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Biphonon Spectra in Disordered Crystals

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In the coherent potential approximation (CPA) calculations have been made for the light absorption coefficient and the density of states in biphonon band for a disordered isotopic-mixed crystal over the whole range of mixture concentrations. Models of one-dimensional and three-dimensional crystals have been considered. It is shown that even in three-dimensional crystals such situations may arise when in the region of the fundamental tone at any concentrations no splitting of the impurity band occurs while in the overtone region due to anharmonicity such splitting takes place at any compositions of the mixture.

1. INTRODUCTION. COHERENT POTENTIAL APPROXIMATION FOR BIPHONONS

Recently the studies of those peculiarities of crystal vibrational spectra which are conditioned by the possibility of the formation in them optical phonons bonded with one another (biphonons), have been attracting still growing interest.[1,2] Such states are analogous to biexcitons (excitonic molecules) which are realized in the electronic spectral region. However, in contrast to biexcitons, biphonons make no appreciable contribution to luminescence. Therefore, their observation for some crystals turned out to be possible only while studying Raman spectra of light scattering by polaritons (see Ref. 3) and also while studying IR spectra.[4]

In the presence of impurities or lattice defects local biphonons can be formed. As shown in Ref. 2 (see also Ref. 5) the conditions of the formation of these states differ considerably from those when local phonons appear. Therefore, for example, such situations can arise when in spite of the presence of impurities the local or quasi-local states in the fundamental tone region are absent and they appear only in the region of overtones or combination tones of optical vibrations of the lattice. Such situation was actually observed experimentally in Ref. 6, where Raman spectra of the first and second orders were studied in a $N^{14}H_4Cl$ crystal with the addition of N^{15} isotope. The problem of the validity of conclusions made in Refs. 2, 5 about the splitting of local states for high impurity concentrations has not been studied as yet. In this connection the problem of today is further theoretical analysis of biphonon spectra in disordered media and the present paper deals with this very problem. Here we use the coherent potential approximation[7,8] which was successfully used before for studying electron, phonon and Frenkel exciton spectra in disordered media (see, Refs. 9, 10).

Consider the so-called isotopic-mixed molecular crystals with one molecule in the elementary cell which are formed of molecules of two kinds. Having in mind the study of the vibrational spectrum of the crystal, we assume molecules to be anharmonic oscillators having one and the same anharmonicity constant A and differing only in eigenfrequencies of vibrations. In this case the crystal Hamiltonian can be written in the form[2]

$$\hat{H} = \sum_n E_n B_n^+ B_n + \sum_{nm} V_{n,m} B_n^+ B_m - A \sum_n (B_n^+)^2 B_n^2, \tag{1}$$

where $B_n^+(B_n)$ is the creation (annihilation) operator of the vibrational quantum in the molecule n. E_n are random variables which take on the values $E_n = E_1$ or $E_n = E_2$ depending on which molecule, of the first or second kind placed in the site n; $V_{n,m}$ are matrix elements of the operator of intermolecular interaction energy. Nondiagonal disorder (i.e. $V_{n,m}$ dependence on the kind of molecules) is neglected.

In coordinate representation the wave function $\psi_{n,m}$, which determines crystal states with two vibrational quanta, has the form

$$|2\rangle = \sum_{n,m} \psi_{n,m} B_n^+ B_m^+ |0\rangle, \tag{2}$$

where $|0\rangle$ is the wave function of the crystal ground state.

The energy E and the wave function of biphonons are determined from Schrodinger equation $\hat{H}|2\rangle = E|2\rangle$, which upon the use of Eqs. (1) and (2) becomes:

$$\sum_{p,q} \{[E - E_n - E_m + 2A\delta_{n,m}]\delta_{np}\delta_{mq} - V_{np}\delta_{mq} - \delta_{np}V_{mq}\}\psi_{pq} = 0 \tag{3}$$

Green's function in Eq. (3), which determines the spectrum of two-quasiparticle states depends on random values E_n and E_m:

$$D_{nm,pq} = \{[E - E_n - E_m + 2A\delta_{n,m}]\delta_{np}\delta_{mq} - V_{np}\delta_{mq} - \delta_{np}V_{mq}\}^{-1} \tag{4}$$

For further convenience we introduce the so-called locator Green's function $g_{nm,pq}$, which coincides with $D_{nm,pq}$ at $\hat{V} = 0$:

$$g_{nm,pq}(E) = D_{nm,pq}(E)|_{\hat{V}=0}$$

By expanding Eq. (4) into a series over $\hat{V}$, one can come to the equation of Dyson's type (matrix indices are omitted below):

$$D = g + g(\hat{V}^{\mathrm{I}} + \hat{V}^{\mathrm{II}}) \tag{5}$$

where matrices $\hat{V}^{\mathrm{I}}$, $\hat{V}^{\mathrm{II}}$ correspond to two terms with $\hat{V}$, which enter Eq. (4) in different ways

$$V^{\mathrm{I}}_{nm,pq} = V_{np}\delta_{mq}, \qquad V^{\mathrm{II}}_{nm,pq} = \delta_{np}V_{mq}$$

Now in Eq. (5), determining D, the random value is the locator g.

For the determination of the seeked value of Green's function averaged over all impurity configurations (the dash means averaging) we use some generalization of coherent potential approximation. Within the frames of this approach the desired averaged Green's function $\bar{D}$ is determined from the equation of the type (5), but with the determinate locator σ:

$$\bar{D} = \sigma + \sigma(V^{\mathrm{I}} + V^{\mathrm{II}})\bar{D} \tag{6}$$

The value σ is determined in the following self-consistent way. As it follows from Eqs. (5) and (6)

$$\begin{aligned} g^{-1} &= D^{-1} + (V^{\mathrm{I}} + V^{\mathrm{II}}) \\ \sigma^{-1} &= \bar{D}^{-1} + (V^{\mathrm{I}} + V^{\mathrm{II}}) \end{aligned} \tag{7}$$

From Eq. (7), upon the exclusion of $V^{\mathrm{I}} + V^{\mathrm{II}}$, we obtain directly the bond

$$\bar{D}^{-1} = D^{-1} + (\sigma^{-1} - g^{-1}) \tag{8}$$

and, therefore,

$$D = \bar{D} + \bar{D}(\sigma^{-1} - g^{-1})D \tag{9}$$

Now, if we introduce the T-matrix, then, according to the definition:

$$D = \bar{D} + \bar{D}T\bar{D} \tag{10}$$

and we obtain for it the following relationship:

$$T = [(\sigma^{-1} - g^{-1})^{-1} - \bar{D}]^{-1} \tag{11}$$

As it follows from Eq. (10), the equality $\bar{T} = 0$ must be fulfilled. This equality may be used to determine the value σ. In the theory of disordered media, as applied to one-quasi-particle states, the equation for the value similar to σ was obtained from the condition that the diagonal elements of the matrix T were equal to zero. In the case of two-quasi-particle states natural generalization of this condition also gives the relationship for the determination of the value σ. This condition is given by

$$\overline{[(\sigma^{-1} - g^{-1})^{-1}_{nn,nn} - \bar{D}_{nn,nn}(\sigma)]^{-1}} = 0 \tag{12}$$

In two different limiting cases, i.e. at small concentrations of any of the two components of the mixture, the approach used gives the results coinciding with the results of the exact theory. In the intermediate region the coherent potential method is known[7,8] to give results, corresponding to certain interpolation.

Below it is convenient to seek the value σ in the form

$$\sigma^{-1}_{nm,pq} = [E - \textstyle\sum(E) + 2A\delta_{nm}]\delta_{np}\delta_{mq}, \tag{13}$$

where $\sum(E)$ has the meaning of the self-energy part. In this case Eq. (12) can be represented in the usual way as it is done in the coherent potential method:

$$\frac{C_1}{(2E_1 - \sum)^{-1} - \bar{D}_{nn,nn}} + \frac{C_2}{(2E_2 - \sum)^{-1} - \bar{D}_{nn,nn}} = 0, \tag{12a}$$

where C_1, C_2 are concentration of the component ($C_1 + C_2 = 1$). Some easy simplifications give

$$C_1/(2E_2 - \textstyle\sum) + C_2/(2E_1 - \sum) = \bar{D}_{nn,nn}(\sum) \tag{12b}$$

By substituting Eq. (13) into (6), we find that in the coherent potential approximation

$$\bar{D}_{nm,pq} = \{[E - \textstyle\sum + 2A\delta_{nm}]\delta_{np}\delta_{mq} - V_{np}\delta_{mq} - \delta_{np}V_{mq}\}^{-1} \tag{14}$$

Using this relationship, it can be shown that the value of the matrix element $\bar{D}_{nn,nn}$ in Eq. (12b) is determined as follows:

$$\bar{D}_{nn,nn}(\textstyle\sum) = \frac{1}{N}\sum\limits_{K} \frac{I(\sum, K)}{[1 + 2AI(\sum, K)]}, \tag{15}$$

where N is the number of molecules in the bulk volume,

$$I(\textstyle\sum, K) = \frac{1}{N}\sum\limits_{Q} D^0_{K,Q}(\sum), \tag{15a}$$

$$D^0_{K,Q}(\textstyle\sum) = \{E - \sum - V_{K+Q} - V_{K-Q}\}^{-1}, \tag{15b}$$

V_K is the intermolecular interaction in the momentum representation:

$$V_{nm} = \frac{1}{N}\sum_{K} V_K \exp\{iK(n - m)\}$$

In an ideal crystal formed, for example, of molecules of the kind 1 (i.e. at $C_1 = 1$ and $C_2 = 0$), the value $\sum = 2E_1$. In this case, as it was shown in Ref. 2, and as it follows from Eq. (15) the biphonon energy E is determined from the equation

$$1 + 2AI(2E_1, K) = 0 \tag{16}$$

But if the crystal has as an impurity of the second isotope with small concentration $C_2 \ll 1$, then from the Eq. (12b) at $C_2 \to 0$ and $\sum \to 2E_1$ there follows† the equation for the energy of the local biphonon:

$$\frac{1}{2}(E_2 - E_1)^{-1} = D_{nn,nn}(2E_1) \tag{17a}$$

In the second limiting case, i.e. at $C_2 \to 1$ and $C_1 \ll 1$, $\sum \to 2E_2$ and the equation for the local biphonon acquires the form:

$$\frac{1}{2}(E_1 - E_2)^{-1} = D_{nn,nn}(2E_2) \tag{17b}$$

The relationships Eq. (17) were obtained previously in Refs. 2, 5.

The imaginary part of the Green's function matrix element $\bar{D}_{nn,nn}(\sum)$ (see Eq. (15)) determines the density of the required states of optical phonons in the energy region $E \sim 2E_1, 2E_2$ considered and, moreover, it can be used to determine the dependence of two-phonon light absorption on E. However, the use of the relationship Eq. (15) requires the knowledge of the self-energy part $\sum$ dependence on E.

For the region of arbitrary concentrations the value $\sum(E)$ satisfies the equation (see also Eq. (15a,b))

$$C_1(2E_2 - \textstyle\sum)^{-1} + C_2(2E_1 - \textstyle\sum)^{-1} = \frac{1}{N}\sum_K \frac{1(\sum, K)}{1 + 2AI(\sum, K)} \tag{18}$$

The solution of this equation in the general form is rather difficult. The main difficulty, as compared to the case discussed in Refs. 7, 8, arises from the presence of double summation in Eq. (15) and from the "shift" by the wave vector of the biphonon K in the integrand terms which include the expressions $V_{K+Q} + V_{K-Q}$. This shift impedes the use of the model density of states for an ideal crystal as it used in the theory of disordered media in its application for one-quasi-particle states.

2. BIPHONONS IN DISORDERED ONE-DIMENSIONAL CRYSTAL

In this connection there was considered first the simplest model of an one-dimensional crystal in the approximation of the nearest neighbours interaction. In this case $V_{nm} = V\delta_{n,m\pm 1}$ and the zone addition to the energy of one-particle excitations is known to be $V_K = 2V\cos Ka$ (a is the lattice

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† Note that the term of the type $C_2/(2E_1 - \sum) \to 0$ at $C_2 \to 0$ though in this case $\sum \to 2E_1$. This conclusion can be grounded in the same way as it was done in Refs. 7, 8, and 9 for the similar case.

parameter). Here the function $D^0_{K,Q}$ is determined by the relationship:

$$D^0_{K,Q} = [E - \sum - 4V\cos Ka \cdot \cos Qa]^{-1} \tag{19}$$

Now we go in (15) from the summation over K, Q to integration. The integral with respect to Q in the expression for I can be calculated analytically.[11] In this case the real and imaginary parts of this integral should be considered separately. If it is taken into account that $\sum = \sum' + i\sum''$, we obtain:

$$\begin{aligned} \operatorname{Re} I(\textstyle\sum, K) &= \frac{1}{\sqrt{2}}\Psi^{-1/2}[(E - \textstyle\sum' - 4V\cos Ka)M_-^{-1} \\ &\quad + (E - \textstyle\sum' + 4V\cos Ka)M_+^{-1}], \\ \operatorname{Im} I(\textstyle\sum, K) &= \frac{1}{\sqrt{2}}\Psi^{-1/2}\textstyle\sum''[M_-^{-1} + M_+^{-1}], \end{aligned} \tag{20}$$

where functions Ψ, $M_\pm$ are given by

$$\begin{aligned} M_\pm &= [(E - \textstyle\sum' \pm 4V\cos Ka)^2 + (\textstyle\sum'')^2]^{1/2}, \\ \Psi &= M_+M_- + (E - \textstyle\sum')^2 - 16V^2\cos^2 Ka + (\textstyle\sum'')^2 \end{aligned} \tag{21}$$

Relationships Eqs. (20) and (21) allow to determine, in particular, the zone of biphonon states in an ideal crystal. Substitution of the value $I(\sum, K)$ from Eq. (20) into Eq. (16) gives, for example, for a crystal of the kind 1($\sum'' = 0$, concentration broadening is absent, $\sum' \to 2E_1$):

$$1 = 2A[(E - 2E_1)^2 - 16V^2\cos^2 Ka]^{-1/2}$$

Thus, the energy of biphonons can be given by the following relationship:

$$E(K) = 2E_1 - \sqrt{4A^2 + 16V^2\cos^2 Ka}. \tag{22}$$

From Eq. (22), the same as from the general theory,[2,5] it follows that the width of the biphonon states zone at small V/A has the order of magnitude of V^2/A.

Further analytical integration with respect to K in Eq. (18) is rather difficult due to the complexity of expressions Eq. (20). The other two procedures—integration with respect to K and the solution of the system of 2 transcendent Eq. (18) for $\sum'$ and $\sum''$ have been performed by us numerically by means of a computer, as it was done previously in the theory of disordered media. Calculations were made at different values of parameters $\delta = (E_1 - E_2)/2V$, A/V and C_1.

Figure 1 shows the calculation results for the values $\sum'(E)$ (the dashed line) and $\sum''(E)$ (the solid line) found from Eq. (18) for the parameter value†

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† For the sake of convenience excitation energies of isolated molecules E_1 and E_2 here and below are calculated from the value equal to a half of their sum.

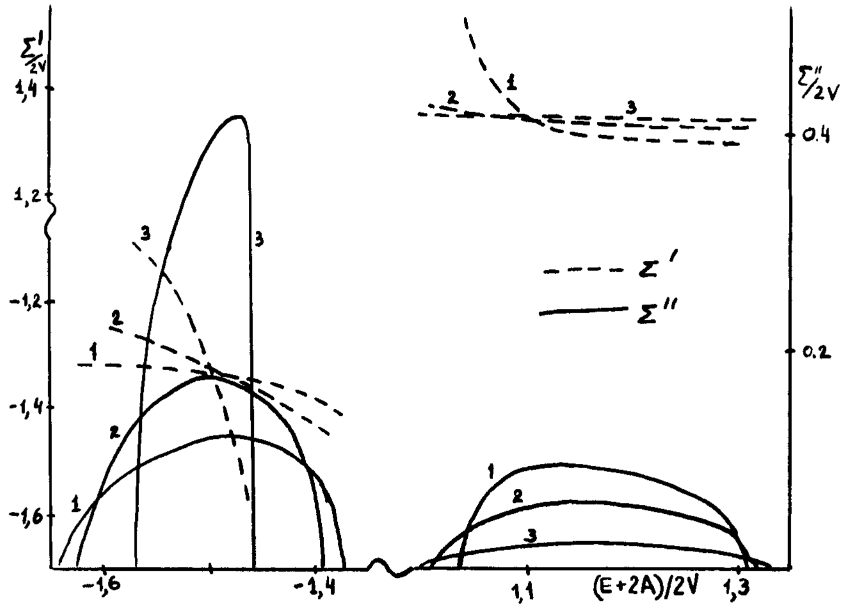

FIGURE 1 Self-energy part for linear crystal ($A/V = 6, E_1/V = 1.33$; $1 - C_1 = 0.5$, $2 - C_1 = 0.7$, $3 - C_1 = 0.9$).

$\delta = 1.33$ ($E_1/V = -E_2/V = 1.33$, as in naphthalene.)[10] In this case considerable overlapping of zones of one-phonon states of ideal crystals (kinds 1 and 2) is realized as well as of the zone of unbound two-phonon states in the region $2E_2 - 2V < E < 2E_1 + 2V$. For the parameter value $A/V = 6$ biphonon zones are completely chip off into the region $E < 2E_2 - 2V$. The development of the impurity zone is observed with the increase of concentration. The general form of energy dependences for functions $\sum'(E)$, $\sum''(E)$ is similar to energy dependences for one-phonon states.

Figure 2 shows the density of states in biphonon band (the solid line). This density was found from the formula

$$\rho(E) = \frac{1}{\pi} \operatorname{Im} \bar{D}_{nn,nn}.$$

It gives also the energy dependence of the intensity of two-phonon light absorption (the dashed line), determined with the accuracy up to the constant multiplier of the value

$$P(E) = \operatorname{Im}\left\{\frac{I(\sum, 0)}{[1 + 2AI(\sum, 0)]}\right\}$$

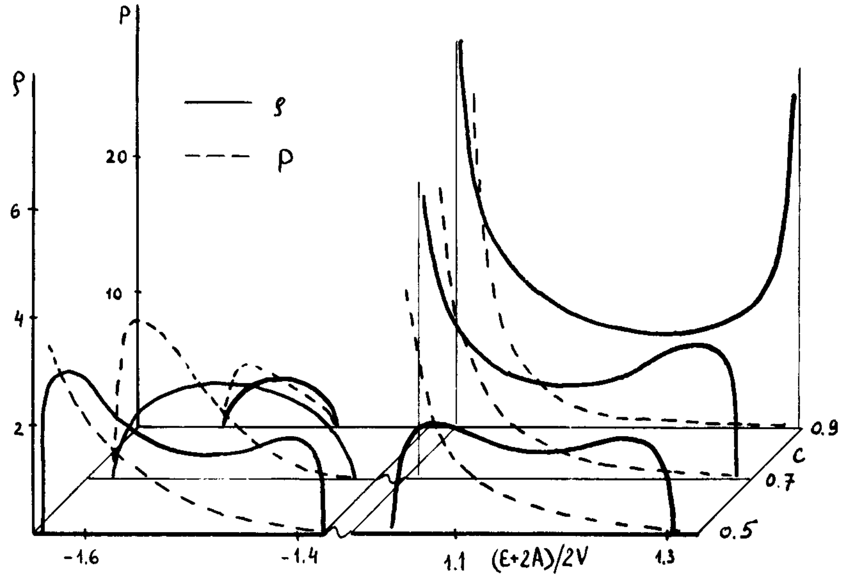

FIGURE 2 The density of states and absorption coefficient for linear crystal ($A/V = 6$, $E_1/V = 1.33$).

In Figure 3 state densities and light absorption coefficients are plotted for two other values of parameters δ and A/V. It is seen that with the decrease of the anharmonicity constant. A the zone of biphonon states approaches the zone of unbound two-particle states and the biphonon zone is broadened which is seen also from the above relationships. In Figure 3b the case is represented when the decrease of parameter δ causes the transition from the situation when biphonon zones are separated, to the situation when such separation of biphonon zones does not occur.

3. BIPHONONS IN DISORDERED THREE-DIMENSIONAL CRYSTAL

The relationships Eqs. (19–21) obtained for the linear chain allow to pass naturally to the consideration of bulk crystals. If for a three-dimensional crystal the nearest neighbours approximation of the interaction is used, then zone addition to the energy of one-particle excitations is given by

$$V_K = 2V \ (\cos K_1 a + \cos K_2 a + \cos K_3 a),$$

where K_i, $i = 1, 2, 3$ are components of the wave vector K. Here for the value

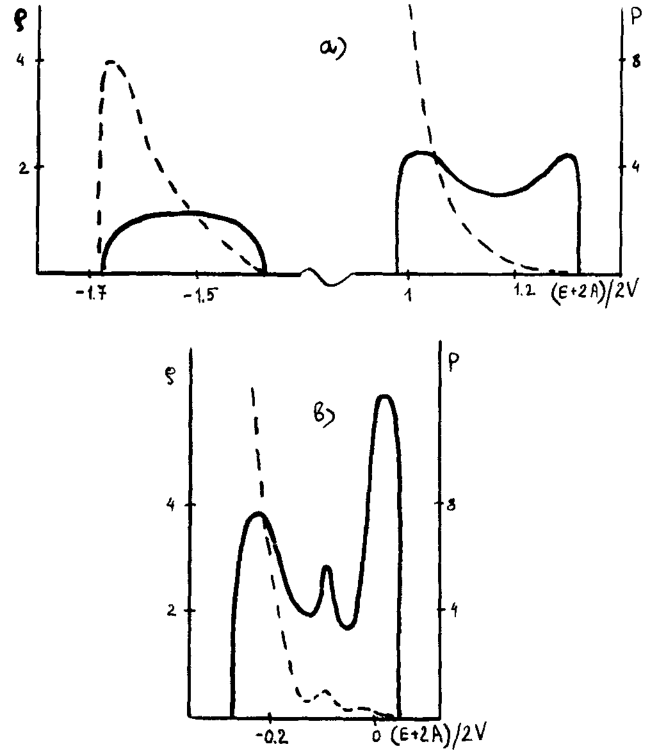

FIGURE 3 The density of states and absorption coefficient for linear crystal (a – $A/V = 5$, $E_1/V = 1.33$, b – $A/V = 6$, $E_1/V = 0.08$).

$V_{K+Q} + V_{K-Q}$ in $I(\sum, K)$ we obtain

$$\begin{aligned} z(Q) &\equiv V_{K+Q} + V_{K-Q} \\ &= 4V(\cos K_1a \cdot \cos Q_1a + \cos K_2a \cdot \cos Q_2a \\ &\quad + \cos K_3a \cdot \cos Q_3a) \end{aligned} \tag{23}$$

Calculation of integrals Eq. (15) with the dependence Eq. (23) is rather difficult. Therefore, we use an approximation method: in Eq. (15) we substitute summation over Q by integration with use of the model density of z values determined by the relationship:

$$\mathrm{d}Q = 2V_K^{-2}[(2V_K)^2 - z^2]^{1/2}\,\mathrm{d}z \tag{24}$$

The limiting values $z(Q)$ are seen from Eq. (23) to equal $\pm 2V_K$ and the behaviour of the model density used in the vicinity of these limits has the usual root dependence. The final form of the sum over Q in Eq. (15) can be represented as follows:

$$M \equiv \frac{1}{N}\sum_{Q}(E - \sum - V_{K+Q} - V_{K-Q})^{-1} = \frac{1}{2\pi V_K^2}\int_{-2|V_K|}^{+2|V_K|}\frac{[4V_K^2 - z^2]^{1/2}}{E - \sum - z}\,\mathrm{d}z \tag{25}$$

The integral in Eq. (25) can be reduced to the form

$$M = \frac{1}{2V_K^2}\{E - \sum - [(E - \sum)^2 - 4V_K^2]J(E, \sum, V_K)\},$$

$$J(E, \sum, V_K) = \frac{1}{\pi}\int_{-2|V_K|}^{2|V_K|}(4V_K^2 - z^2)^{-1/2}(E - \sum - z)^{-1}\,\mathrm{d}z \tag{26}$$

The integral I in Eq. (26) is of the type considered before for a linear crystal and has an analytical representation. As a result we obtain:

$$\begin{aligned} \operatorname{Re} I(\sum, K) &= \frac{1}{2V_K^2}\{E - \sum' - [(E - \sum')^2 - (\sum'')^2 - 4V_K^2]\operatorname{Re} J(\sum, V_K) \\ &\quad - 2\sum''(E - \sum')\operatorname{Im} J(\sum, V_K)\}, \\ \operatorname{Im} I(\sum, K) &= \frac{1}{2V_K^2}\{-\sum'' - [(E - \sum')^2 - (\sum'')^2 - 4V_K^2]\operatorname{Im} J(\sum, V_K) \\ &\quad + 2\sum''(E - \sum')\operatorname{Re} J(\sum, V_K)\}, \end{aligned} \tag{27}$$

where

$$\begin{aligned} \operatorname{Re} J(\sum, V_K) &= (2\varphi)^{-1/2}[(E - \sum' - 2V_K)m_1^{-1} + (E - \sum' + 2V_K)m_2^{-1}], \\ \operatorname{Im} J(\sum, V_K) &= (2\varphi)^{-1/2}(m_1^{-1} + m_2^{-1})\sum'' \end{aligned} \tag{27a}$$

and functions $m_{1,2}$, φ are given by

$$\begin{aligned} m_{1,2} &= [(E - \sum' \pm 2V_K)^2 + (\sum'')^2]^{1/2} \\ \varphi &= m_1 m_2 + (E - \sum')^2 - 4V_K^2 + (\sum'')^2. \end{aligned} \tag{27b}$$

Relationships Eq. (27) determine the energies of biphonon states of an ideal crystal. Substituting the value $I(\sum, K)$ from Eq. (27) into Eq. (16) we obtain, for example, for a crystal of the kind 1 ($E < 2E_1 - 2|V_K|$)

$$V_K^2 + A\{E - 2E_1 + [(E - 2E_1)^2 - 4V_K^2]^{1/2}\} = 0$$

The solution of this dispersion equation gives the biphonon energies:

$$E(K) = 2E_1 - 2A - V_K^2/2A$$

Thus, again in accordance with the general theory,[2,5] the width of the biphonon zone is proportional to T^2/A, where T is the half-width of the one-phonon zone.

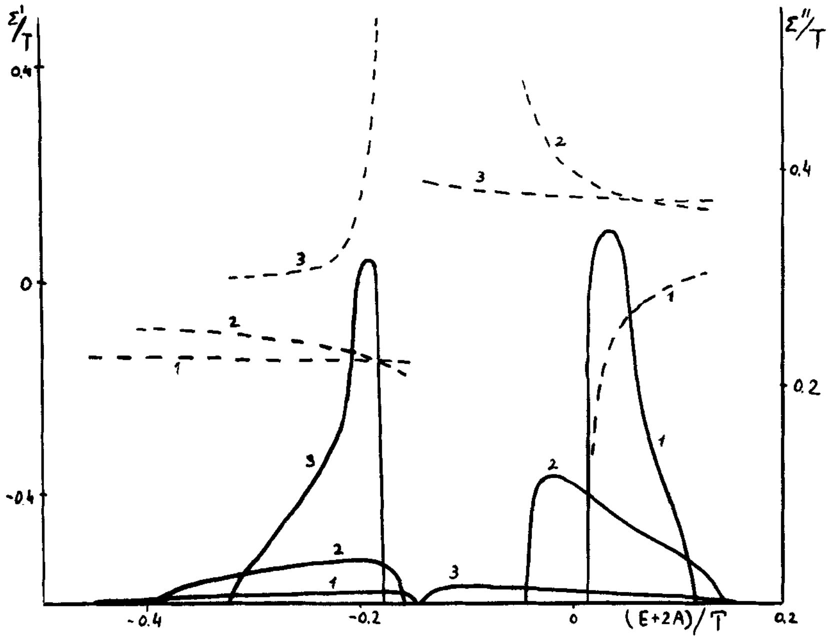

FIGURE 4 Self-energy part for bulk crystal ($2A/T = 3$, $2E_1/T = 0.15$; $1 - C_1 = 0.1$, $2 - C_1 = 0.5$, $3 - C_1 = 0.9$).

The next calculation procedure, i.e. integration with respect to K and the solution of the system of equations for $\sum'(E)$, $\sum''(E)$ have been performed by us numerically—the same as for a linear crystal. Here again integration with respect to K was performed with the use of the model density of one-phonon states of the "elliptical" type:[7,8,9]

$$\rho(E) = \frac{2}{\pi} T^{-2}(T^2 - E^2)^{1/2}$$

Figure 4 gives for different concentrations calculation results for $\sum'(E)$, $\sum''(E)$ for the parameter value $2E_1/T = -2E_2/T = 0, 15$, $A/T = \frac{3}{2}$. For these parameter values there occurs great overlapping of the zones of one-phonon and unbound two-phonon states and with any compositions of the mixture there is no splitting of energy zones corresponding to these states. For the given values of parameters the biphonon zones in ideal crystals of the kinds 1 and 2 are also close (have insignificant overlapping). However, in a crystalline mixture (see Figure 6) separated biphonon zones are formed with any compositions. In this case the system is extremely close to the "percolation" threshold, thus generalizing the conclusion made in Ref. 2 for the case of high concentrations and permitting to reveal more distinctly typical peculiarities of spectral characteristics.

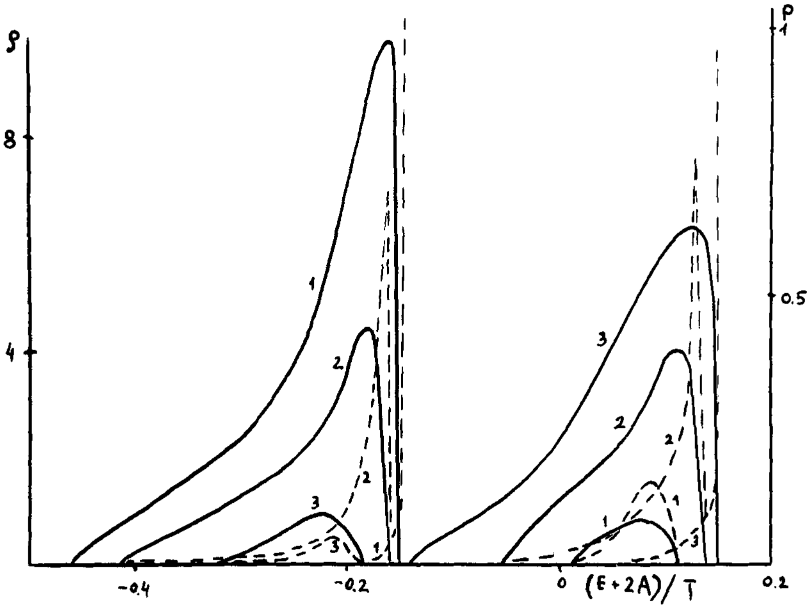

FIGURE 5 The density of states and absorption coefficient for bulk crystal ($2A/T = 3$, $2E_1/T = 0.15$; $1 - C_1 = 0.1$, $2 - C_1 = 0.5$, $3 - C_1 = 0.9$).

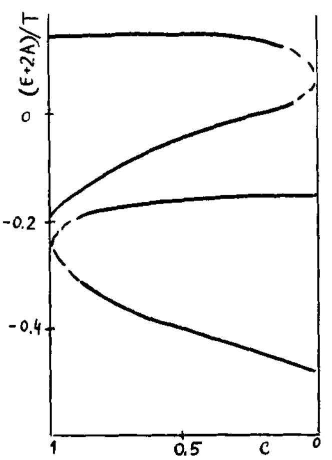

FIGURE 6 Concentration dependence of zone boundaries for bulk crystal ($2A/T = 3$, $2E_1/T = 0.15$).

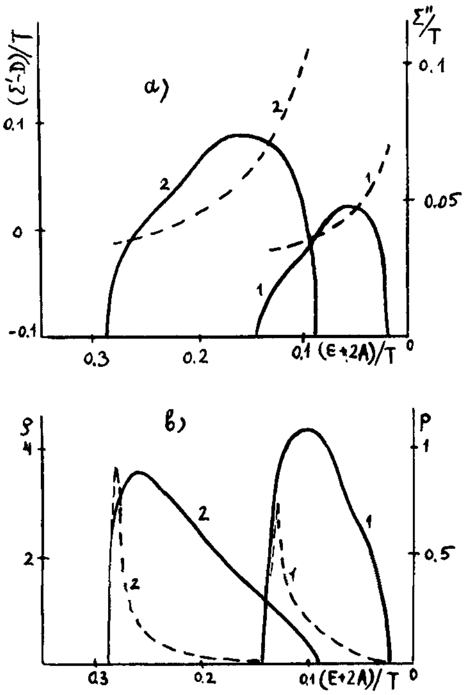

FIGURE 7 (a) Self-energy part, (b) the density of states and absorption coefficient for bulk crystal ($C_1 = 0.5$; $1 - 2A/T = 5$, $2E_1/T = 0.15$; $2 - 2A/T = 3$, $2E_1/T = 0.3$).

Figure 5 gives the energy dependence of the biphonon state densities $\rho(E)$ and the two-phonon light absorption coefficient $P(E)$ for the same parameter values and with different concentrations. It was assumed in the calculation that the upper side of the zone corresponds to the wave vector $K = 0$ ($V(K = 0) = 0$). Note the absence of symmetry similar to that one which is observed for analogous values in the one-phonon region where equations and solutions are symmetrical with respect to the transformation $C_1 \rightarrow 1 - C_1$, $\sum \rightarrow -\sum$, $E \rightarrow -E$. The abovesaid is connected with the fact that for biphonons Eq. (18) has no such symmetry. This is clearly seen also in Figure 6, where concentration dependence is given for the boundaries of biphonon state zones. The dependence found differs considerably from the analogous dependence for the one-phonon spectral region.

Figure 7 gives the values $\sum'(E)$, $\sum''(E)$ and $\rho(E)$, $P(E)$ at $C_1 = 0.5$ for parameters $2E_1/T = -2E_2/T = 0.15$, $2A/T = 5$ and $2E_1/T = -2E_2/T = 0.3$, $2A/T = 3$. Together with appropriate curves ($C_1 \equiv C = 0.5$) in Figures 4–5 this allows qualitative evaluation of the variation of the values $\sum'$, $\sum''$, ρ, P obtained upon varying either parameter $2E_1/T$ or parameter $2A/T$.

We plan further consideration of the Fermi-resonance influence on biphonon spectra in crystalline mixtures and discussion of Raman spectra peculiarities. The calculations for this case was made recently in Ref. 12 in connection with experimental work.[6]

References

1. M. H. Cohen and J. Ruvalds, *Phys. Rev. Lett.*, **23**, 1378 (1969). J. Ruvalds and A. Zawadowski., *Phys. Rev.*, **B2**, 1172 (1970).
2. V. M. Agranovich, *Fiz. Tverd. Tela*, **12**, 562 (1970).
3. G. G. Mitin, V. S. Gorelik, and M. M. Sushchinskii, *Fiz. Tverd. Tela*, **17**, 2422 (1975). V. S. Gorelik, G. G. Mitin, and M. M. Sushchinskii, *ZhETF*, **69**, 823 (1975).
4. M. V. Belousov and D. E. Pogarev, *Fiz. Tverd. Tela*, **17**, 2832 (1975).
5. V. M. Agranovich, M. A. Mekhtiev, and Yu. E. Lozovik, *ZhETF*, **59**, 246 (1970).
6. M. V. Belousov and D. E. Pogarev, *Pisma v ZhETF*, **28**, 692 (1978).
7. P. Soven, *Phys. Rev.*, **156**, 809 (1967).
8. B. Velicky, S. Kirkpatrick, and H. Ehrenreich, *Phys. Rev.*, **175**, 747 (1968).
9. Y. Onodera, and Y. Toyozava, *J. Phys. Soc. Jap.*, **24**, 341 (1968).
10. O. A. Dubovskii and Yu. V. Konobeev, *Fiz. Tverd. Tela*, **12**, 405 (1970).
11. I. S. Gradstein and I. M. Ryzhik, Tables of integrals, sums and products, M, "Nauka", 1971.
12. V. M. Agranovich, O. A. Dubovsky, and K. Stoichev, *Fiz. Tverd. Tela*, **21**, 3012 (1979).