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DIFFUSIVE EXCITATION ENERGY TRANSPORT IN QUASI-ONE-DIMENSIONAL CRYSTALS WITH TRAPS AND IN RELATED SYSTEMS

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The kinetics of the exciton density decay in a quasi-one-dimensional crystal with randomly distributed traps is studied. Assuming that the exciton motion is incoherent (diffusive), we have considered two cases of the initial distribution of excitations over the host crystal molecules: one produced by δ pulse and one by a stationary excitation source. It is shown that the above change in the excitation conditions may result in considerable delay of the decrease of exciton luminescence and in rearrangement of the shape of the luminescence decay curve. The specific features of trap (sensitized) luminescence generated by one-dimensional motion of excitons and trap density fluctuations are indicated. The influence of small concentrations of scattering centers on exciton and trap luminescence kinetics is also discussed. The results derived are applicable to the excitation energy (charge) transport in polymers. In particular, the time dependences of exciton density and trap population can be used to describe the exciton and excimer luminescence in dilute solutions of poly(N-vinylcarbazole). The possibilities to compare the theoretical findings of the paper with the available experimental data are considered.

1. Introduction

Much interest has recently been generated in the electronic excitation energy transport in quasi-one-dimensional crystals. These include molecular crystals of 1,4-dibromonaphthalene [1], 1,2,4,5-tetrachlorobenzene [2,3], weak charge transfer crystals such as naphthalene and tetrachlorophthalic anhydride [4], crystals of $(CH_3)_4NMnCl_3$ (TMMC), $(CH_3)_4NMnBr_3$ (TMMB) [5–7] and others. Exciting radiation produces in the above crystals triplet excitons whose migration is realised primarily along isolated molecular chains. The quasi-one-dimensional character of the exciton motion generates a number of specific features of the excitation energy transport processes which are observed experimentally and studied in the present paper. The structure of our paper is as follows.

In section 2 the exact results on diffusive transport of excitation energy to traps in one-dimensional systems are reviewed. Comparison is made with an approximation such as the average field, the possibilities to compare theory with experiment are discussed. In section 3 we discuss the exciton luminescence kinetics of quasi-one-dimensional crystals with traps under different excitation conditions: short-duration pulses and stationary illumination of a crystal. We also study how this process is influenced by defects such as scattering centers (or barriers). The time dependence of trap luminescence generated by excitation energy transport from the host molecules to the trap due to diffusion, i.e. sensitized luminescence, is analyzed in section 4. The possible manifestation of fluctuations in the density of the defects (traps and barriers) is discussed and reproduced as the kinetic curve of sensitized luminescence.

2. The problem of random walks on a chain with traps and the application of theory to experimental results

To study the transport processes in quasi-one-dimensional crystals, it is of interest to consider the results obtained in solving the problem of random walks on a chain with chaotically distributed traps. In

the simplest statement of the problem it is assumed that the motion of a particle along the chain is realized through random jumps between neighbouring sites, and the absorption of a particle by trap proceeds with unit probability. In ref. [8] an exact result was derived for the average number of steps made by the particle over the sites of an infinite chain with an arbitrary trap concentration, c_{tr}, before it gets trapped. This quantity defines the average lifetime of a particle in a chain containing traps,

$$\bar{T} = 1/2Wc_{tr}^2, \tag{1}$$

where $1/2W$ is the lifetime of a particle on a given site between its two consecutive jumps, W is the unit time probability of a particle jump from one site to the nearest neighbour, so that the average number of steps made by the particle before being trapped is equal to c_{tr}^{-2} [8].

In the theory of continuous time random walks (CTRW) [9], the expression (1) corresponds to zero moment at the average survival probability of a particle in a chain with traps $\rho(t)$

$$M^{(j)} = \int_0^\infty t^j \rho(t)\, dt, \quad j = 0. \tag{2}$$

The survival probability and the moments $M^{(j)}$ are related to experimentally observed quantities. To determine them it is necessary to specify the physical contents of the model.

We now consider the process, detailed below, of incoherent exciton transport in a two-component chain consisting of host molecules and of trap molecules. In this case $\rho(t)$ can be treated as the average exciton population density in the chain at time t, relative to the initial value $\rho(0)$.

The radiative lifetime of an exciton in the following is denoted by β^{-1}, and it is assumed that the jump of an exciton to a trap is realized from the nearest-neighbour host molecule with the unit time probability ω. Then, in the limit $\beta \to 0$, $\omega \to \infty$ we have the result (1) for $M^{(0)}$ [9]. On the other hand, according to the definition of quantum yield (QY),

$$\eta = \beta M^{(0)}, \tag{3}$$

i.e. $\beta\bar{T} = \beta \lim_{\beta \to 0} M^{(0)}$ is the first term in the expansion of η in the small parameter $\beta/2Wc_{tr}^2$ when a molecular chain containing traps is homogeneously excited by a δ pulse. In other words, the QY is defined by eq. (1), provided that $\eta \ll 1$, i.e. the decreasing of the exciton population is mainly due to exciton trapping.

With arbitrary values of the parameters c_{tr}, W, β and ω the general expression for η is derived in ref. [10] (see also ref. [11])

$$\eta = \beta c_{tr}^2 \sum_{n=1}^{\infty} n(1 - c_{tr})^{n-1} m_n^{(0)}, \tag{4}$$

where $m_n^{(0)}$ is the zero moment of the survival probability of a particle in the segment of a chain of n host molecules confined by two traps, the cluster with the length n

$$m_n^{(0)} = \frac{1}{\beta}\left(1 - \frac{2\omega}{\beta n}\frac{z_+^{n+1} - z_+^n - z_+ + (\omega/W - 1)(z_+^n - z_+^{n-1} - z_+) - (z_+ \leftrightarrow z_-)}{(z_+ + \omega/W - 1)^2 z_+^{n-1} - (z_+ \leftrightarrow z_-)}\right), \tag{5}$$

$z_\pm = 1 + \beta/2W \pm \sqrt{\beta^2/4W^2 + \beta/W}$, the parentheses $(z_+ \leftrightarrow z_-)$ imply that next we have terms coinciding with those written accurate to z_+ being replaced by z_-. In particular, when a strong excitation quenching by traps is the case, it follows from (4) and (5)

$$\eta = \frac{\beta}{2Wc_{tr}^2}\left(1 + \frac{2W}{\omega}c_{tr}\right). \tag{6}$$

In the above example of calculating the simplest characteristic of the transport process – QY of the exciton luminescence – we can see the important dependence of the theory predictions on the choice of a model for the trapping process. As is seen from (6), Montroll's result (1) as applied to describe luminescence QY, is valid if, in addition to the condition $2Wc_{tr}^2/\beta \gg 1$, the following inequality is valid:

$$\Lambda \equiv \frac{\omega}{2Wc_{tr}} \gg 1, \tag{7}$$

which is referred to hereafter as the case of fast trapping. When the inversed inequality (slow trapping) is valid, the concentration dependence of η is qualitatively different and, besides, the measured QY does not depend on the diffusion rate.

The difference between fast and slow trapping is also important for studying the kinetics of exciton density decay in a chain with traps but, as far as we know, this was realized only recently [10].

At first, the problem of defining the time dependence $\rho(t)$ has been solved in ref. [12] assuming the trapping to be fast, where it was also supposed that $c_{tr} \ll 1$ [#1]. With these restrictions,

$$\rho(t) = \frac{4}{\pi^2}\int_0^\infty \mathrm{d}x \frac{x}{\sinh x}\exp\left(\frac{-\pi^2 c_{tr}^2 Wt}{x^2} - \beta t\right) \tag{8}$$

$$= \exp(-\beta t)\left(1 - 4c_{tr}\sqrt{Wt/\pi}\right), \qquad \pi^2 c_{tr}^2 Wt \ll 1; \tag{8a}$$

$$= \exp(-\beta t)\left\{16\sqrt{c_{tr}^2 Wt/3\pi}\exp\left[-3\left(\tfrac{1}{4}\pi^2 c_{tr}^2 Wt\right)^{1/3}\right]\right\}, \quad \pi^2 c_{tr}^2 Wt \gg 1. \tag{8b}$$

The asymptotics (8b), obtained within the framework of CTRW theory [12], has subsequently been repeatedly reproduced by other methods [13–17].

A more rigorous evaluation of the integral in (8) for $\tau_1 = 2\pi^2 c_{tr}^2 Wt \gtrsim 1$ yields [18]

$$\rho(t) = \frac{16}{\pi^2}\exp(-\beta t)\left[f_1\left(\sqrt{\tfrac{1}{2}\tau_1}\right) + \sqrt{\tfrac{1}{2}\tau_1}\, f_0\left(\sqrt{\tfrac{1}{2}\tau_1}\right)\right]$$

$$= \frac{16}{\pi}\sqrt{\tau_1/6\pi}\exp\left(-\beta t - \tfrac{3}{2}\tau_1^{1/3}\right)\left[1 + \tfrac{17}{18}\tau_1^{-1/3} + \tfrac{205}{648}\tau_1^{-2/3} + \mathrm{O}\left(\tau_1^{-1}\right)\right], \tag{9}$$

where the functions $f_0(z)$, $f_1(z)$ are defined in ref. [19] [#2]. Comparison of the approximations (8b) and (9) with the exact dependence is represented in fig. 1. We note that expansion (9) is the same as that obtained in ref. [17], although there an integral different from (8) was used to define $\rho(t)$.

In real systems both cases of fast [5,7] and slow [6] trapping can occur, as well as the case of intermediate trapping. Eqs. (8) do not describe all these situations.

When the trapping is slow, $\Lambda \ll 1$, the time dependence of the exciton density is much different from that predicted by the Balagurov and Vaks theory [12]. In addition to the basic asymptotics (9), in this case $\rho(t)$ is characterized by intermediate asymptotics such as [10,18] [#3]

$$\rho(t) = 2\tau_2 \exp(-\beta t) K_2\left(2\sqrt{\tau_2}\right) \tag{10}$$

$$= \exp(-\beta t)(1 - 2c_{tr}\omega t), \qquad \tau_2 \ll 1; \tag{10a}$$

$$= \sqrt{\pi}\,\tau_2^{3/4}\exp\left(-2\sqrt{\tau_2} - \beta t\right)\left(1 + \tfrac{15}{16}\tau_2^{-1/2} + \mathrm{O}\left(\tau_2^{-1}\right)\right), \quad \tau_2 \gg 1, \tag{10b}$$

[#1] We emphasize that the formulas (1), (4) and (6), as distinct from (8), are exact under any trap concentration.

[#2] $f_m(z) = \int_0^\infty t^m \exp(-t^2 - z/t)\,\mathrm{d}t$, $m = 0, 1, \ldots$, see for details ref. [19].

[#3] The same result, but in different context, was obtained in ref. [20]. This was kindly brought to our attention by A.S. Prostnev and M.A. Kozhushner.

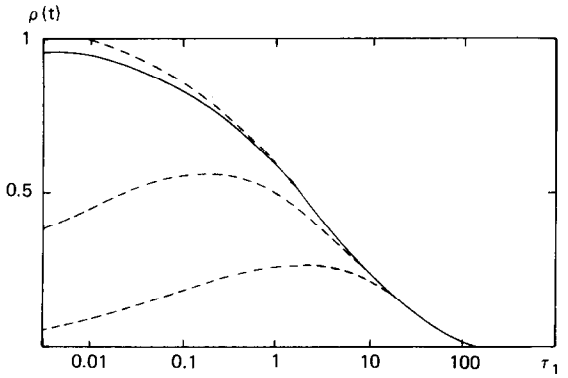

Fig. 1. Comparison of the exact dependence with the approximate dependence. The dependence (8) at $\beta = 0$ is the solid curve. The dotted lines denote the different approximations (8), respectively (from below to above), with one, two and three terms in the square brackets in (9).

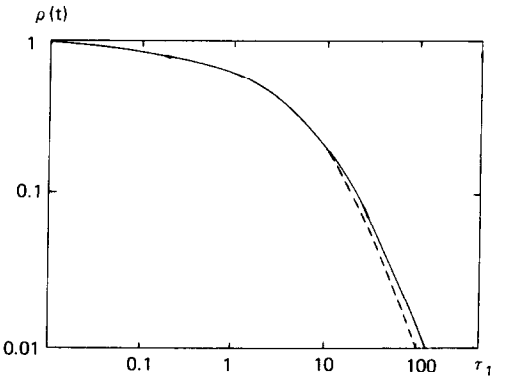

Fig. 2. Comparison of the exact dependence (8) (solid line) with the approximate dependence (13a) ($\beta = 0$). The difference between the curves at $\rho(t) > 0.01\,\rho(0)$ does not exceed 10%.

$\tau_2 = 2c_{tr}\omega t \ll [(\pi^2 W/\omega)c_{tr}]^2$ in (10a) and (10b) ($K_n(z)$ is the modified Bessel function) whereas the dependence (9) is realized at times $\tau_1 \gg (\pi^2 c_{tr} W/\omega)^3$, at which the quantity $\rho(t)$ is practically unobserved, because the number of excitons (particles) that avoid being trapped is small.

Thus, in the case of slow exciton trapping the curve of exciton population decay differs appreciably from (8). The physical reason for the difference in the decay kinetics under fast and slow trapping is that the "trapping reaction" for most clusters proceeds in the first case in the diffusion-controlled (diffusion rate, W, limited), and in the second case in the kinetic (trapping rate, ω, limited) regime.

It is of interest to compare the above results with the theoretical predictions obtained within the traditional approach based on the phenomenological equation for an average exciton concentration

$$d\rho(t)/dt = -\beta\rho(t) - \gamma c_{tr}\rho(t), \tag{11}$$

where γ is the "rate constant" of exciton trapping. The calculation of this quantity using Smolukhovski's bimolecular reaction theory [21,22] yields

$$\gamma(t) = 2\omega \exp(\omega^2 t/W)\,\mathrm{erfc}(\omega\sqrt{t/W}) \tag{12}$$

$$= 2\omega, \qquad (\omega/W)\sqrt{Wt} \ll 1; \tag{12a}$$

$$= 2\sqrt{W/\pi t}, \quad (\omega/W)\sqrt{Wt} \gg 1. \tag{12b}$$

In the case of fast trapping it follows from (11) and (12)

$$\rho(t) = \exp(-\beta t - 4c_{tr}\sqrt{Wt/\pi}), \tag{13a}$$

and in the case of slow trapping

$$\rho(t) = \exp(-\beta t - 2c_{tr}\omega t) \tag{13b}$$

at times that satisfy the condition (12a). At large times defined in (12b), the concentration decay for fast and slow trapping is in this approximation described by the dependence (13a).

As is seen from the comparison of (13) with (8) and (10), the approximate description of the trapping process is, strictly speaking, justified only at small times when $\exp(\beta t)\rho(t) \equiv \tilde{\rho}(t) \approx 1$. Specific calcula-

tions, however, show that the difference between the decay curves defines by the formulas (13) and (8), (10) turns out to be small with $\rho(t)$ changing within 1–0.01. An example of such calculations is given in fig. 2. At large times the discrepancy between exact and approximate dependences becomes pronounced.

Experimental data were processed in refs. [5–7] using the dependences (8) and (13a). In ref. [5], where the migration of triplet excitations in Cu^{2+}-doped TMMC crystals was studied, the observed phosphorescence decay kinetics was equally well described both by (8) and (13a), moreover, the values of the parameters β and W obtained when experimental and theoretical curves exhibit best coincidence turn out to be quite close.

The same crystals (but obtained by a different procedure) were investigated in ref. [6]. The results of that work, in contrast to ref. [5] show that neither (8) nor (13) can fit the observed decay curves of exciton phosphorescence. The authors of ref. [6] assume that the discrepancy may be ascribed to the small trapping rate ω, in their samples, as distinct from those used in ref. [5].

In ref. [7] the exciton population decay after pulsed laser excitation down to $\rho(t) \approx 0.002\rho(0)$ has been examined under an almost ideal one-dimensional triplet exciton transport in the Cu^{2+}-doped TMMB crystals (the ratio of the jump rates along a chain and in transverse direction $> 10^{10}$) and the existence of asymptotics $\exp(-t^{1/3})$, predicted in ref. [12] for long-time kinetics of the trapping process in one-dimensional lattices, has been established experimentally for the first time.

Still as can be seen from the above discussion, the experimental verification of the dependence (8) is not convincing enough in TMMC crystals. As far as we know, the decay curve (10) was not employed at all to interpret experimental results, though this would be quite interesting and informative.

We now want to emphasize the objective difficulties in experimentally verifying the dependences (8) and (10) (or, more general (22), see below). They result from the fact that as the trap concentration varies, as in the experiments of refs. [5–7] (and the accuracy of specifying it is quite limited), the value of the parameter β also changes. This is caused by transverse exciton motion (jumps between neighbouring chains), resulting in a reduced exciton lifetime β^{-1} due to the capture of an exciton generated in one chain by a trap belonging to another. This can be taken into account by adding to the constant β a term proportional to c_{tr}, which at $c_{tr} \ll 1$ describes the trapping under three-dimensional anisotropic diffusion [21] (see also ref. [23]), and we are thus led to the dependence of β on c_{tr} [#4]. Thus, the deviation of the excitation transport from the strictly one-dimensional one effectively increases the exponential decay rate constant and therefore limits the posibilities to observe the nonexponential behaviour of the luminescence decay predicted by (8) and (10) at large times. Moreover, the accuracy of defining the luminescence intensity decreases as it decays.

To reliably define the constants β and W by comparing theory with experiment and to verify the relevance of the theoretical model used, we need at least two independent experiments using a single specimen with a fixed trap concentration. In refs. [5–7] comparison was made with the decay curves obtained theoretically by assuming the crystal to be homogeneously excited by a δ pulse. As a second experiment, we propose to monitor the luminescence intensity decay curve under varying excitation conditions. In section 3 we will give a theoretical expression of the expected decay curve shapes after the stationary crystal excitation. In this case, as shown, the luminescence decay law (depending on the same parameters of the system) can be much different from that defined by (8) or (10). This can be used for reliable determination of the parameters β, ω and W.

[#4] This approximation takes no account of the role of trap density fluctuations in a three-dimensional system. However, the deviation from exponential decay for three-dimensional systems is small [12], and, as numerical calculations show [24], manifests itself at a very remote stage of the process which can hardly be attained in real experiment. Therefore, taking account of the three-dimensional character of the motion by redefining the constant β appears to be justified and will be implied in the following.

We have discussed above the excitation energy transport in quasi-one-dimensional crystals with traps. In real crystals, in addition to defects such as traps, there are also defects that play the role of scattering centers – barriers that reduce the exciton mean-square displacement along the one-dimensional axis. The influence of barriers on the transport processes in the case of a primarily one-dimensional quasiparticle diffusion is, understandably, quite considerable. It was shown in a number of papers, for example, in refs. [1,3–6], that the presence of even a relatively small concentration of scattering impurities sharply lowers the efficiency of excitation energy transfer to traps. A theoretical interpretation of the effect is proposed in refs. [2,23], where the migration of a triplet excitation to traps in dideuterated 1,2,4,5-tetrachlorobenzene (TCB-d_2) was considered as the process of random walks over a superlattice, composed of cages which represent a sequence of host molecules (with or without traps) confined between barriers, TBC-d_2. In other words, it was assumed that the transport is limited by the rate of jumps across high potential barriers and is, therefore, microscopically diffusive irrespective of the character of excitation motion inside the cages.

The model used in refs. [3,23] appears to be applicable only if the barrier concentration is much higher than the trap concentration. When the concentration of defects such as the barriers is $c_b \lesssim c_{tr}$, the theory of ref. [23] cannot be applied. But in this case, too, the influence of scattering centers on the excitation energy transport to the traps can be significant. Below we give some exact results concerning the role of small barrier concentration in forming the kinetic curves of exciton and trap (sensitized) luminescence of quasi-one-dimensional crystals.

In section 3 we consider the exciton luminescence of a crystal under two possible realizations of experimental conditions: δ-pulse homogeneous excitation and instantaneous switching-off of an external source after a stationary regime of crystal excitation is attained.

3. Kinetics of luminescence quenching by traps under different excitation regimes

3.1. Two-component chain

The time dependence of the exciton (host molecule) luminescence under homogeneous excitation averaged over a random trap distribution is defined by [10],

$$\rho(t) = c_{tr}^2 \sum_{n=1}^{\infty} (1-c_{tr})^{n-1} \rho_n(t) \underset{c_{tr} \ll 1}{=} c_{tr}^2 \int_0^{\infty} \exp(-c_{tr} n) \rho_n(t)\, dn, \tag{14}$$

where $\rho_n(t)$ is the exciton population of a cluster of n host molecules ($n^{-1}\rho_n(t)$ has the meaning of the survival probability of a particle executing random walks on a chain of n sites with traps at edge sites).

Assuming the trap concentration to be small, we find

$$\rho_n(t) = \int_0^n \rho(x, t)\, dx, \tag{15}$$

where $\rho(x, t)$ is the excitation distribution in a cluster, defined from a solution of the diffusion equation

$$\frac{\partial \rho(x, t)}{\partial t} = W \frac{\partial^2 \rho(x, t)}{\partial x^2} - \beta \rho(x, t) \tag{16}$$

with boundary conditions

$$\left.\frac{\partial \rho(x, t)}{\partial x}\right|_{x=0} = -\left.\frac{\partial \rho(x, t)}{\partial x}\right|_{x=n} = \frac{\omega}{W} \rho(0, t). \tag{17}$$

An important point in calculating $\rho(t)$ is the choice of an initial condition for the function $\rho(x, t)$. The dependences (8) and (10) correspond to homogeneous excitation of molecules at an initial time,

$$\rho(x, 0) = 1. \tag{18}$$

Experimentally such a distribution can be produced by exciting pulses of homogeneous absorbed radiation the duration of which, τ_{pl}, is much less than the characteristic time of redistribution of the exciton population in clusters through diffusion, $\tau_{pl} \ll (c_{tr}^2 W)^{-1}(1 + 2Wc_{tr}/\omega)$. If the opposite condition holds, most of the clusters of a chain in time τ_{pl} will develop a nonuniform stationary distribution of the exciton population whose profile is defined by a relation between the parameters β, ω, W and cluster length. When a source is switched off instantaneously, the resultant distribution is just initial for solving the nonstationary problem. In this case

$$\rho(x, 0) = \frac{I}{\beta}\left(1 - \frac{\omega}{W}\frac{\cosh\left[l_D^{-1}(x - n/2)\right]}{l_D^{-1}\sinh(n/2l_D) + (\omega/W)\cosh(n/2l_D)}\right), \tag{19}$$

where $l_D = (W\beta^{-1})^{1/2}$ is the diffusion length of excitons in the units of an intermolecular distance in a chain, I is the intensity of the exciting radiation per one host molecule.

Using the solution (16)–(19) derived in ref. [25], we find

$$\rho_n(t) = \exp(-\beta t)8n\sum_{i=1}^{\infty}\theta_{n,i}\sin^2(\alpha_i/2); \tag{20a}$$

$$= \exp(-\beta t)8n\sum_{i=1}^{\infty}\theta_{n,i}\frac{I}{\beta}\sin(\alpha_i/2)\left(\sin(\alpha_i/2)\right.$$

$$\left. - \frac{(\omega/W)\left[(n/\alpha_i l_D)\sinh(n/2l_D)\cos(\alpha_i/2) + \cosh(n/2l_D)\sin(\alpha_i/2)\right]}{\left[(1/l_D)\sinh(n/2l_D) + (\omega/W)\cosh(n/2l_D)\right]\left[1 + (n/\alpha_i l_D)^2\right]}\right), \tag{20b}$$

$$\theta_{n,i} = \alpha_i^{-2}\exp\left(-\alpha_i^2 Wt/n^2\right)\frac{(\omega n/W)^2 + \alpha_i^2}{(\omega n/W)^2 + 2\omega n/W + \alpha_i^2},$$

where the values α_i are defined by the roots of the equation

$$\alpha_i \operatorname{tg}\left(\tfrac{1}{2}\alpha_i\right) = \omega n/W, \tag{21}$$

the equalities (20a) and (20b) correspond to the initial conditions (18) and (19).

It is easy to see that after substituting (20a) in (14), the latter equality transforms into (8) or (10), if fast or slow trapping occurs, respectively. With arbitrary values of the parameter $\Lambda = \omega/Wc_{tr}$, the calculation of $\rho(t)$ with the use of formulas (14) and (20) is quite complicated. We note in this connection that in ref. [18], a simple integral form for the dependence $\rho(t)$ was obtained, which describes the luminescence decay at $\rho(t) \lesssim 0.5\rho(0)$ for any values of Λ,

$$\tilde{\rho}(t) = \frac{5}{6\Lambda^2}\int_0^{\infty} dx \frac{x(x+6)^2}{x^2 + 10x + 30}\exp\left(-\frac{x}{\Lambda} - \frac{\Lambda^2(x+6)}{x^2 + 10x + 30}\frac{10c_{tr}^2 Wt}{x}\right). \tag{22}$$

Use of (22) seems to be instrumental to determine the ratio of the excitation diffusion rate W to the trapping rate ω by observing the shape of the decay curve. Comparison of (22) with exact dependences in the limiting cases of fast (8) and slow (10) trapping, as well as with the dependence $\rho(t)$ for a number of intermediate values of Λ are given in fig. 3.

We now consider the case of nonuniform initial distribution (19), caused by a stationary crystal

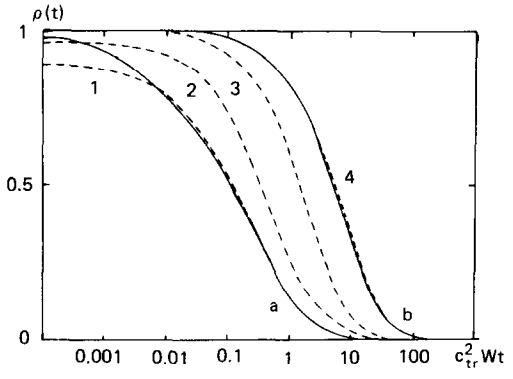

Fig. 3. The dependence (22) (dotted lines) at different values of $\Lambda \equiv \omega/Wc_{tr} = 20$ (1), 2.5 (2), 0.4 (3), 0.1 (4); $\beta = 0$. Curves a and b correspond to the exact dependences (8) and (10).

excitation. At $\Lambda \gg 1$ (fast trapping), substituting (20b) into (14) yields

$$\frac{\rho(t)}{\rho(0)} = \int_0^\infty dx \frac{x^3}{(b^2+x^2)\sinh x} \exp\left(-\frac{\tau_1}{2x^2} - \beta t\right) \left(\int_0^\infty dx \frac{x^3}{(b^2+x^2)\sinh x}\right)^{-1} \tag{23}$$

$$= \exp(-\beta t)\left(1 - \frac{16}{\pi^2} c_{tr}^2 \frac{Wt}{3}\right), \qquad \tau_1 \ll 1 \quad (b \equiv \pi c_{tr} l_D \gg 1); \tag{24a}$$

$$= \exp(-\beta t)\frac{16}{\pi^2}\sqrt{\tfrac{1}{6}\pi}\exp\left(-\tfrac{3}{2}\tau_1^{1/3}\right)\frac{1}{\sqrt{\pi}}\tau_1^{7/6}, \quad \tau_1 \ll b^3; \tag{24b}$$

$$= \exp(-\beta t)\frac{16}{\pi^2}\sqrt{\tfrac{1}{6}\pi}\exp\left(-\tfrac{3}{2}\tau_1^{1/3}\right)\tau_1^{1/2}, \qquad \tau_1 \gg b^3. \tag{24c}$$

The long-time asymptotics of the average exciton density (24c) is the same as (8c). In other words, at $\beta \neq 0$ the decay of $\tilde{\rho}(t)$ at $t \to \infty$ is independent of the initial distribution of excitations in clusters.

For the most interesting interval of not too large times (condition (24b)), when the exciton population decay due to trapping is within a few first orders, the kinetic curves (23) and (8) are very much different, if $c_{tr} l_D \gg 1$ (or $l_D/\bar{l} \gg 1$, $\bar{l}$ is the average cluster length). The validity of the latter inequality for fast trapping implies that most excitons are captured by, i.e. $\eta \ll 1$. Just in this case the excitation distribution in clusters when the pumping is switched off is strongly nonuniform. If, however, the dominant channel of exciton disappearance is the monomolecular excitation decay, the observed kinetic curves of the luminescence under varying duration of exciting pulses will, as was to be expected, be practically the same. The predicted change in the luminescence quenching kinetics manifests itself in a time delay in the luminescence decay when we pass from short- to long-duration exciting pulses within the framework outlined above, fig. 4a.

In the case of slow trapping, $\Lambda \ll 1$, the disappearance of excitons on the traps prevails over the monomolecular decay channel, ($\eta \ll 1$), if $c_{tr} l_D \gg 1$ and $\beta/\omega c_{tr} \ll 1$. We then obtain from (14) and (20b)

$$\frac{\rho(t)}{\rho(0)} = \exp(-\beta t)\ \tau_2^{3/2} K_3\left(2\sqrt{\tau_2}\right) = \exp(-\beta t)\left(1 - \tfrac{1}{2}\tau_2\right), \qquad \tau_2 \ll 1, \quad t \ll \frac{W^2}{\omega^3} c_{tr}\pi^3; \tag{25a}$$

$$= \exp(-\beta t)\tfrac{1}{2}\sqrt{\pi}\,\tau_2^{5/4}\exp\left(-2\sqrt{\tau_2}\right), \qquad \tau_2 \gg 1, \quad t \ll \frac{W^2}{\omega^3} c_{tr}\pi^3; \tag{25b}$$

$$= \exp(-\beta t)\frac{16}{\pi^2}\sqrt{\tfrac{1}{6}\pi\tau_1}\exp\left(-\tfrac{3}{2}\tau_1^{1/3}\right), \qquad t \gg \frac{W^2}{\omega^3} c_{tr}\pi^3. \tag{26}$$

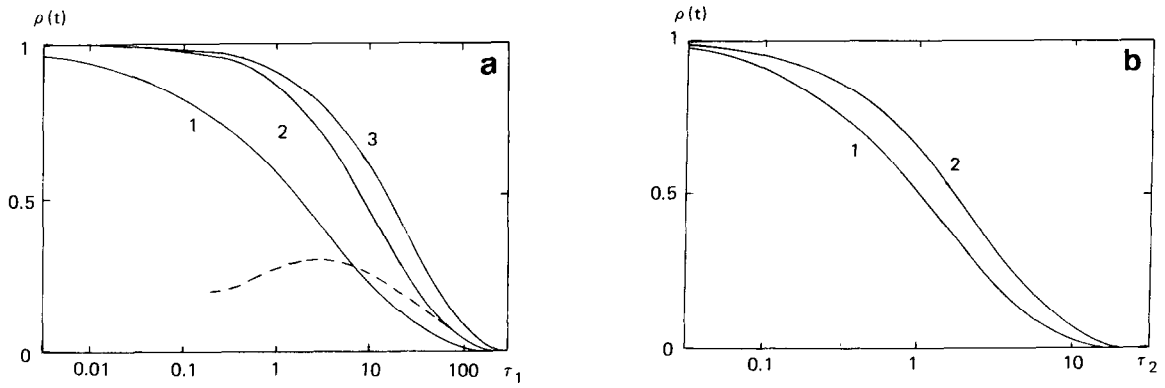

Fig. 4. Average exciton population decay under initial condition (19) (after a stationary source is switched off), $\beta = 0$. (a) Fast trapping, dependence (23). Curves 1, 2 and 3 correspond to the values of the parameter $b = \pi c_{tr} l_D = 0$, 3, 10. The dotted line denotes the dependence (24b). (b) Slow trapping, dependence (25), curve 2. For comparison, the dependence (10) is represented (curve 1) which corresponds to δ-pulse homogeneous excitation.

By analogy with (24b), the function (25b) plays the role or intermediate asymptotics in the dependence $\rho(t)/\rho(0)$, but is different from the basic asymptotics (26) both in a pre-exponential factor and the form of the exponent, which is caused by the change, in addition to the initial distribution, of the regime of exciton trapping in most clusters (see the discussion following eq. (10)).

The influence of the initial excitation distribution on the exciton population decay under slow trapping is illustrated in fig. 4b, where the dependences (10) and (25) are compared. The delay in the decay curve is seen to be present also in the case of slow trapping, but this effect is much less pronounced than under fast trapping. This dependence of the delay effect on the parameter Λ can be used for a reasonable choice of a model for the trapping process.

The calculations performed thus show that the change of (18) to (19), realizable experimentally (that is, the change of homogeneous to inhomogeneous conditions relative to the distribution of excitations in most clusters), will be accompanied by an appreciable rearrangement in the exciton luminescence decay curve observed after a quasi-one-dimensional crystal with traps is excited. It is important that the predicted rearrangement is related to the change in the initial part of the decay curve where the deviation from the exponential form in the dependence $\rho(t)$ is most pronounced, and the error in measurement is minimal. The comparison of the luminescence decay after the crystal is excited by short ($\tau_{pl} \ll (c_{tr}^2 W)^{-1}(1 + 2Wc_{tr}^2/\omega)$) and long ($\tau_{pl} \gg (c_{tr}^2 W)^{-1}(1 + 2Wc_{tr}^2/\omega)$) pulses appears to be a useful tool of checking the relevance of a theoretical model and deriving additional information on the parameters of the system in study.

We note that a qualitatively similar delay effect in the reaction $A + B \to 0$ for the case of a three-dimensional diffusion and an infinite lifetime of "reactants" was recently predicted in ref. [26]. The paper quoted has shown that the asymptotic decay of A(B)-particle concentration in a system "prepared" by a stationary source is described by the law $\sim t^{-1/4}$ (three-dimensional motion of reactants), whereas under a random initial distribution of particles A and B their concentration at large times decreases as $t^{-3/4}$ [27,28]. In our case that formally corresponds to the reaction $A + B \to B$, the asymptotics (8), (23) in the limit $l_D \to \infty$ ($\beta = 0$) are different in logarithmic corrections to the exponent.

3.2. Three-component chain

In quasi-one-dimensional crystals containing, in addition to traps, the defects (impurities) that play the role of scattering centers reflecting the excitons, we can distinguish the three types of clusters: those

involving two barriers at the boundaries (bb), those involving two traps (trtr) and those involving a trap and a barrier (trb). The average excitation density in such a system is defined by [29]

$$\rho(t) = \sum_{n=1}^{\infty} (1-c)^{n-1}\left[c_b^2 \rho_n^{bb}(t) + c_{tr}^2 \rho_n^{trtr}(t) + 2c_{tr}c_b \rho_n^{trb}(t)\right]$$

$$\underset{c_{tr},c_b \ll 1}{=} \int_0^{\infty} dn \exp(-cn)\left[c_b^2 \rho_n^{bb}(t) + c_{tr}^2 \rho_n^{trtr}(t) + 2c_{tr}c_b \rho_n^{trb}(t)\right], \tag{27}$$

where c_b is the barrier concentration; $c = c_{tr} + c_b$. The quantities $\rho_n^{bb}(t)/n$, $\rho_n^{trtr}(t)/n$, $\rho_n^{trb}(t)/n$ have the meaning of exciton survival probabilities for the types of clusters indicated. The calculation of $\rho_n^{bb}(t)$ and $\rho_n^{trb}(t)$ is completely similar to defining the function (15) $\rho_n(t) \equiv \rho_n^{trtr}(t)$ in the case of two-component chain. The boundary condition for eq. (16), defining the excitation distribution functions in the clusters, $\rho^{trb}(x, t)$ and $\rho^{bb}(x, t)$ have the form

$$\left.\frac{\partial \rho^{bb}(x, t)}{\partial x}\right|_{x=0} = \left.\frac{\rho^{bb}(x, t)}{\partial x}\right|_{x=n} = 0 \tag{28a}$$

and

$$\left.\frac{\partial \rho^{trb}(x, t)}{\partial x}\right|_{x=0} = \frac{\omega}{W}\rho^{trb}(0, t), \quad \left.\frac{\partial \rho^{trb}(x, t)}{\partial x}\right|_{x=n} = 0. \tag{28b}$$

Such a choice of boundary conditions corresponds to a complete reflection of excitations from the barriers so that the model used (enabling us to derive exact results) can describe the initial stage of the process when most excitons still have no time to leave "their" cluster, but is not intended to describe the tail of the decay curve.

We consider the case of a uniform initial distribution of excitation on host molecules of a crystal

$$\rho^{bb}(x, 0) = \rho^{trtr}(x, 0) = \rho^{trb}(x, 0) = 1. \tag{29}$$

Substituting into (27) the solution (16) with the boundary conditions (17), (28) and the initial condition (29), we find

$$\rho(t) = c^{-2} \exp(-\beta t)\left[c_b^2 + c_{tr}^2 F(\tau_1') + 2c_{tr}c_b F\left(\tfrac{1}{4}\tau_1'\right)\right], \quad \Lambda \gg 1; \tag{30a}$$

$$= c^{-2} \exp(-\beta t)\left\{2c_b^2 + 2\tau_2'\left[c_{tr}^2 K_2\left(2\sqrt{\tau_2'}\right) + c_{tr}c_b K_2\left(\sqrt{2\tau_2'}\right)\right]\right\},$$

$$\Lambda \ll 1, \quad \tau_2' = 2c\omega t \ll \left(\pi^2 W c/\omega\right)^2, \tag{30b}$$

where $F(\tau_1')$ denotes the dependence (8), in which $\beta = 0$, τ_1 is replaced by $\tau_1' = 2\pi^2 c^2 W t$; the equality (30b), as well as (24b), defines the initial part of the excitation concentration drop curve for slow trapping. At large times, $\tau_2' \gg (\pi^2 W c/\omega)^2$, the intermediate asymptotics (30b) is replaced by the dependence (30a).

Under stationary crystal excitation the clusters containing a trap and a barrier at the boundaries and those containing two traps at the boundaries display a nonuniform distribution such as

$$\rho^{trb}(x, 0) = \frac{I}{\beta}\left(1 + \frac{\omega}{W}\frac{\sinh\left(nl_D^{-1}\right)\sinh\left(xl_D^{-1}\right) - \cosh\left(nl_D^{-1}\right)\cosh\left(xl_D^{-1}\right)}{l_D^{-1}\sinh\left(nl_D^{-1}\right) + (\omega/W)\cosh\left(nl_D^{-1}\right)}\right) \tag{31}$$

and (19), respectively. For the clusters limited by two barriers

$$\rho^{bb}(x, 0) = I/\beta. \tag{32}$$

Using now (19), (31), (32) instead of (29), as an initial condition for solving the equation (16), we find for fast trapping:

$$\frac{\rho(t)}{\rho(0)} = \exp(-\beta t)\left(\left(\tfrac{1}{2}\pi c_b\right)^2 + c_{tr}^2\int_0^\infty dx \frac{x^3 \exp(-\tau_1'/2x^2)}{(b^2+x^2)\sinh x} + 8c_{tr}c_b\int_0^\infty dx \frac{x^3 \exp(-\tau_1'/8x^2)}{(b^2+4x^2)\sinh x}\right)$$
$$\times\left(\left(\tfrac{1}{2}\pi c_b\right)^2 + c_{tr}^2\int_0^\infty dx \frac{x^3}{(b^2+x^2)\sinh x} + 8c_{tr}c_b\int_0^\infty dx \frac{x^3}{(b^2+4x^2)\sinh x}\right)^{-1} \quad (33a)$$

and for slow trapping at times $\tau_2' \ll (\pi^2 Wc/\omega)^2$:

$$\frac{\rho(t)}{\rho(0)} = \exp(-\beta t)\left(c_b^2 + \frac{4\beta c_{tr}}{\omega}\right)^{-2}\left\{c_b^2 + \frac{4\beta c_{tr}}{\omega c}\left[K_3\left(2\sqrt{\tau_2'}\right)c_{tr}\tau_2'^{3/2} + K_3\left(\sqrt{2\tau_2'}\right)c_b\left(\tfrac{1}{2}\tau_2'\right)^{3/2}\right]\right\}. \quad (33b)$$

We note the following: the difference in the time scale in the second and third terms of the dependences (30) and (33) is a direct consequence of the fact that the lifetime of a particle executing random walks on a chain with traps at both boundaries is shorter than that for a chain with one reflecting and one absorbing boundary [30] by four and two times in the case of fast and slow trapping, respectively.

As is seen from (30) and (33), the introduction of defects such as the barriers whose concentration can be varied and controlled [3,5,6], leads to a characteristic change in the exciton luminescence decay for a quasi-one-dimensional crystal. The dependences (30) and (33) are exact for the model of impenetrable barriers. With slow jumps across the barriers taken into account, (30) and (33) correctly describe the initial change in the average exciton population in the range $\rho(t)/\rho(0) \approx 1-c_b^2/c^2$. Their comparison with experiment, for example, measurements of the exciton luminescence decay, similar to ref. [5], should, therefore, be made at concentrations $c_b < c_{tr}$. The theory based on the model of random walks on superlattice [23] then cannot be used to describe the process under consideration.

4. Kinetics of trap (sensitized) luminescence

As follows from the above discussion, the most significant deviation in $\rho(t)$ from the exponential decay law $\sim \exp(-\beta t)$, caused by the one-dimensional character of exciton motion before trapping and fluctuations in defect densities, should be expected at $\eta \ll 1$. Under a small QY of exciton luminescence, however, the measurement of $\rho(t)$ could be difficult. In this connection it is of interest to elucidate the basic features of the kinetics of trap luminescence the QY of which $\eta_{tr} = 1-\eta$, ($c_b = 0$), at $\eta \ll 1$ will be close to unity. The intensity of the luminescence of traps, $\Phi_{tr} = \beta_{tr}\rho_{tr}(t)$, β_{tr} is the probability for a radiative decay of a trapped excitation, is defined by the average trap population $\rho_{tr}(t)$, related to $\rho(t)$ by the obvious balance equation

$$\frac{d\rho_{tr}(t)}{dt} + \frac{d\rho(t)}{dt} = -\beta_{tr}\rho_{tr}(t) - \beta\rho(t). \quad (34)$$

Integrating this equation under the initial condition $\rho(0) = 1$, $\rho_{tr}(0) = 0$ (δ-pulsed crystal excitation) yields

$$\rho_{tr}(t) = \exp(-\beta_{tr}t) - \rho(t) - \Delta\exp(-\beta_{tr}t)\int_0^t \rho(t)\exp(\beta_{tr}t)\,dt, \quad (35)$$

where $\Delta = \beta - \beta_{tr}$.

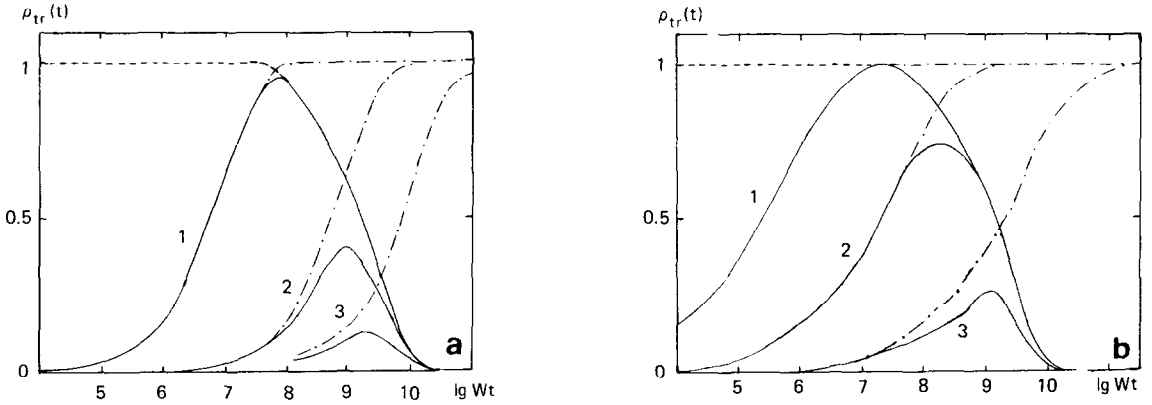

Fig. 5. Trap luminescence intensity $\rho_{tr}(t)$ (solid lines) at $\beta = \beta_{tr}$ (eq. (36)). (a) $\omega/W = 10^3$ (fast trapping), $\rho(t)$ is defined by the dependence (8); (b) $\omega/W = 10^{-6}$ (slow trapping), $\rho(t)$ is defined by the dependence (10). The dash-dotted lines describe the trap occupation kinetics, the dotted lines represent the dependence $\exp(-\beta_{tr}t)$; $c_{tr} = 10^{-2}$ (1), 10^{-4} (2), 10^{-5} (3); $\beta/W = 5.6 \times 10^{-10}$.

We first consider the simplest case of a two-component chain that consists of the host molecules and traps, assuming that $\Delta = 0$. This condition is met, for example, if defects such as traps result from the local reorientation of host molecules, or are concerned with isotopic impurities. The expression (35) is in this case simplified to

$$\rho_{tr}(t) = \exp(-\beta_{tr}t)[1 - \tilde{\rho}(t)]. \tag{36}$$

In (36) the exponential factor describes the decrease in the trap population caused by a radiative excitation decay, and the bracketed expression defines the kinetics of trap population increasing. The exciton population $\tilde{\rho}(t)$ (monomolecular decay channel is disregarded) for slow and fast trapping is defined by formulas (8) and (10), and at an arbitrary value of the parameter Λ by (22).

To illustrate the dependence of the shape of the trap luminescence kinetic curve on the characteristic parameters of a system, fig. 5 represents the dependences $\rho_{tr}(t)$ with the values of c_{tr} over the range 10^{-5}–10^{-3} when the values of the other parameters are fixed. As is seen, the greater the trap concentration, the faster and the earlier is their occupation by captured excitons. The shape of the increasing part of the curve $\rho_{tr}(t)$ for fast and slow trapping is much different, figs. (5a) and (5b). A considerable increase in the height of the trap luminescence maximum with increasing c_{tr} is observed only to $c_{tr} \sim c_{tr}^0$ (c_{tr}^0 is the trap concentration under which most excitons get trapped in time β^{-1}; $c_{tr}^0 \sim l_D^{-1}$ at $\Lambda \gg 1$ and $c_{tr}^0 \sim \beta/\omega$ at $\Lambda \ll 1$). As the trap concentration rises further, the height of the maximum as well as the value of the relative QY $\eta_{tr} \approx 1$ remains practically the same, only the trap luminescence maximum width increases. For curves 1, figs (5a) and (5b) give $\eta_{tr} \approx 1$, for curves 2 the values of η_{tr} and η are comparable and for curves 3 $\eta_{tr} \ll 1$.

The trap luminescence decreasing in the case considered is exponential (see (36)), so that the information on the parameters of motion and excitation trapping (W and ω) is reproduced only by the part of the kinetic curve $\rho_{tr}(t)$ which describes the trap luminescence flaring. We note here some difficulties of verifying the theory for fast trapping. As mentioned above, the dependences $\tilde{\rho}(t)$ calculated with trap density fluctuations taken strictly into account (8) and approximately (13), are slightly different in the range $\tilde{\rho}(t) \approx 1$–$0.01$. It thus follows that specifying the features of the flaring kinetics $\Phi_{tr}(t)$ concerned with trap density fluctuations would be quite difficult at $\beta_{tr} \approx \beta$.

Consider now the case $\Delta \neq 0$. Substituting $\rho(t)$ as (8) and (10) into (35), we have

$$\rho_{tr}(t) = \exp(-\beta_{tr}t)\frac{4}{\pi^2}\int_0^\infty dx \frac{x\left[1-\exp\left(-\Delta t-\tau_1/2x^2\right)\right]}{\left(1+\Delta x^2/\pi^2 c_{tr}^2 W\right)\sinh x}, \quad \Lambda \gg 1;$$

$$= \exp(-\beta_{tr}t)\int_0^\infty dx \frac{x\left[1-\exp(-\Delta t-\tau_2/x)\right]}{(1+\Delta x/2c_{tr}\omega)\exp(x)}, \qquad \Lambda \ll 1, \quad \tau_2 \ll \left(\pi^2 W c_{tr}/\omega\right)^2 \tag{37}$$

for fast and slow trapping, respectively.

The evaluation of these integrals by the Laplace method shows that the difference in the lifetimes of β_{tr}^{-1} and β^{-1} is manifest in the trap luminescence kinetics at times

$$Wt \gtrsim \left(c_{tr}/2\pi^2\right)(W/|\Delta|)^{3/2}, \quad \Lambda \gg 1;$$

$$\omega t \gtrsim 2c_{tr}(\omega/|\Delta|)^2, \qquad \Lambda \ll 1. \tag{38}$$

When the inverse inequalities are valid, the dependence (37) is practically the same as (36) obtained at $\Delta = 0$. It is thus clear that the shape of the kinetic curve $\rho_{tr}(t)$ may be quite different from that described above only at large $|\Delta|$ (see (38)).

The trap luminescence flaring and decay kinetics is much dependent upon the sign of Δ. If the monomolecular decay probability, β, is much greater than β_{tr}, the dependence (37) under the condition (38) can be rewritten as

$$\rho_{tr}(t) = \exp(-\beta_{tr}t)\left[f_1(\Delta) - \sqrt{\tfrac{2}{3}\pi}\,2^{-1/3}(8W/\Delta)c_{tr}^2\tau_1^{-1/6}\exp(-\Delta t)\right], \quad \Lambda \gg 1;$$

$$= \exp(-\beta_{tr}t)\left[f_2(\Delta) - 2\sqrt{\pi}\,(c_{tr}\omega/\Delta)\tau_2^{1/4}\exp(-\Delta t)\right], \qquad \Lambda \ll 1, \tag{39}$$

where

$$f_1(\Delta) = \frac{4}{\pi^2}\int_0^\infty \frac{dx}{\sinh x}\frac{x}{1+\Delta x^2/\pi^2 c_{tr}^2 W}, \quad f_2(\Delta) = \int_0^\infty \frac{dx}{\exp(x)}\frac{x}{1+\Delta x/2c_{tr}\omega}.$$

In the opposite limit case of large negative values of Δ, it follows from (37), with (38) taken into account

$$\rho_{tr}(t) = \exp\left(-\beta t - \tfrac{3}{2}\tau_1^{1/3}\right)\sqrt{\tfrac{2}{3}\pi}\left(8Wc_{tr}^2/2^{1/3}|\Delta|\right)\tau_1^{-1/6}, \quad \Lambda \gg 1, \quad \tau \gg 1;$$

$$= \exp\left(-\beta t - 2\sqrt{\tau_2}\right)2\sqrt{\pi}\,(\omega c_{tr}/|\Delta|)\tau_2^{1/4}, \qquad \Lambda \gg 1, \quad 1 \ll \tau_2 \ll \left(\pi^2 W c_{tr}/\omega\right)^2. \tag{40}$$

The latter dependence is seen to be similar to $\rho(t)$ for the same times; under a sufficiently fast trap luminescence its decay law is close to $\rho(t)$, i.e. it can deviate much from an exponential one. Conversely, at $\beta \gg \beta_{tr}$ the trap luminescence flaring and decay kinetics is primarily controlled by the parameters β and β_{tr}, see (39).

The above results are directly generalized to the case of a quasi-one-dimensional crystal with defects such as traps and barriers, if we consider, as in section 3, the exciton reflection from the barriers to be complete. It is easy to show that in the present model the average trap population can be represented as

$$\rho_{tr}(t) = c^{-2}\left[c_{tr}^2\rho_{tr}^{trtr}(t) + 2c_{tr}c_b\rho_{tr}^{trb}(t)\right], \tag{41}$$

where, similar to (27), the first and the second terms are determined by the contributions from clusters with two traps, and those with a trap and a barrier at the boundaries, respectively. In particular, at $\Lambda \gg 1$ and $\Lambda \ll 1$ the explicit form of $\rho_{tr}^{trtr}(t)$ is as (37), if τ_1 and τ_2 are replaced by $\tau_1' = 2\pi^2 c^2 W t$ and $\tau_2' = 2c\omega t$,

and $\rho_{tr}^{trb}(t)$ is different from $\rho_{tr}^{trtr}(t)$ only in τ_1' replaced by $\tau_1'/4$ at $\Lambda \gg 1$ and τ_2' replaced by $\tau_2'/2$ at $\Lambda \ll 1$. The results of analyzing the dependence (37) can thus be used for (41).

As mentioned above, the defect-barrier concentration can be varied, so that the measurement of the time dependence of trap luminescence at different values of c_b and the comparison with (41) can produce an additional information on the kinetic parameters of the system under consideration.

5. Conclusions and relation to existing and proposed experiments

The model comparable with real quasi-one-dimensional systems has been used to study the basic feature regularities of the quasiparticle trapping process (exciton, electron, etc.), which can manifest themselves in the transport process in polymers (dilute solutions), quasi-one-dimensional crystals and similar objects. The results obtained in the framework of the model specified for exciton trapping but applicable for lots of similar processes take strict account of trap density fluctuations and the fact that the value of the ratio between the particle diffusion rate and the particle trapping rate is finite.

Under uniform or, equivalently, random initial distribution of excitations over host molecules, i.e. chain sites free of traps, which was discussed earlier assuming an infinitely fast trapping [10,12,14–18], the average exciton population in a chain, $\rho(t)$, decreases by the law $\sim \exp(-\frac{3}{2}\tau_1^{1/3} - \beta t)$ at $\tau_1 = 2\pi^2 c_{tr}^2 W t \gg 1$, see (8). It is shown that the same dependence is realized also at finite values of ω that satisfy the fast trapping condition, $\Lambda \equiv \omega/W c_{tr} \gg 1$. In the case of slow trapping, $\Lambda \ll 1$, we have an intermediate asymptotics $\rho(t) \sim \exp(-2\sqrt{\tau_2} - \beta t)$ at $\tau_2 = 2c_{tr}\omega t \gg 1$, see (10), and the shape of the decay curve $\rho(t)$ is changed qualitatively.

The interpolation formula (22) was proposed to describe the exciton luminescence decay at arbitrary values of the trapping parameter, Λ. Since there are no objective (i.e. experimentally derived) data to evaluate the ratio ω/W, the shape of the decay curve calculated by (22) may be compared with the observed one to provide a criterion for a correct choice of a model for the trapping process (trapping is often a priori postulated to be fast).

In a very recent publication Knochenmuss and Güdel [6] presented strong evidence that the trapping of triplet excitons in TMMC crystals is not perfect and evaluated the trapping efficiency p (i.e. the trapping probability connected with the parameter $k = \omega/W$ by the simple relation $p = k/(k+1)$ [31]) to be the quantity of the order 10^{-4}. For such a small trapping rate, in accordance with our results, the trapping cannot be treated to be fast in the whole concentration range investigated in ref. [6], $c_{tr} \approx 10^{-3}$–10^{-5}. The condition (7) of fast trapping is fulfilled only for $c_{tr} \lesssim 10^{-5}$. For the most of the concentration values used in ref. [6], the trapping process should be classified as intermediated or slow for $c_{tr} \gtrsim 10^{-3}$. Consequently, the dependences (10) or (22) should be used to fit the experimental curves. It seems that the relatively good coincidence of experimental results with those predicted by (8) at $c_{tr} \lesssim 10^{-5}$ on the one hand, and the marked disagreement between the experiment and the Balagurov–Vaks theory [12] (the theory had originated almost 10 years before similar results by Movaghar, Sauer and Würtz were presented [15]) at higher concentrations on the other hand, can serve as an argument in favour of the small trapping efficiency in TMMC crystals. Unfortunately, the authors of ref. [6] were not acquainted with the dependences (10) (which is exact for slow trapping) and (22) (which reproduces the behaviour of $\rho(t)$ when $\rho(t) \lesssim 0.5\ \rho(0)$ for arbitrary trapping efficiency, see fig. 3) and used the Laplace transform of $\rho(t)$ obtained in ref. [32] to fit their experimental data. Some difficulties of such a procedure are discussed in ref. [6]. Besides, we want to point out that the expression of Kenkre and Parris (used in eq. (10) in ref. [6]) is approximate (of the mean-field theory version) without a definite region of parameters of its applicability. This adds confusion to the interpretation of experimental data. Moreover, it is known that mean-field approaches often lead to incorrect conclusions especially in the case of low-dimensional systems. Thus, it is highly desirable to re-examine the results of refs. [5,6] on the basis of eqs. (10) and (22).

Another convincing support among the findings of Knochenmuss and Güdel to prove the small trapping rate in TMMC is the strong deviation of η ($\langle t \rangle = \eta/\beta$ in notations in ref. [6]) from the dependence c_{tr}^{-2} first predicted by Montroll [8] for the case of perfect trapping. This expectation also follows from our theory, see eq. (6). But as indicated, the latter equation works well only when $\eta \ll 1$, in other words, when the part of trapped excitons is great. In the other case, the exact expression for η given by (4) and (5) shoud be used. In ref. [6] an estimation formula analogous to eq. (6) was employed, therefore this part of handling of experimental results should also be improved.

Although the exciton decay kinetics in doped TMMC was studied experimentally, in great detail [5,6], it cannot now be definitely concluded, as was pointed out in ref. [6], whether excitation trapping is nearly perfect or not. From this point of view performing experiments with prolonged excitation in the sense discussed above seems to be able to supply the necessary evidence to prove one of the two oppossing assumptions on the trapping efficiency made in refs. [5,6]. Besides, our results show that in general, special attention should be paid to the duration of excitation pulses in interpreting experimental results. If the condition of short pulses (see above) is fulfilled, one can try to use eqs. (8), (10) or (22) for fitting calculations. If the condition mentioned is violated, the use of the theoretical results obtained for δ-pulse excitation can be misleading, because in this case the form of excitation pulses can effect the observed exciton decay kinetics considerably.

Theoretically solving of the corresponding problem for an arbitrary form of excitation pulses is desired, yet remains a very difficult task hardly capable of leading to analytical expressions for the observables. Therefore, we obtain analytic results only for the extreme situation (in contrast to δ-pulse excitation) when the initial distribution of excitons over a molecular chain with traps is generated by a stationary source which is switched off when the stationary distribution of quasiparticles is achieved. Such conditions or those resembling them seem to be realizable. Prediction of the delay effect in the average exciton (other particle) density in a quasi-one-dimensional crystal with traps when the exciting pulse duration increases and calculation of the explicit form of $\rho(t)$ in the case of an initial distribution "prepared" by a stationary source of external excitation are the basic results of the present paper. As is shown, the change of the exciton excitation condition (from δ-pulsed to stationary excitation) can result in an appreciable rearrangement of the exciton luminescence decay curve. The magnitude and the character of the change indicated are defined by specific values of the parameters ω, W and c_{tr}, therefore the comparison of experimental data with the kinetic curves (23), (25), (30) and (33) appears to be a convenient tool to derive reliable information on the exciton trapping and diffusion rates and the trap concentration.

The kinetics of trap (sensitized) luminescence produced by trapping of host molecular excitations has also been considered. In the limiting cases of fast and slow trapping, analytical expression for the average trap population by excitons $\rho_{tr}(t)$ have been derived under a uniform (random) initial distribution of excitations over host molecules. It is shown that at trap radiation rates less than or comparable with the monomolecular exciton decay rate the peculiarities of the trapping kinetics concerned with trap density fluctuations can be manifested only in the initial part of the curve $\rho_{tr}(t)$ which corresponds to trap luminescence flaring. Under fast trap luminescence ($\beta_{tr} \gg \beta$), the dependence $\rho_{tr}(t)$ is close to $\rho(t)$.

The influence of defects such as scattering centers on the quasiparticle trapping process in the model of impenetrable barriers has been investigated. The results can be used, for example, to describe the initial stage of the decay in exciton (and the increase in trap) luminescence intensity, also for the case of a finite, yet small probability of an exciton jump through a barrier. It is shown that the presence of the defects mentioned above in fast and slow trapping results in a two-rate kinetics: the change of $\rho(t)$, $\rho_{tr}(t)$, see (30), (33) and (41), is described by a superposition of two dependences different only in the characteristic time scale.

To conclude, we emphasize that the results derived in the present paper are obtained disregarding the interaction between diffusing quasiparticles. Their application, therefore, is limited by the condition that the number of the particles participating in the energy (or charge) transport processes should be small per site (trap), i.e. for excitons the intensity of an exciting radiation should be sufficiently low.

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