

Singularities of absorption spectra of directionally deformed naphthalene crystals

N. I. Ostapenko, G. Yu. Khotyaintseva, M. P. Chernomorets, and M. T. Shpak

Physics Institute, Ukrainian Academy of Sciences

(Submitted January 29, 1976)

Pis'ma Zh. Eksp. Teor. Fiz. **23**, No. 6, 377–380 (20 March 1976)

It is shown that directed compression of naphthalene crystals causes splitting of weakly polarized bands to be observed in the absorption spectrum. This can be attributed to a lowering of the crystal symmetry by the deformation. The exciton bands remain single in this case.

PACS numbers: 61.50.Sa, 78.65.+t

Investigations of deformed molecular crystals yield information on the dependence of their energy spectra on the intermolecular distances and the orientation of the molecules, on the exciton-phonon interaction, etc. The optical spectra of such crystals have yielded many interesting results. In particular, a study was made of the exciton-band parameters.^[1-4] In this case, the most effective turned out to be the deformations produced by cooling crystals that were in optical contact with quartz. However, these deformations produce limited results, for if they are homogeneous, then the symmetry of the crystal remains unchanged. On the other hand, a change of the symmetry of crystals such as anthracene and naphthalene can lead to appreciable changes in their spectra.^[5]

We present here the results of an experimental investigation of the absorption spectra of pure directionally-deformed single crystals of naphthalene in polarized light at $T = 4.2^\circ\text{K}$. We investigated the regions of the pure electronic transition and of the vibronic transitions with participation of non-fully-symmetrical oscillations. We used for the investigations naphthalene films (developed ab plane) up to $1\ \mu$ thick, grown by sublimation. The deformation was produced, as before, by placing the investigated crystal in optical contact with the substrate at room temperature, followed by cooling to liquid-helium temperature. The innovation was in the choice of substrate. For the sample symmetry to change, the substrate dimensions should change isotropically when the temperature is lowered, and by a large amount. Such properties are possessed by molecular crystals, and indole was therefore used for this purpose.¹⁾ By varying the angle between the crystallographic axes of the substrate and the sample, we could vary the direction at which the greatest force was applied. The substrate thickness (several dozen microns) greatly exceeded the naphthalene crystal thickness. The magnified surface of the deformed crystal was projected on the slit of a DFS-13/2 spectrograph (inverse linear dispersion $2\ \text{\AA}/\text{mm}$); we chose for the investigations a section with good contact and without cracks.

Figure 1 shows micrograms of the absorption spectra (a component, region 0–0 and 0–1 transitions, the so-called A and M bands) of deformed naphthalene crystals as a function of the angle α between the corresponding crystallographic axes of the naphthalene and the indole. The dashed curves show, for compari-

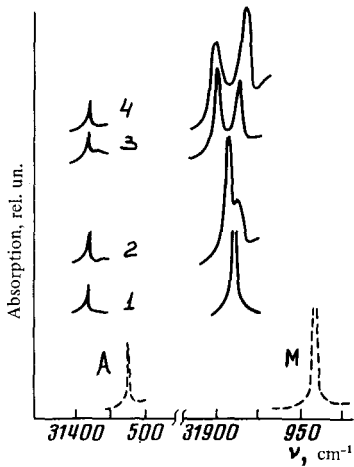


FIG. 1. Micrograms of the a component of the absorption spectra (A and M bands) of deformed naphthalene single crystals at different angles between the crystal and substrate axes, $T = 4.2^\circ\text{K}$. The dashed line shows the spectrum of the free sample: 1) $\alpha = 0^\circ$, 2) $\alpha = 5^\circ$, 3) $\alpha = 15^\circ$, 4) $\alpha = 30^\circ$.

son, the spectrum of the undeformed crystal. It is seen from the figure that the spectrum of the deformed sample differs from the spectrum of the free sample primarily in that all the lines are shifted to the long-wave side by up to 60 cm^{-1} . This shift, according to [1], is connected with the change of the intermolecular distances in the crystal upon deformation. The magnitude of the Davydov splitting in the spectrum of the deformed crystal increases then by 20 cm^{-1} , i. e., it becomes equal to 170 cm^{-1} .

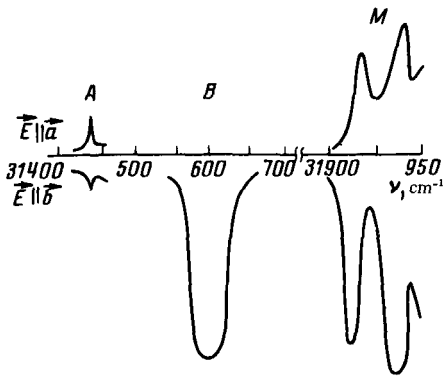


FIG. 2. The absorption spectrum of the deformed naphthalene crystal (region of $0-0$ and $0-1$ transitions) in polarized light at $T = 4.2^\circ\text{K}$ and $\alpha = 40^\circ$.

If the axes of the crystal and of the substrate differ in angle, then, besides an overall shift of the spectrum, splitting of the vibronic bands is observed due to transitions in which non-fully-symmetrical oscillations take part. The exciton bands, on the other hand, are not split. The magnitude of the indicated splitting depends essentially on the angle between the axes. For example, it is seen from Fig. 1 that when the angle α is increased from 0 (the axes are aligned) to 30° , the M band changes from a singlet ($\nu = 31908\text{ cm}^{-1}$) into a doublet of bands ν_1 and ν_2 , the distance between which reaches 18 cm^{-1} ($\nu_1 = 31900\text{ cm}^{-1}$ and $\nu_2 = 31918\text{ cm}^{-1}$). The doublet bands are quite narrow and their width does not exceed 10 cm^{-1} .

Notice should be taken of two more singularities observed in the spectra when the crystal is deformed. Figure 2 shows micrograms of both components of the absorption spectrum of a deformed crystal at $\alpha = 40^\circ$. It is seen from the figure that a) the exciton *A* band is observed also in the *b* component of the spectrum; b) the *M* band is split in both components of the spectrum, but in the *b* component the doublet is shifted relative to the doublet in the *a* component by several reciprocal centimeters. The magnitude of this shift increases weakly with increasing angle α .

The results can be explained by starting from the following considerations: All the *M* bands correspond to vibronic transitions with participation of nonfully-symmetrical oscillations. These excitations are localized. The naphthalene crystal contains two translationally-nonequivalent molecules per unit cell, but these can be made to go over into each other with the aid of two elements of the crystal symmetry group (C_2^b and σ^b), and this makes them equivalent in energy. This results in double degeneracy of all the localized transitions. If the naphthalene crystals are compressed in some direction at an angle to the monoclinic axis, then their symmetry is lowered. This should lead to a difference between the excitation energies of the translationally-nonequivalent molecules, i. e., to lifting of the degeneracy and to splitting of the bands in the optical spectra corresponding to the localized transitions, as is indeed confirmed by experiment. This model also explains the experimentally observed dependence of the splitting on the direction of the applied forces.

The different positions of the split *M* band in the *a* and *b* components of the spectrum has not yet been satisfactorily explained.

In the case of the exciton bands, the deformations considered above should not lead to their splitting, since the degeneracy for the exciton transition has already been lifted by the resonant interaction. The observed depolarization of the exciton band is explained by the fact that when the non-equivalent molecules are shifted as a result of the deformation, the sum and difference of their dipole moments reverse direction, i. e., the dipole moments of the transitions to the exciton states do not coincide in direction with the crystallographic axes of the crystal.

The authors thank V. I. Sugakov for a useful discussion.

¹The indole crystal is of rhombic syngony. ^[6]

¹V. L. Broude, O. S. Pakhomova, and A. F. Prikhot'ko. Opt. Spektrosk. **2**, 323 (1975).

²M. S. Soskin, Ukr. Fiz. Zh. **6**, 806 (1961).

³V. L. Broude and A. K. Tomashchik, Ukr. Fiz. Zh. **9**, 39 (1964).

⁴V. L. Broude, Opt. Spektrosk. **24**, 475 (1968).

⁵V. I. Sugakov, Fiz. Tverd. Tela **15**, 2513 (1973) [Sov. Phys. Solid State **15**, 1670 (1974)].

⁶P. Roychowdhury and B. S. Basak, Acta Crystallogr. **B31**, 1559 (1975).