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Delayed luminescence kinetics of nanocrystals and its interpretation

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The kinetics of luminescence decay of nanocrystals (NCs) contains important information about the excited states of the NCs, the type and number of traps of charge carriers (electrons, holes) or excitation-energy acceptors (molecules, other NCs), the trap energy distribution, and the mechanism of electron excitation-energy transfer from NCs to acceptors. Usually, the kinetics of NC luminescence decay is non-exponential and can be approximated with good accuracy by the sum of two or three exponentials. In recent years, it has been experimentally observed that after pulsed excitation, the luminescence intensity of an ensemble of NCs decreases at large times according to a power law. To explain this regularity, a new model of the NC ensemble and a corresponding new function for fitting the kinetics of luminescence decay are proposed. This function is obtained on the basis of the balance equations and assuming an exponential distribution of traps by energies and reversible return of charge carriers from the traps to the NCs. Fitting experimental data with the proposed function allows to estimate the trapping rate of charge carriers and the parameters of the trap energy distribution function.

Keywords: nanocrystals, luminescence decay kinetics, delayed luminescence.

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Introduction

The luminescence decay kinetics of nanocrystals (NCs) semiconductor quantum dots (QDs), nanowires, nanoplatelets, and nano-rings) contains important information about the structure of the electronic energy levels of the NCs and the mechanisms of NC interaction with acceptors of electronic excitation energy (molecules, other NCs) or with charge carriers (electrons, holes) in NCs with traps. The analysis of the luminescence decay kinetics (based on currently existing models) makes it possible to determine the number of traps or excitation energy acceptors, the traps energy, identify the mechanism of electron excitation energy transfer from NCs to acceptors, and determine the charge carriers trapping rate and the rate of detrapping to the NC emitting state [1–19].

Generally, the kinetics of luminescence decay of a NC ensemble $I(t)$ is non-exponential and can be approximated with good precision using a sum of two or three exponents:

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}. \qquad (1)$$

In equation (1) the fitting parameters are the time constants (τ_1, τ_2, τ_3) and amplitudes (A_1, A_2 and A_3). Taking into account the normalization condition for $I(t)$ (in the initial moment of time $I(0) = 1$, and $A_1 + A_2 + A_3 = 1$), the function (1) has five independent fitting parameters (three time constants and two amplitudes). The physical meaning of these parameters is not always clear [18,20].

Often, the exponent with the longest decay time is associated either with the luminescence of NCs without traps or acceptors, or with delayed luminescence of NCs due to detrapping of charge carriers to the emitting state of the NCs. In [20], several models of NC interaction with traps and acceptors are analyzed, in which the approximation of $I(t)$ by a sum of two or three exponents (1) has a clear physical meaning, and a relationship is established between the fitting parameters (between the time constants τ_1, τ_2, τ_3). This allows reducing the number of fitting parameters in equation (1) up to four.

In the present work, two models of NC ensemble are analyzed, explaining the increase in the duration of the NC luminescence. In the first model, different NCs in the ensemble have a different number of identical traps, from which the charge carriers may return to the NC emitting state. The different number of traps and the detrapping of charge carriers lead to the non-exponential kinetics of luminescence decay of the NC ensemble. In addition, the detrapping of charge carriers increases the duration of NC luminescence, i.e. leads to delayed luminescence.

In the second model, the traps are not identical (Fig. 1): they have different energies (the trap energy is calculated relative to the conduction band edge energy level for electron traps or relative to the valence band edge energy level for the hole traps) and are characterized by some energy distribution function. Note that the highest and lowest quantum size energy levels in NCs are called conduction band edge and valence band edge levels in analogy to the situation in bulk solids. It can be shown that if the energy distribution function of the traps decreases exponentially with the energy growth, then the luminescence intensity $I(t)$ of the NC ensemble decreases according to the power-law pattern at long times. Such behavior $I(t)$ in ensembles

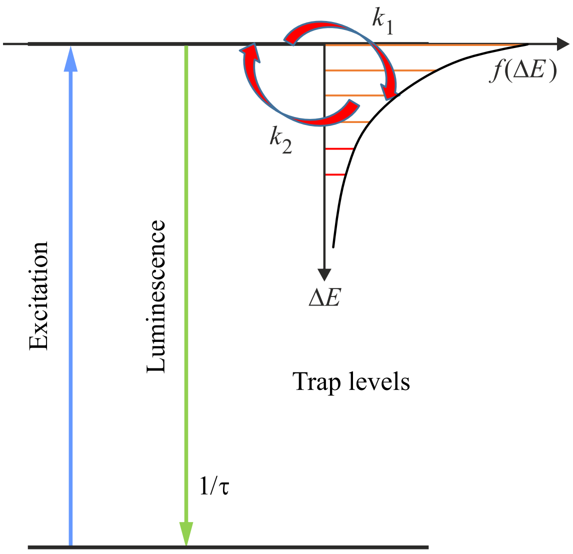

Figure 1. Graph of NC ensemble electronic levels with non-identical traps: τ is lifetime of NC emitting state in the absence of traps ($1/\tau$ is luminescence decay rate), k_1 and k_2 are rates of electron capture by traps and electron detrapping to NC emitting state, $f(\Delta E)$ is function of trap distribution by energies.

of QDs, nano-wires, nanoplatelets, and nano-rings was observed experimentally in the works [21–24].

Kinetics of NC ensemble luminescence decay with different number of identical traps

The problem of the kinetics $I(t)$ of NC ensemble luminescence decay in the case of reversible trapping of charge carriers was addressed in the works jcite7-9. It was assumed that 1) each NC has a different number (N) of traps, 2) the number of traps per NC follows a Poisson distribution, 3) the traps are identical, i.e. the trapping rates (k_1) and the detrapping rates (k_2) of charge carriers are the same for all traps. Under these assumptions, the corresponding balance equations were solved, and the following expression was obtained for the normalized kinetics of NC ensemble luminescence decay after pulsed excitation:

$$I(t) = \sum_{N=0}^{\infty} e^{-\bar{N}} \frac{\bar{N}^N}{N!} A_N e^{-\alpha_1(N)t/\tau} + \sum_{N=0}^{\infty} e^{-\bar{N}} \frac{\bar{N}^N}{N!} B_N e^{-\alpha_2(N)t/\tau}. \tag{2}$$

In equation (2) $\bar{N}$ is average number of traps per one NC, τ is NC luminescence decay time in the absence of traps. (It should be stressed that in the case of QDs characterized by energetically close bright (emitting) and dark states, τ is equal to the twice the lifetime of the bright state [3,25–27] at room temperatures, since at these temperatures the populations of bright and dark states become equal due to the electron-vibrational interaction.)

Other parameters in equation (2) are defined by the following equations:
The exponents

$$\alpha_1(N) = \frac{1}{2}(1 + NK_1 + K_2) + \sqrt{\frac{1}{4}(1 + NK_1 + K_2)^2 - K_2}, \tag{3}$$

$$\alpha_2(N) = \frac{1}{2}(1 + NK_1 + K_2) - \sqrt{\frac{1}{4}(1 + NK_1 + K_2)^2 - K_2}, \tag{4}$$

the amplitudes are given by

$$A_N = \frac{1 + NK_1 - \alpha_2(N)}{\alpha_1(N) - \alpha_2(N)}, \quad B_N = 1 - A_N, \tag{5}$$

and the dimensionless trapping and detrapping rate constants of the charges carriers are respectively equal to

$$K_1 = k_1\tau, \quad K_2 = k_2\tau. \tag{6}$$

The equation (2) was used to fitting the kinetics of NC luminescence decay in papers [7,8,12,14–17].

Note that since $\alpha_2(N) < \alpha_1(N)$, the first sum in the equation (2) decreases faster over time than the second one. The second sum determines the delayed luminescence caused by the detrapping of charge carriers to NCs emitting state (at $K_2 = 0$, the second sum becomes zero, since under this condition the amplitudes $B_N = 0$).

In the present work we focus on delayed luminescence, i.e., on the study of the second sum in equation (2). Let us denote this sum as $I_d(t)$. Let us consider the special case — luminescence decay kinetics at $1 \ll K_2 \ll K_1$, i.e. given that the rates of the charge carriers trapping and their detrapping to NC emitting state are larger compared to the rate $1/\tau$. Then equation (2) is converted to the form

$$I(t) = e^{-\bar{N}-t/\tau} + \sum_{N=1}^{\infty} e^{-\bar{N}} \frac{\bar{N}^N}{N!} \left(1 - \frac{1}{N}\frac{K_2}{K_1}\right) e^{-NK_1 t/\tau} + \sum_{N=1}^{\infty} e^{-\bar{N}} \frac{\bar{N}^N}{N!} \frac{1}{N} \frac{K_2}{K_1} e^{-\frac{1}{N}\frac{K_2}{K_1}t/\tau}. \tag{7}$$

All terms of the first sum in (7) are rapidly decreased over time: $NK_1 \gg 1$, and the terms of the second sum decrease slowly: $K_2/(NK_1) \ll 1$.

Thus, under considered conditions, the kinetics of delayed luminescence of NC $I_d(t)$ is expressed as

$$I_d(t) = \sum_{N=1}^{\infty} e^{-\bar{N}} \frac{\bar{N}^N}{N!} \frac{1}{N} \frac{K_2}{K_1} e^{-\frac{1}{N}\frac{K_2}{K_1}t/\tau} \tag{8}$$

and provides the major contribution to the full luminescence intensity (7).

From the formula (8) it follows that $I_d(t)$ does not directly depend on the rate of charge carrier trapping K_1, but depends on the ratio of rates K_2/K_1 and the average number of traps per NC.

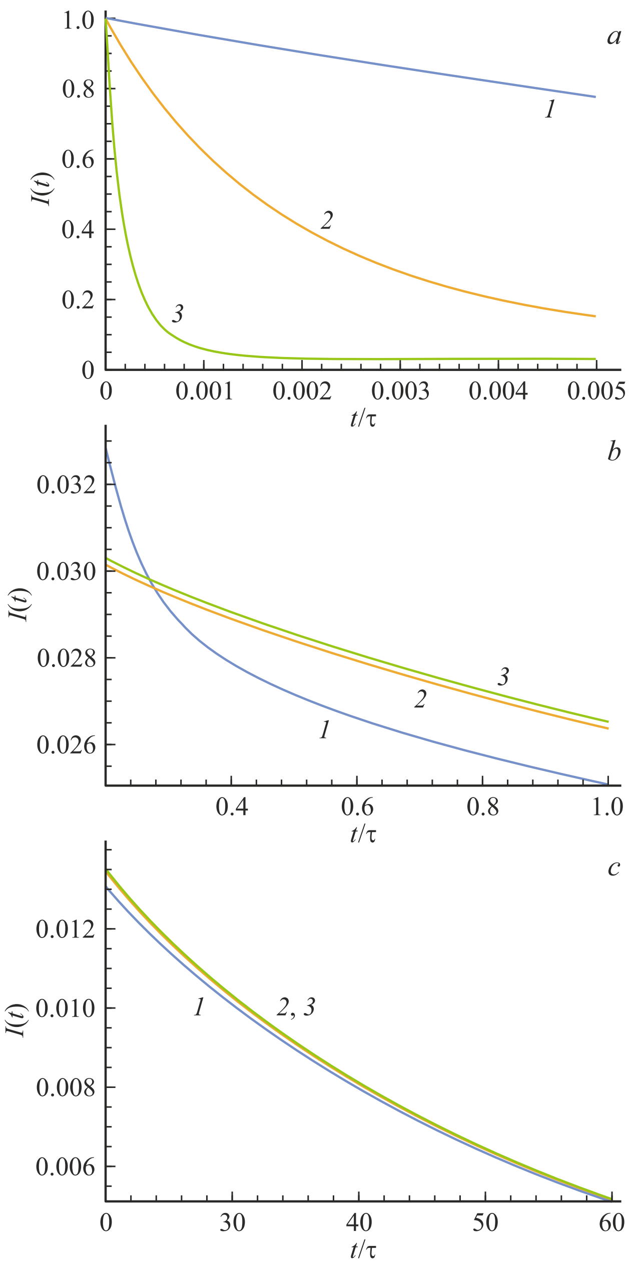

Figure 2. Kinetics of luminescence decay (2) at different values of trapping rate of charge carriers: (*a*) $K_1 = 10$ (curve *1*, top, blue), 100 (*2*,_ middle, yellow) and 1000 (*3*, bottom, green). $K_2/K_1 = 0.1$, $\bar{N} = 5$; (*b*) over time, the relative position of the curves starts to change (curve *1*, blue, becomes bottom); (*c*) at large time ($t/\tau \geq 50$) all curves practically coincide (according to formula (8)), since all curves are calculated at one and the same value $K_2/K_1 = 0.1$.

Figure 2 illustrates the kinetics of luminescence decay $I(t)$ calculated by formula (2) at different time intervals with various values K_1 (10, 100 and 1000) and $K_2/K_1 = 0.1$. The calculations demonstrate the correctness of formula (8) even at relatively small values of K_1 and K_2: all curves calculated for $K_1 = 10$, 100 and 100, at large times (Fig. 2, *c*) practically coincide, since for all curves $K_2/K_1 = 0.1$.

Thus, according to equation (8), the intensity of delayed luminescence $I_d(t)$ and, consequently, the total luminescence intensity of the NC ensemble (2) at large times (i. e. the asymptote $I(t)$) are described by the sum of exponentials with different values of the indexes $K_2/(NK_1)$. Hence, in the considered NC model $I_d(t)$ and $I(t)$ decrease over time in the non-exponentially.

Kinetics of NC ensemble luminescence decay with different number of non-identical traps

In the works [21–24] it was experimentally found that the luminescence intensity $I(t)$ for some NCs at large times (i.e. asymptotic behavior $I(t)$) decreases with time as an inverse power law: $I(t) \sim 1/t^c$, where c is constant. This behavior $I(t)$ was explained within the framework of a three-level NC model (the ground and emitting states of NC and the trap level), in which the distribution of rates of detrapping of charge carriers k_2 to the emitting state of NC is described by some broad distribution function $f_s(k_2)$. In [21] this function was assumed to be exponential, while in [22–24] it was assumed to be a log-normal distribution (similar distribution was used in [28] to approximate the QD luminescence kinetics at large times).

In the present work, in order to explain the behaviour observed in [21–24] the following assumptions are made:

1) different NCs in the ensemble have different number of traps,

2) the number of traps per NC_follows a Poisson distribution (with an average value of $\bar{N}$),

3) the levels of electrons (holes) traps are located at different energy distances ΔE from the emitting (ground) state of NC (Fig. 1),

4) the principle of detailed balance is valid, i.e. the charge carrier trapping rate k_1 and detrapping rate k_2 to the emitting state of NC are related by

$$k_2/k_1 = \exp(-\Delta E/kT), \tag{9}$$

5) the traps distribution across energies ΔE is described by the function

$$f(\Delta E) = \beta \exp(-\beta \Delta E), \tag{10}$$

where β is constant ($\beta > 0$).

Such energy distribution of electron traps in colloidal QDs of CdS was proposed in [29], and was used to explain the long-time phosphorescence of solids [30]; it coincides with the dependence of the light absorption coefficient of some solids (including semiconductors) on the photon energy near the optical absorption edge (Urbach's rule [31]).

Based on the assumptions made and the corresponding balance equations, we propose a new function that can be used for fitting the experimental kinetics of NC ensemble luminescence decay, whose asymptotic behavior at large times is a decrease according to a power law. The fitting parameters are the following: charge carriers trapping rate constant k_1, parameter β in the trap energy distribution function (10), average number of traps $\bar{N}$ per NC, and the time constant of NC luminescence decay in the absence of traps τ.

The balance equations for the population of NC emitting state with N traps, $p(N, \Delta E, t)$, and the population of the trap state, $p_{\text{trap}}(t)$, used in this study are identical to the corresponding equations in [7,8]. Taking into account the assumptions made above, these equations are expressed as follows:

$$\frac{dp(N,\Delta E,t)}{dt} = -\frac{1}{\tau}p(N,\Delta E,t) - Nk_1 p(N,\Delta E,t) + Nk_2 p_{\text{trap}}(t), \quad (11)$$

$$\frac{dp_{\text{trap}}(t)}{dt} = -k_2 p_{\text{trap}}(t) + k_1 p(N,\Delta E,t). \quad (12)$$

Under pulse excitation of NC (i.e. under initial condition $p(N, \Delta E, 0) = 1$) these equations have solution as a sum of two exponents:

$$p(N,\Delta E,t) = A_N e^{-\alpha_1(N)t/\tau} + B_N e^{-\alpha_2(N)t/\tau}. \quad (13)$$

Coefficients $\alpha_1(N), \alpha_2(N), A_N$ and B_N in equation (13) are defined by previous formulae (3)–(5). However, given the detailed balance principle (9) and the above-described dimensionless rates K_1 and K_2 (formulae (6)) coefficients $\alpha_1(N)$ and $\alpha_2(N)$ are transformed to

$$\alpha_1(N) = \frac{1}{2}\left(1 + K_1(N + e^{-\Delta E/kT})\right) + \sqrt{\frac{1}{4}\left(1 + K_1(N + e^{-\Delta E/kT})\right)^2 - K_1 e^{-\Delta E/kT}}, \quad (14)$$

$$\alpha_2(N) = \frac{1}{2}\left(1 + K_1(N + e^{-\Delta E/kT})\right) - \sqrt{\frac{1}{4}\left(1 + K_1(N + e^{-\Delta E/kT})\right)^2 - K_1 e^{-\Delta E/kT}}, \quad (15)$$

$$\alpha_2(N) - \alpha_2(N) = = 2\sqrt{\frac{1}{4}\left(1 + K_1(N + e^{-\Delta E/kT})\right)^2 - K_1 e^{-\Delta E/kT}}. \quad (16)$$

To obtain the kinetics of NC ensemble luminescence decay, it is necessary to average the population of the emitting state of NC $p(N, \Delta E, t)$ (13) over the trap energies (with the distribution function (10)) and the number of traps in NC (using Poisson distribution), which leads to the equation

$$I(t) = \sum_{N=0}^{\infty} e^{-\bar{N}}\frac{\bar{N}^N}{N!}\int_0^{\infty} \beta e^{-\beta\Delta E} p(N,\Delta E,t)\,d(\Delta E). \quad (17)$$

For the convenience of further numerical computations and obtaining analytical results, we shall perform the following transformations of formula (17). First, we calculate the kinetics of NC ensemble luminescence decay with a fixed number of traps N on each NC, $I(N, t)$, but with different values ΔE, i.e., let us first perform in equation (17) the averaging over ΔE:

$$I(N,t) = \int_0^{\infty} \beta e^{-\beta\Delta E} p(N,\Delta E,t)\,d(\Delta E). \quad (18)$$

According to equation (17), the kinetics of luminescence decay of the entire NC ensemble is obtained by averaging the function (18) over N with the Poisson distribution function:

$$I(t) = \sum_{N=0}^{\infty} e^{-\bar{N}}\frac{\bar{N}^N}{N!} I(N,t). \quad (19)$$

For convenience of numerical computations, let us introduce in expression (18) the dimensionless variable x and the dimensionless parameter b:

$$x = \Delta E/kT, \quad b = \beta kT. \quad (20)$$

Then the distribution function (10) and the kinetics of NC ensemble luminescence decay with a fixed number of traps N (18) are written as

$$f(x) = be^{-bx}, \quad (21)$$

$$I(N,t) = b\int_0^{\infty} e^{-bx} p(N,x,t)\,dx. \quad (22)$$

Let us change the integration variable again:

$$y = e^{-x}. \quad (23)$$

When x varies from 0 to ∞ the variable y changes from 1 to 0, $dx = -dy/y$, and the kinetics $I(N, t)$ (22) in the new variables becomes

$$I(N,t) = b\int_0^{\infty} y^{b-1} p(N,y,t)\,dy. \quad (24)$$

Coefficients $\alpha_1(N)$ and $\alpha_2(N)$ defining the temporal dependence of population $p(N, y, t)$ (formula (13)), then take the form:

$$\alpha_1(N) = \frac{1}{2}\left(1 + K_1(N + y)\right) + \sqrt{\frac{1}{4}\left(1 + K_1(N + y)\right)^2 - K_1 y}, \quad (25)$$

$$\alpha_2(N) = \frac{1}{2}\left(1 + K_1(N + y)\right) + \sqrt{\frac{1}{4}\left(1 + K_1(N + y)\right)^2 - K_1 y}, \quad (26)$$

$$\alpha_1(N) - \alpha_2(N) = 2\sqrt{\frac{1}{4}\left(1 + K_1(N + y)\right)^2 - K_1 y}. \quad (27)$$

Let us investigate the behavior of the function (24) at large times, i.e. calculate its asymptotic behavior. The asymptote of function (24) is determined by the second exponent in the formula (13) with the smallest exponent $\alpha_2(N)$ $\big(\alpha_2(N) < \alpha_1(N)\big)$, consequently,

$$p(N, y, t) \propto B_N e^{-\alpha_2(N)t/\tau}. \tag{28}$$

By substituting (28) into (22), in the asymptotic limit (at $t \to \infty$) we obtain (Appendix A)

$$I(N, t) \propto b \int_0^\infty e^{-bx} B_N e^{-\alpha_2(N)t/\tau} dx \propto b\Gamma(b+1)N^b \left(\frac{\tau}{t}\right)^{b+1}, \tag{29}$$

where $\Gamma(b+1) = \int\limits_0^\infty w^b e^{-w} dw$ is gamma-function.

Thus, the function (29) (i.e. kinetics of NC luminescence decay with fixed number of traps, $I(N, t)$) decreases at large times according to an inverse power law as $1/t^{b+1}$ and increases with increasing number of traps in the NCs as N^b.

The kinetics of the entire NC ensemble luminescence decay (19), $I(t)$, and its asymptote are obtained by averaging the expressions (24) and (29) with Poisson distribution function, respectively. In the new variables

$$I(t) = \sum_{N=0}^{\infty} e^{-\bar{N}} \frac{\bar{N}^N}{N!} b \int_0^\infty y^{b-1} p(N, y, t) dy, \tag{30}$$

and at large times, given formula (29), we obtain

$$I(t) \propto b\Gamma(b+1)\overline{N^b} \left(\frac{\tau}{t}\right)^{b+1}, \tag{31}$$

where

$$\overline{N^b} = \sum_{N=0}^{\infty} N^b e^{-\bar{N}} \frac{\bar{N}^N}{N!}. \tag{32}$$

Thus, in the proposed model, the kinetics of NC ensemble luminescence decay decreases over long times in a power-law manner (as $1/t^{b+1}$), determined by the trap energy distribution function (10), namely by the coefficient $b = \beta kT$. The amplitude of the asymptote (31), given by $b\Gamma(b+1)\overline{N^b}$, increases with the average number of traps as $\overline{N^b}$.

Figure 3 illustrates the functions (30), $I(t)$, and (24), $I(N, t)$, for equal values of parameters K_1 and b and $\bar{N} = N$. The functions coincide at small ($t/\tau < 0.1$, Fig. 3, *a*) and large times ($t/\tau > 50$, Fig. 3, *c*). At intermediate times (Fig. 3, *b*) a large divergence is observed.

Figure 4 shows the kinetics of luminescence decay (30) at different values of the average number of traps $\bar{N}$ in NC and equal values of other parameters (b and K_1). As expected, at small times, the kinetics of NC luminescence decay with the largest average number of traps (Fig. 4, *a*, $\bar{N} = 4$, curve *1*, blue) decreases faster. At long times (Fig. 4, *b*), the position of the curves changes according to the formula (31): the numerical coefficient $b\Gamma(b+1)\overline{N^b}$ in the asymptote (31) for $(\tau/t)^{b+1}$ is equal to 2.21, 1.23 and 0.67 for $\bar{N} = 4$, 2 and 1, respectively.

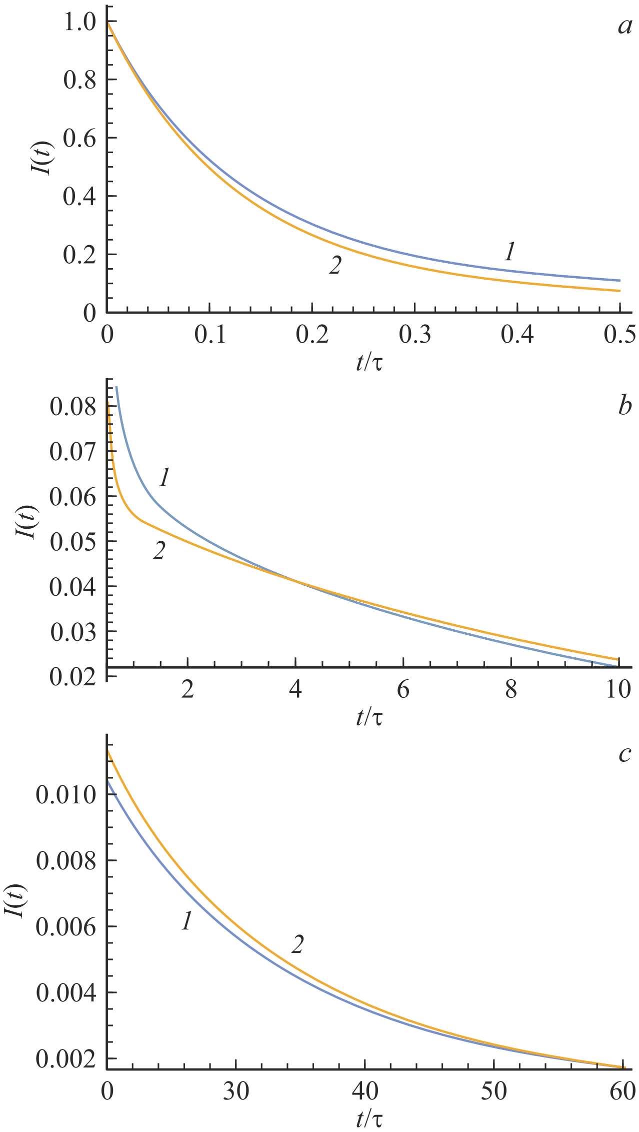

Figure 3. Comparison of the luminescence decay $I(t)$ (30) of NC ensemble (curve *1*, blue) with kinetics of luminescence decay $I(N, t)$ (24) of NC with a fixed number of traps (curve *2*, yellow) in different time intervals. Parameters: $\bar{N} = N = 5$, $K_1 = 1.2$, $b = 0.8$. (*a*) Functions $I(t)$ and $I(N, t)$ coincide at small times ($t/\tau < 0.1$), (*b*) change their positions at in intermediate times, (*c*) at large times (at $t/\tau > 50$) the luminescence decay kinetics (30) and (24) (their asymptotes) coincide again which was predicted from the formulae (31) and (29) at $\bar{N} = N$.

Figure 5 shows the kinetics of luminescence decay (30) at different values b ($b = \beta kT$), equal values K_1 and average number of traps $\bar{N}$ in NC. At short times (Fig. 5, *a*), the luminescence corresponding to the lowest value of b (curve *1*, blue) decreases faster, since in this case the proportion of deep traps in the NC ensemble is large (according to formula (10)), from where the detrapping rate to NC emitting state is small. At long times (Fig. 5, *b*) the position of curves starts to change: curve *1* (blue) becomes the upper curve. This follows from the asymptote (31):

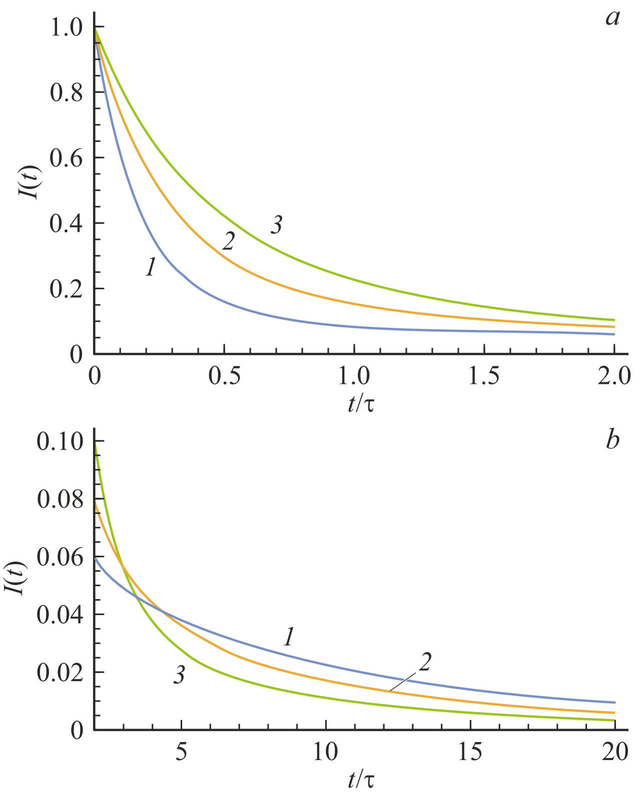

Figure 4. Kinetics of luminescence decay $I(t)$ (30) at various values $\bar{N}$: 4 (curve *1*, blue), 2 (*2*, yellow) and 1 (*1*, green); $b = 0.8$, $K_1 = 1.1$. At large times (Fig. *b*) the curve *1* (blue) becomes the upper curve, as expected from the asymptotic behavior (31), since numerical coefficient $b\Gamma(b+1)\overline{N^b}$ in asymptote (31) at $(\tau/t)^{b+1}$ is equal to 2.21, 1.23 and 0.67, respectively for $\bar{N} = 4$, 2 and 1.

all curves are approaching the time axis according to the inverse power law, but at $\tau/t \ll 1$ with the increase of b the values $(\tau/t)^{b+1}$ in (31) become smaller.

Figure 6 compares the long-time behavior of luminescence decay kinetics (30) with asymptote (31) at small values $K_1 = 1.1$. As can be seen even at small values K_1 at long times ($t/\tau > 30$) the exact function (30) coincides with its asymptote (31).

Note that the power-law character of luminescence decay (31) over long periods of time (in the proposed NC ensemble model) is due to the exponential form of the trap energy distribution function (10) and the detailed balance condition (9). From deriving the formula (29) (Appendix A) it follows that any other function of trap distribution over energies $f(\Delta E)$, which differs from (10) at small ΔE, but decreases exponentially with increasing ΔE at large ΔE, also results in asymptotic behavior (31), i.e., to the inverse power law of luminescence decay (30) at long times.

By using formulae (9) and (10), we may calculate the corresponding distribution function, $f_s(K_2)$, for traps over the dimensionless rates of detrapping (K_2) of the charge carriers to NC emitting state. It is easy to check that

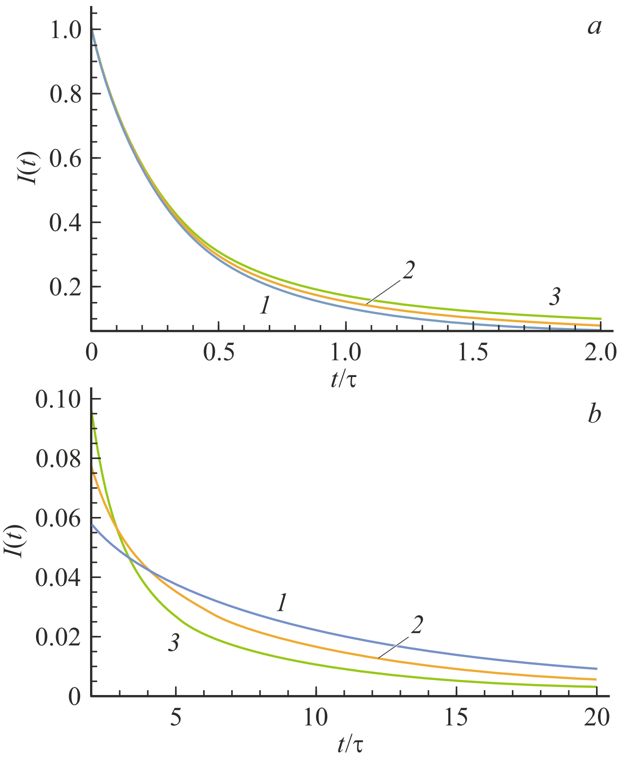

Figure 5. Kinetics of luminescence decay $I(t)$ (30) at different values b: (*a*) 0.4 (curve *1*, blue, bottom curve), 0.8 (*2*, yellow, middle curve) and 1.6 (*3*, green, top curve). $\bar{N} = 2$, $K_1 = 1.1$. (*b*) At large times the positions of curves start to change: the curve *1* (blue) becomes the top curve. This follows from the asymptote (31): all curves are approaching the time axis according to an inverse power law, but at $\tau/t \ll 1$ with the increase of parameter b the values $(\tau/t)^{b+1}$ in formula (31) decrease faster with time.

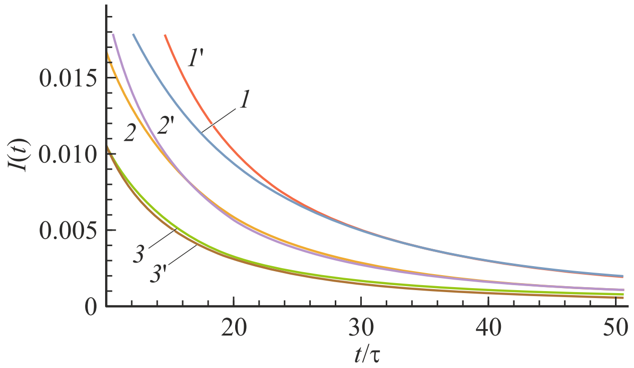

Figure 6. Kinetics of luminescence decay $I(t)$ (30) (curves *1, 2, 3*) and its asymptote (31) (curves *1', 2', 3'*) at different values $\bar{N}$: 4 (curves *1, 1'*), 2 (curves *2, 2'*) and 1 (curves *3, 3'*). $b = 0.8$, $K_1 = 1.1$. At large times ($t/\tau > 30$), the kinetics of luminescence decay $I(t)$ (30) coincides with the asymptote (31).

$$f_s(K_2) = \frac{b}{K_1^b} K_2^{b-1}, \qquad (33)$$

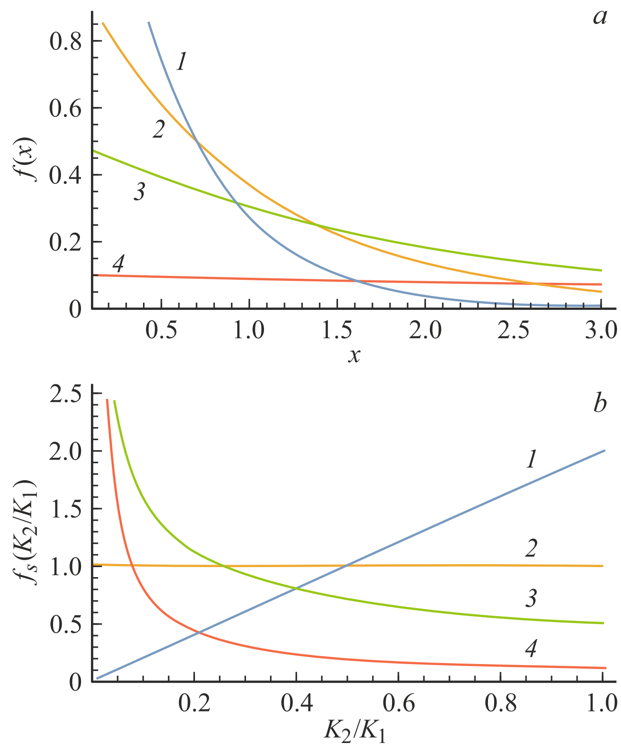

Figure 7. Functions of traps distribution (a) over energies, $f(x)$ (21) ($x = \Delta E/kT$), and (b) over the rates of the charge carriers detrapping to NC emitting state, $f_s(K_2/K_1)$ (33). Parameter $b = 2$ (curves *1*, blue), 1 (curves *2*, yellow), 0.5 (curves *3*, green), 0.1 (curves *4*, red).

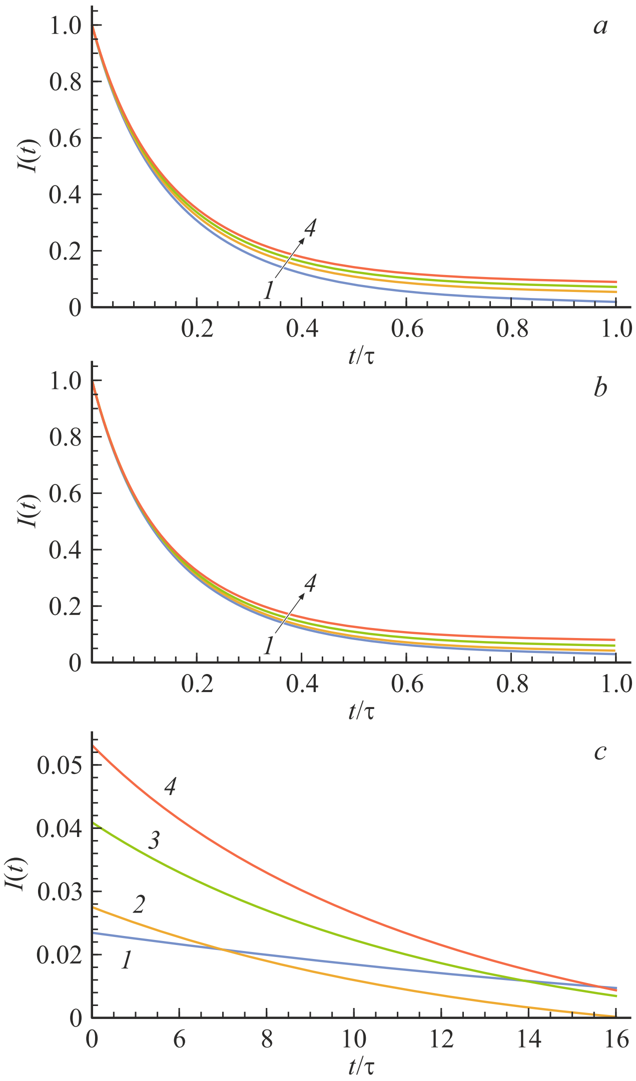

Figure 8. Luminescence decay kinetics (2) (curves *1*, blue) compared with kinetics (30), calculated at equal values $\overline{N}$ ($\overline{N} = 5$) and $K_1 = 1.1$. The luminescence decay kinetics (30) was calculated at different values *b*: 0.4 (curve *2*, yellow, second from bottom), 0.8 (curve *3*, green, third from bottom) and 1.6 (curve *4*, orange, fourth from bottom). The luminescence decay kinetics (2) (curve *1*, blue, first from bottom) was calculated at $K_2 = 0.01$ (a) and $K_2 = 0.2$ (b, c).

and, thus,

$$f_s(K_2)dK_2 = b\left(\frac{K_2}{K_1}\right)^{b-1} d\left(\frac{K_2}{K_1}\right) = f_s\left(\frac{K_2}{K_1}\right) d\left(\frac{K_2}{K_1}\right). \quad (34)$$

According to detailed balance principle (9), K_2 changes from 0 to K_1, and, hence, the ratio K_2/K_1 changes from 0 to 1. Figure 7 illustrates the dependencies of distribution functions $f(x)$ (19) and $f_s(K_2/K_1)$ for different values $b = 0.1, 0.5, 1, 2$.

Note that it is precisely this type of (33) distribution function $f_s(K_2)$ in [21] that explains the power-law decrease in the luminescence intensity of semiconductor NCs at long times and indicates the relationship of the discovered pattern with the blinking of single NCs luminescence.

Two models of NC ensemble compared: kinetics of luminescence decay (2) and (30)

Let us now compare the kinetics of luminescence decay (2) and (30), corresponding to different models of NC ensemble with traps, for the same values $\overline{N}$ and K_1 (Fig. 8).

As seen from Fig. 8, a, at short periods of time ($t/\tau < 1$) the curves corresponding to functions (2) and (30) are coinciding. By increasing the parameter K_2 in formula (2) it is possible to increase the initial time interval from 0.01 to 0.2, where these curves practically coincide (Fig. 7, b). However, at longer periods the curves divergence is quite sufficient (Fig. 8, c). This may serve as a basis for choosing the appropriate model of NC ensemble with traps.

Now let us compare the models of kinetics of luminescence decay (2) and (30) for the purposes of fitting experimental results. Let the function (2) ideally represent the experimental kinetics of the luminescence decay (curve *1*, blue, in Fig. 9), while the accuracy of experimental data is 0.01 of the maximum luminescence intensity (i.e., at the initial moment of time). In these assumptions the experimental values shall lie within the curves $I(t) - 0.01$

(curve *2*, green, in Fig. 9) and $I(t)+0.01$ (curve *3*, yellow, in Fig. 9), where $I(t)$ is the function (2). Let us now select the parameters of the function (30) so that its values describe the experiment in the best way, i.e. fall within the range specified above: from $I(t)-0.01$ to $I(t)+0.01$. Naturally, for coincidence of functions (2) and (30) at initial time interval their parameters $\overline{N}$ and K_1 shall coincide. For the values of function (30) to lie in the above-mentioned interval (from $I(t)-0.01$ to $I(t)+0.01$) at large time we change the parameter b in the function (30). Figure 9 illustrates the behavior of functions (2) and (30) at optimized parameters ($b=0.4$, $K_2=0.2$).

From Fig. 9 it follows that both models of NC ensemble (functions (2) and (30)) can equally well (within the error of 1%) reproduce the experimental results (in the considered time interval $0 \le t/\tau \le 150$). More accurate measurements and longer time intervals for measuring the kinetics of luminescence decay are needed in order to select the appropriate model of NC ensemble with traps based on comparison of theory and experiment.

In Appendix B a simplified version of the function is proposed for approximating $I(t)$, decreasing according to the inverse power law over long times.

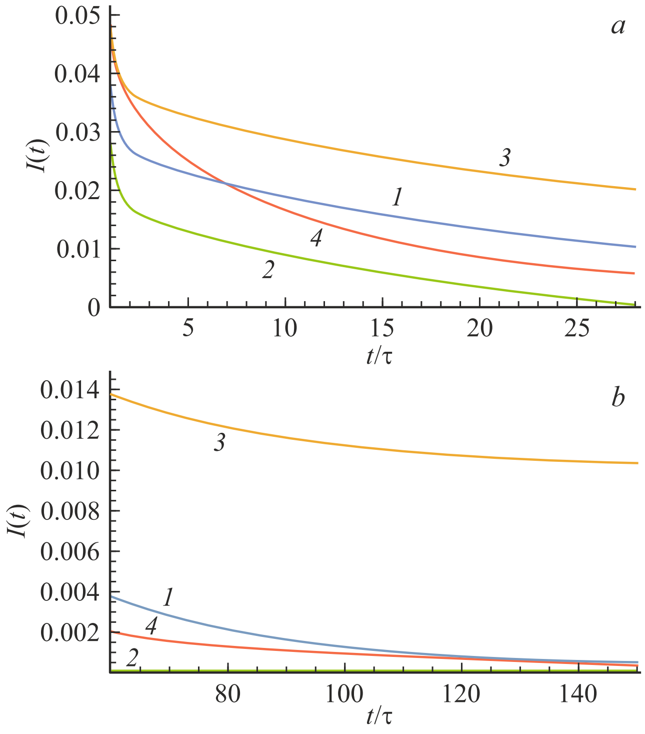

Figure 9. Comparison of luminescence decay kinetics (2) (curve *1*, blue — $I(t)$; curve *2*, green — $I(t)-0.01$ and curve *3*, yellow — $I(t)+0.01$) and kinetics (30) (curve *4*, red) at short (*a*) and long (*b*) times. Parameter values: $\overline{N}=5$, $K_1=1.1$, $K_2=0.2$, $b=0.4$. As can be seen from the Figure, the kinetics (30) (curve *4*, red) within the error (±0.01) correctly reproduces the „experimental data“ (lying between the curves *2*, blue, and *3*, green) within the time interval $0 \le t/\tau \le 150$.

Conclusion

A comparative analysis of two functions proposed for modeling the kinetics of NC delayed luminescence decay is carried out. The functions were obtained within the framework of two NC ensemble models with traps, from which the reversible return of the charge carriers to the emitting state of NC is carried out, leading to non-exponential delayed luminescence decay.

In the first model, the traps are considered identical (in particular, their energy is fixed), the number of traps in NC is different (described by the Poisson distribution), and the charge carriers are reversibly returned from the traps to the emitting state of NC. As a result, the kinetics of luminescence decay over long periods is the sum of exponentially decreasing functions of time.

The following is proposed for the second model. As in the first model, we assume that (a) the number of traps in NC is different and is described by the Poisson distribution, (b) from the traps, the charge carriers are reversibly returned to the emitting state of NC. Additionally, we assume that (c) traps have different energy levels, the distribution of traps over energy is described by an exponentially decreasing function of energy, and (d) the principle of detailed balance is valid. On this basis, a new function was obtained for fitting the experimental kinetics of luminescence decay of a NC ensemble. At large times, this function predicts delayed luminescence decay according to an inverse power law. The power exponent in this law depends on the rate of decrease of the trap distribution function with the energy increase, the intensity of delayed luminescence increases with increasing average number of traps in the NCs.

Appendix A

Derivation of formula (29)

Let us investigate the behavior of the function (24) at large times, i.e. calculate its asymptotic behavior. The time dependence of function (24) over long periods is determined by the second exponent in the formula (13) with the lowest exponent $\alpha_2(N)$ ($\alpha_2(N) < \alpha_1(N)$):

$$p(N,y,t) \propto B_N e^{-\alpha_2(N)t/\tau}. \qquad \text{(A1)}$$

This dependence is explained by detrapping of the charge carriers to the NC emitting state, leading to delayed luminescence.

The largest contribution to the delayed luminescence of NC at long periods of time is provided by the so-called „deep“ traps, from where the charge carriers return to NC emitting state at low rate. For these traps $\Delta E/kT > 1$, and, hence, $K_2 \ll K_1$ and $y=\exp(-\Delta R/kT) \ll 1$.

Further, we shall assume that $K_1 \gg 1$. Under this condition, the traps capture a significant portion of charge carriers from NC emitting state, which leads to an increase in the intensity of delayed luminescence. At $K_1 \gg 1$ and

$y < y_0 \ll 1$ (where $y_0 = e^{-\Delta E_0/kT}$ is a boundary parameter which conventionally divides the traps into „deep“ traps with $\Delta E \geq \Delta E_0$ and „shallow“ traps with $\Delta E < \Delta E_0$) from equations (5), (25)–(28) it follows that

$$\alpha_2(N) = \frac{y}{N}, \quad B_N = \frac{y}{N}, \tag{A2}$$

$$p(N, y, t) \propto \frac{y}{N} e^{-\frac{y}{N}\frac{t}{\tau}}. \tag{A3}$$

Deep traps for which $y \leq y_0$ contribute to the asymptotic kinetics of luminescence decay (24). Therefore, to get the asymptote, in (24) we shall use only integration over y from 0 to y_0. We thus obtain

$$I(N, t) \propto b \int\limits_0^{y_0} \frac{y^b}{N} e^{-\frac{y}{N}\frac{t}{\tau}} dy. \tag{A4}$$

Let us make another substitution of variables: $T = t/\tau$, $z = Ty$. Then $dz = Tdy$, $dy = dz/T$. When y varies from 0 to y_0 the variable z changes from 0 to $y_0 T$. Using these variables the equation (A4) is be expressed as

$$I(N, t) \propto \frac{b}{T^{b+1}} \int\limits_0^{y_0 T} \frac{z^b}{N} e^{-z/N} dz. \tag{A5}$$

In the asymptotic limit (at $T \to \infty$) from (A5) we obtain the formula (29):

$$I(N, t) \propto \frac{b}{T^{b+1}} \int\limits_0^{\infty} \frac{z^b}{N} e^{-z/N} dz$$

$$= \frac{bN^b}{T^{b+1}} \int\limits_0^{\infty} \left(\frac{z}{N}\right)^b e^{-z/N} d\left(\frac{z}{N}\right) = b\Gamma(b+1) N^b \left(\frac{\tau}{t}\right)^{b+1}, \tag{A6}$$

where $\Gamma(b+1) = \int\limits_0^{\infty} w^b e^{-w} dw$ is gamma-function.

Appendix B

A simple function for fitting the kinetics of luminescence decay

Taking into account the exponential nature of the decrease of luminescence intensity (30) at short time periods and the power-law pattern at long time periods (31), we can propose a simplified version of the function for fitting experimental data:

$$I(t) = \theta(t_{\text{gr}} - t) e^{-Kt} + \theta(t - t_{\text{gr}}) e^{-kt_{\text{gr}}} \left(\frac{t_{\text{gr}}}{t}\right)^{b+1}, \tag{B1}$$

where θ is Heaviside function, t_{gr} is time when the first and second terms of equation (B1) becomes equal. Three parameters are considered as fitting: K, t_{gr}, and b.

For smoothing the dependence (B1) at a moment of time t_{gr} (i.e. for removal of jump of the derivative function (B1) at $t = t_{\text{gr}}$) it is required to replace θ-function, for example, by its approximated equivalent — a function of

$$\theta(t_{\text{gr}} - t) \approx 1 - \exp\left(-(t/t_{\text{gr}})^2\right). \tag{B2}$$

Then a simple fitting function takes the form

$$I(t) = e^{-Kt} + \left[1 - \exp\left(-(t/t_{\text{gr}})^2\right)\right] e^{-Kt_{\text{gr}}} \left(\frac{t_{\text{gr}}}{t}\right)^{b+1}. \tag{B3}$$

Such function equivalent to (B3) was used in papers [22–24,28].

Conflict of interest

The author declares that he has no conflict of interest.

References

[1] R. Koole, B. Luigjes, M. Tachiya, R. Pool, T.J.H. Vlugt, C. de Mello Donegá, A. Meijerink, D. Vanmaekelbergh. J. Phys. Chem. C, **111**, 11208 (2007). DOI: 10.1021/jp072407x

[2] S. Sadhu, M. Tachiya, A. Patra. J. Phys. Chem. C, **113** (45), 19488 (2009). DOI: 10.1021/jp906160z

[3] E.N. Bodunov, V.V. Danilov, A.S. Panfutova, A.L. Simões Gamboa. Ann. Phys., **528**, 272 (2016). DOI: 10.1002/andp.201500350

[4] E.N. Bodunov, Yu.A. Antonov, A.L. Simões Gamboa. J. Chem. Phys., **146**, 114102 (2017). DOI: 10.1063/1.4978396

[5] E.N. Bodunov, A.L. Simões Gamboa. J. Phys. Chem. C, **122**, 10637 (2018). DOI: 10.1021/acs.jpcc.8b02779

[6] E.N. Bodunov, A.L. Simões Gamboa. Semiconductors, **52** (5), 587 (2018). DOI: 10.1134/S1063782618050044

[7] E.N. Bodunov, A.L. Simões Gamboa. J. Phys. Chem. C, **123**, 25515 (2019). DOI: 10.1021/acs.jpcc.9b07619

[8] E.N. Bodunov, A.L. Simões Gamboa. Semiconductors, **53** (16), 2133 (2019). DOI: 10.1134/S1063782619120078

[9] A.L. Simões Gamboa, E.N. Bodunov. In: *2022 International Conference Laser Optics* (*ICLO*) (IEEE, 2022). DOI: 10.1109/ICLO54117.2022.9839822

[10] A. Sahu, D. Kumar. J. Alloys and Compounds, **924**, 166508 (2022). DOI: 10.1016/j.jallcom.2022.166508

[11] J.R. Martins, V. Krivenkov, C.R. Bernardo, P. Samokhvalov, I. Nabiev, Yu.P. Rakovich, M.I. Vasilevskiy. J. Phys. Chem. C, **126** (48), 20480–20490 (2022). DOI: 10.1021/acs.jpcc.2c06134

[12] J. Xiao, Y. Liu, V. Steinmetz, M. Çağlar, J. Mc Hugh, T. Baikie, N. Gauriot, M. Nguyen, E. Ruggeri, Z. Andaji-Garmaroudi, S.D. Stranks, L. Legrand, T. Barisien, R.H. Friend, N.C. Greenham, A. Rao, R. Pandya. ACS Nano, **14**, 14740 (2020). DOI: 10.1021/acsnano.0c01752

[13] O. Stroyuk, A. Raevskaya, F. Spranger, N. Gaponik, D.R.T. Zahn. Chem. Phys. Chem., **20** (12), 1640 (2019). DOI: 10.1002/cphc.201900088

[14] A.S. Kulagina, A.I. Khrebtov, R.R. Reznik, E.V. Ubyivovk, A.P. Litvin, I.D. Skurlov, G.E. Cirlin, E.N. Bodunov, V.V. Danilov. Opt. Spectrosc., **128** (1), 119 (2020). DOI: 10.1134/S0030400X20010129

[15] H. Leng, J. Loy, V. Amin, E.A. Weiss, M. Pelton. ACS Energy Lett., **1**, 9 (2016). DOI: 10.1021/acsenergylett.6b00047

[16] Li Liu, Keliang Pan, Ke Xu, Jin Z. Zhang. ACS Phys. Chem. Au, **2**, 156–170 (2022). DOI: 10.1021/acsphyschemau.1c00047

[17] Zitao Zhao, Qian Wang, Fei Gao, Donghui Luo, Yan Zhang, Huan Liu. AIP Advances, **14**, 105115 (2024). DOI: 10.1063/5.0228028

[18] A.A. Rempel, O.V. Ovchinnikov, I.A. Weinstein, S.V. Rempel, u.V. Kuznetsova, A.V. Naumov, M.S. Smirnov, I.Yu. Eremchev, A.S. Vokhmintsev, S.S. Savchenko. Russ. Chem. Rev., **93** (4), RCR5114 (2024). DOI: 10.59761/RCR5114.

[19] I.G. Grevtseva, O.V. Ovchinnikov, M.S. Smirnov, K.S. Chirkov, A.N. Latyshev. Opt. i spektr., **132** (6), 675–682 (2024) (in Russian). DOI: 10.61011/OS.2024.06.58646.6194-24

[20] E.N. Bodunov. Opt. Spectrosc., **131** (1), 96–99 (2023). DOI: 10.21883/EOS.2023.01.55524.91-22

[21] P.H. Sher, J.M. Smith, P.A. Dalgarno, R.J. Warburton, X. Chen, P.J. Dobson, S.M. Daniels, N.L. Pickett, P. O'Brien. Appl. Phys. Lett., **92**, 101111 (2004). DOI: 10.1063/1.2894193

[22] F.T. Rabouw, M. Kamp, R.J. van Dijk-Moes, D.R. Gamelin, A.F. Koenderink, A. Meijerink, D. Vanmaekelbergh. Nano Lett., **15**, 7718–7725 (2015). DOI: 10.1021/acs.nanolett.5b03818

[23] F.T. Rabouw, J.C. van der Bok, P. Spinicelli, B. Mahler, M. Nasilowski, S. Pedetti, B. Dubertret, D. Vanmaekelbergh. Nano Lett., **16**, 2047–2053 (2016). DOI: 10.1021/acs.nanolett.6b00053

[24] F. Montanarella, M. Biondi, S.O.M. Hinterding, D. Vanmaekelbergh, F.T. Rabouw. Nano Lett., **18**, 5867–5874 (2018). DOI: 10.1021/acs.nanolett.8b02538

[25] Al.L. Efros. Phys. Rev. B, **46**, 7448–7458 (1992). DOI: 10.1103/PhysRevB.46.7448

[26] O. Labeau, P. Tamarat, B. Lounis. Phys. Rev. Lett., **90** (25), 257404(4) (2023). DOI: 10.1103/PhysRevLett.90.257404

[27] V.I. Klimov. J. Phys. Chem. B, **110**, 16827 (2006). DOI: 10.1021/jp0615959

[28] A. Marchioro, P.J. Whitham, K.E. Knowles, T.B. Kilburn, P.J. Reid, D.R. Gamelin. J. Phys. Chem. C, **120**, 27040–27049 (2016). DOI: 10.1021/acs.jpcc.6b08336

[29] A. Hässelbarth, A. Eychmüller, H. Weller. Chem. Phys. Lett., **203** (2, 3), 271–276 (1993). DOI: 10.1016/0009-2614(93)85400-I

[30] J.T. Randall, M.H.F. Wilkins. Proc. R. Soc. Lond. A, **184**, 390–407 (1945). DOI: 10.1098/rspa.1945.0025

[31] F. Urbach. Phys. Rev., **92**, 1324 (1953). DOI: 10.1103/PhysRev.92.1324

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