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Different mechanisms of nonlinear quenching of luminescence

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An analytic solution for the kinetics of nonlinear (upconversion) luminescence quenching in solid-state laser materials and other luminophosphors is obtained under the assumptions of hopping character of migration-assisted energy transfer and finite excitation lifetime. It is shown how the observables of the luminescence experiment depend on microparameters of the energy transfer and ion concentrations. The critical ion concentrations separating different upconversion regimes are determined. The predictions of the theory are in agreement with experimental observations reported in the literature. [S0163-1829(97)04013-7]

I. INTRODUCTION

A radiationless energy transfer from one type of excited centers (donors) to another type of centers (acceptors) is typical for laser materials and many other solid and liquid solutions.[1] When acceptors are the already excited particles, an energy transfer and a quenching of donor luminescence are referred to as ''nonlinear'' or ''upconversion.'' At strong pumping density, upconversion interactions influence population inversion in many solid-state lasers, for example, in 3 μm Er lasers,[2–4] 2 μm Ho lasers[5,6] and many others.

Experimentally, nonlinear luminescence quenching manifests itself in shortening the effective decay-time of luminescence and in changing the shape of luminescence kinetics. In the most of publications, the influence of upconversion on excited state concentration is accounted for by using a simple term αn^2 in the rate equation, where α is the upconversion macroparameter and n is the concentration of excited centers. However, as was shown in Refs. 7–9, in many practically important cases the experimental upconversion kinetics cannot be described in terms of αn^2. For example, in Ref. 7 the characteristic shape of the upconversion luminescence kinetics changed with the change of temperature that turned the migration of energy over donors on and off. In Ref. 8, a similar change occurred also with the change of the total ion concentration. Both of these effects cannot be explained with a simple model of upconversion. This suggests that a the more detailed analysis of the energy transfer processes is needed to describe the experiment.

An energy transfer from ion donors to ion acceptors can be static or migration assisted. In the former case, a donor excitation is transferred to an acceptor directly. In the later case an excitation migrates over donors before it reaches an acceptor. The migration helps excitations to find such donor centers (normally centers with one or several closely colocated acceptors) from where an energy can be transferred to acceptors in the mostly efficient way. That is why the migration of excitations over donors accelerates the energy transfer to acceptors.

Depending on the multipolarity and the microparameters of donor-donor (C_{DD}) and donor-acceptor (C_{DA}) interaction, a migration-assisted energy transfer can have a diffusion character or a hopping character. In the case of the diffusion mechanism of migration-assisted energy transfer, the average distance between two neighboring donor centers is much less than the characteristic spatial scale of donor-acceptor interaction, which is equal to a radius of so-called ''black'' quenching sphere surrounding acceptors (by definition, at the edge of the black sphere a donor excitation has an equal probability to be quenched by acceptor or to migrate out of the sphere[1]). In this situation, the neighboring donors are excited practically uniformly and the density of donor excitation changes in space gradually. This allows one to describe the temporal and spatial behavior of donor excitation using a regular diffusion equation. As was shown by Perepechko *et al.*,[10] the conditions where the migration-assisted energy transfer can be described in terms of diffusion are not typical to rare-earth (RE) doped laser crystals (although the diffusion regime of energy transfer in laser crystals is often assumed in the literature).

In the case of the hopping regime of migration-assisted energy transfer, the average distance between neighboring donors is much larger than the radius of the quenching sphere and an excitation takes only one hop to enter the sphere or exit the sphere. Obviously, in this situation the spatial distribution of donor excitation cannot be considered as a continuum and the diffusion equation is not applicable. As was shown by Zusman,[11,12] to describe the evolution of donor excitation in the case of the hopping regime of luminescence quenching, instead of using the diffusion equation, one should consider a detailed balance of excitation probability for one donor and then average the result over all donors in the ensemble. Unlike the diffusion regime, the hopping mechanism of migration-controlled energy transfer (including upconversion) is very common in RE-doped laser materials. This is the motivation for the detailed study of the migration-assisted nonlinear luminescence quenching in the hopping regime. This study can help one in optimization of the dopant concentration in solid-state laser materials and of the operation regimes of solid-state lasers.

The hopping regime of migration-assisted energy transfer realizes at $C_{\mathrm{DA}}/C_{\mathrm{DD}} \ll N^{(s-m)/3}$;[11] accordingly, the diffusion regime realizes at $C_{\mathrm{DA}}/C_{\mathrm{DD}} \gg N^{(s-m)/3}$, where N is the net concentration of donors and s and m are the multipolarities of donor-donor and donor-acceptor interaction). The so-called ''kinetic limit'' regime is an extreme case of the ''hopping'' regime. It realizes when the mean rate of one migration hop, τ_0^{-1}, is higher than the rate of donor-acceptor interaction at the minimum distance between ions.[1]

A complicated pattern of upconversion dynamics was studied in details in the cases of static (no migration) energy transfer in Ref. 13 and migration-assisted energy transfer in the diffusion approximation in Refs. 13 and 14. The differential equations describing nonlinear migration-assisted luminescence quenching in the hopping regime were derived and analyzed in the general form by Sverchkov and Sverchkov in Ref. 15. This derivation was done using the routine first introduced by Zusman in Refs. 11 and 12. The differential equations mentioned above were solved analytically in Ref. 15 in the case of the ''pure nonlinear'' migration-assisted quenching of luminescence, when the excitation lifetime is assumed to be infinite. However, the assumption of infinite excitation lifetime does not allow one to use the results of Ref. 15 for the analysis of experimental luminescence kinetics.

In the present paper,[16] taking into account the results of Ref. 15, we obtain an analytic solution for donor dynamics $n(t)$ in the static, hopping, and kinetic limit regimes of upconversion, for arbitrary multipolarity of interaction and finite excitation lifetime. We also determine the boundary ion concentrations separating different upconversion regimes. The theory is consisted with experimental observations described in the literature.

II. THEORY

As it was discussed in Sec. I, to describe the decay kinetics of excited donors in the hopping regime of migration-assisted energy transfer, one should consider a balance of excitation probability for one donor and then average the result over the ensemble of donors.[11,12] Following this technique in the case of nonlinear quenching of luminescence, the dynamics of excited state concentration $n(t)$ (after excitation of the material with a short pulse of light) can be presented in the form

$$\frac{\delta f(r,t)}{\delta t} = -W(r) f(r,t) - \frac{1}{\tau_0} f(r,t) + \frac{1}{\tau_0}, \tag{1a}$$

$$F(t) = \int_0^{\infty} W(r) f(r,t) 4\pi r^2 dr, \tag{1b}$$

$$\frac{dn(t)}{dt} = -\frac{n(t)}{\tau_D} - F(t) n^2(t), \tag{1c}$$

where $f(r,t)$ is the probability that excited donor did not transfer its energy for the time period t to an acceptor at the distance r (another excited donor plays in this case a role of acceptor); $F(t)$ is the nonlinear quenching rate [in a simple mentioned above model describing upconversion in terms of αn^2, $F(t)$ is assumed to be a time-independent value, $F(t) = \alpha$]; $W(r) = C_{\mathrm{DA}}/r^m$ is the probability of multipolar donor-acceptor interaction, where m is the multipolarity factor of interaction, τ_0^{-1} is the most probable rate of excitation hop to nonexcited donors,[1] and τ_D is the excitation lifetime.

The solution of the system of Equations (1a)–(1c) has a form

$$n(t) = \frac{n(0)\exp(-t/\tau_D)}{1 + n(0)\tau_D \dfrac{4\pi}{m} \Gamma[1-(3/m)](C_{\mathrm{DA}}^{3/m}/\tau_0^{1-3/m})\{[1+(\tau_0/\tau_D)]^{1-(3/m)}\Phi[3/m;(1/\tau_0+1/\tau_D)t] - \exp^{-t/\tau_D}\Phi[3/m;t/\tau_0]\}}, \tag{2}$$

where $\Gamma(x) = \int_0^{\infty} t^{x-1}\exp(-t)dt$ is the Eihler's Gamma function[17] and $\Phi(a,x) = \int_0^x t^{a-1}\exp(-t)dt$ is the incomplete Gamma function.[17] In dipole-dipole approximation ($m=6$), formula (2) yields

$$n(t) = \frac{n(0)\exp(-t/\tau_D)}{1 + n(0)\tau_D(2\pi^2/3)\sqrt{C_{\mathrm{DA}}/\tau_0}\{\sqrt{1+\tau_0/\tau_D}\,\mathrm{erf}(\sqrt{t(1/\tau_0+1/\tau_D)}) - \exp(-t/\tau_D)\mathrm{erf}(\sqrt{t/\tau_0})\}}, \tag{3}$$

where $\mathrm{erf}(x) = 2/\sqrt{\pi}\int_0^x \exp(-t^2)dt$ is the error function.[17]

Let us analyze expressions (2) and (3) in several important limiting cases.

(1) As $t \to 0$, Eqs. (2) and (3) yield an infinitely high rate of nonlinear quenching $[dn(t)/dt \to -\infty]$, due to the fact that a nonzero minimum distance between donor and acceptor R_0 determined by the host material is not accounted for in Eqs. (1a)–(1c). If the minimum distance R_0 is taken into account, then at $t \ll (C_{\mathrm{DA}}/R_0^m)^{-1} \equiv t_1$ (here t_1 is the rate of donor-acceptor interaction at the minimum distance R_0) the quenching rate F is time independent and equal to

$$F(t) = \frac{1}{N_0} C_{\mathrm{DA}} \sum_i \frac{1}{R_i^m} \equiv \alpha_1 \tag{4}$$

[here α_1 is the time-independent upconversion macroparameter at $t \ll t_1$; N_0 is the net concentration of the lattice sites that potentially can be occupied by acceptors, R_i is the distance between donor and acceptor, and $\Sigma_i(1/R_i^m)$ is a lattice sum taken over all the potential ion sites in the crystal]. In this case, the dynamics of excited state concentration $n(t)$ can be described with the only rate equation (1c), where F is defined by Eq. (4). The solution of Eq. (1c) with $F=\alpha_1$ yields

$$n(t)=\frac{n(0)\exp(-t/\tau_D)}{1+\alpha\tau_D n(0)[1-\exp(-t/\tau_D)]}, \tag{5}$$

where $\alpha=\alpha_1$.

(2) If a nonlinear luminescence quenching is migration-assisted and the ''kinetic limit'' regime[1] of the energy transfer realizes, $\tau_0 \ll (C_{\mathrm{DA}}/R_0^m)^{-1}$, then Eqs. (4) and (5) hold in the whole time range $0<t<\infty$.

(3) Let us consider the case when $\tau_0, \tau_D \gg t_1$.

(a) At $\tau_0 \gg \tau_D$ and $t \gg t_1$, the kinetics $n(t)$ has a form

$$n(t)=\frac{n(0)\exp(-t/\tau_D)}{1+n(0)\tau_D^{3/m}(4\pi/m)\Gamma[1-(3/m)]C_{\mathrm{DA}}^{3/m}\Phi[3/m;t/\tau_D]}. \tag{6a}$$

In dipole-dipole approximation ($m=6$), this result is consistent with that obtained in Ref. 13 for a pure static nonlinear quenching:

$$n(t)=\frac{n(0)\exp(-t/\tau_D)}{1+\dfrac{2}{3}\,n(0)\sqrt{\tau_D C_{\mathrm{DA}}}\,\pi^2\operatorname{erf}(\sqrt{t/\tau_D})}. \tag{6b}$$

At $t \gg \tau_D$, Eq. (6a) can be rewritten as

$$n(t)=\frac{n(0)\exp(-t/\tau_D)}{1+n(0)\tau_D^{3/m}(4\pi/m)\Gamma[1-(3/m)]\Gamma(3/m)C_{\mathrm{DA}}^{3/m}}. \tag{7}$$

This implies that, at $t \gg \tau_D$, the decay kinetics is exponential with the decay-time equal to the excitation lifetime τ_D. The results (6a), (6b), and (7) can be easily understood. In fact, at $t<\tau_0$, excitation do not have enough time for migration hopping and luminescence quenching occurs in the static regime, Eq. (6a). At $t \gg \tau_D$, the excited state concentration $n(t)$ is sufficiently small and nonlinear (upconversion) quenching cannot compete with radiation and multiphonon decay which have a rate equal to τ_D^{-1}.

(b) In the opposite case, at $\tau_D \gg \tau_0$, excitation makes many hops over donors during the lifetime τ_D. In this case, at $\tau_0 \gg t \gg t_1$ Eq. (2) can be presented in the form

$$n(t)=\frac{n(0)\exp(-t/\tau_D)}{1+n(0)\,\dfrac{4\pi}{m}\,[1-(3/m)]\Gamma[1-(3/m)](C_{\mathrm{DA}}\tau_0)^{3/m}\Phi(3/m;t/\tau_0)} \tag{8}$$

[compare with Eq. (6a)] and describes a static nonordered decay of excitations located in so called black spheres[1] surrounding acceptors (see the definition for the black sphere in Sec. I).

In the time range $t \gg \tau_0$, Eq. (2) can be presented in the form (5), where

$$\alpha=\alpha_2 \equiv \frac{4\pi}{m}\,\Gamma\left(1-\frac{3}{m}\right)\Gamma\left(\frac{3}{m}\right)\frac{C_{\mathrm{DA}}^{3/m}}{\tau_0^{1-3/m}} \tag{9}$$

(here α_2 is the value of time-independent upconversion macroparameter at $\tau_D \gg \tau_0 \gg t_1$ and $t \gg t_0$).

Note, that at high pumping density, when the rate of upconversion interaction is comparable to the rate of radiation and multiphonon relaxation τ_D^{-1} the condition above, $\tau_D \gg \tau_0$, changes to $\tau_{\mathrm{eff}} \gg \tau_0$, where τ_{eff} is the pumping-dependent effective decay time determined both by τ_D^{-1} and upconversion. Thus, in certain systems the inequality $\tau_{\mathrm{eff}} \gg \tau_0$ can hold only at relatively weak excitation and be invalid at high pumping density. In this case, with an increase of the pumping density, one can expect to observe a gradual transformation of the kinetics shape from that typical to the migration controlled one [Eq. (5)] to the shape typical for static luminescence quenching [Eq. (6a)].

According to Ref. 1, the most probable rate of migration hop τ_0^{-1} is equal to

$$\tau_0^{-1}=\frac{4\{(2\pi/3)\Gamma(1-(3/s))\}^{s/3}}{s\Gamma(s/3)}\,C_{\mathrm{DD}}N^{s/3}, \tag{10}$$

where C_{DD} and s are the microparameter and multipolarity factor for donor-donor interaction and N is the net ion concentration. Substituting Eq. (10) into Eq. (9), one has

$$\begin{aligned}\alpha=\alpha_2 &\equiv \frac{4\pi}{m}\,\Gamma(1-(3/m))\Gamma\left(\frac{3}{m}\right)C_{\mathrm{DA}}^{3/m}\\ &\times\left[\frac{4\left\{\dfrac{2\pi}{3}\,\Gamma[1-(3/s)]\right\}^{s/3}}{s\Gamma(s/3)}\,C_{\mathrm{DD}}N^{s/3}\right]^{1-3/m}\\ &\propto C_{\mathrm{DA}}^{3/m}C_{\mathrm{DD}}^{1-3/m}N^{s/3-s/m}.\end{aligned} \tag{11}$$

In dipole-dipole approximation ($m=s=6$), Eq. (11) can be simplified and presented in the form

$$\alpha=\alpha_2 \equiv \frac{3}{2}\left(\frac{2\pi}{3}\right)^{7/2}\sqrt{C_{\mathrm{DA}}C_{\mathrm{DD}}}N. \tag{12}$$

III. DISCUSSION, COMPARISON WITH EXPERIMENT

A. Critical ion concentrations separating different regimes of upconversion

As it was stated in Sec. I, in the most of studies the upconversion rate is described in terms of αn^2 without any

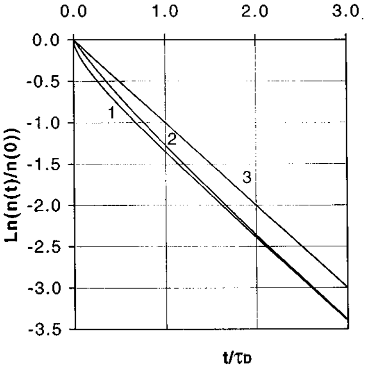

FIG. 1. The calculated kinetics $n(t)$ of nonlinear static [trace 1, Eq. (6b)], and migration-controlled [trace 2, Eq. (5)] dipole-dipole luminescence quenching, plotted according to coordinates $\{\ln(n(t)/n(0))\}$ vs $\{t\}$. Trace 3: the calculated dependence $\exp(-t/\tau_D)$. In the calculations we put $n(0)\tau_D\alpha = n(0)(2\pi^2/3)\sqrt{C_{\rm DA}\tau_D}=0.5$.

discussion of the validity of such approximation. In the present work we have shown that in the hopping regime of migration-assisted energy transfer the description of upconversion in terms of αn^2 holds only for certain time ranges and certain relationships between characteristic time constants of the system, cases (1), (2), and (3b) (at $t \gg \tau_0$), but is not valid in many other experimental situations (for example, at static luminescence quenching).

According to our theory, upconversion cannot be described in terms of αn^2 at $\tau_D < \tau_0$. Substituting $\tau_0=\tau_D$ in Eq. (10), one can determine the critical boundary concentration N_1. Below that concentration the upconversion cannot be described in terms of Eq. (5):

$$N_1=\left(\frac{1}{4}\right)^{3/s}\left[s\Gamma\left(\frac{s}{3}\right)\right]^{3/s}\frac{3}{2\pi\Gamma[1-(3/s)]}(C_{\rm DD}\tau_D)^{-3/s}. \tag{13}$$

At $N_1 < N < N_2$ (where N_2 is the critical concentration for the ‘‘kinetic limit’’ regime of migration-assisted energy transfer) the upconversion parameter α is proportional to $N^{s/3-s/m}$, Eq. (11). At $N > N_2$, the concentration dependence of α vs N saturates to the value given by Eq. (4) and α does not depend on concentration. Equating the right-hand side parts of Eqs. (4) and (11), one can determine the second boundary concentration N_2 as

$$N_2=\frac{3m^{\{3/[s(1-3/m)]\}}}{2\pi\Gamma[1-(3/s)]}\left(\frac{s\Gamma(s/3)}{4}\right)^{3/s} \times\left(\frac{\Sigma_i(1/R_i^m)}{4\pi N_0\Gamma(1-3/m)\Gamma(3/m)}\right)^{3/[s(1-3/m)]}(C_{\rm DA}/C_{\rm DD})^{3/s}. \tag{14}$$

In dipole-dipole approximation ($m=s=6$), Eqs. (13) and (14) yield

$$N_1=\left(\frac{3}{2\pi}\right)^{3/2}(C_{\rm DD}\tau_{\rm D})^{-1/2} \tag{15}$$

and

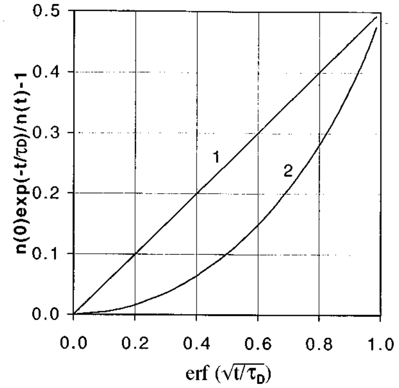

FIG. 2. The calculated kinetics $n(t)$ of nonlinear static [trace 1, Eq. (6b)], and migration-controlled [trace 2, Eq. (5)] dipole-dipole luminescence quenching plotted according to coordinates $\{n(0)\exp(-t/\tau_D)/n(t)-1\}$ vs $\{\mathrm{erf}(\sqrt{t/\tau_D})\}$. In the calculations we put $n(0)\tau_D\alpha=n(0)(2\pi^2/3)\sqrt{C_{\rm DA}\tau_D}=0.5$.

$$N_2=\frac{2}{3}\left(\frac{2\pi}{3}\right)^{-7/2}\frac{1}{N_0}\sum_i\frac{1}{R_i^6}\sqrt{\frac{C_{\rm DA}}{C_{\rm DD}}}. \tag{16}$$

In the most of the laser crystals, $\Sigma_i(1/R_i^6)$ is of the same order of magnitude as N_0^2. Thus, the critical boundary concentration N_2 separating the hopping and the kinetic limit quenching regimes Eq. (16), is in a reasonable agreement with that of Ref. 1, $N_0\sqrt{C_{\rm DA}/C_{\rm DD}}$.

Varying the ion concentration N, one can change in the same type of RE-doped crystal the mechanism of nonlinear (upconversion) luminescence quenching from the static one to the migration-assisted (hopping or kinetics limit) one. A similar change of the character of the energy transfer is well known in the case when acceptors of energy are nonexcited centers.[1]

B. Convenient graphic presentations of luminescence kinetics

In dipole-dipole approximation ($m=s=6$), decay-curves for the static [$\tau_0 \gg \tau_D$, Eq. (6b)] and migration-assisted [$\tau_0 \gg \tau_D$, Eqs. (5) and (12)] nonlinear luminescence quenching were calculated and plotted according to the basis {ln(n(0)/n(t))} vs $\{t/\tau_D\}$ (Fig. 1), $\{[n(0)\exp(-t/\tau_D)]/n(t)-1\}$ vs $\{1-\exp(-t/\tau_D)\}$ (Fig. 2), and $\{[n(0)\exp(-t/\tau_D)]/n(t)-1\}$ vs $\{\mathrm{erf}(\sqrt{t/\tau_D})\}$ (Fig. 3). In the calculations, we put $\{n(0)\tau_D\alpha\}$ to be equal to 0.5 in the case of migration accelerated quenching and we put $\{n(0)\times(2\pi^2/3)\sqrt{C_{\rm DA}\tau_D}\}$ to be equal to 0.5 in the case of static upconversion. Thus, at $t \gg \tau_D$ kinetics (6b) and (5), (12) have the same asymptote:

$$n(t)=\exp(-t/\tau_D)/1.5. \tag{17}$$

Figures 1, 2, and 3 show that the decay kinetics $n(t)$ have very different shapes in static and migration-assisted (hopping) regimes of upconversion quenching. In the static regime of nonlinear quenching of luminescence, $\{[n(0)\exp(-t/\tau_D)]/n(t)-1\}$ is linear when plotted against $\{\mathrm{erf}(\sqrt{t/\tau_D})\}$; while in the hopping regime, $\{[n(0)\exp(-t/\tau_D)]/n(t)-1\}$ is linear when plotted against

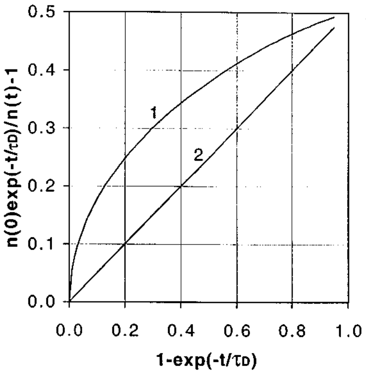

FIG. 3. The calculated kinetics $n(t)$ of nonlinear static [trace 1, Eq. (6b)], and migration-controlled [trace 2, Eq. (5)] dipole-dipole luminescence quenching plotted according to coordinates $\{n(0)\exp(-t/\tau_D)/n(t)-1\}$ vs $\{1-\exp(-t/\tau_D)\}$. In the calculations we put $n(0)\tau_D\alpha = n(0)(2\pi^2/3)\sqrt{C_{\mathrm{DA}}\tau_D} = 0.5$.

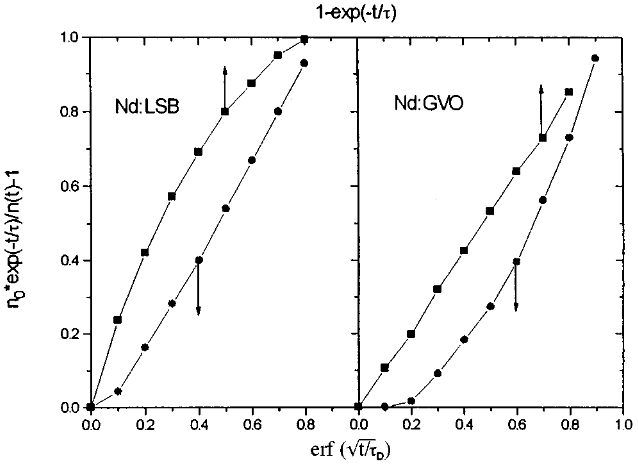

FIG. 4. The experimental kinetics of Nd luminescence in Nd:LaSc$_3$(BO$_3$)$_4$ and Nd:GdVO$_4$ crystals, plotted as $\{n(0)\exp(-t/\tau_D)/n(t)-1\}$ vs $\{\mathrm{erf}(\sqrt{t/\tau_D})\}$ (circles) and $\{n(0)\exp(-t/\tau_D)/n(t)-1\}$ vs $\{1-\exp(-t/\tau_D)\}$ (squares). (Adopted from Ref. 9).

$\{(1-\exp(-t/\tau_D)\}$. Thus, plotting $\{[n(0)\exp(-t/\tau_D)]/n(t)-1\}$ against $\{\mathrm{erf}(\sqrt{t/\tau_D})\}$ or $\{1-\exp(-t/\tau_D)\}$ one can easily differentiate between the static and migration-assisted upconversion regimes.

In Ref. 9, the method of graphic presentation described above was used to differentiate between the static and the migration-assisted regimes of upconversion in Nd-doped LaSc$_3$(BO$_3$)$_4$ and GdVO$_4$ laser crystals. According to Fig. 4 reproduced from Ref. 9, in Nd:LaSc$_3$(BO$_3$)$_4$ the function $\{[n(0)\exp(-t/\tau_D)]/n(t)-1\}$ is linear when plotted against $\{\mathrm{erf}(\sqrt{t/\tau_D})\}$, that implies a static character of upconversion in this material. On the other hand, a linear dependence $\{[n(0)\exp(-t/\tau_D)]/n(t)-1\}$ vs $\{1-\exp(-t/\tau_D)\}$ obtained in Nd:GdVO$_4$ manifests a migration-assisted nonlinear quenching of luminescence.

The change of the upconversion mechanism with the change of ion concentration was experimentally observed in Cr:LiSrGaF$_6$.[8] At 100% Cr doping, $\{[n(0)\exp(-t/\tau_D)]/n(t)-1\}$ was linear when plotted against $\{1-\exp(-t/\tau_D)\}$. At the same time, at lower Cr concentration (10%), $\{[n(0)\exp(-t/\tau_D)]/n(t)-1\}$ was not linear when plotted against either $\{1-\exp(-t/\tau_D)\}$ or $\{\mathrm{erf}(\sqrt{t/\tau_D})\}$. This implies an intermediate case between the migration-assisted and the static energy transfer regimes. [However, in Cr:LiSrGaF$_6$ the relationship $C_{\mathrm{DD}}/C_{\mathrm{DA}}<1$ (Ref. 8) implies not hopping but rather diffusion character of migration-accelerated energy transfer (Ref. 1).]

C. Application of the developed model to solid-state lasers

As was stated above, at high pumping density upconversion strongly influences a population inversion in solid-state lasers. In some cases upconversion damps the population of the upper laser level, as it happens, for example, in 2 μm Ho lasers.[5,6] On the other hand, in upconversion lasers,[18] the interaction of excited ions is the only process populating the upper laser level. In the both cases, the optimization of the dopant concentrations in laser materials and of operation regimes of lasers should be based on a precise analysis of upconversion interaction.

As it was shown in Refs. 13 and 14, the description of upconversion in terms of αn^2 is not applicable to the case of static nonlinear quenching of luminescence and is very limited in the case migration-assisted upconversion in the diffusion regime. In this paper, we have shown that the description of upconversion in terms of αn^2 is also very limited in the case of the hopping regime of migration-assisted energy transfer, the mostly typical regime of luminescence quenching in RE-doped solid-state laser materials. In the hopping regime of upconversion, the luminescence decay curve should be described in terms of microparameters of donor-acceptor and donor-donor interactions (C_{DA} and C_{DD}) rather that in terms of αn^2. We have shown that the description of upconversion in terms of αn^2 holds only in the three situations: (1) at the very initial stage of decay, $t \ll t_1$, (2) in the kinetic limit regime, and (3) at $t_D \gg t_0 \gg t_1$ and $t \gg t_0$ [Sec. II, case (3b)]. In the first and the second cases above, the upconversion macroparameter α is independent of total concentration N and in the third case $\alpha \propto N^{s/3-s/m}$, where s and m are the multipolarities of donor-donor and donor-acceptor interactions. Note, that the theoretical result above is consistent with that of experimental work,[4] where the upconversion parameter α in Er:Y$_3$Sc$_2$Ga$_3$O$_{12}$ laser crystal was found to be concentration independent at Er concentrations exceeding 1×10^{21} cm^{-3}. This result is very different from the dependence $\alpha \propto N^2$ typically considered in the literature.[19] As far as we can discern, the assumption $\alpha \propto N^2$ made in many publications implies a static mechanism of upconversion; but as we show, in this regime upconversion cannot be correctly described in terms of αn^2.

The following two mistakes in the analysis of the decay kinetics are possible if the detailed model accounting for microparameters of the energy transfer is neglected.

(1) At relatively weak migration, the nonlinearity of the luminescence decay-curve plotted in logarithmic scale is much higher than that predicted by the theory accounting for αn^2 term (Fig. 1). Occasionally, the initial part of such decay kinetics can be reasonably good fitted with a simple model accounting for a three-particle upconversion interaction, that is described in terms of βn^3 (here β is the macroparameter of

three-body interaction). Thus, the mechanism of the upconversion process can be completely misinterpreted.

(2) If the upconversion parameter α is determined on the basis of the experimental kinetics that cannot be precisely fitted in terms of αn^2, different values of α can be obtained, depending on which part of the decay curve is taken into consideration. Similarly, the value of α will strongly depend on the duration of the excitation pulse. To our minds, this is one of the most probable reasons why the upconversion parameters reported for the same material in the papers of different authors sometimes are much different.

IV. SUMMARY

We have obtained an analytic solution for the kinetics of nonlinear (upconversion) quenching of donor luminescence under the assumptions of hopping character of migration assisted energy transfer and finite excitation lifetime. It is shown that under certain assumptions [cases (1), (2), and (3b) $(\tau_D \gg \tau_0)$] the kinetics of nonlinear quenching of luminescence can be described in conventional terms of αn^2. However, in many other cases the pattern of nonlinear luminescence quenching is much more complex. The critical ion concentrations separating different upconversion regimes are determined. It is shown how the observables of the luminescence experiment depend on microparameters of energy transfer and ion concentrations. The theoretical results obtained in this paper are consistent with experimental observations described in the literature.

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