Three-particle complex consisting of a bound state of a fully symmetrical phonon and an impurity exciton

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The three-particle impurity + exciton + phonon complexes in the spectrum of crystalline napthalene are investigated experimentally and theoretically. Calculation leads to a series of bound states of the phonon with the impurity exciton. Two bands belonging to this series are observed in experiment.

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In molecular crystals in which the width of the exciton band is less than the frequency ν_0 of the intramolecular phonon, the spectrum of the vibronic (i.e., the electron-vibrational) excitations can be regarded as a spectrum of two interacting quasiparticles—an exciton and a phonon.[1,2] The interaction in the final state, i.e., the interaction between an optically produced exciton and phonon determines the structure of the spectrum, namely, the existence of bound (single-particle) states, the distribution of the intensities and the polarization of the bands in the absorption spectrum, etc. The law governing the exciton-phonon interaction depends essentially on the phonon symmetry; it is of particular interest for fully symmetrical (FS) a_g phonons.

Impurity crystals can acquire three-particle impurity + exciton + phonon complexes. We have investigated an impurity-vibrational complex with participation of a fully symmetrical phonon in crystalline napthalene. This is apparently the first investigation of such a complex. Calculation has shown that the spectrum of the bound states includes a rapidly converging series with a zeroth term that deviates from the regular series. The successive terms of the series correspond to states in which the exciton remains localized predominantly at the impurity site, and the phonon moves progressively away from it. It is convenient to imagine them as bound states of a phonon with an impurity exciton. We have observed in experiment two bands belonging to this series.

For an isotopic impurity, the Hamiltonian of the system, in accordance with the dynamic theory of vibronic spectra,[1] includes the following terms:

$$H_o = \sum_{n\alpha \neq m\beta} M_{n\alpha m\beta} a_{n\alpha}^+ a_{m\beta} + \nu_o \sum_{n\alpha} b_{n\alpha}^+ b_{n\alpha} , \tag{1}$$

$$H_{ex-imp} = \Delta_{ex} a_o^+ a_o , \qquad H_{ph-imp} = \Delta_{ph} b_o^+ b_o , \tag{2}$$

$$H_{ex-ph} = \Delta \sum_{n\alpha} a_{n\alpha}^+ a_{n\alpha} b_{n\alpha}^+ b_{n\alpha}$$

$$+ \gamma^2 \sum_{n\alpha \neq m\beta} M_{n\alpha m\beta} a_{n\alpha}^+ a_{m\beta} (b_{n\alpha}^+ b_{m\beta} + b_{m\beta}^+ b_{n\alpha} - b_{n\alpha}^+ b_{n\alpha} - b_{m\beta}^+ b_{m\beta}) . \tag{3}$$

Here $a_{n\alpha}$ and $b_{n\alpha}$ are the exciton and phonon amplitudes, the subscripts $n\alpha$ number the cells and the molecules inside the cells, and the subscript zero corresponds to the impurity site. In the last operator, Δ is the shift of the vibrational frequency following electron excitation of the molecule, and γ is the dimensionless constant of the linear electron-phonon coupling; for the a_g vibration with $\nu_0 = 764$ cm^{-1} in napthalene[3] we have $\Delta = -57$ cm^{-1} and $\gamma^2 = 0.20$. The last term in H_{ex-ph} is peculiar to fully symmetrical phonons; it is precisely this term which makes it possible, as a result of exciton-phonon interaction for the dispersionless fully symmetrical phonons to move over the crystal. For an impurity of napthalene (d_0) in octadeuteronapthalene (d_8) the isotopic shifts for the exciton and phonon are $\Delta_{ex} = -115$ and $\Delta_{ph} = 69$ cm^{-1}, respectively.

The numerical calculation was carried out for a bounded flat grid in the approximation of the interaction of the nearest translationally-nonequivalent neighbors; the matrix element of this interaction is $M = 22.5$ cm^{-1}. We calculated the levels to which optical transitions are allowed by symmetry. The calculation does not contain arbitrary parameters. The levels will henceforth be reckoned from the frequency $\epsilon_0 + \nu_0$, where ϵ_0 is the electronic term (i.e., the center of gravity of the exciton band).

There is a level -111 cm^{-1}, to which we ascribe a quantum number $m = 0$. A configuration with an exciton and a phonon at the impurity site predominates in the ψ function of this level; this configuration corresponds to a "potential" energy $-115 + 69 - 57 = -103$ cm^{-1}. The contribution of this configuration to the normalization integral is $\approx 93\%$. Since only superimposed configurations (ex-

citon and phonon on a single site) contributes to the band intensity, the intensity of this band should be high.

There is also a dense series of levels $m = 1,2,3,\ldots,\infty$, which converges rapidly in the high-frequency direction. The binding energy is ≈ 2 cm^{-1} and the energy of the $m = 1$ level is $- 132$ cm^{-1}. The configurations that predominate in the ψ function of the mth level are those with an exciton at the impurity site and with a phonon on the mth configuration sphere ("potential" energy $- 115$ cm^{-1}). Their contribution to the normalization integral at $m = 1-3$ is approximately 80%. Owing to the decreased overlap of the wave functions of the exciton and the phonon, the intensity decreases rapidly with increasing m. The position of the band $m = 0$ drops out completely from the regular series; this is due to the large positive value of Δ_{ph}.

The low-temperature (4.2 K) absorption spectra of the d_8 crystals with d_0 impurity in the a component were obtained with a DFS-13 spectrograph having a linear dispersion 2 Å/mm. The crystals were grown from the melt in thin-layer cells. Thicknesses ranged from 3 to 10 μm. The $\kappa(\omega)$ curves shown in Fig. 1 were obtained by photometry of one photographic plate for each impurity crystal. The Photometry results were reproducible within 3%. The error in the background value κ for different photographic plates and crystals of different thicknesses did not exceed 10%.

It is seen from Fig. 1 that a band whose intensity increases with the impurity concentration is located precisely in the region of the calculated position of
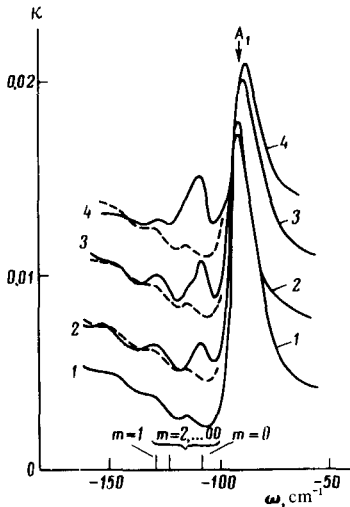

FIG. 1. a) Absorption component of napthalene d_8 crystal with a d_0 impurity at 4.2 K in the region of the vibronic transition with a fully symmetrical phonon 764 cm^{-1}. The different curves correspond to the following values of the concentration d_0: 1—10%; 2—2%; 3—5%; 4—10%. The ordinates of the three last curves are shifted upward without change in scale; the dashed curves duplicate the absorption of the solvent. The arrow A_1 marks the calculated position of the single-particle of the vibronic band of the solvent. The calculated positions of the impurity bands are indicated above the abscissa scale.

$m = 0$ level. More difficult to separate is the second band, which corresponds to levels $m \gtrsim 1$. In curve 2 it is of the same level as the background, but in curve 3 it is clearly seen. According to calculation, it should be approximately one-third as weak as the $m = 0$ band; the experimental data do not contradict this estimate. On curve 4, this band becomes noticably broader. This is natural since the concentration broadening should manifest itself more strongly for states with a larger radius.

Impurity vibronic spectra with participation of nonfully-symmetrical phonons were investigated earlier. [1,4,5] For nonfully-symmetrical phonons, Eq. (3) contains only the first term. As a result, the phonon is at rest, its position is a quantum number that labels the levels, and each configuration corresponds to two impurity bands located on opposite sides of the intrinsic vibronic M band. In our calculation, the decisive factor is the delocalization of the fully symmetrical phonons. Even in the state $m = 0$, where the delocalization is minimal, failure to take the delocalization into account leads to a tremendous error in the energy, 15 cm^{-1}. One can hardly expect distinct impurity bands to appear, on the high-frequency side of the A_1 band, owing to the large width of the A_1 band and the proximity of the two-particle continuum.

Composite vibronic transitions with participation of one or two fully symmetrical phonons can be treated in analogy with the impurity-vibronic complex. An analysis of such transitions has led to good results. We regard this advance as a direct experimental confirmation of the dynamic theory; this confirmation allows us to proceed to a systematic quantitative description of the vibronic spectra.

We note that the spectra of semiconductors also reveal three-particle complexes consisting of a neutral donor (acceptor) and a phonon[6]; there, however, only one term of the series of bound states has been actually observed so far (for a review see[7]).

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