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STUDY OF TRIPLET EXCITON INTERACTION IN MOLECULAR CRYSTALS

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This research continues the study of interaction and relaxation of triplet excitations and is devoted to the magnetic field effect on spin-lattice relaxation (SLR) of triplet excitons and to the triplet-triplet annihilation properties at high density of excitons.

Introduction

Triplet excitons have some advantages over singlet ones when studying interaction between excitons in molecular crystals. A comparatively long life of triplet excitons facilitates production of their high concentrations. The triplet excitons are characterized by narrow bands (~ 1 cm^{-1}), which promotes manifestation of even weak static interaction between them. Triplet excitons in the benzophenone crystals possess a supplementary property due to the static dipole moment of about 1 Debye. It is a result of the dipole moment variation in the benzophenone molecule with its transfer from the basic state S_0 to the triplet one T_1.

Effect of the magnetic field on the SLR of triplet excitons

Rapid SLR ($10^{-6} \div 10^{-8}$s) is typical of triplet excitons as a result of excitation migration on translation-nonequivalent molecules /1/. The theory prognosticates suppression of this mechanism under the effect of the external magnetic field /2/, providing the mentioned effect to be observed both with a coherent mode of exciton movement and with an incoherent (diffuse) one.

The study of the dependence of the exciton SLR rate in the benzophenone crystals on the magnetic field was based on the known phenomenon of the spin memory in the triplet exciton capture by a trap /3/. With this aim a deuterobenzophenone-d_{10} crystal with 0.2 % benzophenone-h_{10} impurity was taken. The latter served to form triplet traps with the depth about 30 cm^{-1}. Pulse excitation of the host crystal to the singlet state S_1 and rapid intercombination conversion were followed by formation of triplet excitons. Then excitons might either relax or be trapped by impurities. The calculated capture period amounted to about 300 ns. The pumping density was chosen low to neglect annihilation for the capture period.

The experiment has shown that the trap phosphorescence intensity after

cessation of the exciton capture depends on the magnetic field. As the exciton capture period does not depend on the field and localized triplet excitations in the magnetic field B < 10 T relax slowly, the found effect depends on the competition between the SLR of excitons and their capture. The competition result is "stored" by traps.

At the stage of capture the population of spin sublevels of excitons $N_{0,\pm1}$ and traps $n_{0,\pm1}$ are described by six differential equations which may take no account of the phosphorescence of excitons and traps of the relaxation of the latter:

$$\begin{aligned}
\dot{N}_1 &= -KN_1 - W_1(N_1 - \varepsilon N_0) - W_2(N_1 - \varepsilon^2 N_{-1}),\\
\dot{N}_0 &= -KN_0 - W_1(N_0 - \varepsilon N_1) - W_1(\varepsilon N_0 - N_1),\\
\dot{N}_{-1} &= -KN_{-1} - W_1(\varepsilon N_{-1} - N_0) - W_2(\varepsilon^2 N_{-1} - N_1),\\
\dot{n}_1 &= KN_1,\\
\dot{n}_0 &= KN_0,\\
\dot{n}_{-1} &= KN_{-1},
\end{aligned} \tag{1}$$

where $\varepsilon = \exp\left(\frac{g\mu B}{kT}\right)$. Initial conditions are as $N_i(o) = N_i^o$; $n_i(o) = 0$, $i = 0,\pm1$.

After integration of the system (1) by t within the limits from 0 to $\tilde{t}$, where $\tilde{t}$ is the complete capture period, $\tilde{t} \gg K^{-1}$, $\tilde{t} \ll (k_0 + k_1 + k_{-1})^{-1}$ we obtain a system of algebraic equations which binds rates of SLR of excitons W_1 and W_2 with finite populations of spin sublevels of traps $\tilde{n}_i$:

$$\begin{aligned}
N_1^o &= \tilde{n}_1 + W_1K^{-1}(\tilde{n}_1 - \varepsilon\tilde{n}_0) + W_2K^{-1}(\tilde{n}_1 - \varepsilon^2\tilde{n}_{-1}),\\
N_0^o &= \tilde{n}_0 + W_1K^{-1}(\tilde{n}_0 - \varepsilon\tilde{n}_{-1}) + W_1K^{-1}(\varepsilon\tilde{n}_0 - \tilde{n}_1),\\
N_{-1}^o &= \tilde{n}_{-1} + W_1K^{-1}(\varepsilon\tilde{n}_{-1} - \tilde{n}_0) + W_2K^{-1}(\varepsilon^2\tilde{n}_{-1} - \tilde{n}_1).
\end{aligned} \tag{2}$$

The magnetic field-dependent relation between values of $\tilde{n}_i$ was found from the $\frac{J_B}{J_{B=0}}$ dependence on B. Initial populations of exciton sublevels N_i^o were calculated from data on the triplet state of the isolated benzophenone molecule.

The system (2) does not permit finding both relaxation rates W_1 and W_2. The value of W_1 which depends on W_2 as on the parameter has been found from this system. The obtained dependence of rate W_1 on the magnetic field is shown in Fig. 1. The dashed part responds to all possible values W_2. A triangle shows the value τ_1^{-1} obtained in the paper [4].

Thus, the experiment has confirmed suppression of the exciton mechanism of spin relaxation by the magnetic field prognosticated by the theory. The $W_1(B)$ dependence demonstrated in Fig. 1 is similar to the theoretical one expected during incoherent motion of excitons $W \sim B^{-2}$ [2].

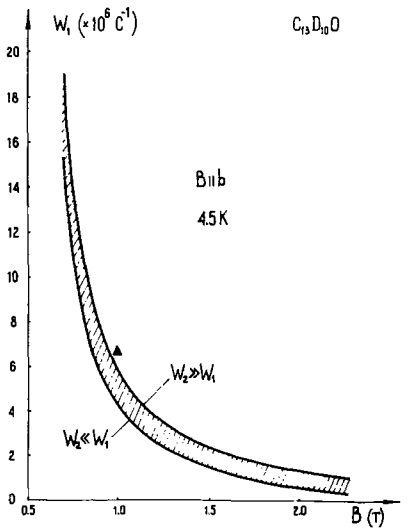

Fig.1. Dependence of rate W_1 on the magnetic field

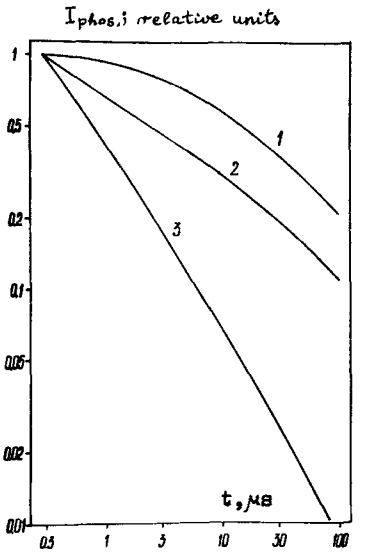

Fig.2. Quenching of the exciton phosphorescence

Self-suppression of exciton-exciton annihilation at high density of triplet excitons

Measurements of the quenching kinetics of exciton phosphorescence of benzophenone crystals after pulse excitation by the nitrogen laser have shown that the exciton-exciton annihilation is the main channel of departure of the triplet excitons, if their initial rate $N_0 > 10^{17}$ cm^{-3}. Fig. 2 shows quenching of the exciton phosphorescence at T = 4.2 K, $N_0 \approx$ $\approx 3 \cdot 10^{17}$ cm^{-3} (curve 1). The respective kinetics is well described by an ordinary equation

$$\frac{dN}{dt} = -\gamma N^2, \qquad (3)$$

where $\gamma = 5 \cdot 10^{-13}$ cm^3/s is an exciton-exciton annihilation constant. In this case the specimen excitation inhomogeneity due to the absorption of the exciting light is taken into account.

At the same time in case of more intensive pumping when $N_0 \approx 10^{20}$ cm^{-3} the observed quenching rate (curve 2, Fig. 2) proves to be considerably less than the calculated one (curve 3).

It is natural to relate an essential decrease in the efficiency of the exciton-exciton annihilation with high density of excitons to retardation of the exciton diffusion, as annihilation of triplet excitations

proceeds, as a rule, the contact way. The cause of the excitons migration retardation is, probably, their interaction. Estimates show that the dipole-dipole part of energy of interaction between two triplet excitons may vary within the ranges from 25 to 30 cm^{-1} depending on their mutual arrangement. Already at $N \sim 10^{19}$ cm^{-3} the dipole-dipole interaction of neighbouring excitons exceeds the resonance one which is less than 1 cm^{-1}. Thus, excitons prove to play the role of movable lattice defects. The defective structure formed (probably it contains exciton clusters) is to weaken exciton diffusion and annihilation resulted from it. The fact that the crystal temperature elevation by several degrees accelerates the annihilation adds to this interpretation.

Main conclusions

It is found that the triplet exciton SLR rate in the magnetic field decreases as a result of the orienting action of the field on the triplet spins.

At high density of triplet excitons their migration and annihilation related to it are retarded. This fact is, probably, a result of static interexciton interaction.

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