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KINETICS OF INCOHERENT EXCITON ANNIHILATION IN NONIDEAL ONE-DIMENSIONAL STRUCTURES

A.I. ONIPKO and I.V. ZOZULENKO

Institute for Theoretical Physics, Acad. Sci. UkSSR, 252130, Kiev–130, USSR

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The annihilation of incoherent excitons in a quasi-one-dimensional (Q1D) crystal containing impurities (which form traps or reflecting barriers) is studied. The distribution function and the survival probability of an annihilating pair of quasi-particles diffusing in a chain with absorbing or reflecting ends are obtained. These results are used to calculate the kinetic curves of the delayed fluorescence (DF) caused by triplet–triplet annihilation in Q1D crystals containing impurities whose concentration is much higher than the concentration of triplet excitons. It is shown that at long times the kinetics of DF is described by the exponential dependence $\exp(-\text{const}\ t^{1/3})$ which differs qualitatively from that predicted for pure Q1D crystals, where a power law of DF decay $\propto t^{-3/2}$ is expected.

1. Introduction

The kinetics of exciton annihilation under one-dimensional diffusion is usually described, by analogy to higher dimensionality systems, by the Smoluchowsky theory [1,2] or similar approximate methods [3,4]. An exact solution to the model problem of annihilation of identical particles in a chain was recently obtained [5,6] showing that the particle concentration at large times varies as $\propto t^{-1/2}$, as distinct from the t^{-1} dependence typical for a three-dimensional system.

The annihilation problem was treated in the above papers for an infinite ideal chain. Real materials in which transfer processes are mainly one-dimensional (for instance, quasi-one-dimensional crystals, polymers) always have defects that can considerably affect the exciton motion, especially if the defects play the role of traps or high potential barriers that obstruct the quasi-particle motion. The quasi-particles, in particular triplet excitons [7–15], are caged in segments bounded by defects, i.e. in linear clusters (which are also called cages [8]), so that it appears to be unacceptable to use an infinite chain as a model to describe transfer processes.

In the present model, triplet exciton annihilation under one-dimensional diffusion is considered, taking into account the effect of quasi-particle caging by defects such as traps or barriers, and assuming that the exciton concentration c_T is much less than the defect concentration c_d. So, when triplet excitons are excited in a crystal, most cages contain only one excited molecule, so that the exciton–exciton interaction has an insignificant effect on exciton phosphorescence. However, in crystals in which the triplet–triplet annihilation leads to delayed fluorescence (DF) (this is also characteristic of quasi-one-dimensional crystals, for example, 1,4-ditromonaphthalene [16]), the annihilation-produced effect is already appreciable at $c_T/c_d \ll 1$ in the sense that the DF, spectrally separated from phosphorescence, can readily be investigated. Thus, under high defect densities the DF kinetics that provides information on the exciton motion and interaction parameters will be determined by the mean value of the survival probability for an

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annihilating exciton pair (its interaction with other excitons being disregarded), that is, we deal with a two-particle problem that is solved exactly in the present paper.

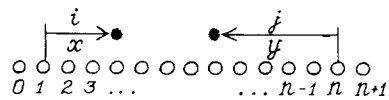
2. Random walks of an annihilating pair of excitons in a chain with reflecting or absorbing boundaries

The typical element of a molecular chain with randomly distributed impurities (defects) that play the role of traps or barriers is a segment of n host molecules at whose boundaries the excitons are absorbed or reflected. We now determine the survival probability for an annihilating pair of excitons, assuming that their motion is realized by jumps between neighbouring lattice sites with a unit time probability W (in what follows we use a dimensionless time in units W^{-1}); when two excitations come to the same site they immediately annihilate, i.e. the annihilation rate is infinite. The latter is the most popular, but is not, of course, a general model of the annihilation process. A more realistic treatment requires a finite annihilation rate. The possible consequences of such a generalization of the model considered will be discussed later.

The position of excitons in a chain at time t is determined by the distribution function $\rho_n(i, j, t)$ that satisfies the master equation

$$\frac{\partial \rho_n(i, j, t)}{\partial t} = -4\rho_n(i, j, t) + \rho_n(i+1, j, t) + \rho_n(i-1, j, t) + \rho_n(i, j+1, t) + \rho_n(i, j-1, t)$$
$$i + j \neq n$$
$$-2\beta_T \rho_n(i, j, t); \tag{1}$$
$$\rho_n(i, j, t) = 0, \quad i + j = n.$$

$\rho_n(0, j, t) = \rho_n(i, n+1, t) = 0$, if the sites 0 and $n+1$ are occupied by traps (the trapping is assumed to be instantaneous), and $\rho_n(0, j, t) = \rho_n(1, j, t)$, $\rho_n(i, n, t) = \rho_n(i, n+1, t)$, if the sites 0 and $n+1$ are occupied by reflecting barriers; β_T^{-1} is the lifetime of an exciton in units W^{-1}. The meaning of the discrete variables i and j that determine the position of a pair of incoherent excitons is clear from the following diagram:



Assuming the distribution functions $\rho_n(i, j, t)$ to be smooth at distances of a lattice constant a (this may be expected at $n \gg 1$ and $t \gg 1$) we pass from a discrete to a continuous description, introducing continuous variables $x = ai$, $y = aj$.

We then have instead of eqs. (1),

$$\frac{\partial \rho_n(x, y, t)}{\partial t} = \frac{\partial^2 \rho_n(x, y, t)}{\partial x^2} + \frac{\partial^2 \rho_n(x, y, t)}{\partial y^2} - 2\beta_T \rho_n(x, y, t) \tag{2}$$

in the region

$$0 \leq x + y \leq n; \tag{2a}$$

all the quantities of length dimension are henceforth expressed in units of a.

The boundary condition at $x + y = n$,

$$\rho_n(x, y, t)|_{x+y=n} = 0, \tag{3}$$

implies that a pair of excitations at the same site annihilates instantaneously.

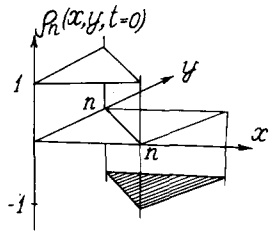


Fig. 1. The extension of the initial condition $\rho_n(x, y, t=0)=1$ given in the region $0<x+y<n$ to the region $x<n$, $y<n$, $x+y>n$ in an odd way (shaded triangle).

The boundary condition

$$\rho_n(x, y, t)|_{x=0}=\rho_n(x, y, t)|_{y=0}=0, \tag{4}$$

corresponds to a case when traps are located at the chain ends, and the boundary condition

$$\left.\frac{\partial\rho_n(x, y, t)}{\partial x}\right|_{x=0}=\left.\frac{\partial\rho_n(x, y, t)}{\partial y}\right|_{y=0}=0 \tag{5}$$

corresponds to excitons being reflected from the chain ends (barriers).

As an initial condition we choose

$$\rho_n(x, y, t=0)=1, \quad 0<x+y<n, \tag{6}$$

which corresponds to a homogeneous excitation of a crystal at time $t=0$.

To solve the problem in eqs. (2)–(6), it is convenient to extend the condition (6) in an odd parity way to the region $x<n$, $y<n$, $x+y>n$

$$\rho_n(x, y, t=0)=-1, \; x<n, \quad y<n, \quad x+y>n, \tag{7}$$

thus completing the range of the variables x, y to a square (see fig. 1).

The boundary conditions at $x=n$, $y=n$ are chosen for a chain with traps as

$$\rho_n(x, y, t)|_{x=n}=\rho_n(x, y, t)|_{y=n}=0, \tag{8}$$

and for a chain with barriers as

$$\left.\frac{\partial\rho_n(x, y, t)}{\partial x}\right|_{x=n}=\left.\frac{\partial\rho_n(x, y, t)}{\partial y}\right|_{y=n}=0. \tag{9}$$

It is then easy to see that the solution of eq. (2) with boundary conditions (4), (8) or (5), (9) and initial condition (6), (7) is the same as that of the initial problem (eq. (2) with boundary conditions (4) and (5) and initial condition (6)) in the region $0\le x+y\le n$.

Deriving the Green's functions of eq. (2) under the boundary conditions (4), (8) [17]:

$$G_n^{\mathrm{tr}}(x, y, x', y', t)\,\mathrm{e}^{2\beta_{\mathrm{T}}t}=\frac{4}{n^2}\sum_{m=1}^{\infty}\sum_{l=1}^{\infty}\exp\left(-\frac{\pi^2}{n^2}(m^2+l^2)t\right)\sin\frac{\pi mx}{n}\sin\frac{\pi ly}{n}\sin\frac{\pi mx'}{n}\sin\frac{\pi ly'}{n}, \tag{10}$$

and (5), (9):

$$G_n^{\mathrm{b}}(x, y, x', y', t)\,\mathrm{e}^{2\beta_{\mathrm{T}}t}=\frac{1}{n^2}\left\{1+2\sum_{m=1}^{\infty}\exp\left(-\frac{\pi^2m^2t}{n^2}\right)\cos\frac{\pi mx}{n}\cos\frac{\pi mx'}{n}\right\}$$
$$\times\left\{1+2\sum_{l=1}^{\infty}\exp\left(-\frac{\pi^2l^2t}{n^2}\right)\cos\frac{\pi ly}{n}\cos\frac{\pi ly'}{n}\right\}, \tag{11}$$

we write the solution to the diffusion equation (2) as

$$\rho_n^{\mathrm{tr(b)}}(x, y, t) = \int_0^n \mathrm{d}x' \int_0^n \mathrm{d}y' G_n^{\mathrm{tr(b)}}(x, y, x', y', t) \rho_n^{\mathrm{tr(b)}}(x', y', t=0)$$
$$= \int_0^n \mathrm{d}x' \int_0^{n-x'} \mathrm{d}y' G_n^{\mathrm{tr(b)}}(x, y, x', y', t) - \int_0^n \mathrm{d}x' \int_{n-x'}^n \mathrm{d}y' G_n^{\mathrm{tr(b)}}(x, y, x', y', t), \tag{12}$$

or, substituting the expressions for the Green's functions (10), (11), as

$$\rho_n^{\mathrm{tr}}(x, y, t) = \left(\frac{2}{\pi}\right)^2 \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \frac{\exp\left(-\frac{\pi^2}{n^2}(m^2+l^2)t - 2\beta_{\mathrm{T}} t\right)}{m^2 - l^2} \frac{m}{l}\left(1-(-1)^l\right)\left(1+(-1)^m\right)$$
$$\times \left[\sin\frac{\pi m x}{n}\sin\frac{\pi l y}{n} + \sin\frac{\pi l x}{n}\sin\frac{\pi m y}{n}\right], \tag{13}$$

$$\rho_n^{\mathrm{b}}(x, y, t) = \left(\frac{2}{\pi}\right)^2 \sum_{m=1}^{\infty} \frac{\exp\left(-\frac{\pi^2 m^2 t}{n^2} - 2\beta_{\mathrm{T}} t\right)}{m^2}\left(1-(-1)^m\right)\left[\cos\frac{\pi m y}{n} + \cos\frac{\pi m x}{n}\right]$$
$$+ \frac{8}{\pi^2} \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \frac{\exp\left(-\frac{\pi^2}{n^2}(m^2+l^2)t - 2\beta_{\mathrm{T}} t\right)}{l^2 - m^2}\left((-1)^m - (-1)^l\right)\cos\frac{\pi l y}{n}\cos\frac{\pi m x}{n}, \tag{14}$$

where the indices tr and b correspond to choosing a boundary condition as (3), (4) and (3), (5), i.e. they belong to the case of a chain with absorbing and reflecting boundaries.

We now use the solutions obtained to determine the probability for a pair of excitons to survive by time t in a chain of length n:

$$\Omega_n^{\mathrm{d}}(t) = \frac{2}{n^2}\int_0^n \mathrm{d}x \int_0^{n-x} \mathrm{d}y \rho_n^{\mathrm{d}}(x, y, t), \tag{15}$$

with absorbing (d = tr)

$$\Omega_n^{\mathrm{tr}}(t)\, \mathrm{e}^{2\beta_{\mathrm{T}} t} = 8\left(\frac{2}{\pi}\right)^4 \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \frac{\exp\left(-\frac{\pi^2}{n^2}\left((2m)^2 + (2l-1)^2\right)t\right)}{\left((2m)^2 - (2l-1)^2\right)^2}\left(\frac{2m}{2l-1}\right)^2 \tag{16}$$

$$= \frac{32}{9}\left(\frac{2}{\pi}\right)^4 \exp\left(-\frac{5\pi^2 t}{n^2}\right), \quad \frac{t}{n^2} \gg 1, \tag{16a}$$

and reflecting boundaries (d = b)

$$\Omega_n^{\mathrm{b}}(t)\, \mathrm{e}^{2\beta_{\mathrm{T}} t} = 4\left(\frac{2}{\pi}\right)^4 \left\{ \sum_{l=1}^{\infty} \frac{\exp\left(-\frac{\pi^2}{n^2}(2l-1)^2 t\right)}{(2l-1)^4} + 2\sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \frac{\exp\left(-\frac{\pi^2}{n^2}\left((2m)^2 + (2l-1)^2\right)t\right)}{\left((2m)^2 - (2l-1)^2\right)^2} \right\} \tag{17}$$

$$= 4\left(\frac{2}{\pi}\right)^4 \exp\left(-\frac{\pi^2 t}{n^2}\right), \quad \frac{t}{n^2} \gg 1. \tag{17a}$$

The expressions (16a) and (17a) are obtained with the dominant term in (16) and (17) at $m = 1$, $l = 1$ being preserved, which is justified at $t/n^2 \gg 1$. At small times, calculating $\Omega_n(t)$ with the aid of (16), (17) is

much complicated, because it involves summing over all m, l. Therefore, to find $\Omega_n(t)$ at $t/n^2 \ll 1$, we use in (13), (14) the Poisson formula (see ref. [17], Ch. X)

$$\sum_{m=1}^{\infty} \cos\frac{\pi m(x \pm x')}{n} \exp\left(-\frac{\pi^2 m^2 t}{n^2}\right) = \frac{n}{2\sqrt{\pi t}} \sum_{j=-\infty}^{\infty} \exp\left(-\frac{(x \pm x' + 2nj)^2}{4t}\right) - \frac{1}{2}. \tag{18}$$

This enables us to pass from a sum such as

$$\sum_m \exp(-mt/n^2)$$

to a sum such as

$$\sum_j \exp(-j^2 n^2/t),$$

obtaining

$$G_n^{\mathrm{tr}(b)}(x, y, x', y', t)\, \mathrm{e}^{2\beta_T t} = \frac{1}{4\pi t} \sum_{j=-\infty}^{\infty} \left(\mathrm{e}^{-(x-x'+2nj)^2/4t} (\mp)\, \mathrm{e}^{-(x+x'+2nj)^2/4t}\right) \sum_{j=-\infty}^{\infty} \left(\mathrm{e}^{-(y-y'+2nj)^2/4t} (\mp)\, \mathrm{e}^{-(y+y'+2nj)^2/4t}\right). \tag{19}$$

Using the definition of $\Omega_n^{\mathrm{d}}(t)$ (15), we have from (12), (19)

$$\Omega_n^{\mathrm{tr}}(t)\, \mathrm{e}^{2\beta_T t} = 1 - \frac{8 + 4\sqrt{2}}{\sqrt{\pi}} \frac{\sqrt{t}}{n}, \tag{20a}$$

$$\Omega_n^{\mathrm{b}}(t)\, \mathrm{e}^{2\beta_T t} = 1 - \frac{4\sqrt{2}}{\sqrt{\pi}} \frac{\sqrt{t}}{n}, \quad \frac{t}{n^2} \ll 1. \tag{20b}$$

We compare the limiting expressions for $\Omega_n^{\mathrm{d}}(t)$ (at $\beta_T = 0$) with similar relations for $\rho_n^{(1)}(t)$, the probability for survival of a single particle that diffuses in a chain with absorbing boundaries for which [18]

$$\rho_n^{(1)}(t)\, \mathrm{e}^{\beta_T t} = \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{\exp\left(-\frac{\pi^2}{n^2}(2i+1)^2 t\right)}{(2i+1)^2} \tag{21}$$

$$= \begin{cases} 1 - \frac{4}{n}\sqrt{\frac{t}{\pi}}, & \frac{t}{n^2} \ll 1, \quad (22) \\ \frac{8}{\pi^2} \exp\left(-\frac{\pi^2}{n^2} t\right), & \frac{t}{n^2} \gg 1. \quad (23) \end{cases}$$

At large times the exponential decay constants (of course, we mean those unrelated to the monomolecular lifetime of a particle β_T^{-1}) $\Omega_n^{\mathrm{b}}(t)$ and $\rho_n^{(1)}(t)$ are seen to be the same, whereas the value for $\Omega_n^{\mathrm{tr}}(t)$ has turned out to be 5 times as great.

At small times the decay rates of $\Omega_n^{\mathrm{b}}(t)$ and $\rho_n^{(1)}(t)$ are different, the formal difference of (20b) from (22) being that the diffusion coefficient is doubled (i.e. t is replaced by $t/2$). For the case of a particle pair this is to be expected, because the annihilation rate, unlike the trapping rate, is associated with the diffusion coefficient for relative motion of a pair not of a single particle). At large times, however, the

above difference between $\Omega_n^{\mathrm{b}}(t)$ and $\rho_n^{(1)}(t)$ vanishes; whereas in an infinite chain, we have a relation such as $\rho_\infty^{(1)}(t) = \Omega_\infty^{\delta}(t/2)$.

Comparing (20) with (22) shows that at small times the rate at which a pair vanishes,

$$R_n(t) \equiv -\mathrm{d}\Omega_n^{\mathrm{tr}}(t)\,|_{\beta_{\mathrm{T}}=0}/\mathrm{d}t$$

is equal to the sum of the rates at which each of the particles are trapped,

$$R_n^{\mathrm{tr}}(t) \equiv -\mathrm{d}\rho_n^{(1)}(t)\,|_{\beta_{\mathrm{T}}=0}/\mathrm{d}t = 2/(n\sqrt{\pi t})$$

and their annihilation rate

$$R_n^{\mathrm{an}}(t) \equiv -\mathrm{d}\Omega_n^{\mathrm{b}}(t)\,|_{\beta_{\mathrm{T}}=0}/\mathrm{d}t = 2\sqrt{2}\,/(n\sqrt{\pi t}),$$

i.e. the trapping and annihilation channels for particle disappearance are independent. At large times, however, the processes of particle disappearance caused by trapping and annihilation cannot be regarded as uncorrelated.

It is of interest to note that the expressions for

$$nR_n^{\mathrm{tr}}(t) = \frac{2}{\sqrt{\pi t}} = \gamma_{\mathrm{tr}}(t), \tag{24}$$

and

$$nR_n^{\mathrm{an}}(t) = 2\sqrt{\frac{2}{\pi t}} = \gamma_{\mathrm{an}}(t) \tag{25}$$

are exactly the same as the trapping and annihilation rates of diffusing particles that are calculated with the help of Smoluchowsky's method (see, for example, ref. [2]) for an infinite one-dimensional system and used in equations for the mean particle concentration similar to those given below (see eq. (35)).

3. Delayed fluorescence kinetics

We use the expressions for the probability for a pair of particles to survive in a chain with reflecting and absorbing boundaries, to calculate the time dependence of the DF intensity in quasi-one-dimensional crystals with impurities that play the role of traps or reflecting barriers. Here we assume that one of the channels through which triplet excitons, excited in a crystal, decay is by mutual annihilation generating singlet excitons. We also assume that a randomly disordered chain that consists of molecules of two types (hosts and guests) randomly distributed over a periodic one-dimensional lattice is the basic structural unit of quasi-one-dimensional crystals. The triplet excitons diffuse and annihilate in the chain segments of host molecules and can be trapped (or reflected) by the guest molecules which bound a segment.

It is possible to observe the DF when the range of two-triplet exciton excitation energies is close to the energy of a singlet state S. While describing the DF that occurs after triplet excitons get excited, we restrict ourselves to the initial time interval in which most excitons cannot go from the cluster where they were born to others (the transfer process is predominantly one-dimensional, and the caging effect of triplet excitons mentioned in the Introduction is practically complete). This restriction arises from the model formulated above which does not take into account the slow but always present interchain and (or) over-defect jumps.

We first consider the annihilation process for a cluster of length n containing initially two triplet excitons. The probability of finding a singlet excitation $\Omega^{\mathrm{d}}_{n,\mathrm{S}}(t)$ in such a cluster obeys the following equation:

$$\frac{\partial \Omega^{\mathrm{d}}_{n,\mathrm{S}}(t)}{\partial t} = -\left.\frac{\partial \Omega^{\mathrm{d}}_{n}(t)}{\partial t}\right|_{\mathrm{an}} - \beta_{\mathrm{S}}\Omega^{\mathrm{d}}_{n,\mathrm{S}}(t), \tag{26}$$

where the first term on the right-hand side of (26) is the annihilation rate of a pair of triplet excitons; β_{S}^{-1} is the monomolecular lifetime of a singlet excitation (the final state after triplet annihilation).

To determine $\partial\Omega/\partial t|_{\mathrm{an}}$ we integrate eq. (2) over x, y in the region $0 \le x + y \le n$, obtaining

$$\frac{\partial \Omega^{\mathrm{d}}_{n}(t)}{\partial t} = -\frac{4}{n^2}\int_0^n \mathrm{d}y \left.\frac{\partial \rho^{\mathrm{d}}_{n}(x,\,y,\,t)}{\partial x}\right|_{x=0} + \frac{4}{n^2}\int_0^n \mathrm{d}y \left.\frac{\partial \rho^{\mathrm{d}}_{n}(x,\,y,\,t)}{\partial x}\right|_{x=n-y} - 2\beta_{\mathrm{T}}\Omega^{\mathrm{d}}_{n}(t). \tag{27}$$

The first term on the right-hand side of (27) (equal to zero at d = b) has the meaning of a net excitation flux towards traps. The last term corresponds to the change in the number of excitations in a chain due to monomolecular decay. The second term defines the flux of excitations towards each other and, consequently, the change in the survival probability of an exciton pair in a cage, which is caused by mutual annihilation of excitons, so that

$$\left.\frac{\partial \Omega^{\mathrm{d}}_{n}(t)}{\partial t}\right|_{\mathrm{an}} = -\frac{4}{n^2}\int_0^n \mathrm{d}y \left.\frac{\partial \rho^{\mathrm{d}}_{n}(x,\,y,\,t)}{\partial x}\right|_{x=n-y}. \tag{28}$$

The intensity of the DF of a quasi-one-dimensional crystal with defects is determined by averaging the probability $\Omega^{\mathrm{d}}_{n,\mathrm{S}}(t)$ over a random distribution of defects in a chain

$$\Phi^{\mathrm{d}}(t) = \beta_S \rho^{\mathrm{d}}_{\mathrm{S}}(t); \quad \rho^{\mathrm{d}}_{\mathrm{S}}(t) = \frac{c_{\mathrm{d}}^3}{2}\int_0^\infty \mathrm{d}n n^2\, \mathrm{e}^{-c_{\mathrm{d}}n}\Omega^{\mathrm{d}}_{n,\mathrm{S}}(t) \tag{29}$$

where $\rho^{\mathrm{d}}_{\mathrm{S}}(t)$ is the mean density of singlet excitations in a chain with randomly distributed guest and host molecules. Using the expression for the distribution functions $\rho^{\mathrm{d}}_{n}(x,\,y,\,t)$ (13), (14) and the initial condition $\Omega^{\mathrm{d}}_{n,s}(0) = 0$ we have from (26), (28), (19), for the case of a chain with traps,

$$\left.\frac{\partial \Omega^{\mathrm{tr}}_{n}(t)}{\partial t}\right|_{\mathrm{an}} = -\frac{64}{n^2}\left(\frac{2}{\pi}\right)^2 \sum_{i=2,4,\ldots}^{\infty}\ \sum_{j=1,3,\ldots} \frac{\exp\left(-\dfrac{\pi^2}{n^2}(i^2+j^2)t - 2\beta_{\mathrm{T}}t\right)}{(i^2-j^2)^2} i^2, \tag{30}$$

$$\rho^{\mathrm{tr}}_{\mathrm{S}}(t) = 32 c_{\mathrm{tr}}^2\left(\frac{2}{\pi}\right)^2 \int_0^\infty \mathrm{d}n n^2\, \mathrm{e}^{-c_{\mathrm{tr}}n} \sum_{i=2,4,\ldots}^{\infty}\ \sum_{j=1,3,\ldots}^{\infty} \frac{\mathrm{e}^{-\beta_{\mathrm{S}}t} - \mathrm{e}^{-(\pi^2/n^2)(i^2+j^2)t - 2\beta_{\mathrm{T}}t}}{\pi^2(i^2+j^2) + (2\beta_{\mathrm{T}} - \beta_{\mathrm{S}})n^2} \frac{i^2}{(i^2-j^2)^2}, \tag{31}$$

and for the case of a chain with barriers

$$\left.\frac{\partial \Omega^{\mathrm{b}}_{n}(t)}{\partial t}\right|_{\mathrm{an}} = -\frac{16}{n^2}\left(\frac{2}{\pi}\right)^2 \left\{ \sum_{j=1,3,\ldots}^{\infty} \frac{\exp\left(-\dfrac{\pi^2 j^2 t}{n^2} - 2\beta_{\mathrm{T}}t\right)}{j^2} \right.$$

$$\left. + 2\sum_{i=2,4,\ldots}^{\infty}\ \sum_{j=1,3,\ldots}^{\infty} \frac{\exp\left(-\dfrac{\pi^2}{n^2}(i^2+j^2)t - 2\beta_{\mathrm{T}}t\right)}{(i^2-j^2)^2}(i^2+j^2) \right\}; \tag{32}$$

$$\rho_S^b(t) = 8c_b^3\left(\frac{2}{\pi}\right)^2 \int_0^\infty dn n^2\, e^{-c_b n}$$

$$\times \left\{ \sum_{j=1,3,\ldots}^{\infty} \frac{e^{-\beta_S t} - e^{-\pi^2 j^2 t - 2\beta_T t}}{(\pi^2 j^2 + (2\beta_T - \beta_S)n^2)\, j^2} \right.$$

$$\left. + 2 \sum_{i=2,4,\ldots} \sum_{j=1,3,\ldots} \frac{e^{-\beta_S t} - e^{-(\pi^2/n^2)(i^2+j^2)t - 2\beta_T t}}{\pi^2(i^2+j^2) + (2\beta_T - \beta_S)n^2} \frac{i^2+j^2}{(i^2-j^2)^2} \right\}. \tag{33}$$

The rate of a monomolecular decay of singlet excitations in molecular crystals and polymers is several orders greater than that of triplets, so that it is sufficient to consider the case $\beta_S \gg \beta_T$ while analyzing the dependence $\rho_S^d(t)$. From (31), (33) we have

$$\rho_S^d(t) = \begin{cases} 2\sqrt{\frac{2}{\pi}}\, c_d \sqrt{t}, \quad \tau_d \ll 1, \quad \beta_S t \ll 1, & (34a) \\ \sqrt{\frac{2}{\pi}}\, \frac{c_d}{\beta_S} \frac{e^{-2\beta_T t}}{\sqrt{t}}, \quad 1 \ll \beta_S t \ll z^{-2}, & (34b) \\ A_d \frac{16}{45}\left(\frac{2}{\pi}\right)^4 e^{-\beta_S t}\left(1 - \sqrt{\frac{\pi}{6}}\, \tau_d^{5/6}\, e^{-(3/2)\tau_d^{1/3}}\right), \quad 1 \ll \tau_d \ll z^3, & (34c) \\ A_d 8\left(\frac{4}{3\pi}\right)^2 \sqrt{\frac{2\pi}{3}}\, \tau_d^{1/6} \frac{c_d^2}{\beta_S} e^{-(3/2)\tau_d^{1/3} - 2\beta_T t} \quad \tau_d \gg \max\{1,\, z^3\}, & (34d) \end{cases}$$

where

$$z = c_d\sqrt{1/\beta_S}, \quad \tau_{tr} = 10\pi^2 c_{tr}^2 t, \quad \tau_b = 2\pi^2 c_b^2 t, \quad A_{tr} = 4, \quad A_b = 1.$$

We stress that the dependences (34) follow from the exact expressions (31), (33) and therefore take strict account of the fluctuations in defect density.

The dependences (34b), (34c) play the role of intermediate asymptotic approximations: (34c) describes the DF intensity rise and decay near its maximum, and (34b) only the DF decay. When the singlet excitation monomolecular decay is sufficiently fast, $z \ll 1$, the region described by (34c) is absent; if the opposite condition $z \gg 1$ is valid, the region (34b) is absent.

The long-time asymptotic expression (34d) describes the late stage of the annihilation process, in which the DF intensity follows (with an accuracy up to logarithmic corrections in the exponent) the survival probability (15), averaged over the random distribution of guest and host molecules in a chain. The latter is calculated in refs. [19,20]. It is also to be noted that the characteristic scale of times that determine the DF decay rate in a chain with traps is 5 times as large as the relevant scale in the dependence of phosphorescence intensity decay in the same crystal, see eq. (41) (a detailed discussion of this point is given in the concluding section).

It is helpful to compare the dependence $\rho_S^d(t)$ with the theoretical predictions derived by solving the set of phenomenological equations

$$\begin{cases} \frac{dc_T(t)}{dt} = -(\beta_T - \gamma_{tr}(t)c_{tr})c_T(t) - \gamma_{an}(t)c_T^2(t), & (35a) \\ \frac{dc_S(t)}{dt} = -\beta_S c_S(t) + \frac{1}{2}\gamma_{an}(t)c_T^2(t), & (35b) \end{cases}$$

that correspond to the process under consideration (trapping + annihilation) and are used to interpret

experimental results. In (35), $c_{T(S)}(t)$ is the mean concentration of triplet (singlet) excitons. The quantities $\gamma_{an(trapping)}(t)$ in these equations have the meaning of exciton annihilation (trapping) rates; they are usually calculated by Smoluchowsky's two-particle approach and have a form like in (24), (25) [2]. Substituting the expressions (24), (25) into the solution of (35) under the conditions $c_T(0) \ll c_{tr}$, $c_S(0) = 0$ yields *

$$c_S(t) = ic_T^2(0)\sqrt{\frac{2}{\beta_S - 2\beta_T}}\exp\left[-\left(\beta_S t + \frac{16c_{tr}^2}{\pi(\beta_S - 2\beta_T)}\right)\right]$$

$$\times\left\{\operatorname{erf}\left[-i\sqrt{(\beta_S - 2\beta_T)t} + i\frac{4c_{tr}}{\sqrt{\pi(\beta_S - 2\beta_T)}}\right] - \operatorname{erf}\left(i\frac{4c_{tr}}{\sqrt{\pi(\beta_S - 2\beta_T)}}\right)\right\} \tag{36}$$

At short times $\tau_{tr} \ll 1$, (36) is the same as (34a), (34b), with the same restrictions on time intervals. Let us compare the dependence (34c) (intermediate range) with the result

$$c_S(t) \sim \exp(-\beta_S t)\left\{1 - \exp\left(-\frac{4}{\pi^{3/2}}\sqrt{\tfrac{2}{5}}\,\tau_{tr}^{1/2}\right)\right\}, \quad 1 \ll \tau_{tr} \ll z^3, \tag{37}$$

which was derived from (36) for the same part of a kinetic curve. It is seen that defect density fluctuations are important in this case, both in determining the position and the form of the maximum of DF time dependence and in establishing a relation between the characteristics of an observed kinetic curve and the values of the defect concentration and the triplet exciton diffusion coefficient.

The difference in the predictions based on the phenomenological and the present microscopic approaches is also manifest in the appreciable difference between the dependence (34d) and the long-time dependence that follows from (36):

$$c_S(t) = 2\sqrt{\pi}\,\frac{c_{tr}}{\beta_S}\tau_{tr}^{-1/2}\exp\left(-\frac{4}{\pi^{3/2}}\sqrt{\tfrac{2}{5}}\,\tau_{tr}^{1/2} - 2\beta_T t\right), \quad \tau_{tr} \gg \max\{z^2,\ z^4\}. \tag{38}$$

Thus, at $z \ll 1$ ("fast" decay of the DF intensity) the phenomenological equations (35) together with the definitions (24), (25) describe fairly accurately the increase and decrease of the DF intensity except the long-time tail of the kinetic curve, but to define the asymptotic tail of luminescence of singlet excitons, we must take trap density fluctuations accurately into account. At $z \gg 1$, the time dependence of the survival probability for a pair of annihilating excitons takes an asymptotic form at times $\lesssim \beta_S^{-1}$, so that fluctuation effects are important to define the greater part of the DF kinetic curve, whereas the phenomenological description using (24), (25), (35) may, strictly speaking, be used only at the initial stage of the DF rise.

For a crystal with barriers, the behaviour of $\rho_S^b(t)$ is easily seen to be identical to that of $\rho_S^{tr}(t)$ (34) with an accuracy to the replacement $\tau_{tr} \to \tau_b$, so that in this case, too, we can expect an asymptotic exponential dependence of DF, proportional to $\exp(-\text{const}\ t^{1/3})$. In ideal infinite one-dimensional systems (without defects), we have $dc_T/dt \propto t^{-3/2}$ at times $c_T^{-2}(0) \ll t \ll \beta_T^{-1}$ (i.e. the triplet exciton concentration is already much reduced by annihilation, with the bimolecular decay channel still remaining dominant).

As a result,

$$\Phi(t) \propto \exp(-2\beta_T t)t^{-3/2}, \quad \beta_S t \gg 1. \tag{39}$$

This estimate follows from the solution (35) at $c_{tr} = 0$, as well as from an exact solution of the annihilation problem in one dimension [5,6]. So, the triplet exciton caging effect, with impurities introduced as potential barriers, should manifest itself in a qualitatively changed DF decay law: the power law (39)

* When comparing the approximate (36) and the exact (31), (33) dependences, it should be remembered that according to the adopted definition of the average (29), the quantity $\rho_S^d(t)$ is related to the concentration $c_S(t)$ by $c_S(t) = c_T^2(0)\ \rho_S^d(t)$.

observed in a crystal without defects changes to an exponential one such as

$$\Phi^{d}(t) \propto \exp\left(-\text{const}\ t^{1/3} - 2\beta_{T}t\right), \tag{40}$$

observed in a crystal with defect barriers (or traps). As the estimates show [8,9], the value of the concentration c_b may be quite small, whereas the caging effect may be quite pronounced.

We emphasize that the predicted influence of barriers on DF kinetics can be observed only at times smaller than, or comparable with, the time of exciton jump over a barrier.

4. Conclusion

Employing an exact solution for the survival probability of a pair of quasiparticles that diffuse and annihilate in a chain with absorbing or reflecting ends, the time dependence of delayed fluorescence (DF) in Q1D crystals has been calculated in the framework of the model of a molecular chain with randomly distribution defects such as traps or reflecting barriers. Defect density fluctuations have been taken into account in our calculation procedure. The theory developed is accurate under the condition c_T (triplet exciton concentration) $\ll c_d$ (defect (traps or barriers) concentration); c_T, $c_d \ll 1$, relevant to most real Q1D systems – crystals, polymers, etc.

Another restriction on the applicability of our approach to describe real processes is the assumption that the quasiparticle motion is purely one-dimensional. Thus, the application of our results to the DF kinetics is reasonable for the time $t < \tau_{\perp}$, which is the characteristic parameter of the transverse triplet exciton motion, determined by the rate of excitation jump between adjacent chains of the Q1D crystal. In spite of the constraints mentioned above, our previous discussion enables some predictions as to the experimentally accessible quantities, which seem to be useful in verifying our basic ideas concerning, in the first place, the dynamics of an isolated pair of annihilating quasi-particles in Q1D systems and then the role of defect density fluctuations in determining long-time decay laws in processes such as $A + B \rightarrow B$ and $A + A \rightarrow 0$.

It is shown that taking the fluctuations into account leads to time dependence of the decrease in the concentration of singlet excitons (generated by triplet–triplet annihilation) that is of the form $\rho_S^{tr}(t) \propto \exp(-3/2(\tau_{tr})^{1/3} - 2\beta_T t)$ at long times, see eq. (34d). Almost the same expression is known to be relevant to triplet exciton concentration, $\rho_T(t)$, in Q1D crystals with traps (see ref. [21] and refs. therein):

$$\rho_{T}(t) \propto \exp\left(-3/2\tau^{1/3} - \beta_{T}t\right), \quad \tau \equiv 2\pi^{2}c_{tr}^{2}Wt. \tag{41}$$

Thus, the long-time kinetics of the DF in the case when triplet excitons can alternatively annihilates or be trapped and the kinetics of the phosphorescence in the same Q1D crystal are similar in character, but the characteristic time scales of $\rho_S^{tr}(t)$ and $\rho_T(t)$ are different by a factor of 5, i.e. $\tau_{tr}/\tau = 5$. This means that monitoring the phosphorescence and the DF in the same Q1D crystal doped with traps, one should expect the $\exp(-t^{1/3})$ decay law of the phosphorescence (documented, for example, in TMMB crystals [11]) to be also observed in the DF kinetics but on the reduced (five-fold) time scale.

The similarity between the time dependences of the DF, eq. (34d), and the phosphorescence, eq. (41), originates from the close resemblance between the annihilation and trapping processes, and this is not surprising in any way. Moreover, this fact may be used to answer the question: are the conclusions made for the infinite annihilation rate model also applicable to the realistic case of finite annihilation rate, ω_{an}, and to what extent? One can expect that the small values of ω_{an} will manifest themselves in the DF kinetics in the same way as the small trapping rates ω_{tr} in the phosphorescence kinetics. The various aspects of trapping kinetics in 1D systems under an arbitrary trapping rate were studied in refs. [21–23].

One of the most important points in those papers is that the decay law (41) is valid not only for $\omega_{tr} = \infty$, but it is also obeyed whenever the condition for fast trapping

$$\omega_{tr}/Wc_{tr} \gg 1 \tag{42}$$

holds. The corresponding condition of "fast annihilation", for which the conclusions drawn above are correct, should read

$$\omega_{an}/Wc_{tr} \gg 1, \tag{43}$$

at least we do not see any reason why this should not be so.

It is seen that the range of annihilation rates satisfying (43) is very wide. There can be lots of real systems where fast annihilation is the case and thus the predictions of our theory can be tested.

For the case of slow annihilation (when an inequality opposite to (43) holds) we expect essential qualitative changes in the DF kinetics similar to those predicted in the phosphorescence kinetics under slow trapping [21]. But the discussion of such a situation is beyond the framework of the present paper.

In a crystal without traps, but with impurities acting like reflecting barriers, the DF intensity fall is also described by an exponential law of the type mentioned above, as distinct from the power dependence $\propto t^{-3/2}$ expected for one-dimensional motion of excitons in an ideal crystal (without impurities). At small values of monomolecular singlet excitation decay rate, $c_d\sqrt{D/\beta_S} \gg 1$ (D is the triplet exciton diffusion coefficient), the impurity density fluctuations determine the position and the form of the maximum of the DF kinetic curve. In this case the kinetics of the population of the singlet state due to triplet exciton annihilation is determined by the asymptotic time dependence of the survival probability of an annihilating exciton pair averaged over random impurity distribution.

It should be emphasized that the above results cannot be derived within the mean-field approximation associated with a set of kinetic equations commonly used to describe the DF. Specifically, the assumption that the triplet exciton annihilation and trapping are independent processes and the introduction of two relevant rates is unacceptable in the general case. The range of applicability of the above approximation is determined.

The predicted properties of DF kinetics in quasi-one-dimensional crystals with impurities of the above type can be observed at times less than the characteristic time of interchain exciton jumps. Of course, tunneling of excitations between adjacent chains will smear the predicted effects which are pronounced in the case of pure one-dimensional motion only. Still, we believe that experimental verification of the dependences (34) and (40) will become possible just as in the case of the phosphorescence decay law (41), which has the same physical nature as (34d), and was first observed in ref. [11], 13 years after it was predicted [18].

References

[1] V. Gösele, Reaction Kinetics and Diffusion in Condensed Matter (Habilitationsschrift, Stuttgart, 1983).
[2] A.I. Onipko, in: Physics of Many-Particle Systems, Vol. 2, ed. A.S. Davydov (Naukova Dumka, Kiev, 1982).
[3] P.V. Elyutin, J. Phys. C. 17 (1984) 1867.
[4] R.D. Burkhart, Chem. Phys. Lett. 133 (1987) 568.
[5] A.A. Lushnikov, Zh. Ekp. Teor. Fiz. 91 (1986) 1376 (Engl. transl.: Sov. Phys. JETP 64 (1986) 811).
[6] A.S. Prostnev and B.P. Shub, Kinetica i kataliz 28 (1987) 1402.
[7] R.M. Hochstrasser and J.D. Whiteman, J. Chem. Phys. 56 (1972) 5942.
[8] D.D. Dlott, M.D. Fayer and R.D. Wieting, J. Chem. Phys. 69 (1978) 2752.
[9] V.A. Karachevtsev, Fiz. Tverd. Tela 28 (1986) 1400.
[10] R.A. Auerbach and G.L. McPherson, Phys. Rev. B 33 (1986) 6815.
[11] W.J. Rodrigues, R.A. Auerbach and G.L. McPherson, J. Chem. Phys. 85 (1986) 6442.
[12] R. Knochenmuss and H.V. Gudel, J. Chem. Phys. 86 (1987) 1104.

[13] M. Buijs and G. Blasse, J. Lumin. 34 (1986) 263.
[14] M. Buijs, J.P.M. van Vliet and G. Blasse, J. Lumin. 35 (1986) 213.
[15] M. Buijs, J.I. Vree and G. Blasse, Chem. Phys. Lett. 137 (1987) 381.
[16] H. Bouchrina, V. Ern, J.L. Fave, C. Guthmann and M. Schott, Chem. Phys. Lett. 53 (1978) 288.
[17] H.S. Carslaw and J.C. Jaeger, Conduction of Heat in Solids (Oxford Univ. Press, Oxford, 1959).
[18] B.Ya. Balagurov and V.G. Vaks, Zh. Exp. Teor. Fiz. 65 (1973) 1939 (English transl.: Sov. Phys. JETP 38 (1974) 968).
[19] I.V. Zozulenko and A.I. Onipko, Fiz. Tverd. Tela 30 (1988) 2665.
[20] Yu.B. Gaididei, A.I. Onipko and I.V. Zozulenko, Phys. Lett. A 132 (1988) 329.
[21] A.I. Onipko, L.I. Malysheva and I.V. Zozulenko, Chem. Phys. 121 (1988) 99.
[22] L.I. Galchuk and A.I. Onipko, Ukr. Fiz. Zh. 32 (1987) 946.
[23] A.I. Onipko and L.I. Galchuk, Khim. Fiz. 6 (1987) 825.