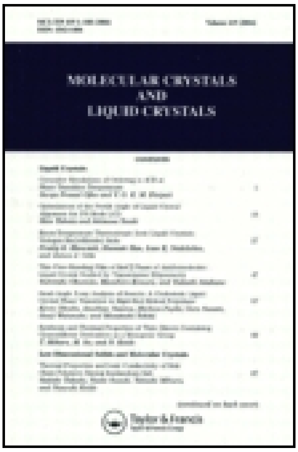

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Enhancement of ODMR Effect in a System of Triplet Excitons at Threshold of Annihilational Bistability in Organic Crystals Containing Traps

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Enhancement of ODMR Effect in a System of Triplet Excitons at Threshold of Annihilational Bistability in Organic Crystals Containing Traps

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It is shown that the sensitivity of a system of triplet excitons in organic crystals to microwave radiation under conditions that give rise to the development of a annihilational bistability significantly increases. A possibility to change intensity of crystal phosphorescence by an order of magnitude by applying microwave field resonant to the transitions between spin sublevels of trapped excitons has been demonstrated.

Keywords: Triplet exciton, bistability, microwave irradiation

1. INTRODUCTION

Recently it was found that the system of excitons in organic crystals may develop annihilational instability under intense light irradiation.[1,2] This instability results in either bistability or self-oscillations of exciton density and temperature. Both phenomena were observed for the system of triplet excitons in deutero-benzophenone crystal with benzophenone impurities.[3]

In this paper it will be shown that owing to the triplet character of excitons in the crystal the development of instability may be effected with application of external microwave field. On the other hand response of the exciton luminescence to the microwave field, that may be detected by means of ODMR (optical detection of magnetic resonance) technique, enhances significantly at the threshold of instability.

Annihilational instability in organic crystals with impurities arises due to the annihilation induced positive feedback between the temperature rise and exciton escape from traps. The instability develops this way: a temperature rise facilitates the escape of excitons captured on traps and that enhances annihilation processes due to the greater mobility of free excitons. Since annihilation is accompanied with energy transfer to the crystal lattice those processes result in further temperature increase. As exciton annihilation is a nonlinear process the development of instability requires certain exciton density that is created with external light irradiation. Thus there exists a certain value of intensity of irradiation at which crystal temperature begins to grow rapidly. Below that value there is an intensity range in which the system may be in one of two states with low or high temperature (the thermostat temperature being the same) and with different levels of luminescence intensity. It is important to note that the exciton density is controlled by two different exciton decay mechanisms, one of which (annihilation) is nonlinear and promotes temperature rise. The second mechanism of exciton decay that is the reemission of a light quantum contributes to luminescence of the crystal.

Account for the triplet nature of excitons provides the possibility to control the development of bistability by applying external microwave field with the frequency resonant to the frequency of transitions between spin sublevels of triplet states. This possibility arises due to the fact that by changing the population of different spin sublevels by applying a microwave radiation one can influence the mean lifetime of excitons in the system thus shifting the balance between two competing decay mechanisms. It will be shown in the paper that microwave irradiation enlarges the region in which bistability arises. So one can expect to switch the system between two stable states with different temperature by decreasing the intensity of microwave radiation. This is accompanied by the decrease of the phosphorescence by an order of magnitude.

2. MODEL OF THE SYSTEM

Let us consider a crystal with impurities that form exciton traps. The crystal is excited with ultraviolet light (level scheme is shown in Figure 1). Levels of triplet excitons are populated due to the process of intercombination conversion. Let the quantum yield of the crystal be close to unity for low intensity of light irradiation. The magnetic spin–spin interaction and spin-orbit interaction in excited molecules results in the splitting of spin sublevels even in zero magnetic field. To describe the dynamics of triplet excitons, one should introduce six variables of exciton density for three subbands of free excitons and three sublevels of trapped excitons. However, the time of spin-lattice relaxation for three spin states of free excitons is small ($10^{-7}-10^{-8}$ s)[4] due to the modulation of the fine structure during the exciton motion.[5,6] Therefore the populations of spin states of free excitons are similar and one can describe free excitons with a single variable of the total population of the free exciton band disregarding their spin states. The time of spin-lattice relaxation of trapped excitons is much greater $\sim 10^{-5}-10^{-6}$ s. Due to the low relaxation rate and radiative lifetimes that may differ by an order of magnitude for the three spin sublevels the populations of different sublevels of trapped exciton may be significantly different. This fact in particular enables the strong influence of external microvawe radiation that changes the population of different sublevels and as a result the total population of trapped excitons. In this paper we shall consider a situation when the frequency of microwave radiation is close to the frequency of a transition between spin states with short and long lifetimes with respect to emission.

It is easy to show that for the equal populations of spin states of free excitons the *mean* (*with* respect to the spin states) exciton capture and escape rates averaged over the spin states of *free* excitons do not depend on the spin state of the trap. Therefore we

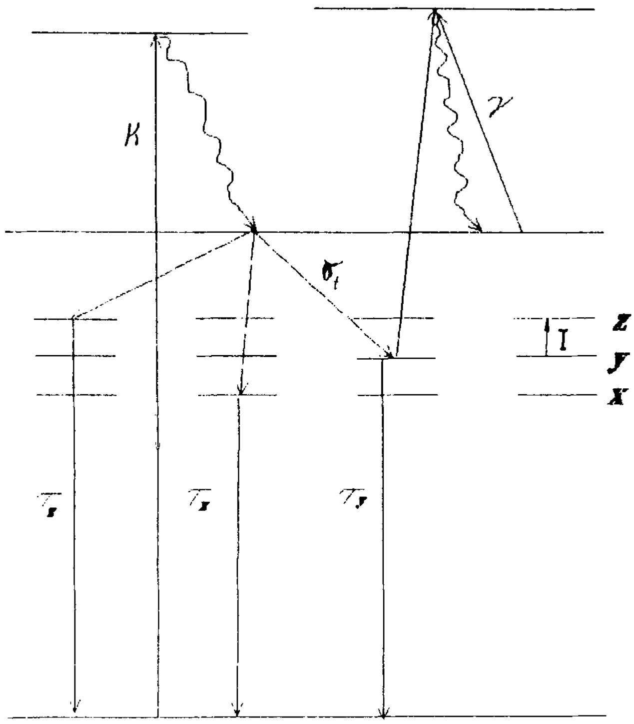

FIGURE 1 The scheme of levels of excitations for the considered triplet exciton system in molecular crystal with exciton traps.

suppose the rates of the exciton capture by a trap to be independent of the resulting spin states of trapped exciton.

Let us consider a thin slab of molecular crystal in which the light irradiation creates K excitons in unit volume in unit time. The slab is in a thermostat with the temperature T_{th}. If the slab is thin and the thermoconductivity of the crystal is high, temperature equilibrium within the plate is established much quicker than the equilibrium between the slab and the thermostat. In this case the sample temperature will be uniform across the slab, and differ from the thermostat temperature, depending significantly on processes within the crystal. The exciton density distribution in the crystal and crystal temperature may be described with the following system of equations.

$$\frac{dn}{dt} = K - n/\tau - \gamma_{00}n^2 - \tfrac{1}{2}\sum_{i=x,y,z} \gamma_{0i}nn_i - \gamma_i n(n_t - n_x - n_y - n_z)$$
$$+ \gamma_t N \sum_{i=x,y,z} n_i \exp(-\varepsilon_i/T), \tag{1}$$

$$\frac{dn_x}{dt} = -n_x/\tau_x - \tfrac{1}{2}\gamma_{0x}nn_x - \gamma_t Nn_x \exp(-\varepsilon_x/T)$$
$$- W_{xy}n_x + W_{yx}n_y - W_{xz}n_x + W_{zx}n_z + \tfrac{1}{3}\gamma_t n(n_t - n_x - n_y - n_z), \tag{2}$$

$$\frac{dn_y}{dt} = -n_y/\tau_y - \tfrac{1}{2}\gamma_{0y}nn_y - \gamma_t Nn_y \exp(-\varepsilon_y/T) - I(n_y - n_z)$$
$$- W_{yx}n_y + W_{xy}n_x - W_{yz}n_y + W_{zy}n_z + \tfrac{1}{3}\gamma_t n(n_t - n_x - n_y - n_z), \quad (3)$$

$$\frac{dn_z}{dt} = -n_z/\tau_z - \tfrac{1}{2}\gamma_{0z}nn_z - \gamma_t Nn_z \exp(-\varepsilon_z/T) - I(n_z - n_y)$$
$$- W_{zx}n_z + W_{xz}n_x - W_{zy}n_z + W_{yz}n_y + \tfrac{1}{3}\gamma_t n(n_t - n_x - n_y - n_z), \quad (4)$$

$$c_v\frac{dT}{dt} = E\gamma_{00}n^2 + E\sum_{i=x,y,z}\gamma_{0i}nn_i - \beta(T - T_{th}), \quad (5)$$

where n is the density of free excitons, n_x, n_y, n_z are the densities of population of the three levels of trapped excitons, τ is the radiation lifetime of free excitons, τ_i are the radiation lifetimes for the three levels of trapped excitons, ε is the trap depth, T is crystal temperature and $T_{\rm th}$ is that of the thermostat, γ_{00} and γ_{0i} are the constants describing the annihilation rates for two free excitons or a free and a trapped excitons, γ_t is a constant describing trapping of a free exciton, n_t is the concentration of traps, $c_v = \alpha T^3$ is the heat capacity of the crystal at low temperature, E is the energy that is released at the annihilation of two excitons, $\beta = v/2L$, where L is the slab thickness and v is the heat exchange coefficient that enters Newton's boundary condition $\kappa\nabla T = v(T - T_{\rm th})$, κ being the thermoconductivity. Coefficients W_{ij} describe the spin relaxation between triplet levels i and j of a trap. The term $I(n_y - n_z)$ is due to the change of level population induced by the microwave radiation. Here $I = 2\pi g\mu_B H^2 f(\omega)$, where μ_B is the Bohr magneton, g is a spectroscopic factor, H is the magnetic component of the electromagnetic field, $f(\omega)$ is the function of line shape maximal for the resonance $f(\omega) = 1/\gamma$, where γ is the line halfwidth in the case of Lorentz line shape.

3. NUMERICAL CALCULATIONS AND DISCUSSION

Numerical calculations were carried out for the parameters of the deuterobenzophenone crystal doped with the admixture of benzophenone molecules in which the bistability was observed experimentally.[3] The impurity molecules create exciton traps with the depth of 34 cm^{-1}. The radiative lifetime of a free exciton is $\tau = 10^{-3}$ s and for the three levels of trapped excitons the decay rates are equal $\tau_x^{-1} = 60\,\mathrm{s}^{-1}$, $\tau_y^{-1} = 70\,\mathrm{s}^{-1}$ and $\tau_z^{-1} = 768\,\mathrm{s}^{-1}$.[7] Coefficients γ_{0j} were chosen to be same and equal to $5 \times 10^{-13}\,\mathrm{cm}^2\,\mathrm{s}$. The concentration of traps was equal to 5% of all molecules of the crystal. The bistability was observed in a thermostat whose temperature ranged from 2–4 K. Within that range, the probability of spin relaxation of trapped excitons is small and was neglected in the calculations. Account for the relaxation rates $W_{i,j}$ narrows the region of the microwave radiation induced bistability. For the high temperature states the spin relaxation is no longer small but then an additional and more powerful relaxation mechanism (it will be discussed below) arises so one can neglect $W_{i,j}$ in that region too.

Figure 2 shows the dependence of the temperature of the slab (the temperature of the thermostat remains the same) on the rate of creation of excitons (pumping rate) for different values of the applied microwave field. There exists a range of the pumping rate and the thermostat temperature in which the system has three stationary points two of which are stable. The corresponding states will be called hereafter, low and high temperature states. In the former, the radiative mechanism of exciton decay prevails and that prevents the growth of crystal temperature. In the high temperature state the main mechanism of exciton decay is the annihilation with energy transfer to the lattice which maintains the temperature much greater than that of the thermostat. As the result of turning on the microwave field the population of the spin levels of trapped excitons tends to became equal. Therefore the population of the level with a short lifetime increases causing the increase of the luminescence of the system. Thus the role of radiative exciton decay becomes more significant and the system may remain in the low temperature state for greater values of pumping rate (see Figure 2b). Meanwhile the effect of the microwave radiation on the high temperature state turns out to be small. This is due to the effect of a mechanism of the spin relaxation intrinsic for the considered system.[8] It works this way: a trapped exciton escapes from a trap, moves some time in the band and is captured back by the same or another trap. While moving along the crystal the exciton quickly forgets its spin state so it may return to any spin sublevel of a trap. So relaxation would occur. Temperature induced escape of the trapped exciton is the cause of the existence of the bistability itself and it also limits the effect of microwave radiation to the lowest branch of the hysteresis loop. The upper parts of all the curves coincide.

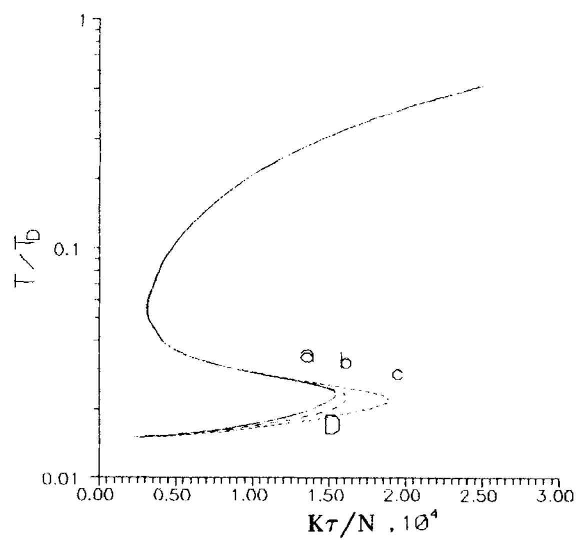

FIGURE 2 Crystal temperature dependence on the pumping rate in the stationary states for different intensities of microwave field: a) without field (solid), b) 10^{-4} Wt/cm^2 (dashed), c) 10^{-3} Wt/cm^2 (dotted). T_D is Debye temperature. Parameters for which calculations were performed are: $T_{th}/T_D = 0.015$, $N = 4 \times 10^{21}$ cm^{-3}, $\alpha = 11.4 \times 10^{-6}$ J/K^4 cm^3, $\beta = 2.76 \times 10^{-14}$ J/cm^{3}Ks. Other parameters are in the text.

Calculations show that in the vicinity to the bifurcation point at which the low temperature state disappears an increase of ODMR response of the system should be observed. This is due to the fact that the balance between two ways of exciton decay becomes more even due to an increase in exciton annihilation rate and a growth of slab temperature prior to bifurcation. Since greater microwave field shifts the balance toward greater role of radiative decay the luminescence of the system should grow. This effect is especially pronounced in the immediate vicinity of the onset of instability. Figure 3 shows dependence of the quantum yield on the frequency of applied microwave field for three values of pumping rate and demonstrates this increase of ODMR response.

To illustrate the possibility of switching between the low temperature and high temperature states with decreasing the intensity of microwave field, Figure 4 shows the numeric solution of the system of Equations (1)–(5). When calculating the system was at first suggested to be placed in the microwave field. After the stationary low temperature state had been reached the microwave field was turned off. As the result the sharp decrease of the phosphorescence in the system was reached accompanied with the rapid growth of temperature. It is worth to note that the transition occurs after some delay since as it is well known all temporal processes slow down in the vicinity to the bifurcation point. At the first moment after switching off the microwave field the total number of excitons in the system even grows since the mechanism of the exciton transfer to the short living state stops to function. But with time, this very effect causes the increase of annihilation rate that is followed with the rapid heating. The time of the switching between the states is of order of several τ and so the decrease of the

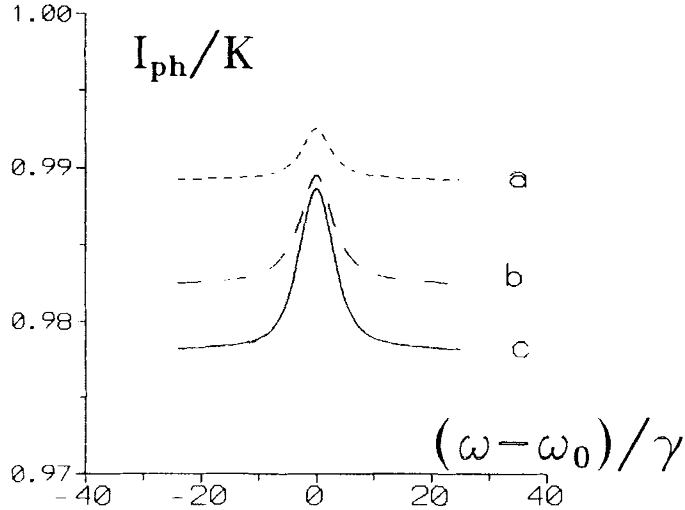

FIGURE 3 Quantum yield of the crystal dependence on the frequency of microwave radiation for three values of pumping rate approaching the bifurcation point (K_r/N) are: a) 10^{-4}; b) 1.4×10^{-4}; c) 1.5×10^{-4} -that is the immediate vicinity to the bifurcation point. Microwave field intensity was 10^{-3} Wt/cm^2, other parameters of the system as in Figure 2.

phosphorescence intensity occurs in the considered system in time of order of 10 ms. The equilibrium temperature is established much later due to the growth of the crystal heat capacity with the temperature.

As was noted above, the significant influence of the microwave field on the bistability in the exciton system is possible at low temperatures when the relaxation between the levels of triplet states is slow, particularly the one induced by the escape of an exciton from a trap and return capture into the different spin state, and the crystal heat capacity is small. The characteristic temperature range in which the effect takes place is about 2–4 K for the parameters of benzophenone crystal. The external irradiation should create about 10^{19}–$10^{20}\,cm^{-3}\,s^{-1}$ triplet excitons, and the concentration of excitons in the crystal in stationary state should be of order of $10^{16}-10^{17}\,cm^{-3}$. The nature of the effect is resonant and the intensity of microwave radiation required to switch the states is minimal for the microwave radiation frequency that coincides with the frequency of transition between the spin sublevels (the other conditions being equal).

The intensity of the microwave field required for observation of the effect may be very small, down to the level of the noise in the system. That depends very much on the ability to keep the system state as close as possible to the bifurcation point. Thus if the thermostat temperature is below the bifurcation point by 0.01 K (that is a point D in Figure 2), the linewidth of the spin levels is 30 G[7] and the temperature remains low for the field intensity 2×10^{-5} Wt/cm^2, then by switching off the microwave field of this rather small intensity, one can succeed in forcing the system to the high temperature state accompanied with the decrease of phosphorescence by an order of magnitude. The required microwave field may be even weaker when the deviation from

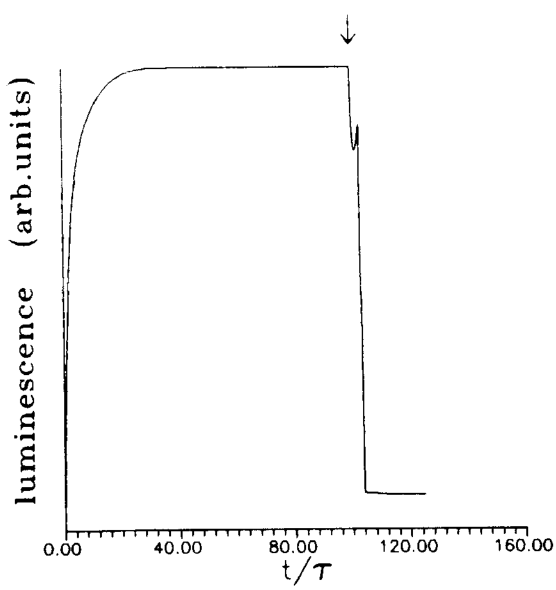

FIGURE 4 Time dependence of the phosphorescence at steady pumping. The moment of time when the microwave field is switched off is indicated by an arrow. $T_{th}/T_D = 0.015$, $K_\tau/N = 1.6 \times 10^{-4}$. Microwave field intensity was 10^{-3} Wt/cm^2, other parameters as in Figure 2.

the bifurcation point requirements in pumping rate and thermostat temperature is smaller, but the study of the behavior of the system in the immediate vicinity of the bifurcation point requires accounting for the fluctuations of temperature and pumping rate and should be considered separately.

Acknowledgments

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