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The Effect of Intermolecular Interaction of an Impurity with its Environment on the Spectral Properties of Molecular Crystals

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The energy spectrum and the spectrum of light absorption by impurity crystal are studied taking into account a nondiagonal perturbation caused by an impurity molecule. The effect of the intermolecular guest-host interaction on the conditions of existence of in-band resonance states is analysed and the frequency dependence of the half-width and the intensity of the resonance impurity absorption peak is obtained. The band absorption spectrum is calculated in the nearest-neighbour-approximation for one-dimensional and three-dimensional impurity crystals.

A great deal of papers is devoted to the spectral properties of impurity crystals. Part of these papers were concerned with the region of an exciton excitation spectrum of molecular crystals where the simplest case of isotopic substitution is studied theoretically in great detail.¹ In the referred and subsequent papers only the out-of-band impurity states and their optical spectrum was usually considered. At the same time the properties of in-band impurity states are poorly studied, although such investigations seem to be very informative and useful.

Besides, in most cases only diagonal perturbation caused by an impurity is taken into account. The peculiarities of the spectrum are less known when the change in the intermolecular guest-host interaction can come into play. For example, in Ref. 2 the nondiagonal perturbation was involved to determine the conditions for the formation of out-of-band impurity levels. However, the effect of this perturbation on the exciton band, its role in

shaping the impurity absorption band and determining its intensity which is important for comparison with experiment, were not studied.

In attempts to fill up this gap, we consider the energy spectrum and the wave function of an impure crystal, find the density of states and the polarizability, taking into account the nondiagonal perturbation caused by an impurity. This approach enables us to derive certain conclusions concerning the points indicated. The general relations and their implications are obtained for cubic crystals characterized by an arbitrary exciton dispersion law.

1 THE ENERGY SPECTRUM AND THE WAVE FUNCTION OF A CRYSTAL WITH IMPURITY

For the crystals formed from molecules whose lowest electronic excitation levels are differed by the value greatly exceeding an energy of intermolecular interactions the Hamiltonian operator defining the crystal excitation spectrum in the lowest exciton band region in the second quantization representation is equal to³

$$H = \sum_{n, n'} [(\varepsilon_n + D_n)\delta_{nn'} + M_{nn'}(1 - \delta_{nn'})] B_n^+ B_{n'}, \quad (1)$$

where B_n^+ , B_n are the Bose creation and annihilation operators of an excitation on the molecule with number n , $\varepsilon_{n \neq 0} = \varepsilon^A$, $\varepsilon_0 = \varepsilon^B$ is the energy of this excitation, $D_{n \neq 0} = \sum_{n' \neq 0} D_{nn'}^{AA} + D_{n0}^{AB}$, $D_0 = \sum_n D_{n0}^{AB}$ is the electrostatic shift of the molecule excitation energy which is due to the interaction of the excited molecule with unexcited molecules of a crystal, $M_{nn'} = M_{nn'}^{AA}$ at $n, n' \neq 0$, $M_{0n} = M_{0n}^{AB}$ are the matrix elements of the energy of the resonance excitation transfer between molecules n and n' , $n = 0$ is the crystal lattice point number occupied by an impurity.

Introducing the notations $\varepsilon = \varepsilon^A + D_{n \neq 0}$, $\Delta = \varepsilon^B + D_0 - \varepsilon$ and neglecting the value $D_{n0}^{AA} - D_{n0}^{AB}$ (this rules out the possibility of existence of local exciton states in the sense of Ref. 4), we can represent the operator (1) in the form

$$H = \sum_{n, n'} [H_{nn'}^0 + V_{nn'}(\delta_{n0} + \delta_{n'0})] B_n^+ B_{n'}, \quad (2)$$

where

$$\begin{aligned} H_{nn'}^0 &= \varepsilon \delta_{nn'} + M_{nn'}^{AA}(1 - \delta_{nn'}), \\ V_{nn'} &= 0.5\Delta \delta_{nn'} + (M_{nn'}^{AB} - M_{nn'}^{AA})(1 - \delta_{nn'}). \end{aligned} \quad (3)$$

The wave function of one-particle excited state of a crystal with the Hamiltonian (2) is equal to

$$\psi = \sum_n a_n B_n^+ |0\rangle, \tag{4}$$

where the expansion coefficient satisfy the set of equations

$$\sum_{n'} [E\delta_{nn'} - H_{nn}^0 - V_{nn'}(\delta_{n0} + \delta_{n'0})] a_{n'} = 0 \tag{5}$$

and $|0\rangle$ is the wave function of the ground state. E is the energy of an excited crystal.

We now transform the set of Eq. (5) using the Green's function defined by the relation

$$(E\hat{I} - H^0)G^0 = \hat{I}, \tag{6}$$

where \hat{I} is the single operator (this method was first used by Lifshitz⁵ to solve a one-impurity problem). As a result, we obtain

$$a_n = G_{n0}^0 \sum_{n'} V_{0n'} a_{n'} + \sum_{n'} G_{nn'}^0 V_{n'0} a_0. \tag{7}$$

Supplementing (7) by the equation for $\sum_{n'} V_{0n'} a_{n'}$, we find

$$a_0 = G_{00}^0 \sum_{n'} V_{0n'} a_{n'} + \sum_{n'} G_{0n'}^0 V_{n'0} a_0.$$

$$\sum_{n'} V_{0n'} a_{n'} = \sum_{n, n'} (V_{0n} G_{n0}^0 V_{0n'} a_{n'} + V_{0n} G_{nn'}^0 V_{n'0} a_0) \tag{8}$$

The condition that the determinant of the set of Eqs. (8) be equal to zero gives an equation to define the energy spectrum in the exciton band region of a crystal

$$\left(1 + \sum_n V_{0n} G_{n0}^0\right)^2 - G_{00}^0 \sum_{n, n'} V_{0n} G_{nn'}^0 V_{n'0} = 0. \tag{9}$$

We now limit the model of an impurity to the case when the interaction of an impurity with its environment has the same character as the interaction between molecules of the host crystal, $M_{0n}^{AB} = \alpha M_{0n}^{AA}$. Using this condition and the relations following from the equations for the matrix elements of the Green's function

$$\sum_n M_{0n}^{AA} G_{n0}^0 = (E - \varepsilon)G_{00}^0 - 1, \tag{10}$$

$$\sum_{n, n'} M_{0n}^{AA} G_{nn'}^0 M_{n'0}^{AA} = (E - \varepsilon)[(E - \varepsilon)G_{00}^0 - 1] \tag{11}$$

Equation (9) can be reduced to the form

$$G_{00}^0[(1 - \alpha^2)(\varepsilon - E) + \Delta] = \alpha^2. \quad (12)$$

In this case the wave function corresponding to the state with energy E is given by the relation

$$a_n = \left[G_{n0}^0 \frac{\Delta - (E - \varepsilon)(1 - \alpha)}{\alpha + (E - \varepsilon)(1 - \alpha)G_{00}^0} + (1 - \alpha)\delta_{n0} \right] a_0 \quad (13)$$

with the normalization condition

$$\sum_n |a_n|^2 = 1. \quad (14)$$

An equation similar to (12) was obtained in Ref. 2 where the exciton band was supposed to be defined by the dipole-dipole interaction between molecules and the guest-host interaction was supposed to be of dipole character.

Since this equation is analyzed in detail in the paper [2], we confine ourselves to some relevant remarks. If the nondiagonal perturbation is absent, $\alpha = 1$ (the case of an isotopic impurity, Eq. (12) changes to a well-known equation

$$G_{00}^0 = \Delta^{-1} \quad (15)$$

whose solutions occupy the energy interval of the exciton band of a perfect crystal.⁵ Besides, isolated roots of Eq. (12), i.e. out-of-band states, are also possible.

Let us consider a particular case of the nondiagonal perturbation $\alpha = 0$ when the resonance interaction between the impurity and the host molecules is absent. Equation (12) then splits into two equations

$$E = \varepsilon + \Delta, \quad (16)$$

and

$$G_{00}^0 = 0 \quad (17)$$

where the first corresponds to a state with an excited impurity, $|a_0|^2 = 1$, $a_{n \neq 0} = 0$ while the second defines the energy of the collective excited states of a crystal. The solutions (17) coincide with the solutions (15) in the limit $|\Delta| \rightarrow \infty$ i.e. an infinitely "deep" impurity and an impurity which does not interact resonantly with the host molecules have the same effect on the band spectrum of a perfect crystal.

Suppose now that the resonance guest-host interaction is small $\alpha \ll 1$. Solving (12) by the successive approximation method and using the energy

(16) as the zero approximation, we find

$$E = \varepsilon + \Delta - \alpha^2 [G_{00}^0(\varepsilon + \Delta) - \Delta] + O(\alpha^4). \quad (18)$$

If the value $\varepsilon + \Delta$ is outside the exciton band, the intermolecular interaction results in a small shift of an impurity level. For $\varepsilon + \Delta$ inside the band we give a supplement to the definition of the Green's function in a usual way by assigning in the energy denominator an infinitesimal positive quantity. This is known to correspond to selecting retarded solutions of the Schrödinger equation.⁶ The solution (18) is then complex $E = E' + iE''$, $E'' \ll E'$,

$$E' = \varepsilon + \Delta - \alpha^2 \left[\frac{\text{Re } G_{00}^0(\varepsilon + \Delta)}{|G_{00}^0(\varepsilon + \Delta)|^2} - \Delta \right], \quad E'' = -\pi\alpha^2 \frac{\rho^0(\varepsilon + \Delta)}{|G_{00}^0(\varepsilon + \Delta)|^2} \quad (19)$$

where $\rho^0(E) = -\pi^{-1} \text{Im } G_{00}^0(E + i\delta)_{\delta \rightarrow +0}$ is the state density of a perfect crystal.

It is easy to verify by employing the relations (14), (13) that for the energy value obtained $|a_0|^2 = 1 + O(\alpha^2)$ and with the same accuracy $a_{n \neq 0} = 0$. The excited state is thus localized primarily on an impurity molecule. The fact that this state is nonstationary can be explained as follows: when the impurity gets excited it will lose its energy by producing divergent waves. This is possible due to the resonant guest-host interaction.

The damping time of the excited impurity state is great if $\alpha \ll 1$ and this restriction may be regarded as the condition of a strong coupling of the excitation with the impurity. Conversely, when $\alpha \gtrsim 1$ Eq. (13) has no solutions with the in-band excitation energy corresponding to the states which are localized on the impurity, and this condition will hereafter be referred to as the case of a weak coupling of the excitation with the impurity.

2 STATE DENSITY

The effect of an impurity on the band spectrum of a perfect crystal is readily analyzed in terms of state density. Besides, the calculation of the state density is of interest of itself.

By definition, the state density is expressed in terms of the retarded Green's function by the

$$\rho(E) = -\frac{1}{\pi N} \text{Im } SpG(E), \quad (20)$$

where N is the number of molecules in a crystal and $G(E)$ is defined from

$$(E\hat{I} - H)G = \hat{I}. \quad (21)$$

The solution for the matrix elements of these equations in the basis of localized functions is

$$\begin{aligned}
 G_{nn'} &= G_{nn'}^0 - G_{n0}^0 G_{0n'}^0 G_{00}^{0^{-1}} \\
 &+ G_{00}^{0^{-1}} \left[\left(1 - \sum_m G_{0m}^0 V_{m0} \right)^2 - G_{00}^0 \sum_{m,m'} V_{0m} G_{mm'}^0 V_{m'0} \right]^{-1} \\
 &\times \left[G_{00}^0 \sum_m G_{nm}^0 V_{m0} + G_{n0}^0 \left(1 - \sum_m G_{0m}^0 V_{m0} \right) \right] \\
 &\times \left[G_{00}^0 \sum_m V_{0m} G_{mn'}^0 + G_{0n'}^0 \left(1 - \sum_m V_{0m} G_{m0}^0 \right) \right]. \quad (22)
 \end{aligned}$$

This yields for the impurity center model in point:

$$G_{nn'} = G_{nn'}^0 - \frac{G_{n0}^0 G_{0n'}^0}{G_{00}^0} \left\{ 1 - \frac{\alpha^2 + \alpha(1 - \alpha)(\delta_{n0} + \delta_{n'0}) + (1 - \alpha)^2 \delta_{n0} \delta_{n'0}}{(E - \varepsilon - \Delta)G_{00}^0 + \alpha^2 [1 - (E - \varepsilon)G_{00}^0]} \right\}. \quad (23)$$

Using (23) and the equation

$$\sum_m G_{nm}^0 G_{mn'}^0 = - \frac{dG_{nn'}^0}{dE} \quad (24)$$

we obtain the following expression for the state density of an impure crystal

$$\rho(E) = \rho^0(E) - \frac{1}{\pi N} \operatorname{Im} \frac{[(1 - \alpha^2)(E - \varepsilon) - \Delta](dG_{00}^0/dE) + (1 - \alpha^2)G_{00}^0}{(E - \varepsilon - \Delta)G_{00}^0 + \alpha^2 [1 - (E - \varepsilon)G_{00}^0]}. \quad (25)$$

Let us investigate this expression for the limiting values of the coupling parameter α .

In the case of strong coupling the state density is

$$\rho(E) = \rho^0(E) - \frac{1}{\pi N} \operatorname{Im} \frac{(E - \varepsilon - \Delta)G_{00}^{0^{-1}}(dG_{00}^0/dE) + 1}{E - \varepsilon - \Delta + \alpha^2(G_{00}^{0^{-1}} - \Delta)}. \quad (26)$$

$$\alpha \ll 1$$

We can see that for $\varepsilon + \Delta$ beyond the exciton band (in addition to a small change in the state density in the region of band spectrum) $\rho(E)$ has a δ -spike near the energy value indicated. If $\varepsilon + \Delta$ is inside the band the effect of an impurity causes an appreciable change in the state density in the band spectrum, too. Really, the second term in (26) at $E \approx \varepsilon + \Delta$ has a maximum whose half-width is equal to $2\pi\alpha^2\rho^0(\varepsilon + \Delta)|G_{00}^0(\varepsilon + \Delta)|^{-2}$, and the intensity is inversely proportional to the small α^2 . In the case of strong coupling the

impurity thus always leads to an occurrence of a sharp peak in the state density of a band spectrum when the impurity level happens to be inside the exciton band at a point where $\rho^0(E)$ has no singularity.

When the crystal energy spectrum is defined by Eq. (15), we have

$$\rho(E) = \rho^0(E) + \frac{\Delta}{\pi N} \operatorname{Im} \frac{dG_{00}^0}{dE} (1 - \Delta G_{00}^0)^{-1}.$$

$$\alpha = 1 \tag{27}$$

When the solutions (15) have an isolated root the state density involves a δ -singularity outside the exciton band. If, in addition, there is a root of the equation $1 - \Delta \operatorname{Re} G_{00}^0 = 0$, $E = E_{\text{res}}$ inside the band, the correction to $\rho^0(E)$ has a maximum at this energy value, but its width, however, is proportional to a quantity of the order of the band width

$$\rho^0(E_{\text{res}}) \left| \frac{d \operatorname{Re} G_{00}^0}{dE} \right|_{E=E_{\text{res}}}^{-1}$$

i.e. the perturbation of the state density is of nonlocal character, so that the change in $\rho^0(E)$ for the present case of small impurity concentrations will be insignificant.

If $\alpha \gtrsim 1$ the energy dependence of $\rho(E)$ will also be close to $\rho^0(E)$ in the exciton band region. Thus in the case of weak coupling the presence of an impurity can come into play in the band crystal spectrum under very specific conditions, in particular when the state density of a perfect crystal is very small in the neighbourhood of $E = E_{\text{res}}$.

3 POLARIZABILITY OF AN IMPURITY CRYSTAL IN THE EXCITON TRANSITION REGION

We now consider the light absorption by a crystal containing impurities. Suppose that a plane wave of a frequency ω with the electric field strength

$$\mathbf{E} = \operatorname{Re} \mathbf{E}_0 \exp[i(\mathbf{QR} - \omega t)] \tag{28}$$

directed along the dipole transition moment of the molecule is incident upon a crystal described by the Hamiltonian (2). The linear response of the system to the field (28) is defined by the polarizability tensor whose resonance part to a long-wave approximation is equal to

$$\beta_{ij} = - \frac{1}{Nv_0} \sum_{n, n'} (\mathbf{P}_n)_i (\mathbf{P}_{n'})_j G_{nn'}^{(\omega)} \tag{29}$$

where v_0 is the average volume per molecule, \mathbf{P}_n is the dipole moment of the transition of a molecule between the ground and the excited state $\mathbf{P}_n = \mathbf{P}_0$, when $n = 0$, $\mathbf{P}_{n \neq 0} = \mathbf{P}$.

Let the dipole transition moment of the molecules be directed along the unity vector \mathbf{i} : $\mathbf{P} = P\mathbf{i}$, $\mathbf{P}_0 = P_0\mathbf{i}$. Then, at small impurity concentration C we find, using (23),

$$\beta_{ii} = \frac{P^2}{v_0} \frac{1}{\varepsilon + \mathcal{E} - \omega} + C \frac{P^2}{v_0} \left\{ \frac{1}{[\varepsilon + \mathcal{E} - \omega]^2 G_{00}^0(\omega)} - \frac{[P_0/P - \alpha + \alpha(\omega - \varepsilon - \mathcal{E})^{-1} G_{00}^{0-1}(\omega)]^2}{(1 - \alpha^2)(\omega - \varepsilon) - \Delta + \alpha^2 G_{00}^{0-1}(\omega)} \right\}, \quad (30)$$

where $\mathcal{E} = \sum_n M_{0n}^{AA}$.

The light wave energy absorbed per unit time per unit crystal volume is proportional to the imaginary part of the dielectric permittivity. Analysis of the formula (30) indicates that the character of intraband impurity absorption is primarily expressed by the behaviour of the state density, except for the case of an inband resonance close to the self-absorption frequency of a perfect crystal. When the excitation is strongly coupled to an impurity molecule, $\alpha \ll 1$, the absorption spectrum will exhibit, in addition to a peak at the exciton-transition frequency, a sharp spike at a frequency close to $\varepsilon + \Delta$. Conversely, under a weak coupling, $\alpha \approx 1$, we can expect a monotonic decrease in the absorption intensity when going away from the proper resonance frequency of a perfect crystal.

If the impurity level happens to be outside the exciton band the dependence of the absorbed energy on the position of the level in the spectrum is also different for the cases of a strong and a weak coupling. For example, for an isotopic impurity formula (30) describes the known Rashba effect,¹ an increase in the impurity absorption intensity as the impurity level approaches the exciton band. This effect will not be observed in the case of a strong coupling, since the impurity band intensity does not depend (up to terms $\sim \alpha^2$) on the distance between the impurity level and the exciton band (because the resonance guest-host interaction is small).

Detailed information on the features of the absorption spectrum of an impurity crystal could be obtained if we know the state density of a perfect crystal which has not yet been specified. Let us suppose that the exciton dispersion law is determined by a short range interaction, which is typical of crystals with small dipole transition strength, such as naphthalene. The parameter α is then equal to the ratio of the matrix element of the resonance interaction energy between the impurity and the neighbouring molecule of a host crystal M^{AB} to the same quantity for a pure crystal M^{AA} . The values of the functions $\text{Re } G_{00}^0$ and $\text{Im } G_{00}^0$ for a cubic crystal are calculated in the

nearest-neighbour-approximation in Ref. 7. These values are used here to calculate the shape of the absorption spectrum.

Figure 1 in which the absorption intensity I is plotted depending on the incident light frequency illustrates the impurity absorptions for various characteristics of an impurity molecule. The calculation was made for excitons with positive effective mass, $M^{AA} < 0$, at $\Delta/2|M^{AA}| = -2$, $X = (\omega - \varepsilon)/2|M^{AA}| + 3$.

The position of resonance at $\alpha = 0, 1$ is defined with high accuracy by the solution (19) in the zeroth approximation in α : $E_{\text{res}} = \varepsilon + \Delta$ and it is reflected in the absorption spectrum by a sharp spike whose intensity decreases with

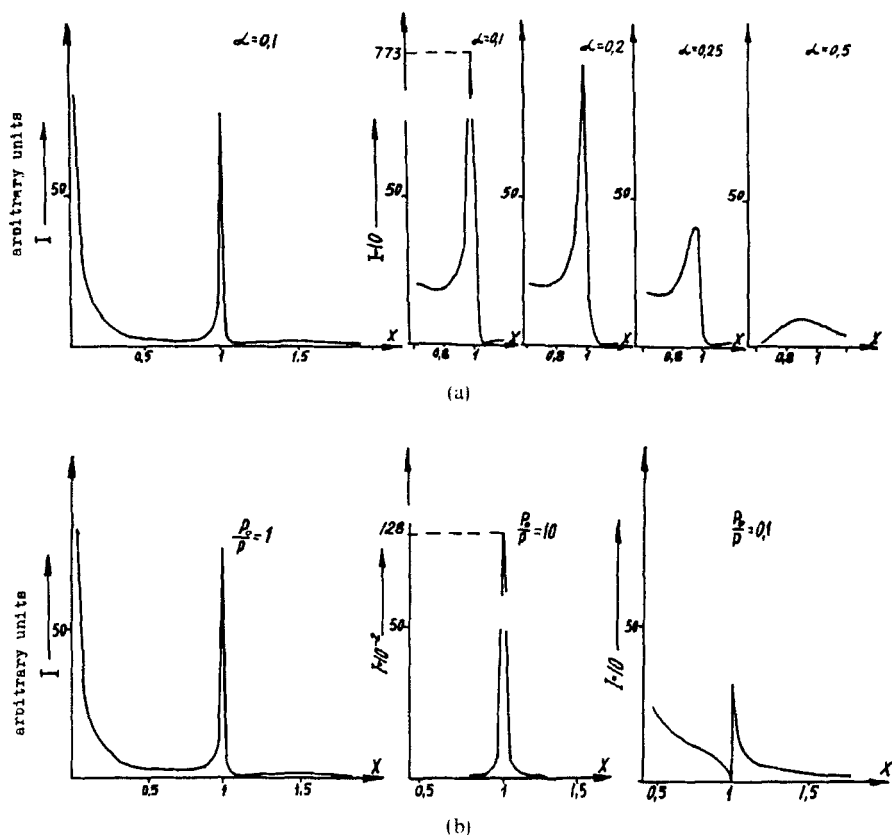


FIGURE 1 The in-band absorption spectrum of a three-dimensional impurity crystal. (a) The intensity and shape dependence of the in-band impurity resonance on the parameter $\alpha = M^{AB}/M^{AA}$ ($P_0/P = 1$). (b) The intensity and shape dependence of the in-band impurity resonance on the parameter P_0/P ($\alpha = 0.1$). P_0, P are the dipole transition moment between the ground and the exciton states for an impurity and a host molecule, respectively. X is the dimensionless light frequency. $X = 0$ corresponds to the exciton band bottom.

increasing coupling of the excitation on an impurity molecule with neighbours. At the same time the spike shifts to the long-wave-length side and broadens, so that even at $\alpha = 0.5$ the impurity in-band resonance becomes very weak against the background of the self-absorption band of a crystal. The intensity of the impurity spike increases in the absorption spectrum if the guest molecule has a larger value of the dipole transition moment as compared with the host molecules. For example, for the present values of the parameters and $P_0 = 10P$ the peak intensity increases by more than two orders. Conversely, as P_0 decreases, the absorption by the impurity level also decreases, and in addition in the neighbourhood of this level there appears sharp dip in the absorption spectrum, indicating the existence of an antiresonance in the system.

Figure 2 represents the data of similar calculations for a one-dimensional crystal which have been studied intensively over the past few years in connection with the discovery of some promising compounds with quasi-one-dimensional properties.

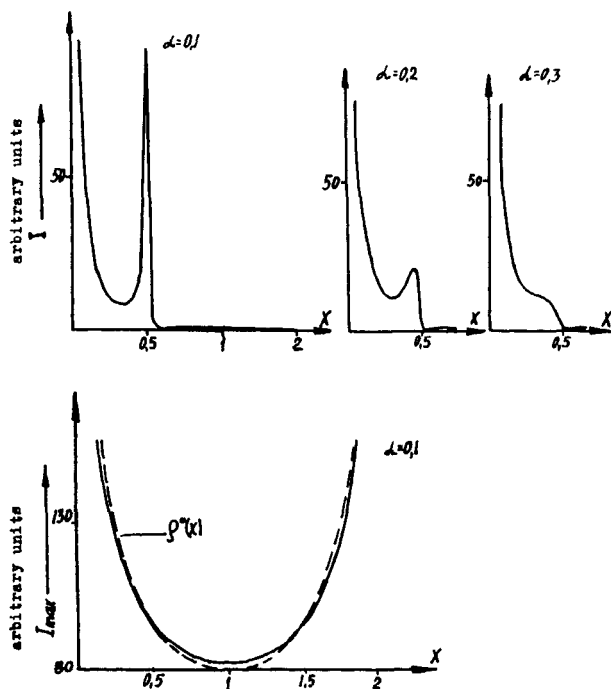


FIGURE 2 The intensity of the in-band absorption spectrum, I , and the intensity maximum of the absorption by the in-band impurity resonance, I_{max} , in a one-dimensional impurity crystal.

In the nearest-neighbour-approximation inside the band $\text{Re } G_{00}^0 = 0$, $-\text{Im } G_{00}^0 = [4(M^{AA})^2 - (E - \varepsilon)^2]^{-1/2}$. The frequency behaviour of the absorption intensity is given for $\Delta/2|M^{AA}| = -0.5$, $P_0/P = 1$, $X = (\omega - \varepsilon)/2|M^{AA}| + 1$. As seen from the figure, the main qualitative features of the impurity in-band resonance, are nearly the same as observed for the three dimensional crystal.

For the same values of the parameters the dependence of the intensity of the resonance absorption peak, I_{max} , is given in Fig. 2. For comparison, the state density of a perfect crystal is shown by a dotted line. We can see that the behaviour of $\rho^0(\omega)$ is well expressed by the dependence I_{max} for frequencies not too close to the exciton band bottom.

CONCLUSIONS

The above discussion enables us to conclude that for impurities whose resonance interaction with crystal molecules is little different from the same interaction between the host molecules or greater than the latter, the absorption into the exciton band has a maximum only at the self-absorption frequency of a crystal and decreases rapidly when going away from it. In this case the frequency behaviour of the in-band absorption intensity is weakly dependent on the other parameters of an impurity molecule and is of monotonic character. The picture of the intraband absorption spectrum is different if the impurity at given transition frequency is characterized by a small resonance interaction with its environment. At the impurity levels which happen to be inside the band there occurs a resonance absorption expressed by a sharp spike which can be detected experimentally. The measurement of the resonance absorption peak half width which is equal to

$$2\pi\alpha^2\rho^0(\omega)|G_{00}^0(\omega)|^{-2}|_{\omega=\varepsilon+\Delta} \quad (31)$$

enables estimates of the magnitude of the guest-host resonance interaction as well as estimates of the state density of a perfect host crystal at the resonance point. Additional information on the state density can be derived from a study of the frequency behaviour of the in-band resonance absorption intensity which is expressed by a dependence inversely proportional to (31) when we are far away from the exciton transition frequency for a pure crystal.

An example of the system suitable for these experiments is the impurity crystal of naphthalene and its deuterio-substituted derivatives. For the lowest electronic transition in combination with the vibrational excitation the impurity molecule of 1-fluorine naphthalene, 2-fluorine naphthalene has a frequency which may fall in the exciton band of crystalline naphthalene (for the pure electronic transition the frequencies are $\sim 100 \text{ cm}^{-1}$ and $\sim 150 \text{ cm}^{-1}$

below the A-band edge in naphthalene for 1- and 2-fluorine naphthalene, respectively). The vibronic excitation of an impurity is characterized by the weak resonance interaction with the crystal molecules, so that the case of a strong coupling of the excitation with the impurity is realized. Single deuteration of naphthalene shifts the exciton band approximately by $15\text{--}20\text{ cm}^{-1}$, leaving the position of the impurity level unchanged. Under complete deuteration the lowest singlet excitation energy increases by $\sim 115\text{ cm}^{-1}$. Under certain experimental conditions the resonance absorption peak at the vibronic impurity level could be observed both outside and inside the exciton band. The in-band impurity resonance would be additionally broadened by the resonance guest-host interaction. Besides, by changing the degree of deuteration we can shift the impurity level relative to the host and perform "probing" the exciton band from measurements of the half-width and the intensity of the impurity absorption peak. This study is to be made at low temperature, to enable a separation of the broadening of the spectral impurity absorption line due to phonons and due to resonance interactions. In this connection, it is worth mentioning Ref. 8 where the state density was established by studying isotopically impure crystals of naphthalene, as well as Refs. 9 and 10 which enabled more detailed characteristics of the exciton band in this crystal derived from a study of local excitons.

Experimental study of the present strongly coupled impurity excitations with reference to intraband absorption at temperatures close to 0°K and comparison with theoretical estimates made for an appropriate crystal model can produce additional information on the energy spectrum, the magnitude of the resonance interaction in a pure crystal and the resonance guest-host interaction both for naphthalene and other crystals.

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References

1. E. I. Rashba, *Optika i Spektroskopiya*, **2**, 568 (1957); *Fiz. tverd. Tela*, **4**, 3301 (1962). D. P. Craig and M. R. Philpott, *Proc. Roy. Soc. (London)*, **A290**, 583, 602 (1966); **A293**, 213 (1966). B. S. Sommer and J. Jortner, *J. Chem. Phys.*, **50**, 187, 822 (1969).
2. R. E. Merrifield, *J. Chem. Phys.*, **38**, 920 (1963).
3. V. M. Agranovich, *The Theory of Excitons*, Nauka, M., 1968.
4. V. I. Sugakov, *Optika i Spektroskopiya*, **21**, 574 (1966).
5. I. M. Lifshitz, *Zh. eksper. teor. Fiz.*, **17**, 1017, 1076 (1947).
6. D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics*, Nauka, M., 1971.

7. T. Wolfram and J. Callaway, *Phys. Rev.*, **130**, 2207 (1963).
8. N. V. Rabin'kina, E. I. Rashba, and E. F. Sheka, *Fiz. tverd. Tela*, **12**, 3579 (1970).
9. D. Hanson, R. Kopelman, and G. W. Robinson, *J. Chem. Phys.*, **51**, 212 (1969).
10. N. I. Ostapenko, V. I. Sugakov, and M. T. Shpak, *Phys. stat. sol. (b)*, **45**, 729 (1971); Local excitons in molecular crystals, in *Excitons in Molecular Crystals*, Naukova dumka, Kiev, 1973.