STRUCTURE OF ABSORPTION SPECTRA OF LOCAL EXCITONS IN A NAPHTHALENE CRYSTAL

N.I. Osipenko and M.T. Shpak
Physics Institute, Ukrainian Academy of Sciences
Submitted 11 September 1972
ZhETF Pis. Red. 16, No. 9, 513 - 516 (5 November 1972)

The theory of electron-vibrational (vibronic) states of pure molecular crystals was developed in a number of papers [1 - 4]. The results of the theory were in satisfactory agreement with the experimental investigations of vibronic spectra of molecular crystals [5]. The scheme of the impurity vibronic spectrum for the case of isotopic impurities was first proposed and analyzed in [2]. The frequencies of the vibrational bands of the local excitons (naphthalene with impurities) was calculated in [6].

We present here the results of experiments on the absorption spectra of naphthalene crystals with heterocyclic impurities (thionaphthene, indole, benzofuran) in the region of the first vibronic transition $^1A_{1g}$ (M-band with frequency 31 959 cm^{-1}). We have shown in [7] that these impurities produce local excitons in the naphthalene crystal. By local excitons are meant states in which the excitation is concentrated at the crystal molecules that are perturbed by the impurity. We used thin single-crystal films ($d \lesssim 1$ μ) for the investigation. The impurity concentration was $C \sim 1\%$.

Figure 1 shows micrograms of the corresponding sections of the absorption spectrum of the pure naphthalene crystal (1) and of naphthalene crystals of varying thicknesses with thionaphthene impurities (2, 3). It is seen from Fig. 1 that introduction of the impurity into the naphthalene crystal leads to appearance in its absorption spectrum in the investigated region, of an entire series of new narrow bands with frequencies 31 879, 31 948, 31 952, 31 967, and 31 970 cm^{-1}, the intensities of which increase with increasing impurity concentration. The 31 879 cm^{-1} band was observed by us earlier [7], and all the remaining bands were observed here for the first time. The most intense are the 31 948 and 31 970 cm^{-1} bands. Polarization investigations have shown that these bands are polarized along the b-direction of the crystal. The frequencies of the new bands depend on the type of impurity. The table lists the frequencies of these bands in the absorption spectra of naphthalene crystals with thionaphthene, indole, and benzofuran impurities.

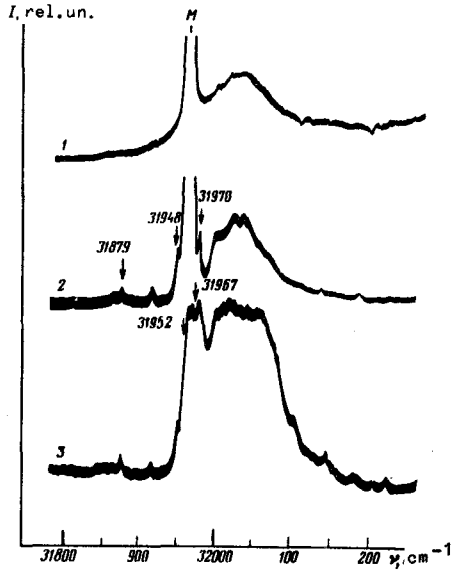

Fig. 1. Micrograms of absorption spectra of a pure naphthalene crystal (1) and of naphthalene crystals of varying thicknesses with thionaphthene impurities (2, 3) ($d_3 > d_2$) in region of the M-band ($T = 4.2°K$). The new bands are marked by arrows.

The new bands can be explained by assuming that they are connected with the appearance of complex vibronic states of local excitons in the spectrum. To this end, we compare the experimental data with the calculated frequencies of the vibronic bands of the local excitons in naphthalene [5] (see the table).

Frequencies of local-exciton bands in the region of the first vibronic transition $^1A_{1g}$ (cm^{-1}).

Impurity in naphthalene	Experimental values	Calculated[1] in [5]
Thionaphthene	31879	–
	31932	–
	31943	–
	31948	31945 a, b
	31952	31950 c
	31967	31967 c
	31970	31969 a, b
Indole	31903	–
	31930	–
	31937	–
	31950	31951 a
	–	31953 b
	–	31956 c
	31972	31971 c
	–	31973 a
	–	31975 b
Benzofuran	31918	–
	31932	–
	31943	–
	–	31955 a
	–	31956 b
	–	31958 c
	–	31977 c
	31976	31980 a, b

[1] The configurations a, b, and c are shown in Fig. 2.

Let us consider the naphthalene-thionaphthene crystal. We assume that the perturbed molecule and the molecule on which the vibration is localized are arranged as shown in Figs. 2a and 2b (non-equivalent position). If the electronic excitation is localized on the perturbed molecule, then there should correspond to the spectrum of this state a band with frequency equal to the sum of the frequencies of the electronic transition of the local exciton and the molecule vibration in the ground state, 31 447 + 509 = 31 956 cm^{-1}. On the other hand, if the electronic excitation is localized on an unperturbed molecule, which is in a perturbed vibrational state, then the M-band (ν = 31 959 cm^{-1}) appears in the spectrum. The resonance of these two states with frequencies 31 956 and 31 959 cm^{-1} causes them to interact strongly, as a result of which two new bands will appear, located on both sides of the M-band. The calculated frequencies are in this case 31 945 and 31 969 cm^{-1} [5], and the experimental values are 31 948 and 31 970 cm^{-1}. On the other hand, if the vibration is localized on a crystal molecule whose position relative to the perturbed molecule is equivalent (Fig. 2c), then the interaction will give rise to a new pair of bands. The calculated values of the frequencies of these bands are 31 950 and 31 967 cm^{-1}, and the experimental ones are 31 952 and 31 967 cm^{-1}. Since the intensities of the bands of these pairs are determined by the degree of

mixing of the interacting states, it follows that the more intense ones should be the pairs in the case of non-equivalent arrangement of the positions of the nearest interacting molecules, as is indeed observed in the experiment.

A similar picture is observed also in the spectra of naphthalene with other impurities (see the table).

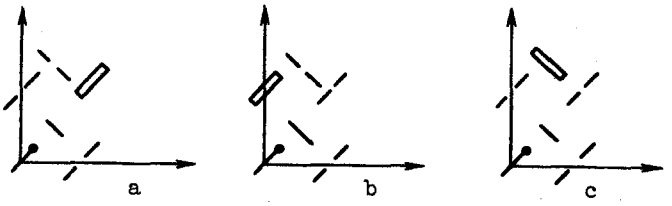

Fig. 2. Possible relative placements of the impurity (——●), impurity-perturbed (-) and unperturbed (---) molecules on which a vibration (rectangle) is localized in the ab plane of a naphthalene crystal.

As to the bands with frequencies (see the table) 31 879 (thionaphthene), 31 903 (indole), and 31 918 cm^{-1} (benzofuran), these bands correspond to the case when the vibration is localized on the molecule perturbed by the impurity. They were observed by us earlier (the so-called L_k-bands), and their frequencies were used in [8] to calculate the parameter Δ, which determines the change of the excitation energy of the molecule in the crystal when the molecule is perturbed by the impurity.

In conclusion, the authors thank V.I. Sugakov for a discussion of the results.

[1] A.S. Davydov, Theory of Light Absorption in Molecular Crystals, Sec. 17, in: Trudy, Phys. Inst. Ukr. Acad. Sciences, 1951.
[2] E.I. Rashba, Zh. Eksp. Teor. Fiz. 50, 1064 (1966) [Sov. Phys.-JETP 23, 708 (1966)].
[3] E.I. Rashba, ibid. 54, 542 (1968) [27, 292 (1968)].
[4] A.S. Davydov and A.A. Serikov, Phys. Stat. Sol. 42, 603 (1970); 44, 127 (1971).
[5] E.F. Sheka, Usp. Fiz. Nauk 104, 593 (1971) [Sov. Phys.-Usp. 14, 484 (1972)].
[6] L. Valkunas and V.I. Sugakov, Ukr. Fiz. Zh. 17, 1575 (1972).
[7] N.I. Ostapenko and M.T. Shpak, Phys. Stat. Sol. 36, 515 (1969).
[8] V.I. Sugakov, Opt. Spektr. 28, 695 (1970).

HALL AND NERNST-ETTINGSHAUSEN EFFECTS IN SINGLE-CRYSTAL RHENIUM

O.K. Kuvandikov, V.I. Ivanovskii, A.V. Cheremushkina, and R.P. Vasil'ev
Moscow State University
Submitted 20 September 1972
ZhETF Pis. Red. 16, No. 9, 517 - 518 (5 November 1972)

The earlier investigations of the Hall effect [1, 2] and the Nernst-Ettingshausen effect [3] in rhenium were performed on polycrystalline samples. We report here an experimental determination of the Hall and Nernst-Ettingshausen coefficients obtained for rhenium single crystals with a resistance ratio R(273°K)/R(4.2°K) = 50. The investigated samples were cut by the electric-spark method from a single-crystal rhenium rod at various angles (15, 40, 90°) relative to the hexagonal axis. The sample thickness was 0.3 - 0.4 mm and their length fluctuated in the range 10.2 - 10.4 mm. The cut samples were ground with emery paper and polished electrolytically. The c-axis orientation in each sample was established with the aid of the Laue patterns. Platinum potential contacts of 0.2 mm diameter and chromel-alumel thermocouples were welded to the sample with an electron beam. A Hall current of 0.1 - 1 A was made to flow through the sample. When measuring the Nernst-Ettingshausen emf, a temperature gradient 10 - 20 deg/cm was produced with two heaters. The Hall and Nernst-