

# Self-suppression of exciton-exciton annihilation in a dense system of molecular excitons

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A sharp decrease in the efficiency of triplet-triplet annihilation has been observed in crystals of benzophenone ( $C_{13}H_{10}O$ ) at exciton densities of  $10^{18}$ – $10^{20}$   $cm^{-3}$  near 4.2 K. This decrease is attributed to a suppression of exciton migration by an exciton-exciton interaction.

Among the various phenomena which can occur in molecular crystals as excitons approach each other, it is exciton-exciton annihilation which has been studied most thoroughly. Only a few experimental studies have been reported on other possible manifestations of interactions of molecular excitons, in particular, on a search for biexcitons and more complex multiexciton formations: clusters and droplets.<sup>1–3</sup>

Questions which are extremely important but which have received the least study are the mechanisms for the interaction of molecular excitons and the nature of the corresponding interaction potential. It is, however, clear that this interaction will be seen most explicitly if the shift of molecular levels which it causes,  $\delta\epsilon(\bar{r})$  ( $\bar{r}$  is the average distance between neighboring excitons), is not small in comparison with the width of the exciton band,  $\Delta$ . Under the condition  $|\delta\epsilon(\bar{r})| \sim \Delta$ , it can be expected that the motion of excitons will be substantially affected by the mobile defect structure which they form.

A similar situation is encountered in a study of the quantum diffusion of impurity atoms in crystals, for which a theory was derived by Kagan and Maksimov.<sup>4</sup> Following Ref. 4, we would expect that a further increase in  $\delta\epsilon(\bar{r})$  (e.g., through an increase in the density of excitons), at a temperature which is not too high,  $kT < |\delta\epsilon(\bar{r})|$ , should lead to a quasiliquid diffusion of excitons, to the formation of exciton clusters, and then to a complete self-localization in the exciton system. In addition, we cannot rule out the formation of a large cluster with a long-range order,<sup>4</sup> i.e., in this case an exciton crystal. The satisfaction of the condition  $\Delta < |\delta\epsilon|$  would be particularly likely for triplet excitons, whose bands are usually narrower than  $5 \text{ cm}^{-1}$  (these bands are determined by a resonant interaction of an exchange nature).

In the experiments which we describe below, a spectral-kinetics method was used to study the effect of the concentration of triplet excitons in crystals of benzophenone on the efficiency at which triplet excitons are annihilated and on their energy distribution. The long lifetime of triplet excitons in this crystal (about 2 ms) and the approximately unit probability for an intercombinational conversion mean that it is possible to achieve high concentrations of triplet excitons by optically pumping the crystal into the first excited singlet state,  $S_1$ . The pumping is carried out with an LGI-21 nitrogen laser, with a pulse length of about 10 ns and a pulse energy of about 20  $\mu\text{J}$ . The

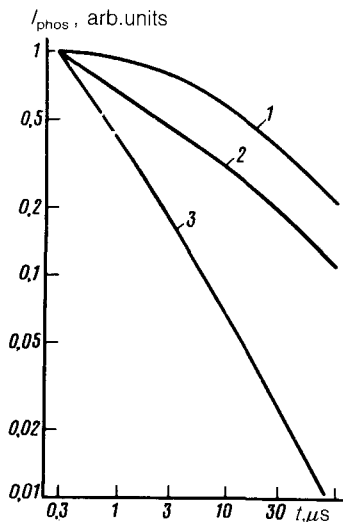


FIG. 1. Decay of the exciton phosphorescence of the benzophenone crystal. 1— $n_0 \approx 3 \times 10^{17} \text{ cm}^{-3}$ ; 2— $n_0 \approx 10^{20} \text{ cm}^{-3}$ ; 3—calculated. The phosphorescence intensity at  $t = 300 \text{ ns}$  is assigned a unit value.

maximum concentration of triplet excitons reaches  $10^{20} \text{ cm}^{-3}$  (this is a calculated value).

Figure 1 shows decay curves of the (spectrally) integrated exciton phosphorescence of a benzophenone crystal measured at  $T = 4.2 \text{ K}$  for two initial concentrations of triplet excitons,  $n_0 \approx 3 \times 10^{17} \text{ cm}^{-3}$  and  $n_0 \approx 10^{20} \text{ cm}^{-3}$ . The first of these curves can be approximated well by the usual equation

$$\frac{dn}{dt} = -\gamma n^2, \quad (1)$$

if we take the exciton-exciton annihilation constant  $\gamma$  to be  $5 \times 10^{-13} \text{ cm}^3/\text{s}$  and if we integrate the solution over the volume of the sample, allowing for the absorption of the exciting light. The decay of the excitons which is linear in  $n$  at  $n > 10^{17} \text{ cm}^{-3}$  can be ignored.

At  $n_0 = 10^{20} \text{ cm}^{-3}$ , a solution of Eq. (1) yields a different decay curve (curve 3 in Fig. 1). The decay rate observed under these conditions (curve 2) is far lower than the calculated rate. The transition from one type of decay to the other occurs gradually in the concentration range  $10^{18} - 3 \times 10^{19} \text{ cm}^{-3}$ .

The most likely reason for the pronounced decrease in the annihilation rate from the calculated value is an interaction of excitons. In this case, the interaction cannot be regarded as slight. As the benzophenone molecule undergoes a transition from the  $S_0$  ground state to the  $T_1$  triplet state, it undergoes a change in static dipole moment (the  $\text{C}_{13}\text{H}_{10}\text{O}$  molecule does not have an inversion center). This change is about 1 D and is directed along the CO bond of the molecule. Effectively, the triplet exciton has a dipole moment. Estimates show that the energy of the dipole-dipole interaction of two triplet excitons lies between  $-25$  and  $30 \text{ cm}^{-1}$ , and even at  $n \sim 10^{19} \text{ cm}^{-3}$  this part of the interaction energy at the average distance exceeds the resonant part ( $\lesssim 1 \text{ cm}^{-1}$ ).

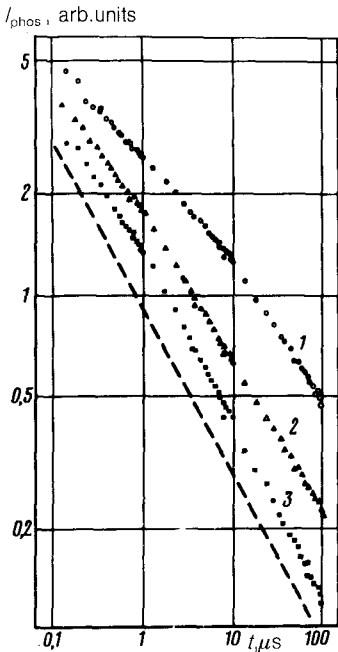


FIG. 2. Decay of the exciton phosphorescence of a benzophenone crystal at  $n_0 \approx 10^{20} \text{ cm}^{-3}$ . 1— $T = 4.2 \text{ K}$  (in liquid helium); 2— $T = 4.5 \text{ K}$ ; 3— $T = 15 \text{ K}$ .

We would naturally expect that this circumstance would hinder the migration of triplet excitons and the annihilation which it brings about.

Evidence in favor of this interpretation comes from the acceleration of the annihilation of triplet excitons at a high concentration at an elevated temperature (Fig. 2). The decay kinetics of the exciton emission at  $T > 4.2 \text{ K}$  is described approximately by  $t^{-1/2}$ , which is characteristic of a long-range dipole-dipole recombination of static excitations. However, the possibility of a recombination of this sort for triplet excitations has not yet been confirmed.

That there is an interaction of excitons in this system can also be deduced from the changes in the phosphorescence spectrum of the excitons. These changes occur at  $n_0 \sim 10^{18} \text{ cm}^{-3}$  and intensify with increasing concentration.

Figure 3 shows the difference between two phosphorescence spectra of a benzophenone crystal pumped at intensities differing by a factor of seven. These spectra have been normalized to a common height of the band corresponding to the purely electronic transition  $\nu_{00} = 24\,194 \text{ cm}^{-1}$ . These spectra were measured over the time interval  $t_1 = 2 \mu\text{s}$  to  $t_2 = 50 \mu\text{s}$  after the pump pulse. The difference spectrum reveals a significant number of excited states below the energy of the 00 transition of free excitons, apparently due to a joining of some of the excitons in clusters.

Since a heating of the crystal by the pump pulse could also cause changes in the spectrum, we experimentally evaluated the temperature of the excited part of the crystal over the pertinent time interval. For this purpose we measured the spectra of mixed crystals consisting of 95% deuterobenzophenone ( $\text{C}_{13}\text{D}_{10}\text{O}$ ) and 5% benzophenone. In this case, the latter forms capture centers with a depth of about  $30 \text{ cm}^{-1}$ .

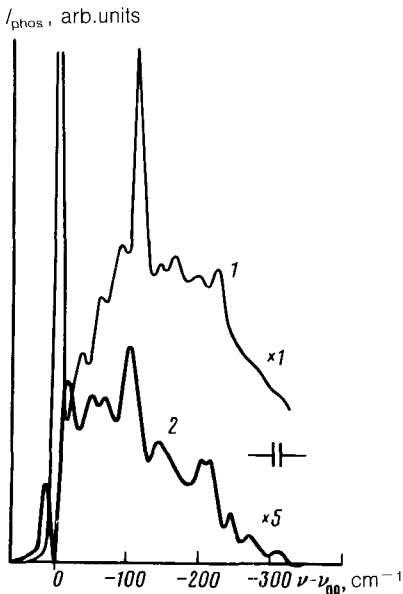


FIG. 3. 1—Initial part of the phosphorescence spectrum of a benzophenone crystal at  $T=4.2$  K ( $n_0 \approx 10^{20}$   $\text{cm}^{-3}$ ); 2—difference between the normalized spectra obtained at  $n_0 \approx 10^{20}$   $\text{cm}^{-3}$  and  $n_0 \approx 1.4 \times 10^{19}$   $\text{cm}^{-3}$ .

From the time-dependent ratio of the emission of excitons and capture centers after the pulse, which excites primarily excitons, we can find an upper estimate on the temperature of the crystal. Taking this approach, we found that  $10 \mu\text{s}$  after the pump pulse the temperature of the emitting part of the crystal, immersed in liquid helium at  $T = 4.2$  K, does not exceed 7 K. The changes in the exciton phosphorescence spectrum of the benzophenone crystal over the temperature interval from 4.2 to 7 K are insignificant.

The observed self-suppression of the diffusion of small-radius excitons as their concentration increases is similar in many ways to the self-localization of impurity atoms in the course of their quantum diffusion in the case of an impurity-impurity interaction. It should be noted, however, that in the case of triplet excitons the scale interaction energy is shifted upward. The effect is to promote an intensification of the interaction of localized excitons with phonons. It probably also interferes with a complete self-localization of excitons.

Deciphering the difference spectrum and finding a quantitative explanation for the decay kinetics of the exciton emission at a high exciton concentration will require more-detailed studies.

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<sup>2</sup>V. A. Benderskii, V. Kh. Brikenstein, Ye. Ya. Misochko, N. A. Vidmont, and V. V. Korshunov, *Mol. Cryst. Liq. Cryst.* **57**, 47 (1980).

<sup>3</sup>B. I. Verkin and A. F. Prikhot'ko (editors), *Krikristally (Cryocrystals)*, Naukova Dumka, Kiev, 1983, p. 526.

<sup>4</sup>Yu. Kagan and L. A. Maksimov, *Zh. Eksp. Teor. Fiz.* **87**, 348 (1984) [*Sov. Phys. JETP* **60**, 201 (1984)]; **88**, 992 (1985) [*Sov. Phys. JETP* **61**, 583 (1985)].

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