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ANHARMONICITY EFFECTS IN THE THEORY OF LOCAL AND SURFACE OSCILLATIONS

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It is shown that allowance for anharmonicity appreciably affects the local oscillation spectrum of an imperfect crystal. In particular, under conditions when local oscillations with the fundamental frequency are absent, anharmonicity may result in the appearance of local overtones. It is shown for a one-dimensional semi-bounded chain that similar effects are also encountered in the theory of surface oscillations.

1. INTRODUCTION

THE theory of local oscillations of a crystal with defects in the harmonic approximation has been the subject of a large number of papers (see, for example,[1,2]). The influence of the anharmonicity on the width and level shift of the local oscillations was also discussed earlier (see, for example,[3]). In this paper we consider some new effects resulting from the presence of anharmonicity in the region of overtones in the presence of impurities in the crystal. These effects are due to the fact that the anharmonicity of the intramolecular oscillations can lead to the appearance of excited states of a crystal, which are bound states of quasiparticles—vibrational[1)] excitons. If the anharmonicity is sufficiently large, these bound states correspond to energy bands whose width turns out to be much smaller than the width of the band of the free quasiparticle (see[4]). Therefore in a crystal with defects this circumstance can, generally speaking, lead to the occurrence of local and surface states in the region of multiple frequencies of local and surface overtones, even in those cases when there are no local and surface states for the individual quasiparticle.

With respect to local overtones, this circumstance was already pointed out in[4]. In the present paper we develop a more general approach than in[4] in the theory in the local overtones in a crystal with impurity. In addition, using as an example a one-dimensional semi-bounded chain, we discuss the states of surface overtones. In both cases, the analysis is limited only to that region of the spectrum of the crystal, which corresponds to the presence in it of only two elementary excitations. Therefore to determine the spectrum of the local states in the vicinity of the defect it is necessary in fact to solve a three-center problem (quasiparticles and a defect all interacting with one another), whereas for surface states the situation, generally speaking, is more complicated, since it is necessary to take into account the interaction of the quasiparticles not only with one another, but also with all the atoms of the surface. Only in the simplest one-dimensional case, which is precisely the one considered below, can the problem again be reduced to a three-center problem.

We note that the excited states of a crystal are considered each time at a specified number of quasiparticles. As already indicated in[4], such an approach is justified if the problem involves quasiparticle-interaction energies and bandwidths that are small compared with the energy of the individual quasiparticle. Therefore the results obtained in that paper pertain more readily to crystal optical oscillations of sufficiently high-frequency, of the type due, for example, to intramolecular or valence oscillations when the crystal is made up of molecules or atoms.

2. THEORY OF LOCAL OVERTONES

Let us consider, for simplicity, a crystal with an isotopic impurity (we shall call an isotopic impurity a molecule that has a different frequency Ω and a different anharmonicity constant A' than the molecule of the host substance). We assume, just as in[4], that the crystal is made up of molecules that are linear anharmonic oscillators, whose energy is determined by the relation (see, for example,[5])

$$E_k = \hbar\omega_0' k - A(k^2 + k), \tag{1}$$

where ω_0' is the frequency of the intramolecular oscillations when no account is taken of the anharmonicity, A is the anharmonicity constant, and k is the quantum number of the oscillator, $k = 0, 1, \ldots$ We introduce the Bose operators B_n^+ and B_n for the creation and annihilation of a quantum of oscillations in the n-th molecule.

Then the Hamiltonian of the molecule n can be represented in the form

$$H_n = \hbar\omega_0 B_n^+ B_n - A(B_n^+)^2 B_n^2, \tag{2}$$

where

$$\omega_0 = \omega_0' - 2A.$$

We now take into consideration the fact that for intramolecular oscillations the energy of the anharmonicity A and the energy of the interaction between the molecules are much smaller than $\hbar\omega_0$. Then the operator of the interaction between the molecules can be represented in the following manner[4]:

$$\hat{H}_{int} = \sum_{n,m} V_{n,m} B_n^+ B_m, \tag{3}$$

where $V_{n,m}$ is the matrix element of the energy of molecule interaction connected with the transition of one quantum from the molecule m to the molecule n.

[1)] "Vibrational" excitons are called here, as in [4], collective excited states lying in the infrared region of the spectrum.

Taking (2) and (3) into account, the Hamiltonian of an ideal crystal is

$$\hat{H}_0=\sum_n \hbar\omega_0 B_n^+B_n+\sum_{n,m} V_{n,m}B_n^+B_m-A\sum_n (B_n^+)^2B_n^2. \tag{4}$$

We shall assume that the isotopic impurity is located at the site n = 0. Then, obviously, the Hamiltonian of the crystal with isotopic impurity can be represented in the form

$$\hat{H}=\hat{H}_0+\hat{H}',\quad \hat{H}'=\hbar\Delta\omega B_0^+B_0-\Delta A(B_0^+)^2B_0^2, \tag{5}$$

where $\Delta\omega = \Omega - \omega_0$ and $\Delta A = A' - A$. We denote by $|0\rangle$ the ground state corresponding to the Hamiltonian $\hat{H}$. The wave functions of the crystal, with one and two vibrational quanta respectively, can be represented in the form

$$|1\rangle=\sum_n \psi(n)B_n^+|0\rangle, \tag{6}$$

$$|2\rangle=\sum_{n,m}\psi(n,m)B_n^+B_m^+|0\rangle. \tag{7}$$

For the states $|1\rangle$, the contribution of the anharmonicity is equal to zero. For these states, the energy E of the oscillation localized at the isotopic impurity is determined, as is well known[1,6], by the equation

$$1=\frac{\hbar\Delta\omega}{N}\sum_{\mathbf{k}}\frac{1}{E-E(\mathbf{k})}, \tag{8}$$

where $\mathbf{k}$ is the wave vector of the exciton and $E(\mathbf{k})$ corresponds to the energy of the vibrational exciton in an ideal crystal. Here and below, we confine ourselves to a crystal with one molecule per unit cell. Equation (8) has a solution corresponding to a local level only when $\hbar\Delta\omega > \Delta$, where Δ is the width of the exciton band (see[1]).

We now obtain the dispersion equation for the local oscillations corresponding to the states $|2\rangle$. Substituting (7) in the Schrödinger equation $\hat{H}\psi = E\psi$, where $\hat{H}$ is given by relation (5), and using the Bose commutation relations for the operator B_n, we obtain an equation for $\psi(n, m)$:

$$(E-2\hbar\omega_0+2A\delta_{\mathbf{mn}})\psi(\mathbf{n},\mathbf{m})-\sum_{\mathbf{n}'}[\psi(\mathbf{n},\mathbf{n}')V_{\mathbf{m},\mathbf{n}'}+\psi(\mathbf{m},\mathbf{n}')V_{\mathbf{nn}'}]$$
$$=[\hbar\Delta\omega(\delta_{\mathbf{m}0}+\delta_{\mathbf{n}0})-2\Delta A\delta_{\mathbf{m}0}\delta_{\mathbf{n}0}]\psi(\mathbf{n},\mathbf{m}). \tag{9}$$

We introduce the Green's function for Eq. (9) without the right-hand side, corresponding to an ideal crystal. It can be represented in the form

$$G(\mathbf{n},\mathbf{m};\mathbf{n}',\mathbf{m}')=\sum_{\mu\mathbf{k}}\frac{\chi^{\mu\mathbf{k}}(\mathbf{n},\mathbf{m})\overset{*}{\chi}{}^{\mu\mathbf{k}}(\mathbf{n}',\mathbf{m}')}{E-E_\mu(\mathbf{k})}, \tag{10}$$

where $E_\mu(\mathbf{k})$ and $\chi^{\mu\mathbf{k}}(n, m)$ are respectively the eigenvalues and the normalized functions of Eq. (9) without the right-hand side.

The vector $\mathbf{k}$ determines the irreducible representation of the translation group, in accordance with which the functions χ are transformed, and μ represents the aggregate of the remaining quantum numbers characterizing the state of the crystal with two excitation quanta. Thus, for example, in the case of two free excitons, the quantity μ includes, besides the numbers of the two exciton bands, also the continuous quantum number determining the wave vector of relative motion of the excitons. Bearing in mind only local oscillations, we rewrite Eq. (9) in a form convenient for future analysis:

$$\psi(\mathbf{n},\mathbf{m})=\sum_{\mathbf{n}'\mathbf{m}'}G(\mathbf{n},\mathbf{m};\mathbf{n}',\mathbf{m}')\varphi(\mathbf{n}',\mathbf{m}'), \tag{11}$$

where $\varphi(n', m')$ is the right-hand side of (9). Putting m = 0, we obtain

$$\psi(\mathbf{n},0)=\sum_{\mu\mathbf{k},\,\mathbf{n}'}\frac{2\chi^{\mu\mathbf{k}}(\mathbf{n},0)\overset{*}{\chi}{}^{\mu\mathbf{k}}(\mathbf{n}',0)[\hbar\Delta\omega-\Delta A\delta_{\mathbf{n}',0}]}{E-E_\mu(\mathbf{k})}\psi(\mathbf{n}',0). \tag{12}$$

The equation determining the spectrum of the local oscillations can be obtained from the condition for the vanishing of the determinant of the system of equations (12), which is linear and homogeneous with respect to $\psi(n, 0)$. This condition obviously has the following form:

$$\det\left|\delta_{\mathbf{nn}'}-2\sum_{\mu\mathbf{k}}\frac{\chi^{\mu\mathbf{k}}(\mathbf{n},0)\overset{*}{\chi}{}^{\mu\mathbf{k}}(\mathbf{n}',0)(\hbar\Delta\omega-\Delta A\delta_{\mathbf{n}'0})}{E-E_\mu(\mathbf{k})}\right|=0. \tag{13}$$

In the general case Eq. (13) determines the local states that are split off both from the band of the two free excitons and from the band of the so-called biexcitons—the band of two bound excitons $E^{(2)}(k)$.

We confine ourselves below to examination of a local level lying near a biexciton band. In the case when the distance from the local level to the biexciton band is small compared with the anharmonicity constant, i.e., when $|E - E^{(2)}(\mathbf{k})| \ll A$, we can confine ourselves in (12) to the contribution of the biexciton band only. If, in addition, we assume that the anharmonicity is strong, i.e., that $\Delta/A \ll 1$, then, as follows from[4], accurate to small $O(\Delta/A)$ the wave function of the biexciton is determined by the expression

$$\chi^{\mu\mathbf{k}}(\mathbf{m},\mathbf{n})=\frac{1}{\sqrt{N}}\delta_{\mathbf{n},\mathbf{m}}.$$

In this approximation we obtain from (12) an equation for the determination of the energy of the sought local level (see also[4]):

$$1=\frac{2(\hbar\Delta\omega-\Delta A)}{N}\sum_{\mathbf{k}}\frac{1}{E-E^{(2)}(\mathbf{k})} \tag{14}$$

In[4] the energy of the biexciton was calculated only at $\mathbf{k} = 0$. However, it is possible to obtain in similar fashion also an equation for $E^{(2)}(\mathbf{k})$ for arbitrary $\mathbf{k}$. It is easy to show that this equation is of the form

$$1=-\frac{2A}{N}\sum\frac{1}{E-2\hbar\omega_0-\Gamma(k+k')-\Gamma(k-k')}, \tag{15}$$

where $\Gamma(k) = \sum_n V_{n,m}e^{ik(n-m)}$. When $|\Gamma(k)/A| \sim \Delta/A \ll 1$ it follows from (15) that

$$E^{(2)}(k)=2\hbar\omega_0-2A-\frac{1}{2NA}\sum_{k'}(\Gamma(k+k')+\Gamma(k-k')). \tag{16}$$

In particular, it follows from (16) that the width of the biexciton band, and incidentally also the splitting of the term of the biexciton in a crystal with several molecules per unit cell (see[4]), have an order of magnitude $\Gamma^2/A \sim \Delta^2/A \ll \Delta$ (with $\Delta/A \ll 1$). Therefore, for analogy with the investigation with the states of local excitons (see[1,6]), a local state with $E < E^{(2)}(k)$ is realized for a biexciton if $|\hbar\Delta\omega - \Delta A| > \gamma\Delta^2/A$, where the coefficient γ depends on the structure of the lattice and is of the order of $\gamma \sim 1$. When $|\Delta A| < |\Delta\omega|$, the indicated inequality can be satisfied even if $\hbar|\Delta\omega| < \Delta$, when the no local states are formed near the fundamental tone. Thus, the anharmonicity leads under the conditions in question to the formation of a local state—a "local overtone," which is missing when no account is taken of the anharmonicity. In the case of strong anharmonicity $(A > \Delta)$ it is easy to show that there appear also higher "local overtones."

We note one more feature of Eq. (14) (see also[4]). It follows from this equation that when $|\Delta A| \sim \hbar|\Delta\omega|$, in the case when $2|\hbar\Delta\omega - \Delta A| < \gamma\Delta^2/A$, the local states in the region of $2\hbar\omega_0$ are not realized, although a local state in the region $\hbar\omega_0$ can exist. Thus, the anharmonicity can lead not only to stabilization of the local states in the region of the overtones, but also, generally speaking, to their suppression.

Finally, as follows from the analysis of (14), the single-pole approximation used above is valid if

$$|\hbar\Delta\omega - \Delta A|/A \ll 1, \quad \text{since} \quad |E - E^{(2)}| \sim |\hbar\Delta\omega - \Delta A|.$$

3. SURFACE OSCILLATIONS IN THE REGION OF THE OVERTONES

Let us consider for simplicity a semi-infinite linear chain of molecules. We assume that on the "surface" there is a molecule of the host substance with a frequency modified by the average field, or else a molecule of a different species.

We consider first surface oscillations in the region of the fundamental tone. Assuming, as before, that the Hamiltonian is of the form (5), we seek the wave function of the surface oscillation in the form (6). In this case we obtain for the coefficients $\psi(n)$ the equation

$$\psi(n)(E - \hbar\omega_n) - \sum_l V_{nl}\psi(l) = 0, \qquad n, l \geqslant 0, \tag{17}$$

where $\omega_n = \omega'$ at $n = 0$ and $\omega_n = \omega$ at $n \neq 0$, while E is the energy of the surface oscillation. The solution of the system (17) (see also, for example,[6], Ch. VIII), is of the form $\psi(n) = A\exp(-\kappa a n)$, $\mathrm{Re}\,\kappa > 0$, where κ is determined, in the nearest-neighbor approximation, from the relation

$$e^{-\kappa a} = \Gamma/\Delta\omega. \tag{18}$$

Here $\Delta\omega' = \omega' - \omega$ and $\Gamma = V_{n,n+1}$. For the surface-oscillation energy we then obtain

$$E = \hbar\omega_0 + 2\Gamma\,\mathrm{ch}\,\kappa a. \tag{19}$$

It follows from (18) that the surface oscillation exists in the region of the fundamental tone if

$$|\Gamma/\Delta\omega| < 1. \tag{20}$$

We now proceed to consider surface oscillations in the region of the overtones. We shall show that, when account is taken of the anharmonicity, the formation of surface oscillations—surface overtones—is possible in this region of the spectrum even in the case when there are no surface oscillations in the region of the fundamental tone. The wave function of the first surface overtone obviously satisfies the following system of equations (see for comparison Eq. (9)):

$$\psi(m,n)(E - 2\hbar\omega_0 + 2A\delta_{m,n}) - \sum_{l\geqslant 0}[V_{ml}\psi(l,n) + V_{nl}\psi(l,m)]$$
$$= [\Delta\omega(\delta_{m0} + \delta_{n0}) - 2\Delta A\delta_{m0}\delta_{n0}]\psi(m,n). \tag{21}$$

In order to simplify the analysis, we shall take into consideration only the interaction between the nearest neighbors. In this case the solution of Eq. (21) for the surface states will be sought in the form

$$\psi(n, m) = e^{-\kappa(n+m)}\varphi(|n - m|), \tag{22}$$

Assuming that

$$|e^{-\kappa}| < 1. \tag{23}$$

It is convenient to distinguish in the system (21) beween the equations with $(m, n) = (0, l)$, $l \geq 0$, which play the role of boundary conditions, and the "interior" equations with $m \geq 1$ and $n \leq 1$. In the approximation considered here, and also when $\Delta A = 0$, these two groups of equations have the following form:

$$(\varepsilon + 2A - 2\Delta\omega)\varphi(0) = 2\Gamma e^{-\kappa}\varphi(1) \quad (m = 0, n = 0), \tag{24a}$$

$$(\varepsilon - \Delta\omega)\varphi(l) - \Gamma\{e^{-\kappa}\varphi(l+1) + 2\,\mathrm{ch}\,\kappa\varphi(l-1)\} = 0,$$
$$m = 0, \quad n \geqslant 1, \quad l = 1, 2, \ldots \tag{24b}$$

and

$$(\varepsilon + 2A)\varphi(0) = 4\Gamma\,\mathrm{ch}\,\kappa\varphi(1), \quad n = m > 0, \tag{25a}$$

$$\varphi(l+1) + \varphi(l-1) = \alpha\varphi(l), \quad l \geqslant 1, \quad n \neq m, \quad n \geqslant 1, \quad m \geqslant 1, \tag{25b}$$

where $\epsilon = E - 2\hbar\omega_0$, $\alpha = \epsilon/2\Gamma\cosh\kappa$, and $\Gamma = V_{n,n+1}$. From (24a) and (25a) it follows that

$$\varepsilon = -2A + 4\Delta\omega e^{-\kappa}\,\mathrm{ch}\,\kappa, \tag{26}$$

$$\varphi(1) = \frac{\Delta\omega}{\Gamma}e^{-\kappa}\varphi(0), \tag{27}$$

and this pair of relations is identically equivalent to the aggregate of Eqs. (24a) and (25a). Equation (25b) can be satisfied for all $l \geq 0$, if the function $\varphi(l)$ is sought in the form

$$\varphi(l) = \varphi(0)e^{-ql}. \tag{28}$$

Substituting (28) in (25b), we find that the quantity e^{-q} must satisfy the equation

$$e^{q} + e^{-q} = \frac{\varepsilon}{2\Gamma\,\mathrm{ch}\,\kappa}. \tag{29}$$

At the same time it follows from (28) and (27) that

$$e^{-q} = \frac{\Delta\omega}{\Gamma}e^{-\kappa}, \tag{30}$$

so that (29) can actually be used to determine the possible values of κ. Using (26) and (30) and solving (29) with respect to the quantity $e^{-2\kappa}$, we get

$$e^{-2\kappa} = \frac{1}{2}\left(-1 + \frac{A}{\Delta\omega} + \frac{\Gamma^2}{(\Delta\omega)^2}\right) \pm$$
$$\pm\frac{1}{2}\sqrt{\left(1 - \frac{A}{\Delta\omega} - \frac{\Gamma^2}{(\Delta\omega)^2}\right)^2 + \frac{4\Gamma^2}{(\Delta\omega)^2}}. \tag{31}$$

Before we proceed to analyze this relation, we note that if relations (26), (28), (29), and (30) are satisfied, then Eq. (24b) is satisfied automatically and becomes an identity. Consequently, the wave function in the form

$$\psi(n, m) = \varphi(0)e^{-\kappa(n+m)}\left(\frac{\Delta\omega}{\Gamma}e^{-\kappa}\right)^{|n-m|} \tag{32}$$

satisfies exactly the system of equations (24) and (25) at a value of the energy

$$E = 2\hbar\omega_0 - 2A + 4\Delta\omega e^{-\kappa}\,\mathrm{ch}\,\kappa \tag{26a}$$

and at a value of κ determined from relation (31). In this case a physical meaning is possessed only by such values of κ for which, besides inequality (23), there is satisfied also the inequality

$$\left|\frac{\Delta\omega}{\Gamma}e^{-\varkappa}\right| \leqslant 1, \tag{33}$$

which ensures a finite norm for the wave function of the relative motion of the quasiparticles in the surface overtone.

If anharmonicity is not taken into account, i.e., if $A = 0$, it follows from (31) that the inequalities (23) and (33) can be satisfied only when $|\Delta\omega| > |\Gamma|$, the only value of κ being determined in this case from the relation

$$e^{-2\varkappa} = (\Gamma / \Delta\omega)^2, \tag{34}$$

so that

$$e^{-\varkappa} = \pm|\Gamma / \Delta\omega|. \tag{35}$$

Using (35) and (32), we find that in this case the wave function $\psi(m, n)$ is equal to the product of wave functions of two surface excitons that are not coupled with each other and whose wave functions and energies are determined by relations (17), (18), and (19). Then the energy of the state $\psi(m, n)$ is equal to double the energy of the surface exciton (19), and is determined by the relation

$$E = 2(\hbar\omega_0 + 2\Gamma \operatorname{ch} \varkappa). \tag{36}$$

When $A \neq 0$, Eq. (31), generally speaking, leads in the region of $E \approx 2\hbar\omega_0$ to the occurrence of two surface states, one of which can be genetically connected with the surface state at $A = 0$, which was considered above, while the second can split from the biexciton band. In the case when

$$|\Delta\omega| < |\Gamma|, \tag{37}$$

i.e., when no surface state is produced in the region of the fundamental tone, the second surface state, which splits away from the biexciton band, may turn out to be the only one. Let us consider this situation in greater detail and let us assume that besides (37) there is also satisfied the inequality

$$A \gg |\Gamma|, \tag{38}$$

which ensures, with a large "margin," the formation of the state of two bound excitons (i.e., a biexciton), in an ideal crystal (for more details see[4]). For this case it follows from (31) that the only root from which the inequalities (23) and (33) are satisfied is determined by the relation

$$e^{-2\varkappa} = \Gamma^2/A\Delta\omega + O\left(\frac{\Gamma^2}{A^2}\right). \tag{39}$$

This value of $e^{-2\kappa}$ turns out to have a modulus smaller than unity, provided only that

$$|\Delta\omega| > \Gamma^2/A, \tag{40}$$

which, of course, can take place if the inequality (38) is satisfied, in spite of the fact that the inequality (37) is satisfied. Thus, in the situation in question, the only surface state is the state that splits away from the biexciton band, and is thus entirely due to the anharmonicity.

In conclusion we note that although the foregoing discussion of the role of the anharmonicity was based on a consideration of very simple crystal models, there is no doubt that the effects indicated above should take place also for more realistic models. In addition, these effects should take place in the region of the spectrum corresponding to higher overtones.

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