

Constants of the deformation potential of exciton-phonon interaction in naphthalene

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The constants of the exciton-phonon interaction of deformed naphthalene crystals are determined, for the first time ever, from their absorption spectra.

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Notwithstanding the decisive role of exciton-phonon interactions in many physical processes,^[1,2] and the large number of theoretical papers on the influence of this interaction on the properties of crystals, no numerical values of the exciton-phonon interaction constants are known for a single molecular crystal. In this paper, using an original procedure of producing strains, we obtain the constants of the exciton-phonon interaction of the naphthalene crystal.

Principles of the method. The method is based on an investigation of the optical spectra of naphthalene single crystals on an anisotropic substrate.^[3] By varying the angle between the crystal axes and the substrate it is possible to produce strains in different directions. Knowing the coefficients of thermal expansion of the crystals, we can determine the strain tensor. By plotting the dependence of the position of the electron bands on the components of the strain tensor, we can obtain the exciton-phonon interaction constants.

Theoretical premises. The main parameters that determine the behavior of the Frenkel excitons are the following^[1,2]: 1) D_α —the change of the static interaction between a molecule situated in position α with the environment as the molecule goes over into the excited state (in undeformed crystals with identical molecules we have $D_\alpha = D$); 2) $M_{n\alpha, m\beta}$ —the resonant interaction between the molecules in the positions $n\alpha$ and $m\alpha$ (in an undeformed crystal we have $M_{n\alpha, m\beta} = M_{n\alpha, m\beta}^0$). In the presence of a strain, in the approximation linear in the strain tensor u_{ik} , we can write

$$\delta D_\alpha = D_\alpha - D = \frac{\partial D_\alpha}{\partial u_{ik}} u_{ik} \quad (1)$$

$$\delta M_{n\alpha, m\beta} = M_{n\alpha, m\beta} - M_{n\alpha, m\beta}^0 = \frac{\partial M_{n\alpha, m\beta}}{\partial u_{ik}} u_{ik} \quad (2)$$

The quantities $\partial D_\alpha / \partial u_{ik}$ and $\partial M_{n\alpha, m\beta} / \partial u_{ik}$ are the sought constants. Owing to the strong anisotropy of the intermolecular interaction in naphthalene,^[4,5] the quantities D_α and $M_{n\alpha, m\beta}$ are more sensitive to changes of the distance between the molecules in the ab plane than to changes of the distance between the planes. We shall therefore assume that they depend only on the components of the strain tensor u_{xx} ,

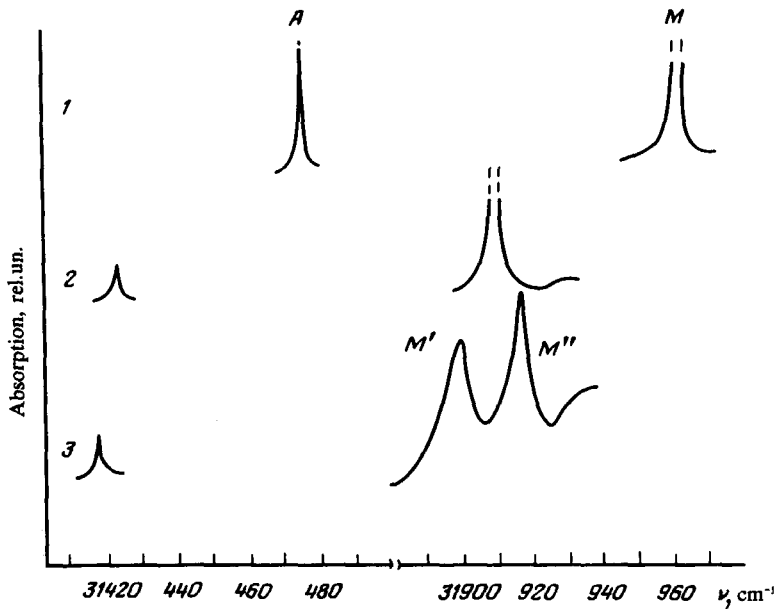


FIG. 1. Comparison of the absorption spectra of naphthalene crystals: free crystal (1) and crystal deformed on an indole substrate (2)— $\phi=0^\circ$ and (3)— $\phi=27^\circ$.

u_{xy} , and u_{yy} (the axes x and y are directed respectively along the a and b axes of the crystal).

In the experiment we investigated naphthalene crystals whose area and thickness were much smaller than those of the substrate. In this case it could be assumed that when the crystal was cooled from 300 to 4.2 K the change in the crystal dimensions followed strictly the change of the substrate dimensions. Then the naphthalene-crystal strain vector is equal to

$$\mathbf{u}_{\parallel}(\mathbf{r}) = \mathbf{u}_{s\parallel}(\mathbf{r}) - \mathbf{u}_{n\parallel}(\mathbf{r}), \quad (3)$$

where $\mathbf{u}_{s\parallel}$ and $\mathbf{u}_{n\parallel}$ are the projections of the displacement vectors of the points of the substrate and the naphthalene on the interface during the course of cooling of the system.

Using Eq. (3) and the linear dependence of $\mathbf{u}_{s\parallel}$ and $\mathbf{u}_{n\parallel}$ on the coordinates, we obtain the following expressions for the components of the strain tensor:

$$u_{xx} = \alpha_s - \alpha_n + (\beta_s - \alpha_s) \sin^2 \phi, \quad (4)$$

$$u_{xy} = (\beta_s - \alpha_s) \frac{\sin 2\phi}{2}, \quad (5)$$

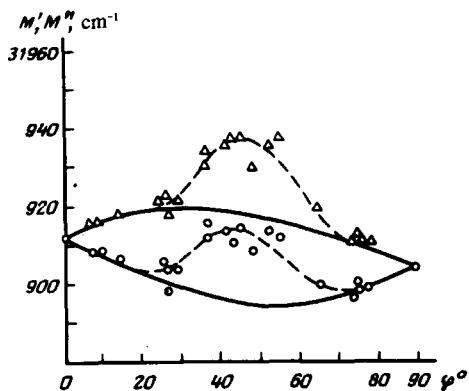


FIG. 2. Comparison of the theoretical (solid curves) and experimental frequencies of the positions M' (circles) and M'' (triangles) of the components of the split M absorption band of naphthalene and indole as functions of the angle ϕ between the axes.

$$u_{yy} = \beta_s - \beta_n - (\beta_s - \alpha_s) \sin^2 \phi, \quad (6)$$

where ϕ is the angle between the axes of the substrate and naphthalene single crystals, α_s, β_s , and α_n, β_n are the relative thermal expansions along the axes x and y of the substrate and naphthalene, respectively, in the case of cooling from 300 to 4.2 K.

The dependence of the position of the excitonic A and B bands on the strain is represented by formula (8) of ⁽⁶⁾, while that of the molecular M band is represented by formula (10) of ⁽⁶⁾ and is determined by the three parameters, $\delta D_1, \sigma D_2$, and δM . In the calculation we took into account the changes, in the course of deformation of only the maximal matrix elements $M_{0,(\pm a+b)/2}$, which take into account the interaction between the nearest non-equivalent neighbors. Therefore

$$\delta M = \frac{1}{2} \left(\delta M_{0, \frac{a+b}{2}} + \delta M_{0, \frac{-a+b}{2}} \right). \quad (7)$$

The procedure for calculating the bands is shown in ⁽⁷⁾.

Measurements. The substrate was chosen to be an indole crystal, which has rhombic symmetry.^[8] The naphthalene and indole single crystals were grown by the sublimation method. The naphthalene, less than a micron thick, was deposited on indole several microns thick. To determine the constants of the deformation potential, we measured the absorption spectra of the naphthalene in the region of the 00 and M bands. The spectra were registered on a DFS-13/4 spectrograph. The scatter of the resonance frequencies for different samples at small angles between the axes ($0^\circ < \phi < 20^\circ$ and $70^\circ < \phi < 90^\circ$) was of the order of 3–4 cm^{-1} . Evidence favoring the homogeneity of the deformation is the small half-width of the A band ($\approx 1 \text{ cm}^{-1}$).

Measurement of the relative elongation was carried out with a specially constructed cryostat in the temperature interval 295–77 K.

The following numerical values were obtained:

$$\text{for indole } \alpha_s = -0,015; \beta_s = -0,028, \quad (8)$$

$$\text{for naphthalene } \alpha_n = -0,0215; \beta_n = -0,0085. \quad (9)$$

The positions of the bands in the spectrum of the naphthalene deformed on the indole, meaning also its deformation, changed little with changing temperature from 77 to 4.2 K (the frequency difference is 3–4 cm^{-1}), so that relations (8) and (9) can be approximated down to $T=4.2$ K.

Figure 1 shows the absorption spectra of naphthalene crystals on an indole substrate for the angles $\phi=0$ and 27° and for the unstressed sample. In the deformed crystal, the spectrum is displaced by $\approx 50 \text{ cm}^{-1}$ towards the longer wavelengths, and a change takes place in the Davydov splitting. At $\phi \neq 0^\circ$, a splitting of the M band into M' and M'' is observed, and its reason is the lowering of the crystal symmetry.^[6,3] At large angles ($\phi \sim 45^\circ$) the splitting reaches 24 cm^{-1} . The split bands have fine structure (not shown in Fig. 1) of as yet unknown origin.

Values of the deformation-potential constants. Using the experimental data on the positions of the exciton A band and M bands of the naphthalene on indole at $\phi=0, 14,$ and 90° , we calculated by means of formulas (8) and (10) of^[6] the values of $\delta D_1, \delta D_2$ and δM . Next, using formulas (4)–(9) we calculated the components of the strain tensor to corresponding values of ϕ . Substituting the values of $\delta D_1, \delta D_2, \delta M, u_{xx}, u_{xy}, u_{yy}$ in (1)–(2), we obtain the constants of the strain potential

$$\begin{aligned} \frac{\partial D_a}{\partial u_{xx}} &= 4,2 \cdot 10^3 \text{ cm}^{-1} \quad ; \quad \frac{\partial D_a}{\partial u_{xy}} = \frac{\partial D_a}{\partial u_{yx}} = (-1)^a 1,9 \cdot 10^3 \text{ cm}^{-1} \quad ; \quad \frac{\partial D_a}{\partial u_{yy}} \\ &= 3,5 \cdot 10^3 \text{ cm}^{-1} \quad , \end{aligned} \quad (10)$$

$$\frac{\partial M}{\partial u_{xx}} = -2,7 \cdot 10^2 \text{ cm}^{-1} \quad ; \quad \frac{\partial M}{\partial u_{yy}} = -2,2 \cdot 10^2 \text{ cm}^{-1}. \quad (11)$$

The relations (10) and (11) were used to determine the position of the M band for other angles ϕ . A comparison of the theoretical and experimental values is shown in Fig. 2. Good agreement is observed, with the exception of the angle region $30^\circ < \phi < 60^\circ$ where the shift of the spectrum is less than predicted by the theory. The discrepancy can be attributed to poor contact between the crystals when the axes of the crystal and the substrate are strongly out of alignment.

Relations (10) and (11) can be used in various studies of effects of exciton-phonon interaction in naphthalene.

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