystal has been reported.<sup>84</sup> A broad band is observed in the region of 204–213 cm<sup>-1</sup> in the Raman spectrum of this crystal with two maxima, apparently associated with extrema of the density of the band of twoparticle states. In the cited study it was also possible to observe the course of the polariton dispersion curve inside this band. The position of the observed break in the polariton curve is associated<sup>84</sup> with the Van Hove critical points. This interpretation is analogous to that treated in this section.

The results of studies of Fermi resonance with polaritons in the CaCO<sub>3</sub> crystal (calcite) obtained with hyper-Raman scattering<sup>85</sup> are of considerable interest. These results are the first demonstration of the potentiality of applying hyper-Raman scattering to study effects of anharmonicity in centrosymmetric crystals, where the process of ordinary Raman scattering by polaritons is forbidden by the selection rules. In the previously mentioned calcite crystal, the anharmonicity is not strong enough for biphonon formation, but it creates decaying states in the bands of two-particle states (quasibiphonons) that are manifested in the infrared absorption spectra. The quasibiphonons give rise to breaks in the polariton curve that are not very broad (see Fig. 12), which have specifically been observed in Ref. 85. The authors were able to compare successfully the theory developed in Refs. 15-17 with experiment (Fig. 18). The data, which were mutually in agreement within the framework of a unitary model for the position, width, and intensity of the Raman lines, as well as for the infrared spectra of calcite, made it possible to determine the anharmonicity constant.

#### 8. CONCLUSION: PROSPECTS OF FURTHER STUDIES

The possibility of formation of biphonons and other, larger phonon complexes substantially enriches the vibrational spectrum of multiparticle states of crystals. Although a number of important results have been obtained already in this field of studies, both in the experimental and theoretical areas, much yet remains to be done. In particular, threephonon and other more complex bound states of phonons merit further study (analysis of them is just beginning<sup>88</sup>).



FIG. 18. Dispersion curves in a GaCO<sub>3</sub> crystal. Dots—polariton frequencies measured in Ref. 85; dotted line—polariton dispersion without allowance for Fermi resonance of the two-particle states; solid lines calculated dispersion relationships with allowance for Fermi resonance.<sup>85</sup>

However, even biphonons and their role in many optical processes have been insufficiently fully studied at present. In connection with what we have said, we wish first of all to call attention to the topicality of calculations of biphonons in crystals of different structures for the field of degenerate vibrational transitions.

Also studies of biphonons in one- and two-dimensional crystals might be of great interest. In crystals of this type, and also in three-dimensional crystals in which certain phonons can be considered quasi-one- or quasi-two-dimensional, the conditions for formation of biphonons must be more favorable, other conditions remaining the same, than in ordinary three-dimensional crystals.

In speaking of biphonons in one-dimensional crystals, we wished to call attention to their possible role in processes of energy transport along protein molecules.<sup>89</sup> These molecules possess vibrations with an energy  $\varepsilon \approx 0.2$  eV. Therefore the formation of stable and mobile complexes consisting of two or three vibrational quanta might prove important in connection with the problem of energy transport with  $\varepsilon \approx 0.5$ eV (see Ref. 89). However, evidently, this type of biphonon energy transport to macroscopic distances, which are important only in biology, can be considered to be real only under the condition that the lifetime of the vibrational quanta is large enough. In this sense, the problem of the lifetime that arises here has the same importance in principle that it has in connection with evaluating the role of soliton transport.<sup>90</sup>

We have already emphasized above that the conditions for formation of local or quasilocal biphonons in disordered crystals can differ substantially from the analogous conditions for formation of local states in the region of the fundamental frequencies. In connection with the already started development of experimental studies of spectra of disordered crystals in the region of overtones and compound tones of the fundamental vibrations, further analysis of the spectra of disordered crystals in the spectral region of multiparticle states seems topical and theoretically interesting. As is known, the coherent-potential method<sup>91</sup> was developed and is being successfully applied for calculating the spectra of one-particle states (electrons, phonons, Fresnel excitons). Yet when the question involves the spectrum of two-

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particle states, then a number of theoretical problems arise in taking account of anharmonicity (see also Ref. 60) that require additional analysis, and which primarily involve the need for ensuring the correct asymptotic behavior of the method at low concentrations of a dopant (going over to the dispersion equation for a local biphonon or quasibiphonon). Also the development of the theory of surface biphonons merits further attention. The conditions for formation of these states also differ from the conditions for formation of surface states in the spectral region of the fundamental vibrations. It has been shown<sup>20</sup> with the model of a bounded one-dimensional crystal that situations are generally possible in which surface phonon states are not formed, and the spectrum of surface states begins only in the region of overtones or compound tones of vibrations.

In closing we emphasize that biphonons and other effects of strong anharmonicity should be manifested not only in the absorption and luminescence spectra of pure and doped crystals, in nonlinear processes, and in Raman spectra and inelastic neutron-scattering spectra, but perhaps also in processes of radiationless decay of electronic excited states of a crystal. The analysis of this problem, as well as many other manifestations of states of phonons bound to one another, is of interest and will probably be a matter for the future.

- <sup>1)</sup> This Hamiltonian is (formally) the Bose analog of Hubbard's Hamiltonian.<sup>96</sup> This situation offered grounds to the authors of Ref. 97 to discuss the possibility of a phase transition for phonons, analogous to the Mott transition for electrons.
- <sup>2)</sup> The converse situation has been studied in Ref. 31,
- <sup>3)</sup> We also note the study of Pitaevskii, <sup>30</sup> which discusses (see also Ref. 34)
- weakly bound biphonons that arise in the limit of small  $|A| < \Delta$ . <sup>4)</sup> When  $\Gamma = 0$ , Eq. (18) is analogous to the known analysis<sup>33</sup> of the conditions for formation of local states of phonons in the neighborhood of an isotopic impurity.
- <sup>5)</sup> Thus the experiments contradict the theory of Ref. 86a according to which the polariton branch cannot enter the band of two-particle states (see also Ref. 86b).
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