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## Strong anharmonicity effects for vibrations in crystals with impurities: local biphonons and triphonons

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The present paper discusses special features in the formation of local vibrations in a crystal having an isotopic defect when these vibrations are in the regions of two and three-particle states of optical phonons and anharmonicity is taken into account. The existence of anharmonicity leads, in some cases, to a cardinal change in the spectrum of local states. Also considered are the conditions for the formation of local biphonons, as well as the available experimental data. Dispersion equations are derived in a number of special cases for triply-bound phonon complexes (triphonons), and conditions are discussed for their localization on an isotopic defect.

### 1. Introduction: local biphonons

The investigation of elementary excitations in imperfect crystals containing crystal defects is a part of solid-state physics. Theoretical investigations in this line were begun by Lifshitz (1947, 1956) and by Montroll and Potts (1955, 1956) in the harmonic approximation. It was shown in these papers that the presence of defects, in general, leads to the formation of a new type of vibrational states—local phonons, localized in the vicinity of the defects. These states appear in spectra of various types in the form of separate lines and bands located outside the continuum of zone states.

In recent years, many more experimental and theoretical investigations have been conducted on systems in which, under definite conditions, the interaction of one-quantum elementary excitations (i.e. phonons) can and do lead to the formation of their bound complexes. The present communication deals mainly with the spectral features of the simplest of the above-mentioned complexes, i.e. biphonons and triphonons.

Many qualitatively new features appear in going over to the spectra of many-particle excitations in crystals having defects. Appropriate theory, requiring in this case that anharmonicity be taken into account, becomes substantially more complex.

For the sake of simplicity we assume that the crystal contains only the simplest point defects: isotopic substitution impurities (the isotopic shift  $\Delta$ ). We point out, first of all, that in the harmonic approximation, for instance in a crystal with one molecule per unit cell, the frequency  $\omega_1^{(1)}$  of local vibrations split off from the zone  $\Omega(\mathbf{k}) = \varepsilon(\mathbf{k})/\hbar$  of non-degenerate optical vibrations, satisfies the equation:

$$1 = \frac{\Delta}{N} \sum_{\mathbf{k}} \frac{1}{\hbar\omega_1^{(1)} - \varepsilon(\mathbf{k})}, \quad (1)$$

where  $N$  is the total number of molecules.

It is a well known fact (see, for example, Lifshitz 1956) that in three-dimensional crystals this equation has a solution for  $\omega_1^{(1)}$ , outside the frequency zone  $\Omega(\mathbf{k})$ , only at sufficiently large values of  $|\Delta|$ , i.e.  $|\Delta| > \Delta_c^{(1)}$ , where  $\Delta_c^{(1)} \approx T_1$  and  $T_1$  is the width of the optical phonon zone in a perfect crystal. If the preceding inequality is complied with, local states appear, not only in the region  $\omega_1^{(1)} \approx \Omega \approx \varepsilon(\mathbf{k})/\hbar$ , but also in the region of the

second and higher overtones, i.e. at the frequencies  $2\omega_1^{(1)}$ ,  $3\omega_1^{(1)}$ , etc. This is, of course, obvious when it is considered that all these states correspond to different quantum numbers ( $n=1, 2, \dots$ ) of a harmonic oscillator, i.e. the normal local vibrations of a crystal having an isotopic impurity. If, however, the inequality  $|\Delta| > \Delta_c^{(1)}$  is not complied with, i.e. if  $|\Delta| < \Delta_c^{(1)}$ , then equation (1) has no solutions for  $\omega_1^{(1)}$  that lie outside the zone  $\Omega(\mathbf{k})$ . In this latter case the presence of an isotopic defect does not lead to the formation of local states. It is clear that in the harmonic approximation such states do not appear either in the fundamental (i.e. at  $\omega_1^{(1)} \approx \Omega$ ) or in the overtone region.

Taking anharmonicity into account can qualitatively change the pattern of the local-states spectrum. Specifically, it can lead to the formation of such states even in cases ( $|\Delta| < \Delta_c^{(1)}$ ) when in the harmonic approximation there are no states whatsoever localized in the region of the defect (Agranovich 1970).

Indeed, let us assume that the anharmonicity constant  $A$  is large compared to the width  $T_1 = 2T$  (where  $T$  is the halfwidth) of the phonon zone. In this case the width of the biphonon zone is of the order of  $T_1^2/A$ , i.e. small compared to the width  $T_1$  of the optical phonon zone. Under these same conditions, i.e. at sufficiently strong anharmonicity, the biphonon state, in a good approximation, is the superposition of the states of twofold-excited molecules. The wavefunction of the relative motion for the biphonon in this case is strongly localized. It is clear then that an elementary generalization of an equation of the type of (1) can be used to find local states. Specifically, the equation for the frequency  $\omega_1^{(2)}$  of a local biphonon, i.e. the localized state split off the biphonon zone, can be written as follows:

$$1 = \frac{2\tilde{\Delta}}{N} \sum_{\mathbf{K}} \frac{1}{\hbar\omega_1^{(2)} - E(\mathbf{K})}, \quad (2)$$

where  $E(\mathbf{K})$  is the energy of a biphonon with a wavevector  $\mathbf{K}$  in a perfect crystal,  $2\tilde{\Delta}$  is the isotopic shift of the twofold-excited state of an impurity molecule:

$$\tilde{\Delta} = \Delta - (A' - A) \quad (3)$$

and  $A'$  is its anharmonicity constant. Since the states of the biphonon, like those of the phonon, are characterized by specifying only a single value of the wavevector, an analysis of equation (2) is analogous to that of equation (1). On the basis of the results of such an analysis, which we have already used for phonons, it can be contended that a local biphonon is formed if

$$2|\tilde{\Delta}| > \Delta_c^{(2)} \quad (4)$$

where  $\Delta_c^{(2)} \approx T_2$ ,  $T_2$  is the width of the biphonon zone ( $T_2 \approx T_1^2/A$ ) or, for example, at  $A' = A$ :

$$2|\Delta| > \Delta_c^{(2)}. \quad (5)$$

It is clear that inequality (4) or (5) can be complied with even in the case when

$$|\tilde{\Delta}| < \Delta_c^{(1)},$$

i.e. when the two following inequalities are simultaneously complied with (for example, at  $A' = A$ ):

$$\frac{T_1^2}{2A} \ll |\Delta| \ll T_1 \quad (6)$$

Complying with the right-hand inequality does not lead to the formation of local states in the region of the fundamental. But if we comply with the second (left-hand)

inequality, splitting off of the level of a local biphonon is provided for. This demonstrates the importance of the role of anharmonicity in forming the spectra of local states. In the limiting situation being discussed the spectrum of local states begins at the energy  $E \approx 2\hbar\Omega$  rather than at  $E \approx \hbar\Omega$ .

We point out still another property of equation (2). From this equation it follows that when  $|\Delta| > \Delta_c^{(1)}$ , but the absolute value of the quantity  $2\tilde{\Delta}$  is less than the biphonon zone width (when  $A' - A \neq 0$ , an anharmonicity defect), a local state in the region  $2\hbar\Omega$  does not result, though one exists in the region  $\hbar\Omega$ . Thus, in this way, anharmonicity can lead, not only to the stabilization of local states in the overtone region, but also, in general, to their inhibition.

We cite here the results obtained in experimental research conducted by Belousov *et al.* (1982). In these investigations they studied the spectrum of local states in the frequency region  $\approx 2800 \text{ cm}^{-1}$  in a  $^{14}\text{NH}_4\text{Br}$  crystal having as an impurity the isotope  $^{15}\text{N}$ . It was first shown experimentally in these investigations that, in accordance with predictions, (Agranovich 1970), anharmonicity actually can lead to the formation of a local biphonon under conditions in which no local phonons exist.

In the Raman spectrum of  $^{15}\text{N}_x^{14}\text{N}_{1-x}\text{H}_4\text{Br}$  (where  $x=0.05$ ) no local one-phonon vibration is set up. Its absence and the typically single-mode nature of the one-phonon spectrum are explained by the fact that the isotopic shift  $\Delta = -6 \text{ cm}^{-1}$  (Price *et al.* 1960) is small compared to the width of the one-phonon zone ( $T_1 = 36 \text{ cm}^{-1}$ ). The picture of a spectrum in this region for a natural isotope  $^{15}\text{N}$  content ( $x=0.0037$ ) is shown in the figure. The narrow line at  $2792.5 \text{ cm}^{-1}$  (see figure (a)), located below the zone of dissociated two-particle states, corresponds, obviously, to the excitation of a biphonon. Its occurrence in a second-order spectrum is thus an indication of quite strong anharmonicity with the characteristic constant  $A \approx 30\text{--}35 \text{ cm}^{-1}$ .

An additional line at  $\hbar\omega'_1 = 2788 \text{ cm}^{-1}$  was found in a crystal with a natural content of the isotope  $^{15}\text{N}$  by Belousov *et al.* (1982).

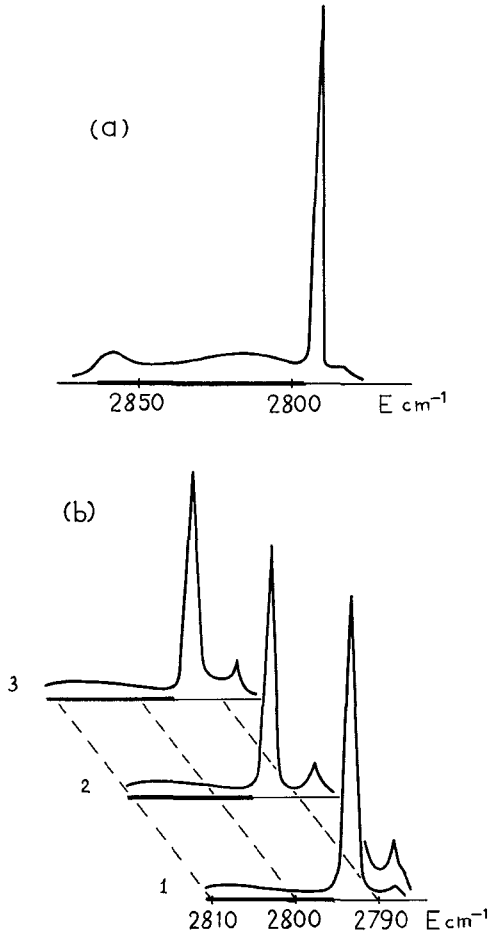
## 2. Triphonons

Let us turn now to an analysis of the triphonon spectra peculiarities. There is at present no experimental data indicating that bound three-phonon states (triphonons) have been observed. Nevertheless, interest is being shown in such states because, as has been pointed out, the two-phonon states (biphonons) discussed above are only the very simplest of phonon complexes.

With anharmonicity of the third and fourth orders in the displacements of the appropriate oscillators (Landau and Lifshitz 1974) taken into account, the model hamiltonian can be represented in the form

$$\hat{H} = \sum_{\mathbf{n}} \hbar\omega \hat{B}_{\mathbf{n}}^{\dagger} B_{\mathbf{n}} + \sum_{\mathbf{n} \neq \mathbf{m}} V_{\mathbf{nm}} \hat{B}_{\mathbf{n}}^{\dagger} B_{\mathbf{m}} - A \sum_{\mathbf{n}} \hat{B}_{\mathbf{n}}^{\dagger 2} B_{\mathbf{n}}^2 - \tilde{A} \sum_{\mathbf{n}} \hat{B}_{\mathbf{n}}^{\dagger 3} B_{\mathbf{n}}^3 \quad (7)$$

Here  $\omega$  is the frequency of the molecular oscillation that is renormalized with anharmonicity:  $\hat{B}_{\mathbf{n}}^{\dagger}$  and  $B_{\mathbf{n}}$  are the Bose creation and annihilation operators for a quantum of oscillations in molecules  $\mathbf{n}$ ,  $V_{\mathbf{nm}}$  is a matrix element of the energy operator for the interaction of molecules  $\mathbf{n}$  and  $\mathbf{m}$ , corresponding to the transition of one quantum of vibrations from molecule  $\mathbf{n}$  to molecule  $\mathbf{m}$ . The anharmonicity constant  $A$  determines the intensity of two-particle contact interaction. The anharmonicity constant  $\tilde{A}$  determines the intensity of three-particle contact interaction. Constants  $A$  and  $\tilde{A}$  should be selected in such a way that the energy values of an isolated molecule in



Raman scattering spectra for  $^{15}\text{N}_x^{14}\text{N}_{1-x}\text{H}_4\text{Br}$  crystals in the region of  $\omega_4(\mathbf{k}) + \omega_4(-\mathbf{k})$  transitions. A heavy line distinguishes the region of two-particle transitions of unbound phonons. The peak  $2788\text{ cm}^{-1}$  corresponds to the excitation of local biphonons. The local phonons do not exist. Concentrations are: (a)  $x = 0.0037$ ; (b) (1)  $x = 0.0037$ ; (2)  $x = 0.05$  and (3)  $x = 0.3$ .

a state with two and three quanta coincide with the experimental values  $E_2^{\text{exp}}$  and  $E_3^{\text{exp}}$ . This means that the value of  $A$  is determined from the relation  $E_2^{\text{exp}} = 2\hbar\omega - 2A$ . At the same time, the value of  $\tilde{A}$  should be determined from the relation  $E_3^{\text{exp}} = 3\hbar\omega - 6(A + \tilde{A})$ . In general,  $A$  and  $\tilde{A}$  are quantities of the same order of magnitude, so that both components of anharmonicity should be taken into account in equation (7) in observing the states of triphonons.

Taking the aforesaid into consideration, we shall seek a wavefunction of three-phonon states of the form

$$|3\rangle = \sum_{\mathbf{nmp}} \Psi_{\mathbf{nmp}} \hat{B}_{\mathbf{n}}^{\dagger} \hat{B}_{\mathbf{m}}^{\dagger} \hat{B}_{\mathbf{p}}^{\dagger} |0\rangle, \tag{8}$$

where  $\Psi_{\mathbf{nmp}}$  is a function symmetrical with respect to any permutation of the indices  $\mathbf{n}$ ,  $\mathbf{m}$  and  $\mathbf{p}$ . It is clear that these quantities have the meaning of the wavefunction of three phonons in the coordinate representation.

The substitution of equation (8) into the Schrödinger equation

$$\hat{H}|3\rangle = E|3\rangle$$

for the Hamiltonian (7) and the use of the appropriate commutation rules for the Bose operators  $\hat{B}_n$  and  $B_n$  lead to the following system of equations:

$$[E - 3\hbar\omega + 2A(\delta_{nm} + \delta_{mp} + \delta_{np}) + 6\tilde{A}\delta_{nm}\delta_{mp}]\Psi_{nmp} = \sum_r [V_{nr}\Psi_{rmp} + V_{mr}\Psi_{nrp} + V_{pr}\Psi_{nmp}] \quad (9)$$

If, we now go over to the Fourier representation

$$\Psi_{nmp} = \sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3} \tilde{\Psi}_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3} \exp [i(\mathbf{k}_1\mathbf{n} + \mathbf{k}_2\mathbf{m} + \mathbf{k}_3\mathbf{p})], \quad (10)$$

then from equation (9) we find that the quantities  $\tilde{\Psi}_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}$  satisfy the system of equations:

$$\tilde{\Psi}_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3} + G_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}(E) \left\{ \frac{2A}{N} \sum_{\mathbf{q}} [\tilde{\Psi}_{\mathbf{k}_1-\mathbf{q},\mathbf{k}_2+\mathbf{q},\mathbf{k}_3} + \tilde{\Psi}_{\mathbf{k}_1-\mathbf{q},\mathbf{k}_2,\mathbf{k}_3+\mathbf{q}} + \tilde{\Psi}_{\mathbf{k}_1,\mathbf{k}_2-\mathbf{q},\mathbf{k}_3+\mathbf{q}}] + \frac{6\tilde{A}}{N^2} \sum_{\mathbf{q}_1\mathbf{q}_2} \tilde{\Psi}_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3-\mathbf{q}_1-\mathbf{q}_2,\mathbf{q}_1,\mathbf{q}_2} \right\} = 0 \quad (11)$$

where

$$G_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}(E) = [E - 3\hbar\omega - V(\mathbf{k}_1) - V(\mathbf{k}_2) - V(\mathbf{k}_3)]^{-1}, \quad (12)$$

$$V(\mathbf{k}) = \sum_{\mathbf{m}(\neq\mathbf{n})} V_{nm} \exp [i\mathbf{k}(\mathbf{n} - \mathbf{m})].$$

Of interest to us in the following are states with a specified value of the total wavevector  $\mathbf{K} = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ . For these states, as follows from equation (11), the function  $\tilde{\Psi}_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}(\mathbf{K})$  is determined by the value of the linear combinations

$$S(\mathbf{k}) = \frac{1}{N} \sum_{\mathbf{q}} \tilde{\Psi}_{\mathbf{k},\mathbf{q},\mathbf{K}-\mathbf{k}-\mathbf{q}}, \quad (13)$$

$$\Pi = \frac{1}{N^2} \sum_{\mathbf{q}_1\mathbf{q}_2} \tilde{\Psi}_{\mathbf{K}-\mathbf{q}_1-\mathbf{q}_2,\mathbf{q}_1,\mathbf{q}_2} \equiv \frac{1}{N} \sum_{\mathbf{k}} S(\mathbf{k}),$$

so that equation (11) can also be written in the form

$$\tilde{\Psi}_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{K}-\mathbf{k}_1-\mathbf{k}_2} + G_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{K}-\mathbf{k}_1-\mathbf{k}_2}(E) \{ 2A[S(\mathbf{k}_1) + S(\mathbf{k}_2) + S(\mathbf{K}-\mathbf{k}_1-\mathbf{k}_2)] + 6\tilde{A}\Pi \} = 0$$

Summing this equation over  $\mathbf{k}_2$  and taking equation (13) into account, we have the following integral equation for  $S(\mathbf{k})$ :

$$S(\mathbf{k}) \left[ 1 + 2A \frac{1}{N} \sum_{\mathbf{q}} G_{\mathbf{k},\mathbf{q},\mathbf{K}-\mathbf{k}-\mathbf{q}}(E) \right] + 4A \frac{1}{N} \sum_{\mathbf{q}} G_{\mathbf{k},\mathbf{q},\mathbf{K}-\mathbf{k}-\mathbf{q}}(E) S(\mathbf{q}) + 6\tilde{A}\Pi \frac{1}{N} \sum_{\mathbf{q}} G_{\mathbf{k},\mathbf{q},\mathbf{K}-\mathbf{k}-\mathbf{q}}(E) = 0 \quad (14)$$

Below we first consider the special case when  $A=0$ , but  $\tilde{A} \neq 0$ . In this case, after making use of the relation between the quantities  $S(\mathbf{k})$  and  $\Pi$ , we find that the energy of three-phonon states  $E$  is determined by the equation

$$1 + 6\tilde{A} \frac{1}{N^2} \sum_{\mathbf{q}_1\mathbf{q}_2} \frac{1}{E - \varepsilon(\mathbf{q}_1) - \varepsilon(\mathbf{q}_2) - \varepsilon(\mathbf{K} - \mathbf{q}_1 - \mathbf{q}_2)} = 0, \\ \varepsilon(\mathbf{q}) = \hbar\omega + V(\mathbf{q}),$$

or

$$1 + 6\tilde{A} \int \frac{\rho_3(\varepsilon, \mathbf{K})}{E - \varepsilon} d\varepsilon = 0, \quad (15)$$

where  $\rho_3(\varepsilon, \mathbf{K})$  is the density of unbound three-particle states having the total wavevector  $\mathbf{K}$ . This equation is analogous to the equation (Agranovich 1970)

$$1 + 2A \int \frac{\rho_2(\varepsilon, \mathbf{K})}{E - \varepsilon} d\varepsilon = 0,$$

that determines the energy of the biphonon with wavevector  $\mathbf{K}$  ( $\rho_2(\varepsilon, \mathbf{K})$  is the density of unbound two-particle states having total wavevector  $\mathbf{K}$ ). An essential, though natural, difference, is the appearance of the three-particle density of states in equation (15). For three-dimensional crystals, this circumstance leads to a comparatively large critical (threshold) value of  $\alpha = (2\tilde{A}/T_1)_c$  (where  $T_1$  is the phonon zone width), beyond which (i.e. at  $(2\tilde{A}/T_1) > (2\tilde{A}/T_1)_c$ ) the formation of a triphonon becomes feasible. By definition the quantity  $\alpha$  is equal to the ratio of the coefficient preceding the integral in equation (15) to the whole width  $3T_1$  of the zone of unbound three-particle states. The analogous ratio for the biphonon  $\beta = (A/T_1)_c < \alpha$ , because the density  $\rho_3(\varepsilon, \mathbf{K})$  of three-particle states at the boundary of the three-particle continuum  $\varepsilon_c$  as  $\varepsilon \rightarrow \varepsilon_c$  in three-dimensional crystals vanishes more rapidly than the density of two-particle states at the boundary of a two-particle continuum (for one-dimensional and two-dimensional crystals  $\alpha = \beta = 0$ ).

Let us turn to the situation when both quantities  $A$  and  $\tilde{A}$  are non-zero, and  $A$  is large compared to the phonon zone width  $T_1$ . In this case the formation of a triphonon can be conveniently regarded as the result of the bonding of a biphonon and a phonon. Since, by assumption,  $T_2 \approx T_1^2/A \ll T_1$ , a biphonon, compared to a free phonon, can be assumed as localized in a certain lattice site. Hence, in this limiting case (high values of  $A$  and arbitrary value of  $\tilde{A}$ ) the formation of a triphonon is formally analogous to the formation of a phonon localized at an isotopic defect. Since the biphonon energy  $E_2 \approx 2\hbar\omega - 2A + O(T_1^2/A)$ , and the energy of a triply excited molecule is  $E_3^{\text{xp}} = 3\hbar\omega - 6(A + \tilde{A})$ , the amount of effective 'isotopic' shift  $\Delta_{\text{eff}} = -(4A + 6\tilde{A})$ . After taking this into account, as well as equation (1), we reach the conclusion that the equation for determining the energy  $E$  of a triphonon is of the form:

$$1 + (4A + 6\tilde{A}) \int \frac{\rho_1(\varepsilon) d\varepsilon}{E - 2\hbar\omega + 2A - \varepsilon} = 0, \quad (16)$$

where  $\rho_1(\varepsilon)$  is the density of one-phonon states.

Next we show how equation (16) follows from (14) and, at the same time, take the dispersion of the triphonon into account. For this purpose we first discuss the energy zone  $\tilde{E}(\mathbf{K}, \mathbf{k})$ , determined by the equation

$$F_{\mathbf{k}}(\tilde{E}, \mathbf{K}) \equiv 1 + 2A \frac{1}{N} \sum_{\mathbf{q}} G_{\mathbf{k}, \mathbf{q}, \mathbf{K} - \mathbf{k} - \mathbf{q}}(\tilde{E}) = 0 \quad (17)$$

After comparing this equation with the equation that determines the energy of a biphonon (see Agranovich 1970), we come to the conclusion that

$$\tilde{E}(\mathbf{K}, \mathbf{k}) = E_2(\mathbf{K} - \mathbf{k}) + \varepsilon(\mathbf{k}) \quad (18)$$

where  $E_2(\mathbf{K} - \mathbf{k})$  is the energy of a biphonon having the wavevector  $\mathbf{K} - \mathbf{k}$ . Thus the

energy zone (18) corresponds to superposition of the states of a free biphonon and a free phonon.

We assume in the following that the anharmonicity constants  $A$  and  $\tilde{A}$  are such that the triphonon state being discussed is split off from the two-particle continuum (18) under conditions in which the dispersion of states in the three-particle continuum can be ignored. It is clear that this is feasible only for triphonons with energy  $E$  for which  $|E - 3\hbar\omega| \gg 3T_1$ , as is assumed below. In this approximation we have

$$\frac{1}{N} \sum_{\mathbf{q}} G_{\mathbf{k}, \mathbf{q}, \mathbf{K} - \mathbf{k} - \mathbf{q}}(E) \approx [E - 3\hbar\omega]^{-1}$$

$$\frac{1}{N} \sum_{\mathbf{q}} G_{\mathbf{k}, \mathbf{q}, \mathbf{K} - \mathbf{k} - \mathbf{q}}(E) S(\mathbf{q}) \approx [E - 3\hbar\omega]^{-1} \Pi,$$

so that equation (14) takes the form

$$[E - 3\hbar\omega] F_{\mathbf{k}}(E, \mathbf{K}) S(\mathbf{k}) + (4A + 6\tilde{A}) \Pi = 0.$$

After taking equation (13) into consideration, we obtain from the preceding equation the dispersion equation

$$1 + \frac{4A + 6\tilde{A}}{N} \sum_{\mathbf{k}} \frac{1}{[E - 3\hbar\omega] F_{\mathbf{k}}(E, \mathbf{K})} = 0. \quad (19)$$

Making use of the identity

$$\frac{2A}{N} \sum_{\mathbf{q}} \frac{1}{E_2(\mathbf{K} - \mathbf{k}) - \varepsilon(\mathbf{q}) - \varepsilon(\mathbf{K} - \mathbf{k} - \mathbf{q})} \equiv -1,$$

we find that

$$F_{\mathbf{k}}(E, \mathbf{K}) \equiv -2A [E - \varepsilon(\mathbf{k}) - E_2(\mathbf{K} - \mathbf{k})]$$

$$\cdot \frac{1}{N} \sum_{\mathbf{q}} \{ [E - \varepsilon(\mathbf{k}) - \varepsilon(\mathbf{q}) - \varepsilon(\mathbf{K} - \mathbf{k} - \mathbf{q})] [E_2(\mathbf{K} - \mathbf{k}) - \varepsilon(\mathbf{q}) - \varepsilon(\mathbf{K} - \mathbf{k} - \mathbf{q})] \}^{-1}$$

With the assumptions ( $|E - 3\hbar\omega| \gg 3T_1$  and  $A \gg T_1$ ) that were made, we have

$$E - \varepsilon(\mathbf{k}) - \varepsilon(\mathbf{q}) - \varepsilon(\mathbf{K} - \mathbf{k} - \mathbf{q}) \approx E - 3\hbar\omega,$$

$$E_2(\mathbf{K} - \mathbf{k}) - \varepsilon(\mathbf{q}) - \varepsilon(\mathbf{K} - \mathbf{k} - \mathbf{q}) \approx -2A,$$

so that instead of equation (19) we obtain the desired dispersion equation

$$1 + \frac{4A + 6\tilde{A}}{N} \sum_{\mathbf{k}} \frac{1}{E - E_2(\mathbf{K} - \mathbf{k}) - \varepsilon(\mathbf{k})} = 0, \quad (20)$$

which coincides to an accuracy of small corrections of the order of  $(T_1/A)^2$  with equation (16). But this equation, in contrast to equation (16), enables the dispersion curve of a triphonon to be determined, i.e. the dependence  $E = E(\mathbf{K})$ . We point out that since  $A$  and  $\tilde{A}$  can have different signs, both in equation (16) and in equation (20) there is the possibility of compensation of the contributions due to two-particle and three-particle anharmonicity (i.e., for example,  $|4A + 6\tilde{A}| \leq T_1$  is feasible). In this case the triphonon energy, as follows from equation (20), is close to the zone of disassociated states [see equation (18)], and the radius of the triphonon can substantially increase.

For the case  $\tilde{A} = 0$ , Mattis and Rudin (1984) employing numerical methods determined the dependence of the energy of bound three-particle states in a crystal on



the anharmonicity constant  $A$ . This showed, among other matters, that in the region where  $A=0.33T_1$  the formation of bound three-particle states, described by Efimov (1970), becomes feasible.

The paper by Mattis and Rudin (1984) does not include an analysis of the dependence of triphonon energy on the wavevector  $\mathbf{K}$ . Such a dependence is necessary for discussing the possibility of the localization and we have one comment to make. In the limiting case of strong anharmonicity ( $A > T_1$  and  $\tilde{A} > 0$ ) both the biphonon and triphonon correspond, to high accuracy, to the state of a crystal in which two phonons (biphonon) or three phonons (triphonon) are localized at one site, and this excited state of the molecule propagates coherently through the crystal. Therefore, to estimate the zone width of the biphonon or that of the triphonon, it is sufficient to estimate the amplitude of the transition of such a localized state from one lattice site to the neighbouring one, using perturbation theory with respect to  $V_{nm}$  (see equation (7)).

For a biphonon such an amplitude is determined by the matrix element

$$W_{nm} = \sum_s \frac{\langle i|\hat{H}|s\rangle\langle s|\hat{H}|f\rangle}{E_i - E_s},$$

where  $i$  is the initial state: both phonons 'sit' at site  $\mathbf{n}$ ;  $s$  is the virtual state: one phonon 'sits' at site  $\mathbf{n}$  and the other at site  $\mathbf{m}$ ;  $f$  is the final state: both phonons 'sit' at site  $\mathbf{m}$ . It is clear that  $E_i = 2\hbar\omega - 2A$ ,  $E_s = 2\hbar\omega$  and  $\langle i|\hat{H}|s\rangle = \langle s|\hat{H}|f\rangle = V_{nm}$ , so that  $W_{nm} = -(V_{nm})^2/2A$ . Consequently, the biphonon zone width  $T_2 \approx T_1^2/2A$ , as previously indicated.

Similarly, for the triphonon

$$W_{nm} = \sum_{s's''} \frac{\langle i|\hat{H}|s'\rangle\langle s'|\hat{H}|s''\rangle\langle s''|\hat{H}|f\rangle}{(E_i - E_{s'})(E_i - E_{s''})},$$

in which there is one phonon in state  $s'$  at site  $\mathbf{m}$ , in state  $s''$  two phonons, etc. An elementary consideration leads to the estimate

$$W_{nm} \approx \frac{T_1^3}{(4A + 6\tilde{A})^2}.$$

It follows from this estimate that for a triphonon the condition of strong anharmonicity corresponds to the inequality

$$T_1 \ll |4A + 6\tilde{A}|.$$

Also of interest is an analysis of the effect of Fermi resonance on triphonon structure (for example, resonance of a phonon and a triphonon, of a biphonon and a triphonon, etc.).

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