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SUPERLUMINESCENCE IN ANTHRACENE CRYSTALS

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When anthracene crystals were intensely excited with a nitrogen laser ($\lambda = 337$ nm) at 4.2°K, a strong increase of the luminescence line and of the vibronic transition to the 1400 cm^{-1} vibrational level was observed. This increase is due to the unique superluminescence which occurs in a thin ($\sim\lambda$) excited layer near the surface of the crystal.

The luminescence spectrum of an anthracene crystal at helium temperature consists of narrow ($\sim$5 - 10 cm^{-1}) bands corresponding to vibronic transitions from the exciton state, and a background apparently connected with superposition of the phonon wings [1, 2]. One observes also a number of narrow lines belonging to uncontrollable impurities [1]. The exciton density attainable by intense excitation is strongly limited by "nonlinear" quenching which is due (in the case of short exciting pulses) to dipole-dipole energy transfer in the interaction of singlet excitons [3]. As noted by us in [4], at an exciting flux of $\sim 10^{23}$ photons-$cm^{-2}sec^{-1}$ the electron density reaches 2×10^{18} cm^{-3}, i.e., about 5×10^{-4} of all the molecules are excited. An increase in the excitation intensity by several more times already damages the crystal.

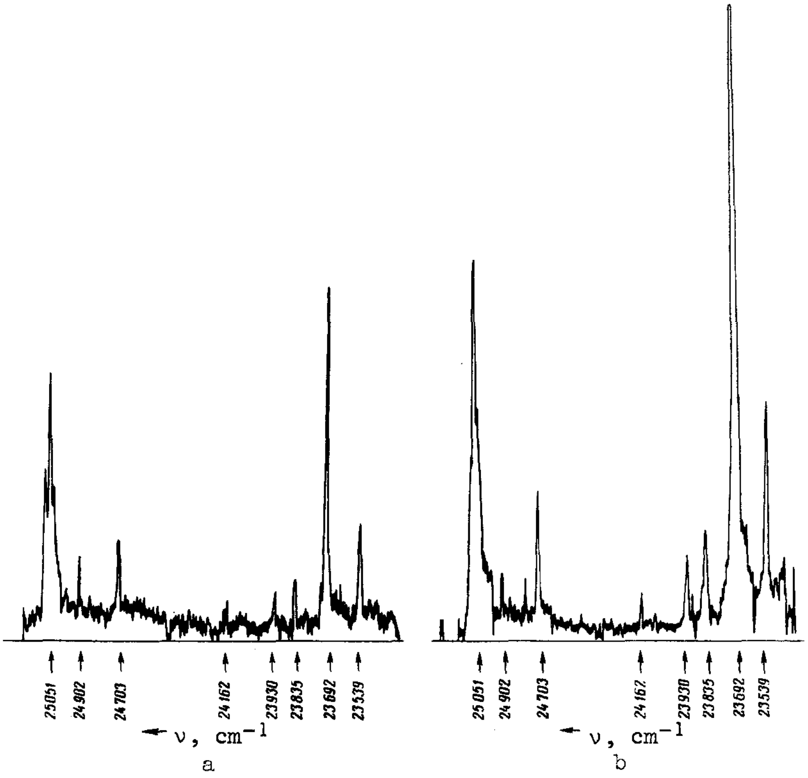

Fig. 1. Luminescence spectrum of anthracene crystal at 4.2°K at excitation intensities 1.4×10^{22} (a) and 1×10^{23} (b) photon-$cm^{-2}sec^{-1}$.

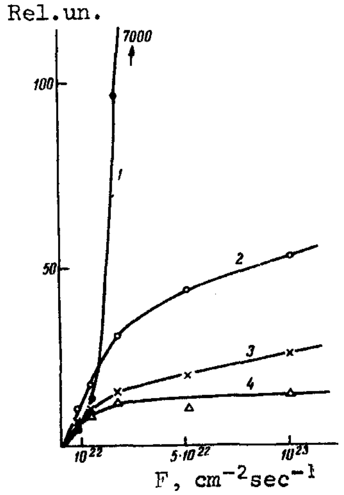

Fig. 2. Dependence of intense luminescence of anthracene crystal on the excitation intensity: 1 - 23692 cm^{-1} line (vibronic transition to the 1400 cm^{-1} vibrational level), 2 - fundamental line 25051 cm^{-1} near 0 - 0 transition, 3 - 24703 cm^{-1} (vibronic transition to the 400 cm^{-1} vibrational level), 4 - 24902 cm^{-1} impurity line.

We used for the excitation a nitrogen laser with pulse duration 15 nsec and repetition frequency 10 Hz (power 1.8 kW in the pulse).

The crystals investigated by us were thin ($\sim$1 μ) plates obtained by sublimation from anthracene purified by zone melting, and were free standing, i.e., without a substrate. The crystals were immersed in the liquid helium and the exciting light was focused into a spot of area less than 0.1 mm^2. The luminescence light emerged in a direction close to normal to the surface of the plate and was focused by a lens on the slit of a DFS-12 monochromator. The pulses from the photomultiplier placed at the exit slit of the monochromator were amplified and the signal was fed through a storage circuit to an automatic recorder. The slit width (0.03 to 0.1 mm) made it possible to take advantage of the resolving power of the monochromator and to determine the widths of the lines.

Figure 1 shows plots of the sections of the luminescence spectra in 25000 - 23500 cm^{-1} region at excitations 1.4×10^{22} and 10^{23} photons-$cm^{-2}sec^{-1}$. When the excitation intensity is increased, two effects can be seen: (1) a very strong increase of the 23692 cm^{-1} vibronic line[1] (exceeding the scale of the instrument), and (2) a relative decrease of the 24902 cm^{-1} impurity line. At frequencies below 23500 cm^{-1} no change in the spectrum was observed with increasing excitation intensity. Figure 2 shows the variation of the line intensity with changing excitation intensity. The initial linear sections correspond to constancy of the luminescence yield. Quenching then sets in for the bands near 25051 and 24703 cm^{-1}, and also for a number of other vibronic bands, and the 24902 cm^{-1} impurity line does not grow at all with the excitation intensity (saturation of the impurity band was noted earlier in [5]).

The 23692 cm^{-1} line has a very strong and superlinear increase. Measurement of the line widths has shown that when the excitation intensity is increased to 10^{23} photons-$cm^{-2}sec^{-1}$ this line narrows down from 5 cm^{-1} at least to 2 cm^{-1}. At the same time, the other lines broaden somewhat, obviously as a result of the heating of the crystal. If we take into consideration the data given in [2], then the line broadening corresponds to a rise of only several degrees. The indicated effects change somewhat quantitatively for different samples, but their general character remains the same.

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[1] No exact calibration against the wavelengths was carried out, and the wave numbers of the lines were taken from [1, 2].

It is natural to assume that the increase and the narrowing of the 23692 cm^{-1} line is due to stimulated emission. The role of stimulated emission in the luminescence of anthracene crystals at high excitation intensities was discussed in [6]. An estimate of the possible gain exponent can be obtained from the well-known formula

$$k = \frac{1}{\tau_0} \frac{N}{8 \pi c \tilde{\nu}^2 \Delta\tilde{\nu} n^2} \beta,$$

where τ_0 is the radiative lifetime, N is the concentration of the excited molecules (the population of the lower level located 1400 cm^{-1} away from the ground level is of course negligibly small), $\tilde{\nu}$ and $\Delta\tilde{\nu}$ are the frequency and the line width expressed in wave numbers, n is the refractive index, and β is the fraction of the given line relative to the entire spectrum.

Assuming $\tau_0 = 5 \times 10^{-9}$ sec, $N = 2 \times 10^{18}$ cm^{-3}, $\Delta\nu = 5$ cm^{-1}, and $\beta = 0.02 - 0.05$ (roughly estimated from the experimental spectrum), we obtain $k = 1000 - 2500$ cm^{-1}. In spite of such a large value of the possible gain exponent, it is still too small to ensure a gain across the excited layer and to explain the observed increase of the line by two orders of magnitude. Indeed, the thickness of the excited layer is determined by the absorption coefficient of the exciting light ($k_{exc} = 3 \times 10^4$ cm^{-1}), i.e., it equals 0.3 μ. The diffusion of the excitons can hardly increase this value to any extent, and in any case it is limited to the thickness of the crystal (∿1 μ). The gain along the excited layer, however, can be quite appreciable. The transverse dimension of the excitation spot is of the order of 0.1 mm, yielding $kx \sim 10 - 25$ or $e^{kx} \sim 10^4 - 10^{10}$. Thus, superluminescence or even lasing can occur along the surface of the crystal, since feedback can be ensured by even a small amount of scattering.

The small thickness of the active layer and the large value of the gain should lead to unique phenomena: a rather appreciable change in the refractive index in the layer, and diffraction of the light through large angles. These are apparently the causes of the gain when the observation is along the normal to the surface of the plate. (We noted no significant difference in the observed effects when the observation was from the surface or from the end face of the plate.)

In conclusion it can be noted that the gain in all the investigated crystals was observed at one and the same line 23692 cm^{-1}, although in many crystals the more intense line in the case of weak excitation was the principal line 25051 cm^{-1}. It is possible that this is due to the larger transparency of the crystal in the region of the vibronic line, or to the larger relaxation rate from the corresponding lower level.

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SUPERLUMINESCENCE AND GENERATION OF STIMULATED RADIATION UNDER INTERNAL-REFLECTION CONDITIONS

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It is customarily assumed that the coefficient R of reflection of light from an interface between two media is a quantity less than or equal to unity.

The purpose of the present communication is to show that in the case of internal reflection of light from an interface between a transparent medium and a medium with inverted population cases with R >> 1 are possible, so that an internal-reflection laser can be constructed.

1. The experimental setup is shown in Fig. 1. The active element was a prism (1) of K-8 glass, the base of which was in contact with a solution (2) of rhodamine-6G mixed with nitrobenzene in ethyl alcohol (4:1). The dye concentration was 10^{-3} mole/liter. The solution was sealed with the aid of a special "pocket" equipped with a heat exchanger, through which thermostatically-controlled water was pumped.

The mirrors (99 and 50%) were installed in such a way that the resonator axis coincided with the path of the ray experiencing the internal reflection from the boundary of the prism with the dye solution. The reflection angle ϕ was approximately 89°. The pump was the second harmonic of a neodymium laser, focused on the surface of the solution with the aid of a cylindrical lens. The pump energy was ~0.1 J.

2. When the refractive index n of the solution is properly chosen (a rough adjustment of n was effected by varying the ratio of the solvent components, and a more accurate one by varying the temperature) generation of radiation in the region of the luminescence of the solution was observed. The divergence of the light beam exceeded somewhat the diffraction divergence and equalled approximately $\sim 10^{-2}$ rad.

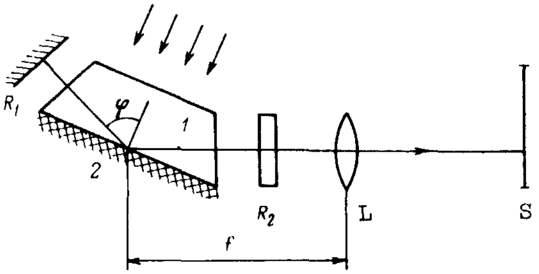

Fig. 1. Experimental setup: 1 - prism, 2 - active medium, R_1 and R_2 - mirrors, L - lens (f = 10 cm), S - spectrograph slit. The arrows show the pump direction.

The light beam was projected on the entrance slit of an STE-1 spectrograph in such a way that rays emerging from the generator at different angles struck different sections of the slit. This made it possible to register simultaneously the emission spectra at different angles of incidence of the light on the boundary between the prism and the dye solution. Figure 2 shows the spectral-angular characteristic of the radiation at different solution temperatures. The generation spectrum usually consists of a small group of narrow lines, the positions of which depend on the refractive index and consequently on the temperature of the solution. The position of the luminescence band remains in this case constant, but the