

Local biexcitons in anthracene crystals

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New bands have been observed in the luminescence spectra of anthracene crystals under conditions of intense laser pumping and are attributed to the formation of local biexciton states near the lattice defect molecules.

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Using intense optical pumping (LGI-21 pulsed nitrogen laser with $\lambda = 3371 \text{ \AA}$) was observed in the region of the intrinsic absorption of the anthracene crystal at helium temperatures the appearance of new intense luminescence-spectrum bands which are missing from the spectra at low pumping levels (mercury lamps). The investigations were made on sublimated plates of anthracene, in whose luminescence spectra we studied in particular detail the region from 24500 to 2400 cm^{-1} , where are located the two phononless lines 24 350 (*B*) and 24 162 cm^{-1} ,^[1] accompanied by phonon wings and belonging to extrinsic emission of the anthracene crystal. The nature of these lines is still not clear. Glockner and Wolf^[1] attribute them to defect states, i.e., with the emission of two sorts of deformed anthracene molecules near a chemical impurity or of a defect in the crystal. Lyons and Warren^[2] on the other hand, suggest that they are due to the impurity emission of one or several isomers of methyl-anthracene in the sample. We propose that the point of view of Glockner and Wolf^[1] is more likely for a number of reasons and will henceforth adhere to it, and analyze the degree to which it agrees with the obtained new singularities in the spectrum.

It was established that the lines *B* and *C* always appear simultaneously in the luminescence spectrum of any specially doped or initially contaminated crystal, and their relative intensity is always practically the same, $I_C/I_B = 1.6 \pm 0.2$. This result agrees with the micrograms of the spectra, which are given in the paper of Lyons and Warren.^[2]

The obtained shifts of the *B* and *C* bands away from the bottom of the anthracene-crystal exciton band ($\sim 25100 \text{ cm}^{-1}$) amounts to 750 and 938 cm^{-1} respectively. These do not seem to be anomalously large values for defect levels, since the shift of the electronic term of the molecules in the crystal field (gas—crystal) in anthracene is approximately 2300 cm^{-1} . The bands *B* and *C* are the starting points of vibronic series, in which part is taken by vibrations at 372, 1169, 1268, 1411 and 1565 cm^{-1} , which are close in magnitude to the vibrations of anthracene (394, 1167, 1262, 1405 and 1558 cm^{-1}). A rough estimate from the luminescence spectrum of a mercury lamp shows that the concentration of the defect molecules is 10^{15} – 10^{16} cm^{-1} .

The luminescence spectra of the pulse-excited anthracene crystals were registered with a time resolution accurate to 0.05 nsec.^[3] Figure 1 shows the investigated spectra obtained by mercury-lamp excitation and by pulsed-laser excitation ($t_p \sim 10 \text{ nsec}$) at different points of time in this pulse (stroboscopic measurements^[3]).

It is seen from Fig. 1 that at certain instants of time an additional intense band *C'* appears in the spectrum and is shifted 72 cm^{-1} away from the phononless line *C* toward the longer wavelengths.

A similar picture is observed also for the defect *B*. In this case the additional band *B'* appears at a distance 40 cm^{-1} from the phononless line *B* on the long-wave side.

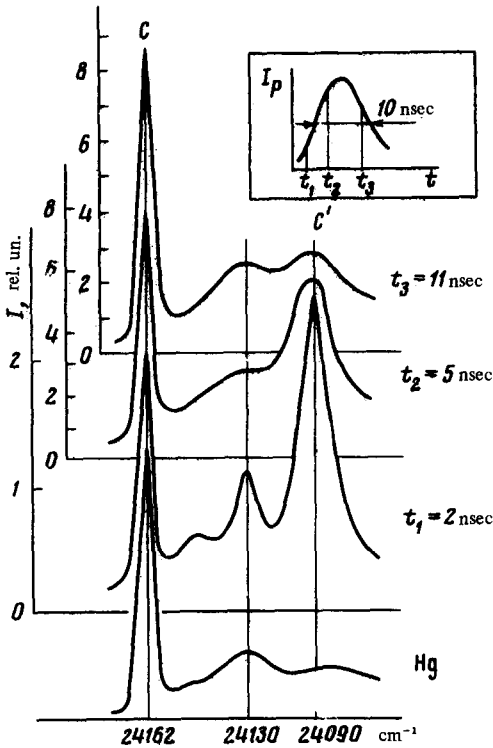


FIG. 1.

Figure 2 shows plots of the intensities of the investigated bands C and C' against time. It is seen from Fig. 2 that the emission in the new band C' has a distinct kinetics that differs noticeably from the emission kinetics of band C . It can be noted here that the emission pulse in the band C' is close on the leading front to the emission pulse of the 23692 cm^{-1} intrinsic vibronic band of the luminescence spectrum of the anthracene crystal. The intensity of this band is proportional to the concentration n_{exc} of the excitons in the absorption layer, and precedes noticeably the emission pulse in band C in time.

Similar emission kinetics are observed also for the bands B and B' . The appearance of new additional bands in the region of the phonon wings can be seen also in the entire series of the vibronic transitions of defect molecules.

Proceeding to the interpretation of the experimental data, we must note immediately that the observed spectral singularities cannot be due to the interaction of the defect centers with the non-equilibrium phonons that accumulate in the crystal.^[4] This statement is substantiated by the absence of any changes whatever in the anti-Stokes region of the defect centers (the short-wave wings near the phononless bands of the defect luminescence).

The proposed interpretation consists of setting the B' and C' bands in correspondence with formation of a bound biexciton state on the defect molecules near a chemical impurity or another lattice disturbance. Within the framework of this assumption it is possible to explain the rapid kinetics of the new state, which can be due to the intense Auger recombination process which is well known for excitons in the anthracene crystal.^[5] It follows also from this interpretation that

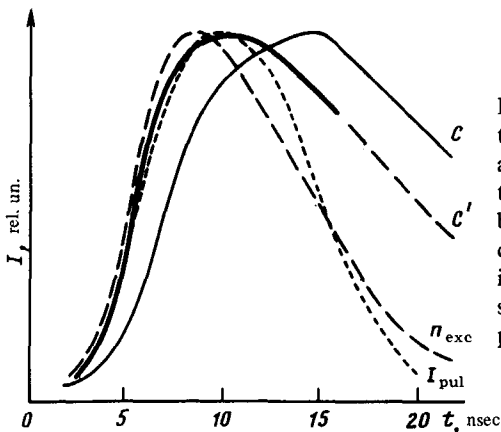


FIG. 2. I_{pul} —waveform of pump pulse, n_{exc} —intensity of the 23692-cm^{-1} vibronic band of the anthracene crystal (proportional to the concentration of the free excitons), C —intensity of the band C , C' —intensity of the band C' ; the latter disappears rapidly from the spectrum on the trailing edge of the pump pulse and the dashed line shows the time dependence of the intensity of the phonon wing at this wavelength (4150 \AA).

there should be no changes at all in the luminescence region of a chemical impurity, such as tetracene, since twofold excitation of the impurity corresponds to a state that lies above the exciton band of the matrix. This was directly confirmed in the measurement of crystals with tetracene-molecule impurities ($\sim 10^{13} \text{ cm}^{-3}$).

It must be recalled that autolocalization of biexcitons under resonant excitation was observed in ionic crystals.^[6]

The results, and in particular the long-wave shift of the biexciton bands B' and C' relative to the direct radiation of the defects—the bands B and C —attests to the presence of the attraction between the excitons and the anthracene crystals. This confirms the previously obtained data on the production of an exciton condensate in anthracene crystals.^[7] The energy structure of the investigated spectrum can be used to estimate the energy of the exciton interaction with one another. The object of our subsequent research will also be the determination of the construction of the defect centers and of the spatial model of the local biexciton.

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