Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: I. Yu. Goliney, V. I. Sugakov & O. N. Shevtsova (1997): Annihilational Multistability in Exciton Luminescence of Organic Crystals with Exciton Traps, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 293:1, 277-285

To link to this article: http://dx.doi.org/10.1080/10587259708042777

Mol. Cryst. Liq. Cryst., 1997, Vol. 293, pp. 277–285
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Annihilational Multistability in Exciton Luminescence of Organic Crystals with Exciton Traps

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(Received 3 June 1996)

Possibility of multistability in exciton luminescence of organic crystals with exciton traps of different depth is shown. Annihilational multistability arises as the effect of the thermally induced escape of trapped excitons leading to a temperature rise due to the enhancement of the annihilation rate of excitons, with subsequent energy transfer to the crystal lattice. Complex hysteresis loops corresponding to multistability are calculated. It shown that quite small number of deeper exciton traps may considerably affect luminescence yield.

Keywords: Excitons; multistability; annihilation; luminescence

1 INTRODUCTION

Annihilational bistability in organic crystals with impurities has been theoretically predicted and experimentally observed in [2]. This effect belongs to the class of selforganization phenomena that attract so much attention nowadays and manifests itself as the development of either bistability or self-oscillations in the crystal under continuous constant light irradiation. The essence of the effect is that exciton annihilation unlike luminescence is accompanied with the transition of a molecule to a highly excited state which relax consequently with energy transfer to the phonon subsystem. Resulting temperature rise will lead to the increase of annihilation rate via thermally stimulated release of trapped excitons. In this way the positive feedback required for the development of instability appears. Exciton sys-

tem in the state close to the development of effect of instability (bistability, auto-oscillations) can show interesting feature, for example, in the case of triplet excitons enhanced ODMR effect [1].

Since bistability in the considered system is due to the exciton escape from traps (increasing their probability to annihilate) it is interesting to study the effect for the crystals with several types of exciton traps with different trap depth in order to look for the conditions at which several (more than two) stable states could exist. This paper deals with the exciton system with two types of traps.

2 BASIC EQUATIONS

Let us consider an organic crystal with impurities in which besides the exciton band there are also exciton traps due to the crystal imperfections and impurities. Let this crystal be irradiated with constant intensity light flux that creates large concentration of triplet excitons by means of intersystem conversion from singlet states. The scheme of the levels in the system is shown in Figure 1. Let the quantum yield of the crystal be close to unity at weak irradiation intensity. Considering the exciton band to be narrow, one may describe exciton motion in frameworks of diffusion approximation.

Let a thin slab made of the organic crystal be placed in the thermostat with temperature T_{th} and irradiated with the steady light source in order to create K excitons in unit volume of the crystal in unit time. The excitons created in this way may further re-emit light quantum, be captured by traps or annihilate with free or trapped excitons. Excitons captured by traps may re-emit light quantum, annihilate with free excitons or escape the traps. The latter is more probable with increasing temperature. In this paper we consider several types of exciton traps with different trap depth. In this case one may indicate several temperature ranges in which different number of exciton traps are involved in this capture-escape interplay. Therefore, depending on the temperature range several stable states may exist.

We consider the slab to be thin enough so that the thermal equilibrium within the crystal would be reached much quicker than the equilibrium between the crystal and thermostat. In this way the crystal temperature may differ from that of the thermostat. At irradiation the crystal is heated due to exciton annihilation, and the greater the mobility of excitons, the higher the crystal temperature would be.

In the framework of this model, the kinetics of the population of levels of trapped or free excitons and the crystal temperature may be described with

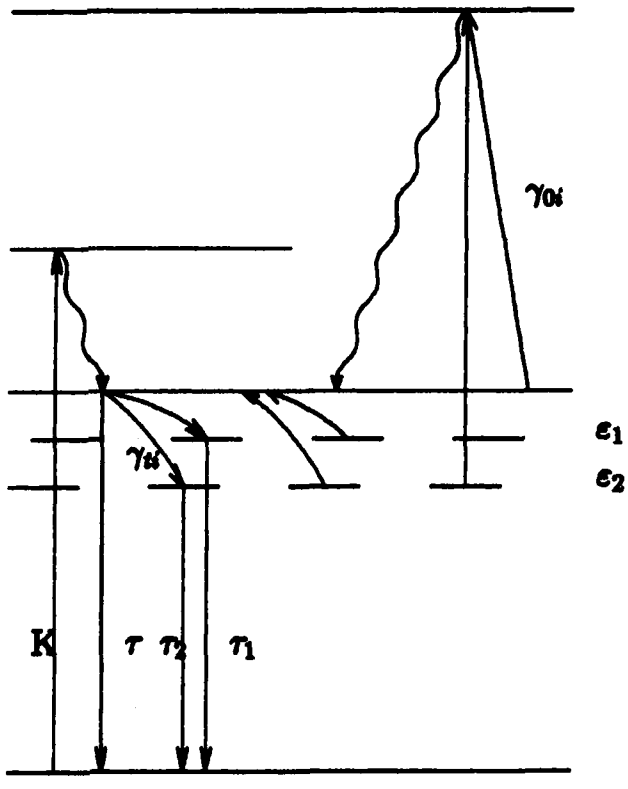

FIGURE 1 Scheme of the levels of an organic crystal with two types of exciton traps. Processes of exciton trapping and thermally induced detrapping, exciton decay with re-emision of a light quantum and as the result of annihilation are shown.

the following set of equations

$$\frac{dn}{dt} = K - n/\tau - \gamma_{00}n^2 - \sum_i \left(\frac{1}{2}\gamma_{0i} n n_i + \gamma_{ti} n(n_{ti} - n_i) - \gamma_{ti} n_i N \exp(-\varepsilon_i/T)\right), \quad (1)$$

$$\frac{dn_i}{dt} = -n_i/\tau_i - \frac{1}{2}\gamma_{0i} n n_i - \gamma_{ti} N n_i \exp(-\varepsilon_i/T) + \gamma_{ti} n(n_{ti} - n_i), \quad (2)$$

$$c_v \frac{dT}{dt} = E\gamma_{00}n^2 + E\sum_i \gamma_{0i} n n_i - \beta(T - T_{th}). \quad (3)$$

Here n is the density of free excitons, n_i is the density of excitons captured by traps of i-th type and ε_i is the depth of the traps of this type, τ and τ_i are

the life times of free and trapped excitons, respectively, γ_{0i} is the coefficient describing exciton annihilation, N is the density of molecules in the crystal. The last two terms in equations (1)–(2) describe exciton trapping and thermally stimulated escape and are written according to the principle of detailed equilibrium. In equation (3) $c_v = \alpha T^3$ is the heat capacity of the crystal at low temperature, E is the energy that is transferred to the crystal lattice at exciton annihilation, $\beta = 2\kappa/L$ is the coefficient of thermal exchange between the crystal and thermostat that is determined by the slab thickness and coefficient κ that enters the Newton equation for thermal equilibrium.

By letting all derivatives in the lefthand sides of equations (1)–(3) to be equal zero one can determine stationary points of the system. Then the stability of these stationary states should be analyzed by letting all variables deviate slightly from the stationary point and determining whether the system would return to that point. This is the procedure to find only stable states. The system may have several stable states and in this way multistability would appear.

3 NUMERICAL CALCULATIONS AND RESULTS

All numerical calculations were carried out for the parameters of deuterobenzophenone crystals in which annihilational bistability was observed [2] in the presence of benzophenone impurity molecules that create exciton trap with the depth of 34 cm^{-1}. In this paper we consider also the second type of exciton traps which are formed by structure imperfection and have depth of 88 cm^{-1}. Those traps were observed experimentally [3], their concentration may change depending on the sample preparation procedure and their physical nature may be connected with the rotation of asymmetrical deuterobenzophenone molecules by 180 degrees [4]. Thus we studied the system with two types of exciton traps.

Figure 2 shows the results of the calculations of the dependence of the temperature of the stationary points of the system on the exciton creation rate K at constant thermostat temperature for various values of the densities of traps of two types. In Figure 2 one can see that for the same value of exciton creation rate there are several values of crystal temperature and exciton density at which lefthand sides of equations (1)–(3) are zero. Analysis has shown that only those of them are stable for which the temperature rises with increasing exciton creation rate. Thus, one can find the range of exciton creation rates for which bistability or multistability (in this case that means three stable states) exist in the system.

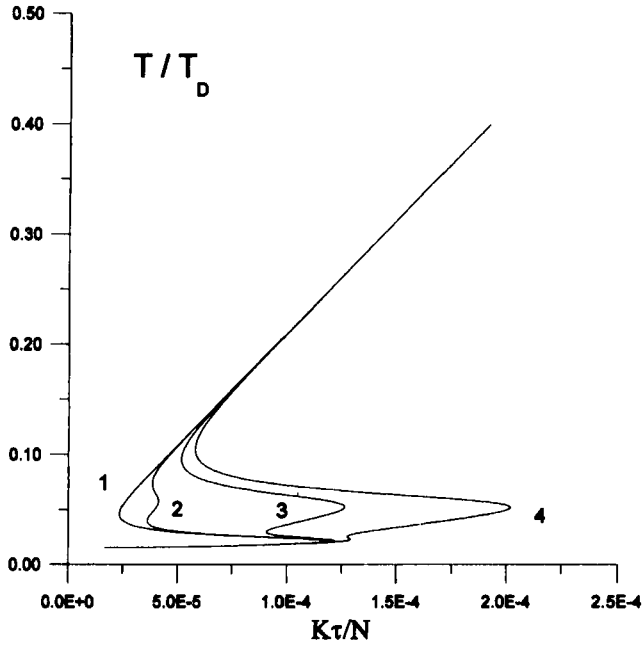

FIGURE 2 Crystal temperature dependence on the exciton creation rate for different densities of traps of two types for fixed total density of traps $n_{t1}+n_{t2}=0.01$. Calculations were carried out for the following parameters: $\tau=2\cdot10^{-3}$ s; $\tau/\tau_1=\tau/\tau_2=0.62$; $\gamma_{t1}N\tau=\gamma_{t2}N\tau=1\cdot10^6$; $\gamma_{0i}N\tau=1\cdot10^6$, $i=0,1,2$; $T_{ih}/T_D=0.015$; $\beta\tau/N=0.1$; $\varepsilon_1=34$ cm^{-1}; $\varepsilon_2=88$ cm^{-1}. The numbers denote the curves for the following values of density of the deeper traps n_{t2}/N: 1-0.0, 2-0.0001, 3-0.0015, 4-0.0040. $T_D=150$ K is Debye temperature.

Manifestation of multistability in luminescence of the system is shown in Figure 3 where luminescence intensity dependence on exciton creation rate is depicted. The curve was calculated solving numerically the system of equations (1)–(3) with the gradual change of exciton creation rate. The solution shows two types of hysteresis loops that can be observed in the system. Their realization depends on history and initial conditions.

With increasing exciton creation rate the system initially is in the state with the greatest luminescence intensity and the lowest temperature. This is the case when almost all excitons are trapped and decay mostly by emitting light quanta and the processes of annihilation are "frozen out". With increasing exciton creation rate the system approaches the threshold of instability that arises due to the exciton escape from more shallow traps. At certain point the system jumps to another branch of the stationary state curve. This is accompanied with the rise of crystal temperature and slight decrease of the luminescence intensity. Here two further scenarios are possible.

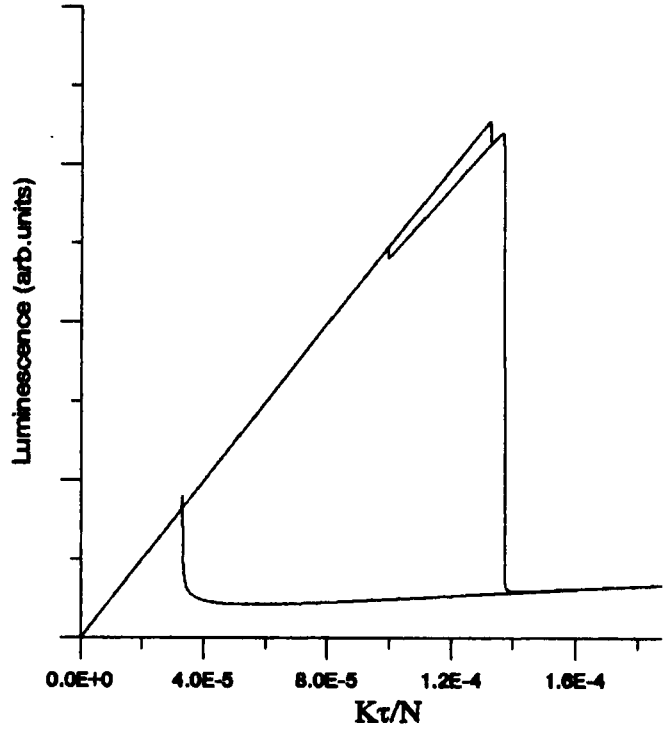

FIGURE 3 Complex hysteresis loop in luminescence dependence on exciton creation rate. $n_{t1}/N = 0.01$ and $n_{t2}/N = 0.002$, $K\tau/N = 1.36 \cdot 10^{-4}$, other parameters as in Figure 2.

If the exciton creation rate decreases from this point then luminescence also decreases gradually till the moment when energy release due to annihilation becomes too small to maintain the temperature that would enable exciton escape from shallow traps. At this point rapid growth of luminescence occurs and the crystal temperature decreases sharply as well.

Another scenario happens if one continues to increase the pumping rate starting from the point where the first sharp decrease in luminescence occurs. Initially the luminescence tries to recover until the moment when the system comes to the state in which excitons captured by deeper traps also become free, temperature increases drastically and luminescence falls by an order of magnitude. Now on decreasing pumping rate the system transfers to the state with lowest temperature passing by the intermediate state.

Figure 4 shows region of multistability versus the pumping rate and thermostat temperature. The greater the thermostat temperature, the less is the pumping rate required for multistability but simultaneously the width of the region decreases. The region of the multistability may be considered as

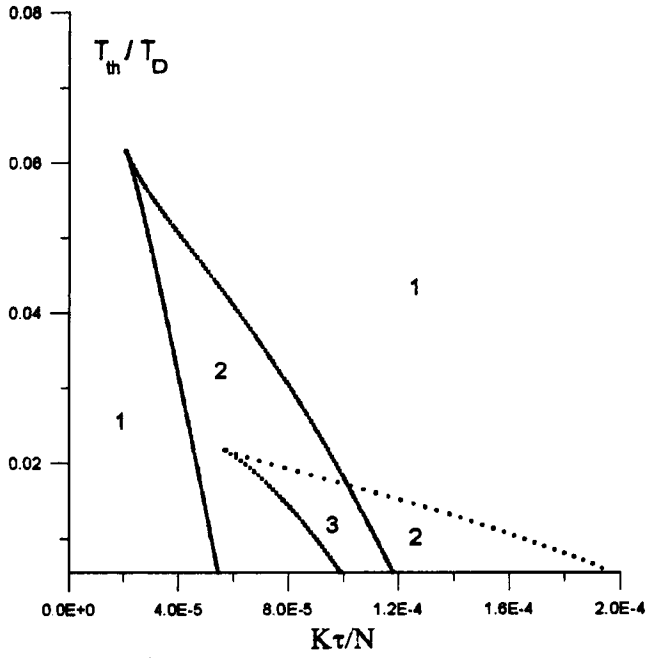

FIGURE 4 Phase diagram of existence of bi- and tristability versus exciton creation rate and thermostat temperature. Ciphers denote number of possible stable states in different regions. $n_{t1}/N = 0.01$ and $n_{t2}/N = 0.002$, other parameters as in Figure 2.

the interposition of the regions of bistability arising due to the presence of two types of exciton traps.

Analysis of curves in Figure 2 shows that multistability arises at a certain threshold value of density of deeper traps. But with further rise of this density the role of shallow levels decreases since the majority of excitons will be captured by the deeper traps. Therefore there is a certain range of trap densities in which multistability is possible. The region of bi- and multistability versus the density of traps of two types is shown in Figure 5. This region takes the form of the "swallow tail". Analysis of the Figure 5 shows that multistability may arise at quite small concentrations of deeper exciton traps (of order of 10^{-4}–10^{-3} for considered case of deuterobenzophenone crystal). This fact means that tiny amount of deep exciton traps that may be considered to be negligible may have significant effect on the intensity of luminescence under certain conditions and even lead to unreproducible results.

Bi- and multistability are most probable in crystals with large exciton life-time, for instance in systems of triplet excitons at helium temperatures in

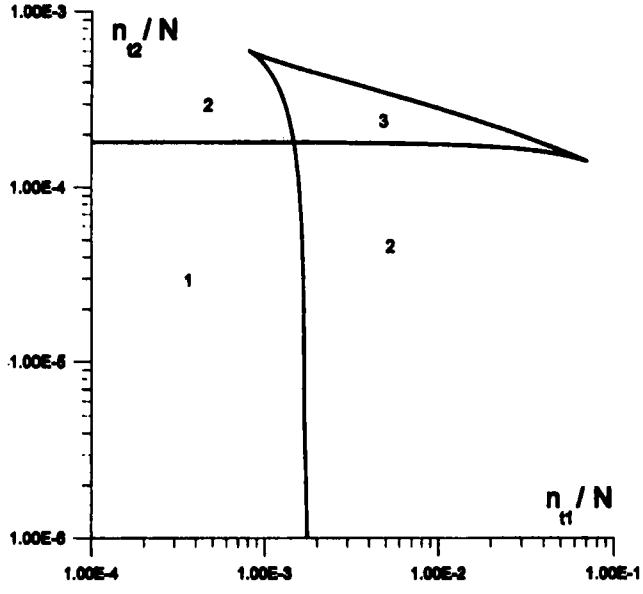

FIGURE 5 Phase diagram of existence of bi- and tristability versus densities of traps of two types. The diagram was calculated for $K\tau/N = 1.5 \cdot 10^{-5}$, other parameters as in Figure 2.

crystals with large quantum yield. Required intensity of light irradiation depends on exciton lifetime. For the deuterobenzophenone crystal the required exciton creation rate is of order of $10^{19}-10^{20}$ excitons per cm^3s. This rate of exciton creation maintains exciton density in crystal of order of $10^{16}-10^{17}$ cm^{-3}.

4 CONCLUSIONS

It is shown that in organic crystals with complex spectrum of exciton traps an annihilational multistability may arise. This multistability manifests itself in the dependence of luminescence on the prehistory of irradiation of the crystal. Multistability arises in crystals with a system of traps of different depth and is a threshold phenomenon. Threshold value depends on the trap concentration.

Acknowledgements

The research described in this publication was supported by The International Soros Science Education Program of International Renaissanse Foundation,

grant ISSEP SPU 042065 and State Committee for Science and Technology of Ukraine.

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