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Anthracene Crystals Under Intensive Optical Pumping

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The fluorescence of a number of anthracene crystals has been studied over a wide range of nitrogen laser optical pumping. The conditions for the separate study of light generation in the plane-parallel anthracene plates and nonlinear fluorescence quenching due to exciton–exciton annihilation have been found. The threshold of generation $I_n^{(1)}$ and quenching constant κ_{ss} have been found to be substantially dependent on the structural perfection of crystals. The values of $I_n^{(1)}$ and κ_{ss} are reduced to 4.10^{19} cm^{-2} sec^{-1} and $\sim 10^{-9}$ cm^3 sec^{-1} respectively in the most perfect subliminated plates. The decrease in the quenching constant is connected with the nontrivial influence of lattice defects on the process of exciton–exciton annihilation.

1 INTRODUCTION

The two nonlinear phenomena connected with the interaction of excitons with one another and with photons can occur at high levels of optical excitation in molecular crystals, particularly, in anthracene crystals.

The former involves a decrease in the quantum yield of the integral luminescence as the pumping level increases. This effect called nonlinear quenching results from the annihilation of excitons during collisions and has been found by Tolstoy and Abramov[1,2–4] in anthracene crystals at room temperature and thoroughly studied. Its main characteristics is the rate constant of the exciton–exciton annihilation which is equal to $(1 \pm 0.5)10^{-8}$ cm^3 sec^{-1} at 310°K[3]. In Ref. 5, the nonlinear quenching was observed at the temperatures from 1.5°K to 77°K.

The second effect is the stimulated emission arising due to the inverse population of the lowest exciton band or the lowest electron-excited impurity levels relative to vibrational sublevels of the ground electron state. The four-level diagram of inverse population producing in molecular crystals and appropriate solutions has been investigated by Broude *et al.*[6] before the first lasers on organic dye solutions came into being. The narrow bands of spontaneous fluorescence and its high quantum yield typical of both molecular pure and impurity crystals should enable one to obtain a high gain of stimulated emission in rather small volumes of active medium. Indeed, the stimulated emission of thin crystalline anthracene flakes has been detected by Broude and Sheka at 77°K;[7] recently, it has been studied more thoroughly by Galanin *et al.*[8] and by the authors of the present work[9] at liquid helium temperatures. A sharp increase ($\sim$ by 10^3-fold) in the intensity of the fluorescence spectrum band at 23692 cm^{-1} which corresponds to the electron-vibration transition with the totally symmetric vibration $\sim 1400\ \text{cm}^{-1}$ was observed in these crystals[8,9] at pumping levels 3–4 times exceeding the arbitrary threshold value. The active volume amounted to $\sim 10^{-6}\ \text{cm}^3$. Also, the light generation was performed on tetracene impurity molecules in anthracene crystals with the same active volume by producing the inverse population on the impurities through energy transfer from the host.[10]

One more field of research associated with the study of interaction between excitons is concerned with molecular crystals behavior at high exciton density. In this case the search for bound states of molecular excitons particularly biexcitons[11] and exciton condensate[12] is of primary interest. Unlike inorganic semiconductor crystals in which owing to large radii of excitons, the condensate embodies the features of electron-hole plasma,[12] the appearance of a new "exciton phase" can be expected in molecular crystals with attraction between excitons. The search for Bose–Einstein condensation of excitons which is possible with repulsion between them[13] is also of interest. Very likely that these phenomena may occur only at very high exciton densities (above $10^{19}\ \text{cm}^{-3}$) and crystal temperatures amounted to 1°K or below.[14]

In view of the above-stated, the present paper deals with:

1) the main features and characteristics of light generation in anthracene crystals;

2) the interrelation between the light amplification in crystals and the nonlinear quenching;

3) the conditions for formation of the greatest exciton density at the lowest temperatures possible.

2 EXPERIMENTAL

The anthracene crystals 0.5 to 20 μ thick obtained by the sublimation of thoroughly purificated substance were investigated. Optical excitation was performed by a laser on molecular nitrogen (3371 Å) with peak power 3 Kwt, pulse duration 12 nsec and repetition frequency 25 Hz. The fluorescence was observed from the back or edge faces of the crystal placed into the helium optical thermostat.

An important circumstance complicating the measurements is the heating of the illuminated region of the crystal which arises due to all possible radiationless transitions both as a result of local conversion of excitation energy (~ 0.57 ev) as well as due to the collisional annihilation of excitons. The total heating value could be determined by half-widths of nongenerated bands.

The temperature dependence of half-widths of spontaneous fluorescence bands measured in the anthracene crystals fitted the well-known data.[15] To eliminate the temperature effect on intensity of several bands and integral fluorescence the bath temperature was adjusted in the way to keep the half-width of control bands constant.† In this connection the temperature of the measurements was rather higher than the boiling temperature of liquid helium.

3 RESULTS AND DISCUSSION

3.1 Light amplification and generation

The dependence of intensity and the half-width of fluorescence bands on pumping is shown to be determined substantially by the quality of the crystals, the perfection of its facets, its thickness, the focus-spot diameter and by the temperature and geometry of fluorescence observation (from the back (front) or edge faces of the plate).

Ideally, light generation can be believed to occur between the edge faces of the plate without noticable issue of stimulated emission from the front and back faces, since in this case the amplification length is maximum. The most perfect sublimated crystals 0.5–2 μ thick with a well pronounced pair of parallel edge faces generation characteristics were found to approach the ideal.

In Figures 1 and 2 are shown the typical curves of intensity and a half-width of the band at 23.692 cm^{-1} as well as the intensity of integral fluorescence versus pumping intensity as observed from the back and edge faces. From these data it follows:

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† Such a method for holding crystal temperature at different pumpings assumes naturally the establishment of thermodynamic equilibrium in the crystal lattice. This however requires an additional study.

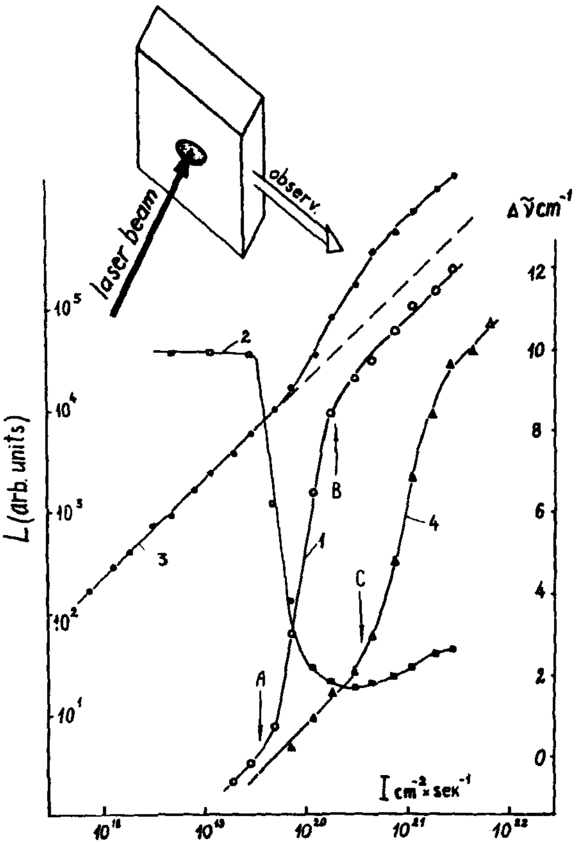

FIGURE 1 Dependence of the anthracene crystal edge fluorescence L on the pumping power I. Fluorescence intensity in maximum of the amplified band at 23,692 cm^{-1}, curve 1. The points A and B correspond to arbitrary threshold values $I_n^{(1)}$ and $I_n^{(2)}$ respectively. Half-width $\Delta\bar{\nu}$ of the amplified band, curve 2. Complete fluorescence spectrum intensity, curve 3. Fluorescence intensity in maximum of the amplified band in the sample with partly destroyed edges ($I_c \simeq 10 I_A$), curve 4.

1) Sharp growth occurs in the 23692 cm^{-1} band beginning from the pumping threshold value $I_n^{(1)}$ of (3–6) × 10^{19} cm^{-2} sec^{-1} for perfect crystals at a thermostat temperature of 4.2°K with a focus-spot diameter of 3–4 mm.

2) The intensity of stimulated emission from the edge faces increases by ~ 10^3-fold as pumping increases by 3–4 times $I_n^{(1)}$. For $I \geq I_n^{(2)}$ the stimulated emission depends linearly on a subsequent increase in excitation intensity.

3) The superlinear increase in the intensity of integral fluorescence from the edge is followed by a sublinear increase in intensity from other directions.

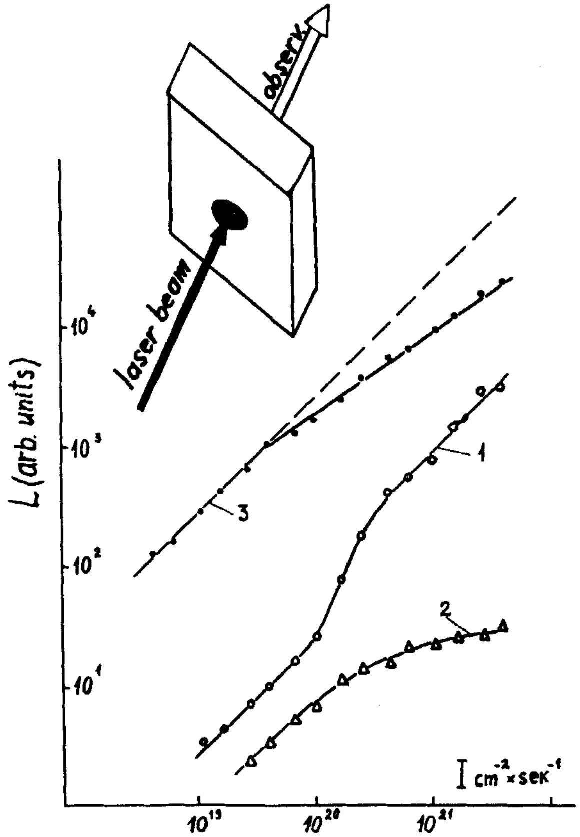

FIGURE 2 Dependence of the anthracene crystal back fluorescence L on the pumping power I. Fluorescence intensity in maximum of the amplified band at 23,692 cm^{-1}, curve 1. Fluorescence intensity of the band at 24,704 cm^{-1}, curve 2. The half-width of the band was kept constant and equal to 11.5 cm^{-1}. Complete fluorescence spectrum intensity, curve 3.

For $I_n \geq I_n^{(2)}$ all the ideal crystal emission is practically concentrated in the amplified band at 23692 cm^{-1} and it emits from the crystal edge.

The amplification factor[6] can be estimated from the pumping threshold value $I_n^{(1)}$:

$$\alpha_0 = \frac{k I_n^{(1)} \eta}{8\pi^2 c\tilde{\nu}\,\Delta\tilde{\nu}}, \qquad (1)$$

where k is the pumping light absorption coefficient, η is the fraction of the amplified band in the spontaneous fluorescence spectrum (~ 0.02), $\tilde{\nu}$ and $\Delta\tilde{\nu}$ are frequencies and the half-width of this band (23692 cm^{-1} and 10 cm^{-1}

at 6°K respectively). The ratio (1) relates to the case of spatially homogeneous pumping. In our case however $kd > 1$ ($k = 2.10^4\ \mathrm{cm}^{-1}$ and the crystal thickness $d \sim 10^{-4}$ cm) and (1) gives an overstated value of the amplification factor equal to 2 cm^{-1}. However, even from this estimate it follows that the observed amplification accompanied with the concentration of the whole emission in a single amplified band, can occur only due to repeating light passages through the active region that is when the many passing generation conditions arise. The direct support of this is an increase in the generation threshold as the perfection of edges is partly disturbed (see Figure 1).

The curves of Figures 1 and 2 are regularly shifted to the region of higher pumping by decreasing the illuminated area S of the crystal, and

$$I_n^{(1)} \sim 1/S \tag{2}$$

Temperature measurements have shown that $I_n^{(1)}$ according to (1) increases proportionally to $\Delta\tilde{\nu}$ over the temperature range from 6 to 30°K. In the most perfect samples, for $I_n^{(1)} \leq 4.10^{19}\ \mathrm{cm}^{-2}\ \mathrm{sec}^{-1}$ at 6°K, an amplification in the 23692 cm^{-1} band is observed up to 170°K where $\Delta\tilde{\nu}$ increases almost by 2 orders of magnitude. For 170°K $I_n^{(1)} \simeq 8.10^{21}\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$.

Unlike the ideal model in the crystals of lower perfection, part of stimulated emission escapes the crystal also through its front (back) surface. In this case however, the generation threshold increases and the amplification of the 23692 cm^{-1} band is smaller than that observed in the edge emission of an ideal sample. In the samples of very low optical quality or in the crystals with disturbed edges, the radiation losses can be so large that the amplification threshold increases even more and the radiation becomes practically isotropic.[8,9] The estimates analogous to those listed above suggest that the one passing superluminescence conditions arise in such samples. It has been found that after irradiating perfect crystals by 10–20 Mrad doses of γ-rays, and thereby creating high concentrations of radiation defects, the generation breaks away.

The measurement of the emission intensity from different zones of a back face indicates that the emission issues mainly through the cracks and surface bends. Because of this, the edge directivity of the emission turns out to be maximum in the crystals 0.8–2 μ thick since thinner crystals are easy to deform especially on cooling and in thicker crystals there appears greater quantity of growing defects.

The maximum temperature at which the generation can be observed at pumping levels less than the limit of damage ($\sim 2.10^{23}\ \mathrm{cm}^{-2}\ \mathrm{sec}^{-1}$) is decreased in imperfect crystals. Also at the pumping levels higher than the damage limit small craters and cracks appear.

The data obtained fit the light generation based on the modes of a total internal reflection.

For a constant pumping light absorption coefficient an increase in the crystal thickness should bring about a decrease in the relative volume of generated modes associated with the active region and as a consequence the threshold of generation should grow. Indeed, for $d \sim 20\,\mu$ the experimental threshold value increases up to $\sim 5.10^{21}$ cm^{-2} sec^{-1}.

Concluding this section it should be noted that the light generation developing in the maximum of the phonon side-band of the pure electronic transition of a tetracene impurity in anthracene (20222 cm^{-1})[10] has the same specific characteristics as those found in this study in pure thin anthracene crystals. In this case, the formation of an inverse impurity population through the energy transfer from the host makes it possible to lower the threshold of generation by 3–4 orders of magnitude over the direct optical impurity pumping.[16] At high pumping levels in the crystals containing $\sim 2.10^{17}$ cm^{-3} tetracene, the generation is observed both in the intrinsic anthracene crystal spectrum band at 23692 cm^{-1} and in the tetracene impurity band at 20222 cm^{-1} with the intensities of the last becoming independent on the pumping which is due to the exciton concentration stabilization in the conditions of intrinsic generation. In this case the primary issue of impurity stimulated emission occurs from edge crystal faces in contrast with the intrinsic one going out from front and back faces due to additional losses of intrinsic radiation connected with tetracene absorption.

3.2 Nonlinear quenching

In reference to the introduction, the nonlinear quenching is provided by radiationless deactivation of excitons under their mutual collisions. In generation conditions, however, the exciton concentration becomes independent of pumping and the experimental dependence of fluorescence intensity on pumping is not associated with the process of exciton interaction at all. On the other hand, the edge generation could be followed by the sublinear dependence of front or back emission on pumping from which the incorrect values of quenching constants can be extracted. Therefore, the nonlinear quenching should be investigated in the conditions of safe absence of the light generation.

The threshold of generation was shown to be dependent on the crystal thickness, a focus-spot diameter and the temperature. This reason allowed ones to increase the threshold of generation so that to investigate the nonlinear quenching with the generation absent.

In Figure 3 is shown the typical curve of nonlinear quenching (1) for the perfect crystal with a well developed edge generation which was subsequently suppressed by decreasing a focus-spot diameter and by disturbing the sample edges. A bath temperature was 4.2°K. The quenching constant is 10^{-9} cm^3 sec^{-1}, which is substantially lower than the value 1.10^{-8} cm^3 sec^{-1} usually

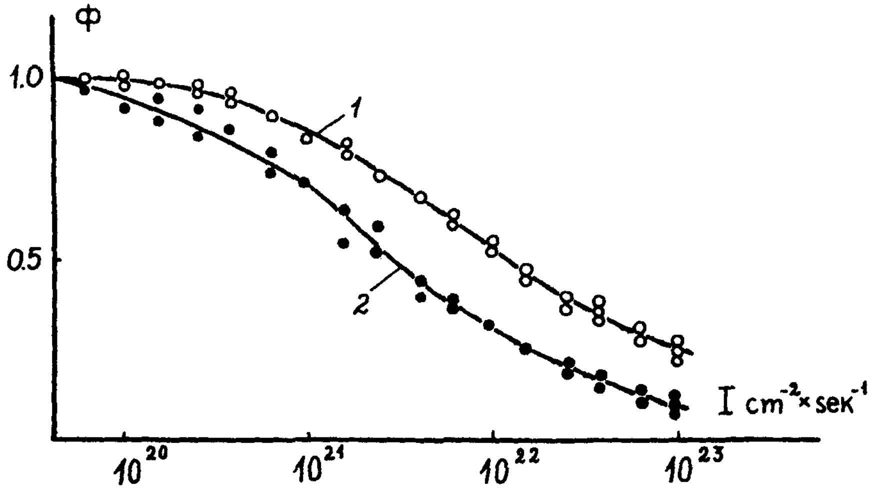

FIGURE 3 Dependence of the quantum yield Φ of the anthracene crystal complete back fluorescence on the pumping power I in perfect sample ($K_{ss} \simeq 10^{-9}$ cm^3 sec^{-1}) curve 1, and in a sample of poor quality ($K_{ss} \simeq 6.10^{-9}$ cm^3 sec^{-1}), curve 2.

cited for the anthracene crystal.[3,5] The same figure gives the curve of nonlinear quenching (2) for a less perfect sample. A lower amplification in the band 23692 cm^{-1} was observed in this crystal at a large focus-spot diameter. The appropriate quenching constant proved to be equal to ~ 6.10^{-9} cm^3 sec^{-1}. In samples cut from an monocrystalline anthracene ingot grown from the melt, the quenching constant ~ 10^{-8} cm^3 sec^{-1} was found as in Ref. 5. The irradiation of the most perfect crystals by the γ-source is also followed by an increase in the quenching constant up to ~ 10^{-8} cm^3 sec^{-1}.

The investigations of the quenching constant dependence on the temperature in the crystals of different perfection have been carried out. The quenching constant of perfect sublimated samples increases from 10^{-9} cm^3 sec^{-1} at 7°K to 6.10^{-9} cm^3 sec^{-1} at 300°K. In defect crystals, the quenching constant (0.5–1.0) 10^{-8} cm^3 sec^{-1} is practically independent on the temperature.

The total set of experimental data is by far indicative of high sensitivity of nonlinear quenching to the structural crystal perfection.

It can be assumed that the quenching constant of the most perfect anthracene crystals approaching 10^{-9} cm^3 sec^{-1} stipulated the direct exciton interaction at rather low temperatures. Its increase in the less perfect samples with different kinds of defects, should be explained by some "catalitic" effect of these disturbances. In this case the exciton annihilation presumably involves the intermediate state of so-called a local biexciton.[17] The temperature dependence of the quenching constant also becomes more or less clear. In the case the quenching constant is determined by defects, the quenching does not depend on the temperature like the concentration of these disturbances. On the other hand, the thermal lattice vibrations and thermodynamics defects determine the temperature dependence of quenching constant of perfect crystals.

The above cited value of the quenching constant in the most perfect crystals means that quenching in a light generation regime may be neglected since the exciton concentration, stabilized on the threshold of generation, is rather small. In less perfect samples with the quenching constant $\sim 10^{-8}$ cm^3 sec^{-1}, the threshold of generation is preceded by the sublinear dependence of fluorescence intensity on pumping for $I < I_n^{(1)}$.

4 CONCLUSION

A thorough study of fluorescence in different anthracene crystals over the wide range of optical pumping makes it possible to find the conditions for separate investigation of light generation and the exciton-exciton radiationless annihilation.

One of the essential results obtained was the detection of high sensitivity of these processes to the structural perfection. Of interest is the nontrivial effect of the third body, and, in particular, of lattice defects in the process of exciton pair annihilation.

Proceeding from the data obtained, the most appropriate conditions for the formation of maximum density exciton gas are realized in the perfect crystals 2–3 μ thick with disturbed edges and with the focus-spot diameter less than 0.4 mm. The estimates show in these conditions, one can achieve the exciton concentration $\sim 2.10^{18}$ cm^{-3} through the nitrogen laser with above cited parameters. The pumping level is herein restricted to $\sim 2.10^{23}$ cm^{-2} sec^{-1} since higher intensities cause crystal damage. If the crystal is placed in this case into the bath with superfluid helium ($\sim$ 1.5°K), its heating by the pumping light can amount to $\sim 6°$.

It should also be expected that the stimulated emission, in turn, offers a number of experimental possibilities for the study of the dynamics of molecular excitons, the mechanisms of energy transfer by excitons and the electronic–vibrational relaxation of the excitation energy. The most obvious of these applications is the determination of temperature dependence of the constants of energy transfer to impurities from the temperature dependence of their flourescence under conditions of generation in the host.

Since the reduction in exciton lifetime caused by stimulated emission is comparable to the effects of other kinds of relaxations, it should be possible to investigate the role played by phonons in the process of energy transfer and in creating nonequilibrium distributions of excitons in the band.

Finally, the excitation of fluorescence by laser light of different wave lengths can allow the determination of the radiationless intra-and intermolecular relaxation rates.

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