INFLUENCE OF STRUCTURAL DEFECTS ON EXCITONIC PHOTOLUMINESCENCE OF PENTACENE

YU.P. PIRYATINSKI, M.V. KURIK

Institute of Physics, Nat. Acad. of Sci. of Ukraine
(46, Prosp. Nauky, Kyiv 03028, Ukraine)

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The exciton reflection, absorption, and photoluminescence spectra for single crystals and polycrystalline films have been studied in the temperature range of 4.2–296 K. A significant influence of structural defects arising during phase transitions on the exciton spectra of pentacene has been detected. The mechanisms of photoluminescence in single crystals and crystalline films of pentacene have been considered.

1. Introduction

Molecular crystals of linear polyacenes, including pentacene, are characterized by a regular growth of the intermolecular interaction in the *ab*-plane of a crystal, which accompanies the increase in the number of benzene rings in the molecule [1], and a weak interplane coupling. The researches of optical properties of molecular crystals (their absorption, reflection, and photoluminescence spectra) at various temperatures allowed the energy structure of single crystals of anthracene [2] and tetracene [3–5] to be studied well. Pentacene crystals have been studied much worse in this aspect. Especially, this concerns the origin of photoluminescence in crystallographically perfect single crystals. To elucidate the nature of photoluminescence in crystalline pentacene, it would be of interest to analyze its optical characteristics in a wide temperature interval. From the viewpoint of exciton physics applied to the crystals of linear polyacenes, it would be interesting to study the exciton spectra of pentacene single crystals (five benzene rings) taking advantage of low-temperature spectroscopy. Of this kind of polyacenes, typical are a high value of the Davydov splitting of excitons, the structural phase transition changing the lattice symmetry (monoclinic – triclinic), and structural defects, which considerably affect the exciton spectra of pentacene.

This work aimed at carrying out a detailed research of the influence of defects in the crystal structure of pentacene single crystals on the exciton manifestation in their optical spectra. Photoluminescence (PL), reflection, and absorption exciton spectra of crystalline pentacene were studied in a wide temperature interval $T = 4.2$–296 K. As specimens, we used thick single crystals and thin single- and polycrystalline films of pentacene, which were freely fixed on a quartz substrate to provide an optical contact between them. The results obtained were explained on the basis of the features in the crystal structure of single crystals and thin polycrystalline films of pentacene, which are sensitive to a deformation of the crystal lattice at the temperature variation. The origin of excitations (molecular and charge transfer excitons free and localized on structure defects) of the observed PL band has been discussed.

2. Experimental Technique

Pentacene single crystals were grown up from well-purified pentacene using the sublimation method in a helium atmosphere at a temperature of 530–550 K. Initial pentacene was subjected to the purification using the multicycle recrystallization. In the course of growth, we obtained single crystals from 100 nm to 50 μm in thickness with a well-developed *ab*-plane. For the majority of single crystals with the thickness $d = 20 \div 50$ μm, one of the crystal *ab*-planes turned out reflecting and the other opaque, which was associated with the features of crystal growth.

Crystalline films of pentacene were fabricated by thermal sputtering in a vacuum of 10^{-5}–10^{-6} mbar onto a quartz substrate at a temperature of 296 K. The optical absorption spectra showed that the deposited pentacene layers consisted of plane, densely packed crystallites, the *ab*-planes of which were mainly oriented in parallel with respect to the substrate surface.

The reflection spectra of pentacene single crystals were measured using the technique of polarized light reflection from the crystal *ab*-plane at a light incidence angle of about 15°. For the B-polarized component of the reflection spectrum, the signal was regulated to provide the maximum intensity of reflection from the crystal *ab*-planes.

The absorption spectra of crystalline pentacene were measured at a normal angle of incidence of natural or linearly polarized light onto the crystal *ab*-plane. While measuring the absorption spectra of a thin ($d = 100$ nm) pentacene single crystal in polarized light, the crystal was arranged between two crossed polarizers and oriented to obtain a zero signal for light passed in the pentacene transparency range. Afterward, the polarizers were mounted to measure the absorption spectra for light polarized, firstly, in parallel and, then, perpendicularly to the crystal *b*-axis (the *B*- and *A*-polarizations, respectively).

The PL spectra of crystalline pentacene were studied in a stationary mode and by the nanosecond time-resolved technique. In another case, PL was excited with the help of a nitrogen laser (the emission wavelength $\lambda_e = 337.1$ nm, the ignition pulse duration $t_I = 9$ ns, the emission pulse power $N = 3$ kW, and the pulse repetition rate $f = 80$ Hz) and the second harmonic generation of an Nd:YAG laser ($\lambda_e = 532$ nm, $t_I = 10$ ns, $N = 100$ kW, and $f = 50$ Hz). The time-resolved registration of PL was carried out using a stroboscopic system [3,4] with various time delays t_d with respect to the pulse of laser radiation.

The PL spectra of crystalline pentacene were registered within the time range of 0–1 ns. A high-aperture grating monochromator MDP-12 was used as a spectral device. The spectral width of a slit at PL spectrum measurements was 0.2–0.4 nm. While registering the PL spectra in the stationary mode, the crystals were excited with a 40-mW He-Cd laser ($\lambda_e = 441.6$ nm). The PL registration was executed in the photon counting mode.

3. Experimental Results and Their Discussion

The PL researches were carried out within the temperature range of 4.2–300 K. PL was observed for pentacene single crystals of the thickness $d = 20 \div 50$ μm and polycrystalline films with $d = 100$ nm obtained by the thermal sputtering in vacuum. In pentacene single crystals (d = 20–50 μm), PL was excited from the side of the smooth surface using the emission of a He–Cd laser ($\lambda_e = 441.6$ nm) and registered in the photon counting mode. We did not managed to detect PL at the excitation of pentacene single crystals (d = 0.1–50 μm) using the emission from a nitrogen laser. The films of crystalline pentacene obtained by the thermal sputtering in vacuum demonstrated PL, when being excited with either a nitrogen or a Nd:YAG laser in the temperature range 4.2–296 K.

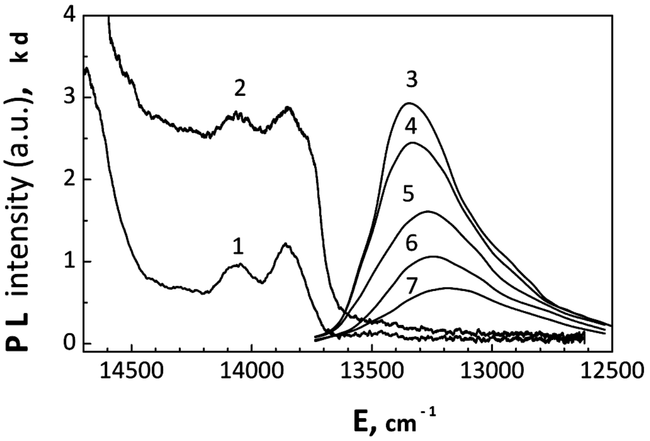

Fig. 1. Absorption, for *B*- (*2*) and *A*- (*1*) polarizations, and photoluminescence, at temperatures $T = 4.2$ (*1–3*), 14 (*4*), 20 (*5*), 25 (*6*), and 30 K (*7*), spectra for a pentacene single crystal with the thickness $d = 20$ μm. The PL spectra were measured from the smooth surface, $\lambda_e = 441.6$ nm

In Fig. 1, the PL spectra of a pentacene single crystal ($d = 20$ μm) excited with a He-Cd laser are depicted. For this single crystal, PL was observed in the temperature interval of 4.2–65 K. At 4.2 K, the pentacene PL spectrum (Fig. 1) was a wide nonstructured band with a maximum at 13300 cm^{-1} and a shoulder extending toward the long-wave side. As the temperature grew to 17 K, the PL intensity did not change substantially. A further temperature increase was accompanied by an exponential decrease of the PL intensity, with the activation energy of this process being equal to 170 cm^{-1}. At a temperature of 65 K, the PL of pentacene cannot be registered.

Figure 1 also exhibits the absorption spectra of a pentacene single crystal under investigation within the crystal transparency interval at 4.2 K. The spectra were measured for both the *A*- (curve *1*) and *B*- (curve *2*) polarizations. Absorption was observed below the exciton band bottom, and it was partially polarized. The bands with maxima located at 13760, 13850, and 14050 cm^{-1} can be resolved in the spectrum for the *B*-polarization and at 13850 and 14050 cm^{-1} for the *A*-polarization of the crystal.

In Fig. 2, the reflection spectra are depicted for the *B*-polarization of a freely fixed pentacene single crystal ($d = 20$ μm), which were measured from the smooth surface of the specimen in the temperature range of 1.85–250 K and the spectral interval of 14000–15000 cm^{-1}. An intensive band with a long-wave maximum at 14460 cm^{-1} is observed for the *B*-component of the reflection spectrum. Attention is also attracted by

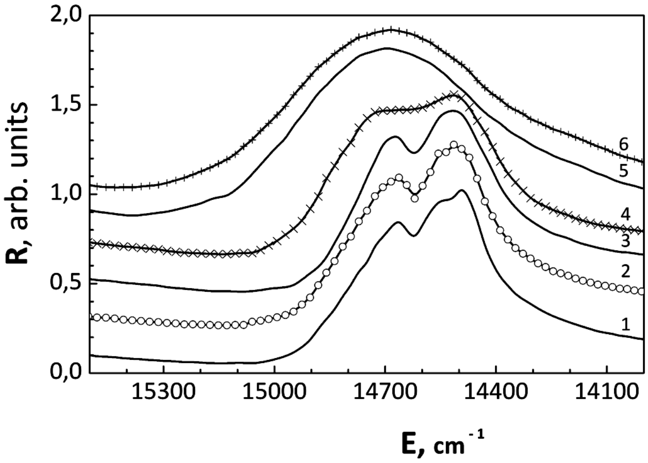

Fig. 2. Reflection spectra for the B-polarization of a freely fixed pentacene single crystal at various temperatures $T = 1.85$ (*1*), 4.2 (*2*), 10 (*3*), 43 (*4*), 200 (*5*), and 250 K (*6*). $d = 20$ μm

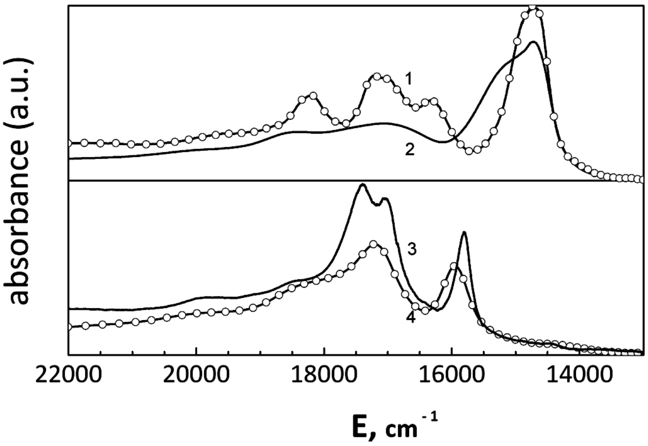

Fig. 3. Absorption spectra for a single-crystalline pentacene film of the thickness $d = 100$ nm, which is in the optical contact with a quartz substrate, for the B- (*1* and *2*) and A- (*3* and *4*) polarizations at $T = 42$ (*1* and *3*) and 296 K (*2* and *4*)

dips with the minima at 14490 and 14600 cm^{-1}, which, similarly to the anthracene [6] and tetracene [3, 5] cases, can be associated with the excitation of surface excitons. When the temperature increased to 43 K, those dips became smoothed out, and they disappeared at higher temperatures.

The exciton reflection spectra given above can be used to determine the position of the exciton band bottom in pentacene single crystals following the method described in work [6]. The position of the long-wave maximum at 14460 cm^{-1} can be identified with the position of the 0-0 transition for a bulk b-exciton.

In the reflection spectrum of pentacene single crystals measured from the opaque surface of a specimen at a temperature of 1.85 K, the reflection B-band is structureless, and no surface excitons are observed. Another peculiarity of the low-temperature reflection spectra is the fact that a jump-like shift of the spectra for the A- and B-components toward the short-wave side is observed at a temperature above 170 K. For the B-component of the reflection spectrum, this shift is close to 180 cm^{-1}. The positions of the long-wave band maxima in the exciton reflection spectrum measured at temperatures of 1.85, 170, and 296 K are as follows: for the B-polarizations, 14460, 14640, and 14720 cm^{-1}, respectively; and for the A-polarization, 15640, 15740, and 15750 cm^{-1}, respectively.

Owing to the triclinic symmetry of pentacene crystals, it is not necessary for the electron transitions in them to be strictly polarized along the b- and a- axes of the crystal. The magnitudes of resonance splitting for pentacene single crystals, being calculated as the energy difference between the a- and b-exciton bands, amount to 1180, 1100, and 1030 cm^{-2}, respectively, for the temperatures indicated above. For pentacene and anthracene single crystals, the resonance splittings of exciton bands at low temperatures amount to 225 [6] and 960 cm^{-1} [3], respectively. For tetracene single crystals, a jump-like shift of exciton reflection spectra at low temperatures was observed, which was associated with a structural phase transition of the first kind in them [3, 5]. In view of a close character of crystal structures in tetracene and pentacene crystals at 296 K (the both crystals are triclinic), the existence of two modifications, high- and low-temperature ones, can also be supposed for the latter. In the case of tetracene crystals, it was shown [3] that the phase transition in it is connected with a change of the crystal symmetry and is stimulated by an increase of the internal pressure in the crystal owing to its squeezing, as the temperature decreases. For pentacene crystals, a pressure-induced modification of the crystal structure was also observed [7], which was detected by a shift of the exciton bands. For this reason, the jump-like shift of the bands in the exciton reflection spectra of pentacene crystals at 170 K can be regarded as that associated with a structural phase transition in it. In work [8], on the basis of the data on electron diffraction in thin pentacene layers, the assumption was put forward that a new, more densely packed lattice is formed in pentacene at low temperatures.

In Fig. 3, the absorption spectra of a single-crystalline pentacene film, which possessed the thickness $d = 100$ nm and was in the optical contact with the quartz substrate, are depicted. The spectra were measured for the *B*- (curves *1* and *2*) and *A*- (curves *3* and *4*) polarizations at temperatures of 4.2 (curves *1* and *3*) and 296 K (curves *2* and *4*). Similarly to what was done in the case of reflection spectra, the differences in the absorption spectra of single-crystalline pentacene films at room temperature and at 4.2 K can be associated with phase transformations occurring in them.

In the absorption spectra of pentacene measured in the range of the first singlet electron transition, S_1, at 4.2 K (curves *1* and *3*), a series of bands is observed. The maxima of the most intensive bands in the absorption spectra are located at 14710, 16320, 17000, 17220, 18220, 18780, 19700, and 21600 cm^{-1} for the *B*-polarization (curve *1*) and at 15810, 17040, 17400, 18400, 19100, 19900, and 21100 cm^{-1} for the *A*-one (curve *3*). When the films of single-crystalline pentacene were heated up to 296 K, the absorption spectra for the *B*- and *A*-polarizations became shifted toward the short-wave side, and the bands are broadened. The most intensive bands in the absorption spectra measured at 296 K had maxima at 14710, 14920, 17070, 18420, and 19800 cm^{-1} for the *B*-polarization (curve *2*) and at 15950, 17200, 18300, and 20000 cm^{-1} for the *A*-one (curve *4*). By comparing the positions of absorption bands at 4.2 and 296 K for the *A*-polarization, it is visible that the long-wave band of the spectrum got shifted toward the short-wave side by 180 cm^{-1}. For the *B*-polarization of the absorption spectrum, a shift of the "center of mass" of the long-wave band can be observed. The maximum of the long-wave absorption band, as it was in the case of the low-temperature spectrum (curve *1*), was located at 14710 cm^{-1} and there was a shoulder on the short-wave side of this band at 14920 cm^{-1}. A considerable broadening of the band toward the short-wave side was associated with the fact that the thin pentacene crystal was in the optical contact with the quartz substrate. As a result, the section of a pentacene specimen, which contacted with quartz, was deformed. This gave rise to the formation of an elevated pressure in this region of the crystal and in the emergence of a low-temperature modification of pentacene characterized by the absorption maximum at 14710 cm^{-1}. The shoulder at 14920 cm^{-1} can be connected with the presence of a high-temperature modification in the single-crystalline pentacene film, which is mainly located nearer to the film free surface. Differences were observed between the reflection spectra of such single-crystalline films measured from the free surface and the surface that contacted with the quartz substrate, which can also be associated with a deformation of the pentacene crystal lattice near the substrate. A reduction of the temperature to 4.2 K resulted in the transition of the whole crystal into the low-temperature modification, for which the absorption band maximum is located at 14710 cm^{-1}.

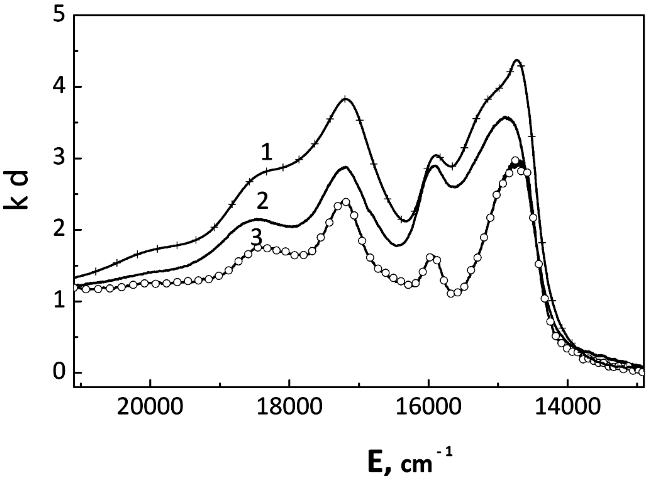

Fig. 4. Absorption spectra for a single-crystalline pentacene film (*1*) and a pentacene film obtained by thermal sputtering in vacuum (*2* and *3*). The film thickness d = 100 nm. Measurements were carried out in natural light at T = 296 (*1* and *2*) and 4.2 K (*2*)

The researches of the absorption spectra of a single-crystalline film (d = 100 nm), which was in the optical contact with a quartz substrate, and a crystalline film of the same thickness, but fabricated by the thermal sputtering in vacuum onto a quartz substrate, showed that they are similar with respect to the measurements using natural light. This circumstance corresponds to the assumption made above that the thin pentacene layers deposited by the thermal sputtering onto quartz plates consist of planar, densely packed crystallites, the *ab*-plane of which is dominantly oriented in parallel to the substrate surface.

In Fig. 4, the absorption spectra of a crystalline film with the thickness d = 100 nm obtained by the thermal sputtering in vacuum are shown. The spectra were measured at 296 (curve *2*) and 4.2 K (curve *3*). For the sake of comparison, the absorption spectrum of a single-crystalline pentacene film of the same thickness, which was in the optical contact with the quartz substrate, measured at 296 K in natural light is also exhibited (curve *1*). In the latter spectrum, the bands with maxima located at 14710, 15070, 15900, 17200, and 18390 cm^{-1} can be resolved. In the absorption spectrum for a polycrystalline pentacene film, the bands with maxima located at 14890, 15910, 17200, and 18500 cm^{-1} are observed at a temperature of 296 K (curve *2*) and at 14710, 15940, 17190, and 18380 cm^{-1} at a temperature of 4.2 K.

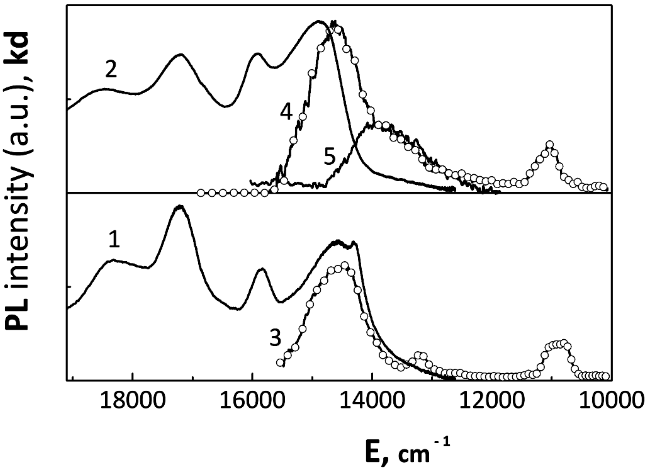

Fig. 5. Absorption (*1* and *2*) and photoluminescence (*3*–*5*) spectra of a thermally sputtered pentacene film with the thickness d = 100 nm at temperatures $T = 4.2$ (*1* and *3*) and 296 K (*2*, *4*, and *5*). $\lambda_e = 532$ (*3* and *4*) and 337.1 nm (*5*)

From Fig. 5, one can see that both high- and low-temperature modifications of pentacene manifest themselves in the absorption spectra measured at room temperature for single-crystalline pentacene films both optically contacting with the quartz substrate and obtained by the thermal sputtering onto it. The presence of a low-temperature modification in crystalline pentacene films at room temperature can be associated with the interaction between the near-surface pentacene layer and the quartz substrate. It is evident that, in the near-surface pentacene layer adjacent to the substrate, there emerge the regions with increased pressure, and a structural phase transition takes place in them. Below the phase transition point, the manifestations of the low-temperature modification of pentacene are mainly observed in the exciton absorption spectra.

The PL spectra of a crystalline pentacene film 100 nm in thickness obtained by the thermal sputtering onto a substrate in vacuum are depicted. They were measured with a nanosecond time resolution ($\not{t}_d = 1$ ns) at 296 (curves *4* and *5*) and 4.2 K (curve *3*). PL spectra *3* and *4* were obtained at the excitation of crystalline pentacene films with a Nd:YAG laser (λ_e = 532 nm). In the PL spectrum of a crystalline film measured at 4.2 K, the bands with maxima located at 14500, 13200, and 10900 cm^{-1} can be resolved. As the temperature grew to 296 K, PL spectrum *4* became shifted toward the short-wave side, and the bands with the maxima at 14610, 13950, and 11070 cm^{-1} can be observed. The 13950-cm^{-1} PL band measured at room temperature correlates with band *5* obtained at PL excitations with a nitrogen laser. PL spectrum *5* of the pentacene film was observed at room temperature; it was obtained under the excitation with a nitrogen laser (λ_e = 337.1 nm) from the quartz substrate side. The same figure displays the absorption spectra of a pentacene film at 4.2 (*1*) and 296 K (*2*).

In a series of linear polyacene crystals (naphthalene, anthracene, tetracene, pentacene), the PL quantum yield essentially depends on the singlet-triplet splitting [9]. For the anthracene crystals, where the splitting of states $S_1 - T_1$ is maximal, the PL quantum yield is also maximal and equals 0.95. The PL quantum yield of tetracene crystals at room temperature is about 0.002, and, for a tetracene molecule, it amounts to 0.21. According to the literature data [9], the PL quantum yield for pentacene single crystals, where this splitting is minimal, is close to zero. This fact was supposed [9] to be associated with a high efficiency of the decay of a singlet exciton into two triplet ones. At the same time, the pentacene molecules, which are located in the crystalline matrix of aromatic carbohydrates, emit rather well [10]. Such a difference between the photoluminescence properties of pentacene crystals and isolated molecules has not obtained a satisfactory explanation and demands further researches.

In work [11], pentacene molecules, being introduced into a matrix of anthracene crystals to the concentration above the solubility threshold, were demonstrated to form clusters. It was predicted that those clusters are nanocrystals or blocks of pentacene molecules located on the external surface of or at dislocations in the anthracene single crystal. At the pentacene content below the solubility limit in anthracene crystals, the low-temperature PL spectra of the anthracene matrix are close to the spectra of pure anthracene. In the well-resolved PL spectrum, a series of narrow peaks emitted by pentacene molecules is observed with the purely electron band at 16395 cm^{-1}. If the pentacene concentration exceeds the solubility threshold, the anthracene emission bands are broadened, and a wide unstructured background stemming from the PL of pentacene clusters appears in the pentacene PL spectra in a vicinity of the pure electron molecular transition.

In work [12], the authors reported on the PL of polycrystalline pentacene films deposited onto substrates made of aerosil and pyroceramics, which was observed at 77 and 300 K. The PL spectrum of those films was similar to that of a solid pentacene solution in naphthalene and consisted of bands at 15500 and 16500 cm^{-1}. Proceeding from this fact, the assumption was made that the PL of polycrystalline pentacene films is related to the presence of the amorphous phase in them. The measured PL lifetime of pentacene molecules at 293 K was 3.4 ns in a polycrystalline film and 10.3 ns in a solid naphthalene solution. The difference between the PL lifetimes, in the authors' opinion, can be explained by the fact that pentacene molecules emit individually (electron transition $^1A_{1g}$–$^1B_{2u}$) in the case of a solid pentacene solution in naphthalene, whereas the structurally deformed cells of crystallites do it in the films.

At high temperatures, the thermal decomposition of pentacene molecules is possible. It is not excluded that, in the course of the crystal growing using the sublimation technique or thermal sputtering of films in vacuum, some pentacene molecules can be thermally decomposed, playing the role of emission centers. Proceeding from this model, the influence of high temperatures on the PL spectra of crystalline pentacene was studied in work [13]. PL obtained in pentacene single crystals as a result of the thermal decomposition of pentacene molecules was considered. While growing pentacene single crystals, it was found that, if the temperature in the crystallizer is elevated above 620 K, individual pentacene molecules undergo irreversible transformations. In contrast to the dark-blue single crystals of pentacene, the crystals grown up at $T > 620$ K were colorless or had a pink tint. Pentacene is known [14] to be thermally decomposed at $T > 620$ K to form dihydropentacene. The researches of the PL spectra of thermally modified pentacene crystals at 4.2 K showed [13] that they are complex. This spectrum can be divided into several spectral intervals, which correspond to the emission by molecular naphthalene, anthracene, and pentacene, and wide structureless bands given by pentacene nanoclusters. The authors of work [15] reported on the PL by crystalline nanoclusters in ultrathin (2.8–7 nm) pentacene films at 77 K. Two bands at 14840 and 15650 cm^{-1} were observed in the PL spectra of pentacene nanoclusters, which are related to the emission by Frenkel excitons, with the Davydov splitting being equal to 810 cm^{-1}. The positions of those PL bands depended on the film thickness and nanocluster dimensions. If the film became thinner, the PL spectrum got slightly shifted toward the short-wave side.

Let us assume that the absence of PL in pentacene crystals is associated with a high decay rate S_1 of a singlet exciton into two triplet ones [9]. Then, at low temperatures, owing to the resonance mismatch between the energies of a singlet and two triplet excitons, the decay rate diminishes, and favorable conditions can emerge for the PL in pentacene single crystals to be observed.

Pentacene crystals considered within the series of linear polyacenes possess the largest distance between the *ab*-planes, which amounts to 1.6 nm. Those crystals are characterized by a strong resonance interaction in the *ab*-plane and a very weak interaction in the *c*-axis direction of the crystal. In view of a weak coupling between *ab*-planes, molecular excitons in pentacene crystals can be regarded as two-dimensional. While studying molecular excitons in perfect one- and two-dimensional crystals, a number of specific features appear. In work [16], the lifetime of excitons with respect to the radiation decomposition was calculated. For one-dimensional excitons, it turned out to equal

$$\tau_{\text{ex}} = \tau_0 4r/3\lambda,$$

where $\tau_0 = 3h^4c^34E(0)^3\mathbf{d}^2$ is the lifetime of the excitation with energy $E(0)$ in an isolated molecule, r is the distance between molecules, λ the radiation wavelength, $\mathbf{d}$ the electric dipole moment, and c the speed of light. Since $r/\lambda \sim 10^{-3}$, the value of τ_{ex} in the case of a one-dimensional molecular chain is thousand times less than τ_0. For the two-dimensional crystal, the exciton lifetime is about $(r/\lambda)^2 \sim 10^{-14}$–$10^{-15}$ s, i.e. it becomes comparable with the period of electron rotation in the crystal and the time of intramolecular vibration relaxation. The quantity $1/\tau_{\text{ex}}$ determines the probability of the exciton excitation by a photon. That is why the probability of the exciton excitation in two-dimensional crystals is 10^5–10^6 times higher than the excitation probability for a free molecule, which is equal to $1/\tau_0$. If the absorption coefficient in a molecular crystal is high, the strong interaction between the excitation and the light-wave field is observed, and polaritons are formed. In the case where the interaction between excitons and the light-wave field exceeds, by magnitude, the interaction between excitons and any other deactivating vibrations in the crystal, the excitons give back their energy to the electromagnetic field of light. For pentacene, this scenario manifests itself in experimentally measured high reflection coefficients at the energies of light irradiation close to that of *b*-exciton at low temperatures. For this reason, PL observed in the temperature range of 4.2–65 K for thick perfect pentacene single crystals can be associated with the multiple scattering of polaritons in the crystal and their capture, owing to the excitonic component, by structural defects.

The observable temperature dependence of PL in pentacene single crystals with a 13300-cm^{-1} maximum at 17 K is typical of predimer states. Such states in low-molecular crystals are usually formed in regions with dislocation defects. Therefore, it can be supposed that the observed PL is associated with the regions of a pentacene crystal, in which molecules are in the predimer state. By comparing the position of the PL band maximum at 4.2 K with the exciton band bottom (14460 cm^{-1}), which was determined from the reflection spectra for the B-polarization (Fig. 2), one can see that the most intense PL band has a long-wave shift of about 1160 cm^{-1}. At the same time, this shift is much larger than the activation energy of PL quenching at a temperature elevation from 17 to 65 K. In this temperature interval, the 13460-cm^{-1} band is observed in the reflection spectra of pentacene single crystals for the B-polarization and a 14300-cm^{-1} band for the A-polarization. Therefore, we may suppose that the observed PL in pentacene single crystals can be induced by inclusions of a new metastable polymorphic pentacene modification, which happens to be in a vicinity of dislocation defects in the temperature range of 4.2–65 K.

For molecular crystals of the pentacene type, there are the channels of intermolecular relaxation associated with the formation of ionic states in addition to the intramolecular channel of radiationless conversion of the vibrationally excited singlet exciton. The direct autoionization of a metastable singlet exciton is observed, if a pentacene crystal is excited in a vicinity of its characteristic photoconductivity threshold ($E_g > 2.8$ eV [17]). At higher excitation energies, a preliminary vibration relaxation to the second excited singlet state (S_2, $E = 3.0$ eV) with the following autoionization is observed. The quantum yield of autoionization for pentacene crystals is close to 1, and this circumstance can be used to explain the fact that no PL was observed under the excitation ($\lambda_e = 337.1$ nm) of thick perfect single crystals above the photoconductivity threshold.

When pentacene crystals are excited below the characteristic photoconductivity threshold, the excitation of molecular excitons is accompanied by the direct excitation of excitons with charge transfer (CT-excitons) [19]. The oscillator strength for the transition with charge transfer to the nearest molecules is close to 0.01 in pentacene crystals. Such a large oscillator strength of CT-transitions in pentacene crystals originates from the mixing of CT-excitons with neutral molecular excitons, which are the nearest by energy, characterized by a large transition oscillator strength. CT-excitons, being intermediate states at the photogeneration, can also give a contribution to PL. As is seen from the absorption spectra of single-crystalline pentacene films depicted in Fig. 3, the oscillatory repetition reckoned from the pure electron transition in the A- and B-polarized spectra, which is typical of pentacene molecules, is not observed. Such deviations in the absorption spectra can be associated with a considerable contribution of the CT-absorption to the total molecular and CT-exciton absorption in crystalline pentacene. For pentacene crystals, the energy of CT-transitions between neighbor molecules in positions (0,0,0)–(1/2,1/2,0), (0,0,0)–(0,1,0), and (0,0,0)–(1,0,0) was determined from the electroreflection spectra [20] to be equal to 2.12, 2.27, and 2.345 eV, respectively. When exciting the pentacene crystal in this spectral region, the most probable is the (0,0,0)–(1/2,1/2,0) transition with the shortest distance between molecules. After the direct excitation of a CT-exciton, it becomes localized, and its energy becomes reduced by 0.3 eV in pentacene crystals [17]. In pentacene crystals, the lowest-by-energy localized state of CT-excitons will be at 1.82 eV (14680 cm^{-1}). The localization of a CT-exciton at a structural defect at low temperatures can also result in PL observed by us for both thick structurally perfect crystals and polycrystalline films.

All the aforesaid concerning the lifetime of excitons in one- and two-dimensional molecular crystals is valid, if the characteristic dimensions of those crystals are not small in comparison with the wavelength of radiation emitted by exciton [16]. For polycrystalline pentacene films, the typical dimensions of crystallites are about 0.1 μm, which is less than the radiation wavelength. Hence, for polycrystalline pentacene films, which demonstrate size effects, the radiation annihilation of molecular excitation can run differently from that for a massive crystal.

Making a comparison between the PL and absorption spectra of polycrystalline pentacene films, one may suppose that the bands at 14500 and 14610 cm^{-1} can be associated with the emission by free excitons in pentacene crystallites, as it was considered in work [21]. The bands at 13200 and 13950 cm^{-1} are produced by excitons localized at structural defects. It is evident from PL spectra *4* and *5* that the largest contribution to the localization of excitons at room temperature is given by structural defects at the crystallite interfaces.

4. Conclusions

Complex spectral researches of peculiarities in the manifestation of exciton states observed at low temperatures in the reflection, absorption, and luminescence spectra have been carried out for a number of pentacene single crystals different by the degree of their structure perfection. New data have been obtained concerning the influence of the crystal structure (single crystals and polycrystals) and the crystal symmetry (the monoclinic and triclinic phases) of pentacene crystals, as well as structural defects, on the exciton energetics and exciton dynamics in the spectra concerned at various temperatures. It has been established experimentally for the first time for the molecular crystals of linear polyacenes, pentacenes, that the magnitude of intermolecular interaction, the symmetry of crystal lattice, and the structural phase transition (monoclinic – triclinic structure) are the basic parameters, which govern the kinetics of excitonic processes.

1. A.I. Kitaigorodskii, *Molecular Crystals and Molecules* (Academic Press, New York, 1973).
2. M.S. Brodin, S.V. Marisova, and A.F. Prikhot'ko, in *Excitons in Molecular Crystals* (Nauka, Moscow, 1973), p. 50 (in Russian).
3. J.M. Turlet and M.P. Philpott, J. Chem. Phys. **62**, 4260 (1975).
4. D.D. Kolendritskii, M.V. Kurik, and Yu.P. Piryatinskii, Opt. Spektrosk. **44**, 281 (1978).
5. D.D. Kolendritskii, M.V. Kurik, and Yu.P. Piryatinskii, Phys. Status Solidi B **91**, 741 (1979).
6. M.P. Philpott and J.M. Turlet, J. Chem. Phys. **64**, 3852 (1976).
7. R.B. Aust, W.H. Bentlei, and H.G. Drickamer, J. Chem. Phys. **41**, 1856 (1964).
8. R. Eiermann, G.M. Parkinson, H. Bassler, and J.M. Thomas, J. Phys. Chem. **87**, 544 (1983).
9. C.E. Swenberg, J. Chem. Phys. **51**, 1753 (1968).
10. I. Hornyak, J. Luminescence **11**, 241 (1975–1976).
11. B.A. Brillante and D.P. Craig, Chem. Phys. Lett. **29**, 17 (1974).
12. G.V. Saidov, M.E. Yudovich, and G.N. Lyalin, Opt. Spektrosk. **46**, 707 (1979).
13. Yu.P. Piryatinski and V.D. Zhukov, Ukr. Fiz. Zh. **31**, 1197 (1986).
14. E. Clar, *Polycyclic Hydrocarbons* (Academic Press, London, 1964).
15. R. He, N.G. Tassi, B. Blanchet, and A. Pinczuk, Appl. Phys. Lett. **87**, 103 (2005).
16. V.M. Agranovich, *Theory of Excitons* (Nauka, Moscow, 1968) (in Russian).
17. E.A. Silinsh, M.V. Kurik, and V. Capek, *Electronic Processes in Organic Molecular Crystals. Localization and Polarization Phenomena* (Zinatne, Riga, 1988) (in Russian).
18. V.D. Zhukov, M.V. Kurik, Yu.P. Piryatinskii, and L.N. Tsikora, Fiz. Tverd. Tela **25**, 1030 (1983).
19. Yu.P. Piryatinski, Fiz. Tverd. Tela **31**, 208 (1989).
20. P.J. Bounds, W. Siebrand, I. Eisenstein, R.W. Munn, and P. Petelenc, Chem. Phys. **95**, 197 (1985).
21. T. Aoki-Matsumoto, K. Furuta, T. Yaada, H. Moriya, K. Mizuno, and A.H. Matsui, Int. J. Mod. Phys. B **15**, 3753 (2001).

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ВПЛИВ СТРУКТУРНИХ ДЕФЕКТІВ НА ЕКСИТОННУ ФОТОЛЮМІНЕСЦЕНЦІЮ ПЕНТАЦЕНУ

Ю.П. Пирятинський, М.В. Курик

Резюме

Досліджено екситонні спектри відбивання, поглинання і фотолюмінесценції монокристалів і полікристалічних плівок пентацену в інтервалі температур 4.2–296 К. Встановлено істотний вплив структурних дефектів, які виникають при фазових перетвореннях, на екситонні спектри пентацену. Розглянуто механізми виникнення фотолюмінесценції в монокристалах і кристалічних плівках пентацену.