Theory of the bound states of phonons with impurity centers

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The interaction of phonons with electrons or excitons that are bound to impurity centers leads to a modification of the phonon spectrum. If the phonon dispersion is small, this interaction produces a system of discrete frequencies. They can be interpreted as belonging to bound states of the phonon with an impurity center, or else as peculiar local modes. Equations are obtained for the bound state spectrum, and formulas are derived for the intensities of individual bands. These general relationships are applied to molecular excitons, for which the phonon binding energy and the intensity of the corresponding band are investigated as a function of the relation between the width of the exciton band, the exciton binding energy, and the phonon frequency.

INTRODUCTION

Most of the theoretical articles concerned with the shape of the impurity absorption and luminescence bands are based on the adiabatic approximation: The ground and the excited electronic states are described by their own adiabatic potentials, which differ by a shift of the equilibrium position of the lattice oscillators, and sometimes also by the spectrum of the vibrational frequencies. It is possible to carry out a rather complete investigation of the shape of the spectrum in such a model; the results of this investigation are contained in the series of review articles[1-3].

The adiabatic approximation is valid only if the ionization potential R of the center significantly exceeds the vibrational frequencies ω_q of the crystal. Although such an approximation is very satisfactory in a whole series of cases (for example, in ionic crystals), it is, of course, not universally satisfied, and it is violated for many electronic centers in typical semiconductors; it is also violated for molecular excitons, which are bound in shallow levels. It should also be noted that, although the contribution to the adiabatic potential which comes from the electron-phonon interaction may in principle be related to the electronic spectrum of this center,[4] in practice this is never done due to the complexity of summing over all the electronic states, and the adiabatic potential is simply represented as an arbitrary quadratic form; some calculations for small-radius centers constitute an exception.

Perturbation theory is usually used if $R \lesssim \omega_q$; and only the lowest nonvanishing term is used when the shape of the phonon satellites is determined. Yet in recent years structure has been observed in the spectra of semiconductors and has been attributed to complexes formed by phonons with impurity centers, magnetopolarons, and excitons (see the review of this data in[5,6]). Its existence indicates that under conditions when the phonon dispersion is small, a realignment of the spectrum of the electron-phonon system occurs and a specific class of states appears; these have already become the object of rather intensive investigation. These states are most clearly manifest in the presence of a resonance between the phonon frequencies and one of the electronic frequencies, but they can also exist away from resonance.

As applied to impurity centers, the impurity center plus phonon complexes can be regarded as local modes that result from the electron-phonon interaction. They have already been observed in semiconductors under both resonance and nonresonance conditions.[7,8] The theory for the resonance situation was suggested by Kogan and Suris,[9] and one of the authors[10] has presented a general equation for the determination of the energy spectrum; in both cases the electron-phonon coupling was assumed to be weak.

The present article begins (Sec. 1) with the derivation and investigation of the previously obtained equation for the spectrum of the local modes.[10] It is written down directly in terms of the Hamiltonian for the electron subsystem and the electron-phonon coupling constant. The eigenvalues of this equation are the frequencies of the local modes, and the eigenfunctions φ characterize the state of the phonon subsystem. Later in Sec. 2 formulas are derived which enable us to calculate the intensity of the phonon satellites in the impurity-exciton spectrum from the functions φ; this enables us to completely solve the problem of the shape of the absorption spectrum. In Sec. 3 we establish the connection between the equations of Sec. 1, which were derived under the assumption of weak coupling, and the equations of the adiabatic theory. It is shown that if $R \gg \omega_q$ the equations of Sec. 1 are valid for arbitrary values of the coupling constant, and for dispersionless phonons they allow us to determine the spectrum of the local modes directly from the electronic Hamiltonian.

In Sec. 4 the general theory, which has been developed in Secs. 1 and 2, is applied to local excitons in molecular crystals. Recent experimental articles[11] demonstrate the presence of an intense phonon sideband associated with the impurity bands in these crystals; the influence of different phonons on the position of the electronic level was considered earlier.[12] From a theoretical point of view molecular excitons represent a convenient model, since the exciton Green's function is known, and therefore simple formulas can be derived for the intensity and position of the phonon satellites in various limiting cases. In particular, it is possible in this model to trace the variation of the binding energy and the intensity of the band as the phonon frequency approaches the energy which binds the exciton to the impurity center.

Experimentally the formation of complexes consisting of a phonon plus an impurity exciton can be observed via a unique structure in the absorption spectrum, a structure which is not present in the corresponding luminescence spectra of impurity excitons. In this connection the criteria for a mirror symmetry of the impurity-absorption and luminescence spectra are discussed in Sec. 5.

1. THE ENERGY SPECTRUM

In this section we present a derivation of the equations[10] which determine the energy spectrum of an impurity center in the presence of the electron-phonon interaction. We shall assume that this interaction has the following properties: 1) it is linear in the phonon amplitudes, 2) it is weak, and 3) the dispersion of the phonon frequencies can be neglected.

We choose the electron-phonon interaction Hamiltonian in the form

$$H_{int}=\sum_{\mathbf{k}\mathbf{q}}\gamma_{\mathbf{k}}(\mathbf{q})a_{\mathbf{k}}^{+}a_{\mathbf{k}-\mathbf{q}}(b_{\mathbf{q}}+b_{-\mathbf{q}}^{+}). \tag{1}$$

The operators $a_{\mathbf{k}}$ can pertain equally well to an electron and to an exciton. The dependence of the coefficients $\gamma_{\mathbf{k}}(\mathbf{q})$ on both the momentum transfer $\mathbf{q}$ and on the momentum k itself is taken into consideration in formula (1); the latter dependence may turn out to be important in certain narrow-band systems, for example, in molecular crystals. If we change to a representation in terms of the eigenfunctions of the electronic subsystem, then

$$H_{int}=\sum_{st\mathbf{q}}\gamma_{st}(\mathbf{q})a_{s}^{+}a_{t}(b_{\mathbf{q}}+b_{-\mathbf{q}}^{+}), \tag{2}$$

$$\gamma_{st}(\mathbf{q})=\sum_{\mathbf{k}}\gamma_{\mathbf{k}}(\mathbf{q})\psi_{s}^{*}(\mathbf{k})\psi_{t}(\mathbf{k}-\mathbf{q}). \tag{3}$$

Here $\psi_s(k)$ ($s = 0, 1, \ldots \infty$) denote the eigenfunctions of the electronic subsystem in the absence of the electron-phonon interaction. From the properties of hermiticity and reality it follows that the functions ψ_s can be chosen such that

$$\gamma_{st}(\mathbf{q})=\gamma_{ts}(\mathbf{q}),\quad \gamma_{st}(-\mathbf{q})=\gamma_{st}^{*}(\mathbf{q}). \tag{4}$$

These conditions turn out to be useful below.

We shall be interested in the spectrum in the energy range near $\epsilon_0+\omega_0$ (ϵ_0 is the lowest energy level of the system, and ω_0 is the limiting phonon frequency), i.e., the region near the threshold for the emission of a phonon. In this region diagrams of the type shown in Fig. 1a give the major contribution to the mass operator, where all of the single-phonon cross sections are dangerous.[13] It is precisely these diagrams, accordingly, which turn out to play a decisive role in the formation of bound states between phonons and various electronic systems;[14] this also pertains, in particular, to impurity centers. Therefore, in the weak-coupling approximation the problem reduces to the summation of the sequence of diagrams of the type shown in Fig. 1a.

The equation for the vertex function is represented graphically in Fig. 1b. After integrating over the frequency Ω', the analytic expression corresponding to the vertex function reduces to

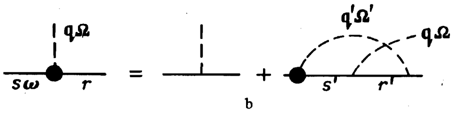

FIG. 1

$$\Gamma_{sr}(\mathbf{q}|\omega,\Omega)=\gamma_{sr}(\mathbf{q})+$$
$$+\sum_{s'r'\mathbf{q}'}\Gamma_{ss'}(\mathbf{q}'|\omega,\omega_{\mathbf{q}'})\gamma_{r'r}(-\mathbf{q}')\gamma_{s'r'}(\mathbf{q})G_{s'}{}^{0}(\omega-\omega_{\mathbf{q}'})G_{r'}{}^{0}(\omega-\omega_{\mathbf{q}'}-\Omega), \tag{5}$$

where G^0 and D are the free electron and free phonon Green's functions. In performing the integration over Ω' it is assumed that Γ, regarded as a function of Ω', does not have any singularities in the lower half-plane; this is easily verified for any diagram of finite order. In the threshold approximation[14] one is restricted to the term $s' = 0$ on the right, which introduces a contribution proportional to $(\omega - \epsilon_0 - \omega_0)^{-1}$ (for dispersionless phonons).

Multiplying by $\gamma_{rt}(-q)G_r^0(\omega - \Omega)D(q\omega)$ and then summing over rq and integrating with respect to Ω, we obtain on the left the usual expression for the mass operator M. It is important that, in the threshold approximation (when only the term $r = 0$ is retained; we assume the ground state to be nondegenerate) and in the absence of phonon dispersion ($\omega_q = \omega_0$), the factors $\Gamma_{ss'}\gamma_{rr'}G_r^0$ with $s' = r = 0$ are also gathered into the mass operator after the summation over q'; here we have taken into account that, according to (4), $\gamma_{r'r} = \gamma_{rr'}$. If we define the matrix

$$A_{st}=\sum_{\mathbf{q}}\gamma_{s0}(\mathbf{q})\gamma_{0t}(-\mathbf{q}), \tag{6}$$

the resultant equation takes the form

$$-\lambda M_{st}(\omega)=A_{st}+\sum_{r}M_{sr}(\omega)G_{r}(\omega-2\omega_0)A_{rt}, \tag{7}$$

where $\lambda = \epsilon_0 + \omega_0 - \omega$. Below we shall be interested in the region near threshold, where $|\lambda| \ll \omega_0$, R.

Thus, owing to the absence of dispersion in the system, the equation for the vertex Γ has been reduced to the equation for the mass operator, and in this respect the problem has been substantially simplified. Nevertheless, since M is off-diagonal in the indices s and t, the determination of the spectrum, i.e., the determination of the poles of G, in such a version of the theory remains, as before, practically impossible.

It is, however, convenient to note that an explicit expression for the inverse operator M^{-1} follows from Eq. (7):

$$M^{-1}(\omega)=-\lambda A^{-1}-G^{0}(\omega-2\omega_0).$$

Using this relation, it is easy to transform the expression for the Green's function in the following manner:

$$\begin{aligned}G(\omega)&=M^{-1}(M^{-1}-G^{0})^{-1}G^{0}\\&=\{\lambda+G^{0}(\omega-2\omega_0)A\}\{\lambda+(G^{0}(\omega)+G^{0}(\omega-2\omega_0))A\}^{-1}G^{0}(\omega).\end{aligned} \tag{8}$$

This formula, which expresses G directly in terms of the matrix A, allows us to obtain convenient formulas for the determination of the spectrum and the optical transition intensities.

The determination of the spectrum reduces to finding the poles of the second factor in (8), which is equivalent to solving the equation

$$\lambda\{(\lambda+H-\varepsilon_0)^2-\omega_0{}^2\}\varphi=2(\lambda+H-\varepsilon_0)A\varphi. \tag{9}$$

Here H is the Hamiltonian of the electronic subsystem. Taking the scalar product of Eq. (9) with ψ_0, we find that $(\psi_0, \varphi) \sim A/\omega_0^2 \ll 1$, owing to the weakness of the electron-phonon coupling. Therefore, one can set $(\psi_0, \varphi) = 0$ and consider only the part of Eq. (9) acting in the subspace of φ which is orthogonal to ψ_0. Under these conditions the secular equation for the determination of the spectrum, following from Eq. (9), takes the form

$$\left|\lambda\delta_{st}-\frac{2(\lambda+\varepsilon_s-\varepsilon_0)}{(\lambda+\varepsilon_s-\varepsilon_0)^2-\omega_0^2}A_{st}\right|=0;\quad s,t=1,2,\dots\infty \tag{10}$$

Equation (10) has an infinite number of roots. We shall briefly investigate their distribution. If a resonance situation arises, i.e., if $\epsilon_s - \epsilon_0 \approx \omega_0$ for some discrete level s, then the corresponding denominators in the second term in (10) become small. This leads to the appearance of two large roots, which are determined by the equation

$$\lambda(\lambda+\varepsilon_s-\varepsilon_0-\omega_0)=A_{ss} \tag{11}$$

and whose order of magnitude is $\lambda \sim A_{ss}^{1/2}$. The existence of these roots was indicated by Kogan and Suris.[9] However, if no resonance is present one can omit λ from the second term in (10) since all $|\lambda| \ll \omega_0$, R for the weak-coupling case. Then (10) reduces to the usual secular determinant, which contains λ only in the diagonal elements

$$\left|\lambda\delta_{st}-\frac{2(\varepsilon_s-\varepsilon_0)}{(\varepsilon_s-\varepsilon_0)^2-\omega_0^2}A_{st}\right|=0;\quad s,t=1,2,\dots\infty. \tag{12}$$

Therefore, the usual algebraic methods of investigating the spectrum can be applied to it.

Since, according to Eqs. (4) and (6), the matrix A has the structure $\gamma\gamma^+$, it is positive; therefore, all of its principal minors are positive. If $\epsilon_s - \epsilon_0 > \omega_0$ for all s, all of the coefficients associated with A_{sr} are positive. Therefore, all of the principal minors of the matrix

$$\left\|\frac{2(\varepsilon_s-\varepsilon_0)}{(\varepsilon_s-\varepsilon_0)^2-\omega_0^2}A_{st}\right\|,$$

will be positive, as well as this matrix itself. Consequently, the whole infinite sequence of roots of Eq. (12) will be located below the threshold and, of course, will be concentrated at the threshold. However, if $\epsilon_s - \epsilon_0 < \omega_0$ for several of the lowest electronic levels, each such s will introduce one change of sign in the sequence of principal minors. Hence roots $\lambda < 0$ appear; according to Jacobi's criterion the number of such roots will be equal to the number of changes in sign, i.e., the number of electronic levels which lie below the threshold. All of the roots $\lambda \leq 0$ correspond to the bound states of a phonon near an impurity center or, what amounts to the same thing, local modes which appear as a consequence of the electron-phonon interaction.

Equation (10) is not convenient for the numerical determination of the roots. It is more convenient to use Eq. (9), which simplifies to the following for nonresonance conditions:

$$\lambda\{(H-\varepsilon_0)^2-\omega_0^2\}\varphi=2(H-\varepsilon_0)A\varphi. \tag{13}$$

A is an integral operator in the coordinate representation. In the simplest case, when $\gamma_k(q) = \gamma(q)$, its kernel is given by

$$A(\mathbf{r},\mathbf{r}')=\psi_0(\mathbf{r})V(\mathbf{r}-\mathbf{r}')\psi_0(\mathbf{r}'),$$
$$V(\mathbf{r})=\sum_{\mathbf{q}}|\gamma(\mathbf{q})|^2e^{i\mathbf{q}\mathbf{r}}. \tag{14}$$

Equation (13) can be solved, for example, by the variational method with the orthogonality conditions $(\varphi, A\varphi_i) = 0$ for $i \neq j$ taken into consideration.

2. THE INTENSITY OF THE TRANSITIONS

The probability for the optical transitions of an electron in an impurity center is usually determined by the two-particle Green's function, and therefore does not reduce to G. But if the topic of discussion is a center to which an exciton (either a Frenkel or a Wannier exciton) is bound, and transitions involving the creation of an impurity exciton are considered, then the absorption intensity is directly determined by the Green's function at zero momentum, Im $G(\omega \mid k = 0, k' = 0)$. Therefore, the problem reduces to finding the residue of G (given by formula (8)) at the pole, a task which is complicated by the fact that the second factor contains the non-Hermitian expression BA with

$$B(\lambda)=-(G^0(\omega)+G^0(\omega-2\omega_0)),$$

which also depends on λ.

One can seek the poles of $G(\omega)$ by determining the eigenvalues λ_i of the equation

$$B(\lambda)A\varphi_i=\lambda_i(\lambda)\varphi_i, \tag{15}$$

where these eigenvalues parametrically depend on λ, and then finding the solution of the equation $\lambda = \lambda_i(\lambda)$. Introducing the new quantities

$$\tilde{A}(\lambda)=B^{1/2}AB^{1/2},\quad \tilde{\varphi}=B^{-1/2}\varphi,\quad (\tilde{\varphi}_i,\tilde{\varphi}_i)=\lambda_i^{-1}, \tag{16}$$

we bring Eq. (15) to Hermitian form, $\tilde{A}(\lambda)\tilde{\varphi} = \lambda_i(\lambda)\tilde{\varphi}$. The normalization condition for φ_i follows from Eqs. (15) and (16):

$$(\varphi_i, A\varphi_i)=1. \tag{17}$$

Using the bilinear representation for the resolvent of the Hermitian operator $\tilde{A}$, which is somewhat modified in comparison with the standard expression as a consequence of the normalization condition (16), we obtain

$$(\lambda-BA)^{-1}=B^{1/2}(\lambda-\tilde{A})^{-1}B^{-1/2}=\sum_i\frac{\lambda_i}{\lambda-\lambda_i}B^{1/2}|\tilde{\varphi}_i\rangle\langle\tilde{\varphi}_i|B^{-1/2}. \tag{18}$$

Evaluating the residue of this expression at the pole λ_i and substituting the result into (8), we obtain

$$\operatorname{Res}_i G=-\frac{G^0(\omega)A|\varphi_i\rangle\langle\varphi_i|AG^0(\omega)}{1-d\lambda_i/d\lambda}. \tag{19}$$

where (15), (16), and also the explicit form of the operator B have been taken into consideration. Again using relations (15) and (16), and also the diagonal nature of the operator $B(\lambda)$ (therefore B commutes with $\partial B/\partial\lambda$), it is easy to obtain the following formula:

$$\frac{\partial\lambda_i}{\partial\lambda}=\left\langle\tilde{\varphi}_i,\frac{\partial\tilde{A}}{\partial\lambda}\tilde{\varphi}_i\right\rangle\Big/\langle\tilde{\varphi}_i,\tilde{\varphi}_i\rangle=\left\langle\varphi_i,A\frac{\partial B}{\partial\lambda}A\varphi_i\right\rangle. \tag{20}$$

Formulas (19) and (20) solve the problem of calculating the intensities from the wave functions φ_i.

3. THE ADIABATIC APPROXIMATION

Everywhere above we assumed the coupling to be weak, i.e., $A \ll \omega_0^2$, R^2. Now let us consider the particular situation $R \gg \omega_0$, when the impurity center can be treated in the adiabatic approximation. In this case it turns out that the criteria for the theory are moderated, and it is sufficient to require $A \ll R\omega_0$; the relation between A and ω_0^2 can be arbitrary. In the adiabatic limit it also turns out to be possible to obtain a classical interpretation of the function φ.

First, however, let us take the limit $R \gg \omega_0$ in Eq. (13). In this case $\epsilon_s - \epsilon_0 \gg \omega_0$ for all $s \neq 0$, and therefore one can omit ω_0^2 on the left. The component $s = 0$ is an exception, because in this case it is precisely the presence of the term ω_0^2 which guarantees fulfilment of the condition $(\psi_0, \varphi) = 0$. Taking this remark into consideration, one can easily understand that at $R \gg \omega_0$ Eq. (13) can be replaced by

$$\lambda(H-\varepsilon_0)\varphi=2\bar{A}\varphi, \tag{21}$$

$$\bar{A}=A-A|\psi_0\rangle\langle\psi_0|-|\psi_0\rangle\langle\psi_0|A+(\psi_0, A\psi_0)|\psi_0\rangle\langle\psi_0|. \tag{22}$$

This equation correctly determines all the components $\varphi_S = (\psi_S, \varphi)$ except φ_0, which generally remains undetermined. Therefore, it is necessary to supplement Eq. (21) with the condition $(\psi_0, \varphi) = 0$. It is obvious that since ψ_0 is an s-type function one can use A in Eq. (21) instead of $\bar{A}$ for the determination of all of the functions φ with angular momenta $l \geq 1$. In applying the variational method one can use the same simplification, having determined

$$\lambda=2\max\frac{\langle\varphi, A\varphi\rangle}{\langle\varphi, (H-\varepsilon_0)\varphi\rangle} \tag{23}$$

under the supplementary condition $(\psi_0, \varphi) = 0$.

Now let us obtain the equations of the adiabatic theory by an independent method. Changing from the operators b_q to complex normal coordinates, we obtain

$$H_{ph}=\frac{\omega_0}{2}\sum_{\mathbf{q}}(P_{\mathbf{q}}P_{-\mathbf{q}}+Q_{\mathbf{q}}Q_{-\mathbf{q}}),$$
$$H_{int}=\sqrt{2}\sum_{\mathbf{q}st}\gamma_{st}(\mathbf{q})a_s^+a_tQ_{\mathbf{q}}; \tag{24}$$

the pairs (P_q, Q_{-q}) are canonically conjugate. For $R \gg \omega_0$ one can eliminate the electronic subsystem, having calculated the correction to the phonon energy in second-order perturbation theory:[4]

$$H_{ph}'=2\sum_{t\neq0}\frac{1}{\varepsilon_0-\varepsilon_t}\left|\sum_{\mathbf{q}}\gamma_{0t}(\mathbf{q})Q_{\mathbf{q}}\right|^2. \tag{25}$$

Now writing down the classical equations of motion of the phonons, we obtain the following relations for the vibrational amplitudes Q_q and the Franck-Condon displacements of the equilibrium positions Q_q^0:

$$(\omega^2-\omega_0^2)Q_{\mathbf{q}}=4\omega_0\sum_{\mathbf{q}'}\sum_{t\neq0}\frac{\gamma_{t0}(-\mathbf{q})\gamma_{0t}(\mathbf{q}')}{\varepsilon_0-\varepsilon_t}Q_{\mathbf{q}'}, \tag{26}$$

$$Q_{\mathbf{q}}^0=-\sqrt{2}\,\gamma_{00}(-\mathbf{q})/\omega_0. \tag{27}$$

With allowance for (27), the condition for the applicability of perturbation theory, $|H_{int}| \ll R$, reduces to $A \ll R\omega_0$. Let us define the quantities

$$\chi_t=\sum_{\mathbf{q}}\frac{\gamma_{t0}(\mathbf{q})Q_{\mathbf{q}}}{\varepsilon_t-\varepsilon_0},\quad t\neq0;\quad \chi_0=0. \tag{28}$$

Then Eq. (26) can be rewritten in the form

$$(\omega^2-\omega_0^2)(\varepsilon_0-\varepsilon_s)\chi_s=4\omega_0\sum_t A_{st}\chi_t,\quad s\neq0. \tag{29}$$

We further take into consideration that, according to (29), $\lambda \sim A/R$, and therefore it follows from $A \ll R\omega_0$ that $\lambda \ll \omega_0$. Then one can easily verify that (29) is equivalent to the system of equations for the quantities $\varphi_S = (\psi_S, \varphi)$ which follow from Eq. (21). Therefore, upon fulfilment of the criterion $\omega_0 \ll R$ for the adiabatic approximation, Eq. (21) is valid in the entire region $A \ll R\omega_0$.

Now let us assume that $\gamma_{\mathbf{k}}(\mathbf{q}) = \gamma(\mathbf{q})$, and let us define the function

$$Q(\mathbf{r})=\sum_{\mathbf{q}}\gamma(\mathbf{q})Q_{\mathbf{q}}e^{i\mathbf{q}\mathbf{r}}. \tag{30}$$

Then, by equating all χ_S and φ_S with $s \neq 0$, we obtain

$$(H-\varepsilon_0)\varphi(\mathbf{r})=(\psi_0(\mathbf{r})Q(\mathbf{r}))_\perp. \tag{31}$$

The subscript in the last expression indicates that the component along ψ_0 is absent. It is clear from Eq. (31) that φ is directly related to the lattice deformation, which is characterized by the function $Q(\mathbf{r})$.

4. THE FRENKEL IMPURITY EXCITON

As an example let us consider an impurity exciton in a molecular crystal, and make a number of simplifying assumptions. The crystal is assumed to be simple cubic and contains one molecule per unit cell. Only the interaction with nearest neighbors is taken into consideration; then the half-width of the band is $\mathfrak{M} = 6|M|$. The matrix element of this interaction $M < 0$; then the point $k = 0$ is located at the bottom of the exciton band. The impurity molecule is isotopic, i.e., it differs from the solvent molecules only by a shift of the energy level by the amount Δ ($\Delta < 0$). The phonons are dispersionless with

$$\gamma_{\mathbf{k}}(\mathbf{q})=\gamma/\mathfrak{N}^{1/2}=\text{const}, \tag{32}$$

where $\mathfrak{N}$ is the number of molecules in the crystal.

By using the standard formulas of degenerate perturbation theory, one can easily write down G^0 and ψ_0 for an isotopic impurity center:

$$G_{\mathbf{nm}}^0=\mathcal{G}_{\mathbf{nm}}+\frac{\Delta}{1-\Delta\mathcal{G}_{00}}\mathcal{G}_{\mathbf{n}0}\mathcal{G}_{0\mathbf{m}},$$
$$\mathcal{G}_{\mathbf{nm}}(\omega)=\frac{1}{\mathfrak{N}}\sum_{\mathbf{k}}\frac{e^{i\mathbf{k}(\mathbf{n}-\mathbf{m})}}{\omega-\varepsilon(\mathbf{k})}, \tag{33}$$
$$\psi_0(\mathbf{n})=\mathcal{G}_{\mathbf{n}0}(-d\mathcal{G}_{00}/d\omega)^{-1/2}.$$

Here $\mathcal{G}_{nm}$ is the Green's function of an exciton in a perfect crystal, $\epsilon(k)$ is the dispersion law of the exciton; the impurity molecule is located at the site $n = 0$. If $|\Delta|$ is not too small, then one discrete level of the impurity exciton appears, $\omega = \epsilon_0$, determined by the equation $\Delta\mathcal{G}_{00}(\epsilon_0) = 1$.

According to Eqs. (14) and (32) the operator A is given by

$$A_{\mathbf{nm}}=\gamma^2\psi_0^2(\mathbf{n})\delta_{\mathbf{nm}}. \tag{34}$$

The phonon spectrum, renormalized as a result of the exciton-phonon interaction, is determined by the equations of Sec. 1. A general schematic diagram of the spectrum is shown in Fig. 2.

Below we shall use Eq. (15) for the determination of the functions φ. Unfortunately, it cannot be solved in general, and therefore below we consider two limiting cases separately.

1. The Case of a Deep Level, $|\Delta| \gg \mathcal{M}$

In this case the exciton function is almost completely concentrated on the impurity molecule and, according to Eqs. (33), $\psi_0(0) \approx 1$ and $\psi_0(1) \approx M/\Delta$ for the six values of 1 ($|1| = 1$) corresponding to the nearest neighbors; at the remaining sites ψ_0 has a higher order of smallness in M/Δ. The depth of the electronic level $R \approx |\Delta - 6M|$. The expansion in $\mathfrak{M}/\Delta$ remains accurate up to $\mathfrak{M}/\Delta \approx 1$.

From Eq. (15) one can easily obtain a system of equations for $\varphi(0)$ and $\varphi(\mathbf{l})$ with $|\mathbf{l}| = 1$ and express the values of $\varphi(\mathbf{l})$ at all remaining sites in terms of them. Since all of the expressions contain integrals of $\mathcal{G}_{nm}(\omega)$, simple formulas can be obtained only in limiting cases corresponding to various ratios between ω_0 and R.

A. The case of a low frequency ω_0. Actually it is required that $|R - \omega_0| \gg \mathfrak{M}$. In this case the function φ is maximal at the sites with $|\mathbf{l}| = 1$. The lowest state among the phonon bound states turns out to be an s-type level:

$$\lambda_s=-14\gamma^2M^2/\Delta(\Delta^2-\omega_0^2). \tag{35}$$

This level is followed by a p-type level and a doubly degenerate level; in the approximation under consideration the latter have identical binding energies, equal to $\lambda_s/7$. λ_s increases with increasing values of ω_0, as is clear from Eq. (35).

Optical transitions are only allowed to the s-level. Calculating according to Eq. (19), the oscillator strength of the corresponding transition is given by

$$f=\frac{6}{7}\left(\frac{\gamma}{\omega_0}\right)^2 f_0, \tag{36}$$

where f_0 is the oscillator strength of the intramolecular transition.

B. The case $|\omega_0 - R| \ll \mathfrak{M}$. Bound states of the phonon are produced for $\omega_0 < R$; for $\omega_0 > R$ they can arise only if $\omega_0 - R \sim \lambda$. In this case the function φ envelops a region substantially exceeding the lattice constant.

For the s-level we find

$$\lambda_s=-7\left(1-\frac{1}{3\alpha}\right)\frac{\gamma^2M}{\Delta^2}, \quad \alpha=\int_0^\infty I_0^3(t)e^{-3t}dt=0{,}50\ldots, \tag{37}$$

i.e., it is larger than in case A by a factor $\sim\Delta/M$ (here I_0 is the Bessel function of imaginary argument). However, in contrast to the case of a resonance between ω_0 and one of the frequencies of the discrete electronic spectrum,[9] here λ retains the same order of magnitude in the coupling constant. The oscillator strength

$$f=\frac{14}{3\alpha^2}\left(\frac{\gamma}{W}\frac{M}{\Delta}\right)^2 f_0 \tag{38}$$

increases sharply with decreasing W, i.e., as the level approaches the bottom of the exciton band; the meaning of W is clear from Fig. 2. For very small $W \lesssim \gamma^4M/\Delta^4$ the term $d\lambda_i/d\lambda$ in the denominator of formula (19) increases and becomes $\gtrsim 1$ (usually it is negligible since it is proportional to γ^2). In this connection the growth of f slows down:

$$f=8\pi|M/W|^{3/2}f_0. \tag{39}$$

The calculation gives $\lambda_p \approx 0.06\,\lambda_s$ and $\lambda_d \approx 0.05\,\lambda_s$ for the p- and d-levels.

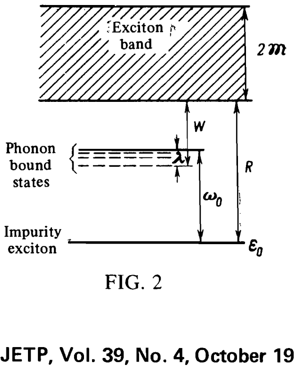

FIG. 2

2. The Case of a Shallow Level, $R \ll \mathcal{M}$

In this case one can obtain a general solution for the lowest phonon level, which goes beyond the framework of the nearest-neighbor approximation adopted above. This possibility is based on the following facts. Since the local exciton level is determined by the zero of the expression $1 - \Delta\mathcal{G}_{00}(\omega)$, when this level is shallow the factor $|1 - \Delta\mathcal{G}_{00}(\omega)|^{-1}$ is large near the edge of the band. Therefore, the second term in the Green's function $\mathcal{G}^0_{nm}(\omega)$ dominates (see formula (33)); therefore, the kernel BA in Eq. (15) factorizes and the equation is easily solved. An additional simplification appears thanks to the fact that the functions $\mathcal{G}_{nm}(\omega)$ remain finite as ω approaches the bottom of the band ($\omega \to \epsilon_{min}$). Therefore, one can replace the functions $\mathcal{G}_{nm}$ by $\mathcal{G}_{nm}(\epsilon_{min})$ in both the operator B and also in the expression for $\psi_0(n)$.

The following expression is finally obtained for λ:

$$\lambda=4\pi^2\zeta\frac{\gamma^2R^{1/2}}{v^2(m^*)^3}\sigma, \quad \sigma=\sum_{\mathbf{n}}|\mathcal{G}_{\mathbf{n}0}(\varepsilon_{min})|^4,$$
$$\zeta=\frac{1}{(R-\omega_0)^{1/2}-R^{1/2}}+\frac{1}{(R+\omega_0)^{1/4}-R^{1/2}}, \tag{40}$$

where v is the volume of the unit cell, and m* is the exciton's effective mass at the bottom of the band. It is obvious that $\sigma \sim \mathfrak{M}^{-4}$; of course, the exact value of this factor can only be determined for a particular band structure.

The oscillator strength f can be calculated in an analogous fashion according to formulas (19) and (20). It is also expressed in terms of σ, and if σ is expressed in terms of λ according to (40), then

$$f=\frac{4\pi}{(2m^*)^{3/2}}\frac{\lambda}{v\zeta W^2}\frac{1}{(\sqrt{R}-\sqrt{W})^2}f_0. \tag{41}$$

For extremely small values $W \lesssim \gamma^4/R\Delta^2$ we obtain

$$f=8\pi v^{-1}(2m^*W)^{-3/2}f_0. \tag{42}$$

instead of expression (41).

From a comparison of (35) and (37), and also from (40) it follows that λ increases as $\omega_0 \to R$, i.e., as the phonon level approaches the edge of the band, but remains finite. Conversely, f increases without limit, and moreover in the immediate vicinity of the band edge it ceases to depend on γ (formulas (39) and (42)). Physically the growth of f will be limited by extraneous mechanisms (polariton effects and the damping of the excitons as a result of their scattering).

5. THE MIRROR SYMMETRY OF THE SPECTRA

The phonon binding energy λ was determined in the preceding section for a number of limiting cases. In this connection an extremely simplified model ($\omega = \omega_0$, $\gamma_k(q) = \text{const}$) was taken as the basis of the calculations. Naturally, taking the phonon dispersion into account might not only lead to a numerical change in the results (which would be most important for a deep level), but might also lead to attenuation of the obtained states. Nevertheless, one can hope that if the phonon dispersion is relatively small, then the basic qualitative results will be preserved. This implies that density-of-states peaks, due to the interaction with the impurity excitons, will appear in the phonon spectrum; the separation of these peaks from the edges of the phonon bands can be determined (or estimated) from the formulas given in the preceding section.

It is obvious that in addition to the "excitonic" mechanism discussed above for the appearance of local modes, there is also an "ordinary" mechanism associated with the mass difference. Local modes of different origin can be experimentally distinguished owing to the fact that, the modes which arise from the excitonic mechanism can only exist in the presence of an impurity exciton, and therefore they must appear (in the form of satellites) exclusively in the impurity exciton absorption spectra, whereas the modes arising from the ordinary mechanism must correspond to comparable frequencies and intensities in the absorption and luminescence spectra. Thus, the modes which are of excitonic origin can be distinguished by the specific nonmirror symmetry of their absorption and luminescence spectra.

Generally speaking the mirror symmetry of the absorption and luminescence spectra occurs only if the adiabatic potentials of the ground and excited states differ by a linear function of the vibrational coordinates, but the transition matrix element does not depend on them;[15] this is possible only if R substantially exceeds $\omega_{\mathbf{q}}$. The picture of the violation of the mirror symmetry as a function of the ratio between R and $\omega_{\mathbf{q}}$ is very simple in the case of weak coupling, when perturbation theory is valid, namely, owing to mixing with band states, the intensity of the absorption contains denominators of the type $R - \omega_{\mathbf{q}}$, and the intensity of the luminescence contains denominators of the type $R + \omega_{\mathbf{q}}$; therefore, the contribution to the absorption spectrum from phonons with $\omega_{\mathbf{q}} \approx R$ will appreciably exceed their contribution to the luminescence spectrum.

The conditions under which the mirror symmetry of the spectra will be satisfied for low-frequency phonons, $\omega_{\mathbf{q}} \ll R$, still have to be established. The well known estimate γ^2/R for the correction to the frequencies[4] follows from formula (25). Therefore, the mirror symmetry of the spectra is satisfied for $\gamma^2/R \ll \omega$ (with the proviso, however, that structure with a scale γ^2/R may appear, corresponding to bound or quasibound states).

The situation is somewhat more complicated if, as usually happens, along with the low-frequency phonons with scale ω there are other phonons with a broad range of frequencies Ω and coupling constants Γ, including phonons with $\Omega \sim R$; then it is impossible to write down an adiabatic potential for the entire phonon system. In this case it is convenient to separate the "high-frequency" phonons for which Ω has the scale R and the "low-frequency" phonons with $\Omega \ll R$. For all of the phonons we demand that the exciton-phonon interaction does not bring about a realignment of the lattice near the center (i.e., so that frequencies whose squares are negative do not appear); the condition for this, $\Gamma^2/R \lesssim \Omega$, when applied to phonons with $\Omega \ll R$ gives $\Gamma \ll R$. The high-frequency phonons together with the electronic subsystem can be regarded as a single system having an excitation energy whose scale is R, and all the terms in the Hamiltonian of the type $\gamma a_0^+ a_n b_{\mathbf{q}}$ and $\Gamma a_0^+ a_n B_{\mathbf{q}}$ can be eliminated in first order by means of the canonical transformation e^{S_1}:

$$S_1 = \sum_{t\neq 0} \frac{a_0{}^+ a_t}{\varepsilon_t - \varepsilon_0} \{\gamma_{0t}(\mathbf{q})\,(b_{\mathbf{q}} + b_{-\mathbf{q}}{}^+) + \Gamma_{0t}(\mathbf{q})\,(B_{\mathbf{q}} + B_{-\mathbf{q}}{}^+)\} - \text{h.c.} \tag{43}$$

it is obvious that $S_1 \sim \gamma/R,\ \Gamma/R \ll 1$.

As a result of this transformation, the terms $\sim S_1^2$ introduce in the adiabatic potential a contribution due to the exciton-phonon interaction; symbolically it can be represented in the form

$$V_{\text{ad}} = b^+ v b + B^+ V B + u(B^+ b + b^+ B), \tag{44}$$

where $v \sim \gamma^2/R$, $V \sim \Gamma^2/R$, and $u \sim \gamma\Gamma/R$. Then, for $\Gamma^2/R \lesssim \Omega$ and $\gamma^2/R \ll \omega$ one can, with the aid of a second canonical transformation $\exp S_2$ with $S_2 \sim u/\Omega$, eliminate the mixed terms $B^+ b$, using the small parameter $u/\Omega \lesssim \gamma(R\Omega)^{-1/2} \ll 1$; corrections to the frequencies ω appear which are $\sim u^2/\Omega \lesssim \gamma^2/R \ll \omega$. Thus, the additional corrections which appear due to the presence of the other phonon branches do not exceed (in order of magnitude) the fundamental corrections $\sim\gamma^2/R$. As to the corrections to the intensities, which appear upon carrying out the transformations $\exp S_1$ and $\exp S_2$ in the corresponding terms which determine the absorption and luminescence spectra, they turn out to be small for reasonably small S_1 and S_2 (that is, $S_1, S_2 \ll 1$). Therefore, even in the general case the criterion $\gamma^2/R \ll \omega$ is sufficient to guarantee the mirrorlike resemblance of the spectra in the region of satellites with frequencies $\omega \ll R$.

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153