

# Bound states of an exciton and a fully symmetrical phonon near defects of a naphthalene crystal

I. V. Brovchenko, L. L. Valkunas,<sup>1)</sup> G. B. Vektaris,<sup>1)</sup> N. I. Ostapenko, and M. T. Shpak

*Institute of Physics, Academy of Sciences of the Ukrainian SSR*

(Submitted 3 May 1983; resubmitted 9 November 1983)

Pis'ma Zh. Eksp. Teor. Fiz. **39**, No. 3, 105–107 (10 February 1984)

Bound and quasilocalized three-particle complexes defect + exciton + fully symmetrical (FS) phonon in the absorption spectra of naphthalene crystals with impurities consisting of heterocyclic compounds in the region of the vibronic transition  ${}^1A_{1g} \rightarrow {}^1B_{2u}a_g$  are observed experimentally and calculated theoretically.

Based on a dynamic theory,<sup>1</sup> vibronic states of molecular crystals are viewed as bound and dissociated states of two quasiparticles: an exciton and an intramolecular phonon. Three-particle complexes can appear in impurity crystals. In addition, the energy spectrum of such crystals must depend on the mutual arrangement of the defective molecules of the crystal and of the impurities, as well as the symmetry of the phonons.<sup>2,3</sup>

This paper is concerned with the theoretical and experimental analysis of the absorption spectra of naphthalene crystals with impurities consisting of heterocyclic compounds (benzofuran, indole, thionaphthene) in the region of the vibronic transition  ${}^1A_{1g} \rightarrow {}^1B_{2u}a_g$ . This analysis, performed for the first time, is based on the model of a local center,<sup>4</sup> which is associated with the transitions in the impurity-perturbed naphthalene molecules. In contrast to problems on localization of the exciton near a nonfully symmetrical (NS) phonon,<sup>4–6</sup> for a FS phonon it is necessary to take into account the motion of the exciton and of the intramolecular phonon. The Hamiltonian of this system has the form

$$H = H_0 + H_{ex - imp} + H_{ex - ph}^{(1)} + H_{ex - ph}^{(2)}, \quad (1)$$

where

$$H_0 = \epsilon_0 \sum_{n\alpha} a_{n\alpha}^+ a_{n\alpha} + \sum_{n\alpha \neq m\beta} M_{n\alpha, m\beta} a_{n\alpha}^+ a_{m\beta} + \nu_0 \sum_{n\alpha} b_{n\alpha}^+ b_{n\alpha}, \quad (2)$$

$$H_{ex - imp} = \Delta_0 a_0^+ a_0 + \Delta a_1^+ a_1, \quad (3)$$

$$H_{ex - ph}^{(1)} = \Delta_\nu \sum_{n\alpha} a_{n\alpha}^+ a_{n\alpha} b_{n\alpha}^+ b_{n\alpha}, \quad (4)$$

$$H_{ex - ph}^{(2)} = \gamma^2 \sum_{n\alpha \neq m\beta} M_{n\alpha, m\beta} a_{n\alpha}^+ a_{m\beta} \times (b_{n\alpha}^+ b_{m\beta} + b_{m\beta}^+ b_{n\alpha} - b_{n\alpha}^+ b_{n\alpha} - b_{m\beta}^+ b_{m\beta}). \quad (5)$$

Here  $a_{n\alpha}^+$  ( $a_{n\alpha}$ ) and  $b_{n\alpha}^+$  ( $b_{n\alpha}$ ) are the exciton and phonon creation (annihilation) operators for an excitation at the  $n\alpha$ th molecule. The index 0 indicates an impurity site, and the index 1 indicates a defect site. The energy  $\epsilon_0$  is the energy of the electronic term of the molecule in the crystal,  $\nu_0$  is the frequency of FS vibrations in the ground state;  $M_{n\alpha, m\beta}$  is the matrix element of the resonant interaction between the  $n\alpha$  and  $m\alpha$  molecules,  $\Delta_0$  and  $\Delta$  are the shift of the energy of the electronic excitation of the impurity and of the defect,  $\Delta_\nu$  is the shift of the vibrational frequency of the molecule accompanying the electronic excitation, and,  $\gamma^2$  is the linear electron-phonon coupling constant. Since the impurity term is situated far from the region being investigated ( $\Delta_0 \gg \Delta$ ,  $M_{n\alpha, m\beta}$ ), while the SF phonon is nondispersive, the probability of localization of both the exciton and phonon on the impurity site can be ignored. For naphthalene,  $\epsilon_0 = 31557 \text{ cm}^{-1}$ ,  $\nu_0 = 764 \text{ cm}^{-1}$ ,  $\Delta_\nu = -57 \text{ cm}^{-1}$ ,  $\gamma^2 = 0.2$ ; for indole,  $\Delta = -72 \text{ cm}^{-1}$ .

The Hamiltonian (1) was diagonalized in two stages. The zeroth-order approximation was obtained without the term  $H_{\text{ex-ph}}^{(2)}$ .<sup>4</sup> The solution was then used to solve the problem numerically on a two-dimensional naphthalene lattice (seven configurational spheres are included) in the nearest-neighbor-interaction approximation, taking into account the term  $H_{\text{ex-ph}}^{(2)}$ , which was assumed to be appreciable in this case. Thus the calculation is performed without any arbitrary parameters.

The calculation for the indole impurity gives an entire series of new levels. The level farthest away from the bottom of the band of two-particle states ( $\nu_D = 32240 \text{ cm}^{-1}$ ) is described primarily by the state when the exciton and intramolecular phonon are localized on a defect, which we shall denote by EPD; we shall denote by ED the state with the exciton localized primarily on the defect and with a phonon moving in the vicinity; and, we shall denote the state with the combined configuration of the exciton and phonon predominating by EP.

We shall examine the results obtained for the system naphthalene + indole. The spectra were recorded on a DFS-13/2 spectrograph with a FÉP-2 photo-attachment (dispersion  $2 \text{ \AA/mm}$ ). Single-crystal petals  $10 \mu\text{m}$  thick were grown by sublimation. Figure 1 shows the absorption spectrum of a single crystal of naphthalene with an indole impurity in the region of the vibronic transition with the FS phonon. The spectrum of pure naphthalene, where the  $A_2$  band corresponds to the bound state of the exciton and the FS phonon, for which  $\nu_{A_2} - \nu_D = -12 \text{ cm}^{-1}$ , is given for comparison. It is evident that the introduction of the indole impurity leads to the appearance of new bands in the spectrum (they are noted by arrows in the figure). The intensity of these bands increases with increasing impurity concentration (from 0.3 to 5%). The computed positions of the new bands agree well with the experimental data.<sup>2)</sup> For example, for indole, the calculation gives  $\epsilon_{\text{EPD}}^T = -50 \text{ cm}^{-1}$  (the reading extends from  $\nu_D$ ), while experimentally  $\epsilon_{\text{EPD}}^e = -52 \text{ cm}^{-1}$ . For the ED and EP series, there are bands in the experiment that correspond to the envelope of the computed bands, since our technique does not permit resolving bands with an interval of  $1\text{--}2 \text{ cm}^{-1}$ . For example, in the case of indole  $\epsilon_{\text{ED}}^T = -(17, 15, 14, 13, 12) \text{ cm}^{-1}$ , while  $\epsilon_{\text{ED}}^e = -17 \text{ cm}^{-1}$ ,  $\epsilon_{\text{EP}}^T = -(8, 7) \text{ cm}^{-1}$ ,  $\epsilon_{\text{EP}}^e = -8 \text{ cm}^{-1}$ . Analogous results were obtained for two other impurities: thionaphthene and benzofuran.

We note the characteristics of the ED and EP states. The ED states are local

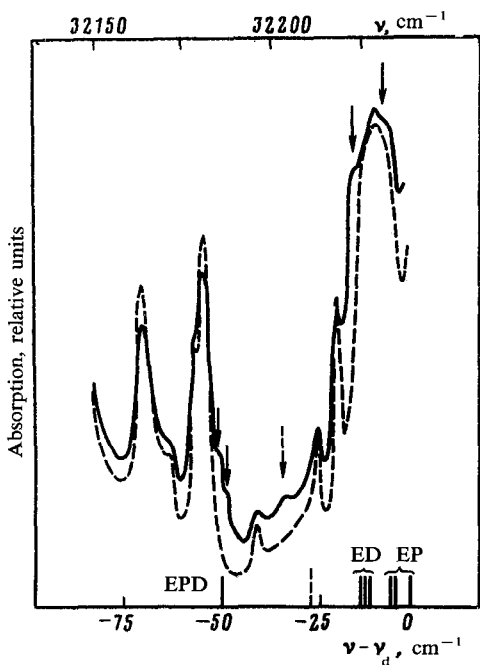


FIG. 1. Absorption spectrum of a single-crystal of naphthalene with an indole impurity in the region of the vibronic transition with FS phonon  $707 \text{ cm}^{-1}$  ( $C = 1\%$ ,  $T = 4.2 \text{ K}$ ). The dashed line shows the spectrum of a pure naphthalene crystal with approximately the same thickness; the ordinates are arbitrary. The bands observed on the long-wavelength side from the  $A_2$  band correspond to a weak electronic-vibrational transition in naphthalene, amplified due to the considerable thickness of the specimen. The arrows denote the experimentally observed bands of local excitons, while the bars on the frequency scale denote the computed bands.

states, as indicated by the behavior of the amplitudes of their wave functions. The calculation shows that for ED, for example, the state with  $\epsilon_{\text{ED}} = -17 \text{ cm}^{-1}$ , the wave function at the lattice sites decreases for the first, third, and fourth configuration spheres as 0.3, 0.1, and 0.004, respectively.

In contrast to ED states, the EP states are quasilocal, since they fall within the  $A_2$  band, whose width is  $30 \text{ cm}^{-1}$ . To confirm that they can be observed the half-width of the quasilocal levels was calculated in the band-structure model with a density of states of the form  $\sqrt{\nu_{A_2}^2 - \nu_{\text{EP}}^2}$  ( $\nu_{A_2}$  is the bottom of the  $A_2$  band, and  $\nu_{\text{EP}}$  is the position of the EP level). Such estimates give half-widths of  $\sim 1\text{--}2 \text{ cm}^{-1}$  for EP levels close to the bottom of the  $A_2$  band.

The good agreement between the theoretical and experimental data shows that the presence of a fine structure in the vibronic spectra of these crystals is related to the interaction of two quasiparticles (exciton and intramolecular phonon) near the defect. This confirms the dynamic theory<sup>1</sup> and the correctness of the model of local excitons<sup>4</sup> in the systems investigated. The quasilocal states of three-particle complexes were observed for the first time, in these studied.

We thank É. I. Rashba and V. I. Sugakov for discussions and for valuable remarks.

<sup>1</sup>Institute of Physics of the Academy of Sciences of the Lithuanian SSR.

<sup>2</sup>The band marked by the dashed arrow in Fig. 1 is apparently related to the more complicated structure of the center due to the perturbation of several molecules in the crystal by the impurity molecule.<sup>7</sup> This explanation agrees qualitatively and quantitatively with the analogous structure in the region of the NS phonon.<sup>5</sup>

---

<sup>1</sup>É. I. Rashba, Zh. Eksp. Teor. Fiz. **50**, 1164 (1966); **54**, 542 (1968) [Sov. Phys. JETP (*SIC*); **27**, 292 (1966)].

<sup>2</sup>V. L. Broude, É. I. Rashba, and E. F. Sheka, *Spektroskopiya molekulyarnykh éksitonov* (Spectroscopy of Molecular Excitons), Énergoizdat, Moscow, 1981.

<sup>3</sup>T. A. Krivenko, A. V. Leïderman, É. I. Rashba, and E. F. Sheka, *Pis'ma Zh. Eksp. Teor. Fiz.* **25**, 538 (1977) [JETP Lett. **25**, 503 (1977)].

<sup>4</sup>N. I. Ostapenko, V. I. Sugakov, and M. T. Shpak, in: *Éksitonyv molekulyarnykh kristallakh* (Excitons in Molecular Crystals), Kiev, 1973, p. 92.

<sup>5</sup>N. I. Ostapenko and M. T. Shpak, *Pis'ma Zh. Eksp. Teor. Fiz.* **16**, 513 (1972) [JETP Lett. **16**, 365 (1972)].

<sup>6</sup>L. L. Valkunas and V. I. Sugakov, *Litovskii Fiz. sbornik* **15**, 647 (1975).

<sup>7</sup>I. V. Brovchenko, L. L. Balkynas, N. I. Ostapenko, S. G. Tret'yakov, and M. T. Shpak, *Fiz. Tverd. Tela* **25**, 465 (1983) [Sov. Fiz. Solid State **25**, 262 (1983)].

Translated by M. E. Alferieff

Edited by S. J. Amoretty