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PUMP INTENSITY DEPENDENCE OF EMISSION QUANTUM EFFICIENCY IN Nd-DOPED MATERIALS

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Abstract. The paper discusses the effects of energy transfer processes that determine the down- and upconversion of excitation on the emission quantum efficiency in Nd-doped laser materials. Using the case of Nd:YAG, it is shown that both these processes contribute to the reduction of emission quantum efficiency in proportion determined by the initial excitation and on the ratio of the energy transfer rates and their relative contribution changes during the emission decay. This analysis shows that consideration of only upconversion transfer is inadequate and accurate account of their joint action is necessary.

Key words: solid-state lasers, de-excitation, energy transfer, emission quantum efficiency.

1. INTRODUCTION

The non-radiative de-excitation of the emitting levels [1, 2] is a major limiting factor for efficiency and power scaling of the solid-state lasers [3–5]. Such de-excitation can be induced by the interaction of the doping ions in the laser materials with the vibrations of the crystalline lattice (electron-phonon interaction); additional non-radiative de-excitation can be determined by the energy transfer processes from the excited ion (donor, D) to other ion (acceptor, A) of similar or different species; by this process, the donor transfers all or part of its excitation to the acceptor, according to the energy level structure of the ions involved in process [6–8]. The energy transfer is determined by static electric multipole or by superexchange interaction between the donor and acceptor that induce simultaneous non-radiative (quasi-) resonant down- and respectively up-pointing transitions between the Stark levels of these ions and thus the energy transfer requires energy level schemes that could grant such gaps. When the initial electronic state of the acceptor is the ground state, the final donor and acceptor energy states are lower than the initial donor energy and the process determines down-conversion of excitation. However, when the initial acceptor state is an

excited state, particularly when this is the same as for the donor initial state, the final energy of the acceptor can be higher than the initial donor state, leading to upconversion of excitation. In many cases the down- and upconversion processes can co-exist and they compete in the de-excitation of the excited levels. The final states of the donor and acceptor could subsequently de-excite by radiative and/or non-radiative processes. Of particular relevance for the laser materials are the energy transfer processes inside the system of laser active ions, which could determine the self-quenching of the emission of the laser emitting level.

The balance between the radiative and non-radiative de-excitation can be characterized by the emission quantum efficiency that expressed the fraction of excited ions that de-excite radiatively. The emission quantum efficiency influences the pump intensity necessary to reach the threshold population inversion for the laser process and thus is a major factor in optimization of laser emission. On the other hand, the electron-phonon de-excitation of the excited level and of the final donor and acceptor states involved in the energy transfer from this level contributes to generation of heat, with deleterious effects on the laser material and process.

The non-radiative de-excitation by electron-phonon interaction depends on the ratio of the energy gap between the excited level and the nearest lower energy level to the phonon energy quantum, *i.e.* on the order of process: its efficiency depends on the phonon occupation number and is thus enhanced with increasing of temperature. However, this interaction does not depend on the pump intensity and on the doping concentration. By contrary, the temperature dependence of the de-excitation by energy transfer is weak, since it could only influence the thermal population of the Stark levels of the ground state and thus the optical absorption transitions in the acceptor act; however, these processes show dependence on doping concentrations as well as on the pump intensity that determines the initial fraction of excited ions, *i.e.* the balance between the down- and upconversion.

The ground electronic configuration of the Nd^{3+} ion has rich energy level scheme; however, the Nd laser materials have a unique metastable state able to give laser emission, the manifold ${}^4\text{F}_{3/2}$, in the region of 11500 cm^{-1} . Due to the large energy gap ($\sim 5500\text{ cm}^{-1}$) to the nearest lower level ${}^4\text{I}_{15/2}$, the electron-phonon interaction has very little contribution to the non-radiative de-excitation of ${}^4\text{F}_{3/2}$ in most laser materials, except for those with very large phonon energies. However, strong energy transfer processes from ${}^4\text{F}_{3/2}$ can take place inside the system of Nd ions in the laser materials, including the yttrium aluminum garnet (YAG), either by down-conversion determined by the interaction of an excited Nd^{3+} ion with another Nd^{3+} ion in its ground state ${}^4\text{I}_{9/2}$, with ${}^4\text{I}_{15/2}$ as final state for both the donor and acceptor ions [9–11] or by upconversion processes determined by the interaction of two excited Nd^{3+} ions, which convert the excitation to higher energy levels [12–14]. The final state of the donor in both processes de-excite completely to the ground state by electron-phonon interaction; however, whereas the final state of the acceptor in down-conversion de-excites non-radiatively to the ground state, in case

of upconversion the final acceptor state de-excites non-radiatively to the initial state ${}^4F_{3/2}$. It is thus evident that these self-quenching energy transfer processes act simultaneously and compete in determining doping concentration and pump intensity dependent reduction of the emission quantum efficiency. Moreover, under the joint action of energy transfer and electron-phonon interaction part of excitation fed into the system of Nd^{3+} laser active ions by pumping is transformed into heat.

The emission quantum efficiency can be measured either by comparing the light emitted from the metastable level with the total amount of excitation fed into this level [15–17] or it can be inferred from the various effects of the heat generated by the non-radiative de-excitation of this level [18–23]. In both cases the measurement is difficult since it could imply painful calibration or utilization of other parameters that are not accurately known. On the other side, the effect of doping concentration or of pump intensity on the emission quantum efficiency can be calculated accurately if the characteristic parameters of the energy transfer responsible for emission quenching are known. Thus, by difference from the electron-phonon de-excitation, which preserves the exponential emission decay after short pulse excitation and introduces concentration-independent acceleration, the energy transfer introduces concentration-dependent departures from exponential and acceleration of decay; these effects can be used for estimation of the characteristics of transfer [9, 10, 24–30]. Such studies have performed on a large variety of Nd laser materials; however, despite of the fact that the two types of energy transfer processes act simultaneously, the studies on emission decay at high excitation densities disregard traditionally the down-conversion and discuss the problem in terms of simplified upconversion models that enable simple analytical solutions [12–14]. This paper presents a unified modeling of emission decay and emission quantum efficiency under the joint effect of these types of energy transfer. In order to make the discussion more clear, the model is illustrated for the Nd-doped yttrium aluminum garnet (YAG), the most popular laser active material.

2. SELF-QUENCHING ENERGY TRANSFER PROCESSES IN Nd-DOPED LASER MATERIALS

The Nd concentration in the melt-grown Nd:YAG laser crystals is limited to [1, 2, 16, 31, 10] energy transfer down-conversion by interaction of the excited ion and another Nd^{3+} ion in its ground state, according to the cross-relaxation scheme (${}^4F_{3/2}$, ${}^4I_{9/2}$) \rightarrow (${}^4I_{15/2}$, ${}^4I_{15/2}$), favored by the fact that the Stark levels of the ${}^4I_{15/2}$ manifold of Nd^{3+} are about mid-way between those of the metastable energy level ${}^4F_{3/2}$ and of the ground manifold ${}^4I_{9/2}$ [11]. Since the final donor and acceptor level ${}^4I_{15/2}$ is de-excited to the ground level by efficient electron-phonon interaction along the ladder of levels ${}^4I_{15/2}$ - ${}^4I_{13/2}$ - ${}^4I_{11/2}$ - ${}^4I_{9/2}$, all the initial excitation of the level ${}^4F_{3/2}$ is finally transformed into heat.

The down-conversion dominates the de-excitation of ${}^4F_{3/2}$ at weak-intensity excitation [26]. However, with increased pump intensity the density of ions in excited state increases and this could onset the energy transfer upconversion of excitation [12–14] by interaction between two excited Nd ions. Several upconversion processes by interaction of two Nd^{3+} ions excited to the ${}^4F_{3/2}$ are shown schematically in Fig. 1. As shown in, due to the dense packing of the energy levels between the terminal levels of the donor ion and the ground state, their excitation relaxes rapidly to the ground state. At the same time, due to the dense packing of levels between the final state of the acceptor ion and the metastable level, almost all upconverted excitation relaxes by electron-phonon interaction to the level ${}^4F_{3/2}$; this implies that from the two excitations in the ${}^4F_{3/2}$ level of the ions involved in upconversion, only one is effectively lost. Moreover, the upconversion process prepares the conditions for down-conversion.

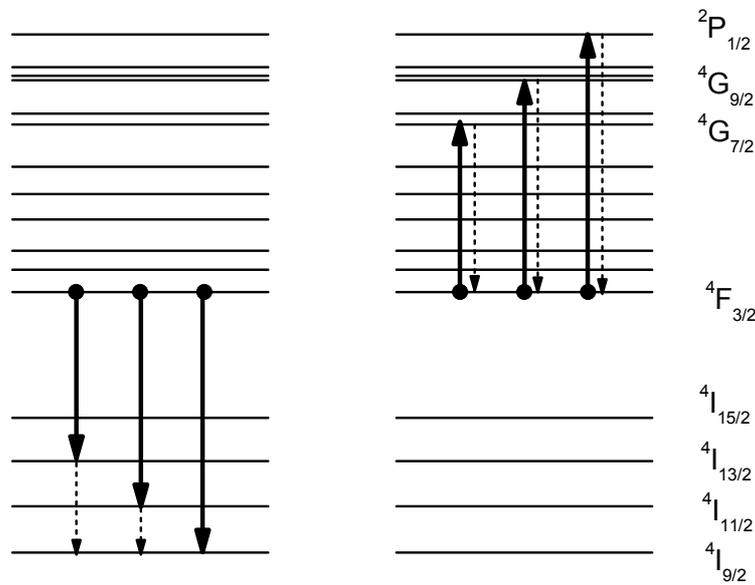


Fig. 1 – Upconversion processes in Nd-doped materials; thick arrows – the energy transfer transitions, dashed arrows – subsequent electron-phonon relaxation.

The energy transfer can be determined by the electric multipole (dipole-d, quadrupole-q) or superexchange interactions between the doping ions and the corresponding de-excitation rate shows specific dependence on the distance R_{DA} between the donor and the acceptor ion involved in transfer. Thus, in case of the

multipolar interactions the energy transfer rate can be written $W_{DA}^{(s)} = \frac{C_{DA}^{(s)}}{R_{DA}^s}$, where

$s = 6, 8$ or 10 for the d-d, d-q and q-q interactions and $C_{DA}^{(s)}$ is the transfer microparameter, dependent on the electronic structure of the doping ions and on the transition probabilities, particularly on the superposition integral of donor emission and acceptor absorption for the transitions involved in transfer, $C_{DA}^{(s)} \propto \frac{1}{\tau_{rad}} \int \sigma_e(D) \sigma_a(A) dv$ [6–8]. The transfer enhances the de-excitation rate of

the donor, to $(1/\tau_D + W_{DA}^{(s)})$, where τ_D is the lifetime in absence of transfer. The multipolarity of the energy transfer interaction is determined for each particular case by the selection rules for the electric multipole transitions in the donor and acceptor ions. The transitions from the metastable level ${}^4F_{3/2}$ to the levels 4I_J , as well as transition ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ are allowed only for electric dipole, whereas some of the transitions from ${}^4F_{3/2}$ to some of the upper levels could be also allowed for electric quadrupole. Thus, in case of the down-conversion ET in Nd^{3+} , both the donor ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ and the acceptor ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ transitions are allowed only for the electric dipole, but forbidden for the electric quadrupole, and the only possible ET component corresponds to $s = 6$. However, in case of upconversion the quadrupole contribution could be allowed in some of the acceptor transitions and thus the transfer rate could contain also $s = 8$ component.

In case of superexchange coupling the energy transfer rate can be written $W_{DA}^{ex} = (1/\tau_{rad}) \exp[\gamma(1 - R_{DA}/R_0)]$ with $\gamma = 2L^{-1}R_0$, where L is the effective Bohr radius and R_0 is the penetration depth of interaction, corresponding to the distance at which the superexchange transfer rate equals the radiative de-excitation rate; in case of Nd^{3+} ions W_{DA}^{ex} diminishes rapidly with distance. The electric multipole and the superexchange interactions act together: however, due to the specific dependence on distance, their relative contribution would depend on R_{DA} .

An excited Nd^{3+} ion can also transfer completely its excitation to a unexcited ion by the cross-relaxation (${}^4F_{3/2}, {}^4I_{9/2} \rightarrow {}^4I_{9/2}, {}^4F_{3/2}$); repetition of this transfer determines the migration of excitation inside the doping ions [32], without loss of excitation. Thus, the migration does not reduce the emission lifetime; however, the excitation could be lost if the last ion from the migration chain loses the excitation by energy transfer down-conversion or upconversion to a near unexcited or excited Nd ion. The cross-relaxation (${}^4F_{3/2}, {}^4I_{9/2} \rightarrow {}^4I_{9/2}, {}^4F_{3/2}$) is characterized by a donor-donor microparameter C_{DD} and the migration-assisted quenching transfer is characterized by a rate proportional to the product $C_{DA}C_{DD}$. The balance between the direct (static) donor-acceptor transfer and the migration-assisted (dynamic) transfer is determined by the ratio of C_{DA} and C_{DD} .

3. THE EFFECT OF ENERGY TRANSFER SELF-QUENCHING ON THE EMISSION DECAY AND QUANTUM EFFICIENCY IN Nd LASER MATERIALS

3.1. ENERGY TRANSFER SELF-QUENCHING IN Nd LASER MATERIALS

The laser active materials contain a large number of doping ions that can be characterized either by the density of doping ions N or by the relative concentration C with respect to the available substitutional sites. In the Nd-doped materials, each Nd^{3+} ion excited by pumping could serve as donor; this ion is surrounded by a particular geometrical configuration of the other Nd ions, placed at various distances R_j , which can act as acceptors in down- or upconversion energy transfer processes. The relative concentrations of the Nd ions that can act as acceptors for down- or upconversion is determined by the fraction of excited ions relative to the total concentration of Nd, $r(t) = n(t)/n_{\text{Nd}}$, which changes during the decay: the concentration of acceptors for upconversion is $C_A^{\text{up}}(t) = r(t)C_{\text{Nd}}$ whereas that for down-conversion equals $C_A^{\text{dw}}(t) = 1 - r(t)C_{\text{Nd}}$.

The de-excitation rate of any donor ion by energy transfer is then the sum of the transfer rates to each of these acceptor ions and depends on the particular configuration of acceptors around this donor, whose global de-excitation rates becomes $(1/\tau_D + \sum W_{DA}(R_j))$. The global emission decay of the sample under investigation will be the sum of decays of all donors, each of them with its particular lifetime. However, since the exact acceptor configurations around each of these donors is not known these particular lifetimes cannot be evaluated; moreover the enormous number of donors would make the summation impossible. Numerically, this problem could be solved by Monte Carlo simulation but the solution is difficult to handle. However, analytically the summation could be replaced by an averaging procedure over the whole ensemble of sites available to the acceptors around the site of the donor. This averaging provides a transfer function $P(t)$, such as $\exp[-P(t)]$ expresses the survival probability of the donor in the excited state in presence of energy transfer at any moment of time t after very short pulse excitation that determines the initial population $n_D(0)$, *i.e.*

$$n_D(t) = n_D(0) \exp\left(-\frac{t}{\tau_D}\right) \exp[-P(t)]; \quad (1)$$

this corresponds to an effective rate equation after the end of the exciting pulse

$$\frac{dn_D}{dt} = -\frac{t}{\tau_D} n_D - [P(t)] n_D. \quad (2)$$

Various models for the distribution of the acceptor ions at the available lattice sites have been utilized in the averaging procedure. Thus, the placement of the doping ions at the available lattice sites can be *correlated*, when additional attractive or repulsive interactions between the doping ions are active, and *non-correlated* distributions, in absence of such interactions. The distributions can be also classified as *discrete*, with the doping ions placed at the specific lattice sites, with the important particular case of non-correlated (random) placement, and *continuous*, which consider the doping concentration as continuous, with specific value at any geometrical point (xyz); a particular case is the continuous uniform distribution, when the density of doping ions is considered equal at any geometrical point. Since the individual donors de-excite with particular rates, it would be expected that the sum of contributions from all donors, as well as the averaged transfer function $P(t)$ will not be exponential in time. A special case in description of the donor emission decay is the *average-distance* model, which considers the acceptor ions placed at distances equal to the average distance equal to $N^{-1/3}$ where N is the absolute Nd doping concentration, ions/cm³, and accounts only for the energy transfer to the nearest acceptor ion. Obviously, from physical point of view, only the discrete placement model is realistic; the presence of correlation of placement can be checked from other types of measurements, such as the relative intensity of the spectral satellite lines due to ensembles of doping ions in near lattice sites.

In case of migration-assisted energy transfer in the usual case for the Nd laser materials when C_{DA} is larger than C_{DD} the excitation migrates over the system of Nd³⁺ ions till it comes very close to another Nd³⁺ ion that can act as trap of excitation by down-conversion. This process introduces a new de-excitation rate whose acceptor ensemble averaged value \bar{W} depends on the square of Nd concentration and determines exponential de-excitation. The emission decay can be then described by the equation of evolution of population

$$\frac{dn_D}{dt} = -\frac{t}{\tau_D} n_D - [P(t)]n_D - \bar{W}n_D \equiv -\frac{t}{\tau_D} n_D - [P'(t)]n_D, \quad (3)$$

which determines the decay law

$$\begin{aligned} n_D(t) &= n_D(0) \exp\left(-\frac{t}{\tau_D}\right) \exp[-P(t)] \exp(-\bar{W}t) \equiv \\ &\equiv n_D(0) \exp\left(-\frac{t}{\tau_D}\right) \exp[-P'(t)]. \end{aligned} \quad (4)$$

Since the emission cross-section of all donor ions is practically identical, the law describing the variation of the emission intensity $I(t)$, *i.e.* the decay law will be similar to that describing the population n_D , Eq. (4). Experimentally the transfer

function $P'(t)$ can be then inferred from the emission decay, according to $[P'(t)]_{\text{exp}} = \ln(I(t)/I(0)) + t/\tau_D$.

As described in Introduction, the early measurements of emission decay of Nd:YAG crystals at the traditional 1 at.% Nd under weak excitation considered the decay as exponential although small departures from exponential at early times were sometimes remarked. The measurement at high Nd concentrations revealed non-exponential decay that was attributed to self-quenching [9]. Subsequent systematic investigation of decay of Nd:YAG crystals with Nd concentrations from 0.1 to 2.5 at.% Nd evidenced four concentration-dependent intervals [24–26], with loose borders, of distinct behavior of $P'(t)$: a very fast drop of emission at early times (below [28–30]). Once the law describing the emission decay at various doping concentrations is known, the effect of doping concentration on the emission quantum efficiency can be obtained by comparing the total amount of luminescence, expressed by the integral of the normalized decay law, in presence and in absence of energy transfer,

$$\eta_{qe} = \frac{\int_0^{\infty} (I(t)/I(0)) dt}{\int_0^{\infty} \exp(-t/\tau_D) dt} = \frac{1}{\tau_D} \int_0^{\infty} (I(t)/I(0)) dt. \quad (5)$$

The emission quantum efficiency can be used to define an effective emission lifetime $\tau_{eff} = \tau_D \eta_{qe}$. In case of the Nd-doped materials, the form of the energy transfer function $P(t)$ for the direct transfer depends on the type of conversion of excitation, which determines the type of acceptors. In turn, as shown above, the type of conversion of excitation is determined by the density of ions in excited state, which is essentially connected with the excitation intensity.

3.2. SELF-QUENCHING AT WEAK EXCITATION INTENSITY

At low excitation intensities the fraction $r(0)$ of Nd ions excited by pumping is low, the down-conversion dominates and upconversion can be safely disregarded, *i.e.* $C_A \approx C_{Nd}$. The mathematical description of the emission decay in presence of transfer is essentially subordinated to the model of distribution of acceptor ions used in the averaging process.

A. *The average-distance model* [33]. The only energy transfer considered in this model refers to the first acceptor placed at the average ion-ion distance defined above and is characterized by a constant transfer rate W_{DA} . In case of multipolar interactions this rate can be related to the Nd concentration by $W_{DA} = C_{DA}^{(s)} C_{Nd}^{s/3}$; for d-d interactions $W_{DA} = C_{DA}^{(6)} C_{Nd}^2$. The rate equation for donor population is

$$\frac{dn_D}{dt} = -\frac{t}{\tau_D} n_D - W_{DA} n_D, \tag{6}$$

the decay is exponential, regardless of interaction,

$$n_D(t) = n_D(0) \exp\left(-\frac{t}{\tau_D}\right) \exp(-W_{DA}t), \tag{7}$$

and the emission quantum efficiency for d-d interaction is

$$\eta_{qe} = \frac{1}{1 + (N_A/N_0)^2}, \tag{8}$$

where $N_0 = (C_{DA}^{(6)}\tau_D)^{-1/2}$ is a characteristic acceptor concentration at which the energy transfer reduces the emission lifetime to its half. Despite of the rude physical reality of this model, the simple equations describing the transfer made it very popular. Nevertheless, the dependences on doping concentrations predicted by this model could be very misleading, leading to wrong physical conclusions.

B. *The continuous uniform model* [6–8]. For the various multipolar interactions

$$P(t) = \Gamma\left(1 - \frac{3}{s}\right) \frac{C}{C_0} \left(\frac{t}{\tau_D}\right)^{3/s} = \gamma^{(s)} t^{3/s}, \tag{9}$$

where $\Gamma(x)$ is the Euler function. In case of d-d interaction

$$P(t) = \gamma^{(d-d)} t^{1/2} = \frac{4}{3} \pi^{3/2} N_A (C_{DA})^{1/2} t^{1/2} \tag{10}$$

is linear in the Nd concentration but non-linear in time. The rate equation and the emission decay are given by equations (1) and (2), but the description of decay in this model is limited to a unique type of ion-ion interaction. Another major shortcoming of this model is that it predicts finite acceptor density at the donor position and thus it does not predict accurately the decay at early times. However, this model enables identification of the specific ion-ion interaction and generally it gives a good description of decay after a given lapse of time.

C. *The discrete random distribution model*. The rate equation for the donor population and the decay law are given by equations (1) and (2) and the energy transfer function for the direct donor-acceptor transfer can be written [34, 35]

$$P(t) = \sum_i \ln[1 - C_A + C_A \exp(-W_i t)], \tag{11}$$

where the summation is performed for all the sites available to the acceptors around the donor sites. This transfer function is an ever decreasing function of

time. Utilization of this transfer function is not simple; however, over definite intervals of time, it can be approximated by simpler forms;

– for small $W_i t$ values, i.e. at early times of decay the transfer function can be approximated by a function linear in time, $P(t) \approx \sum_i C_A W_i t = W_{lin} t$;

– for longer time, the transfer function can be approximated by the function for continuous uniform distribution, eq. (10);

– if a very strong short-distance interaction is active, it could induce a fast drop of emission at beginning of decay, whose extent in intensity corresponds to the number of acceptors involved in this transfer.

A major advantage of this model is that it could accommodate mixed interactions between donor and acceptor. The complex experimental decay in case of Nd:YAG at low excitation can be described very well in the frame of this model: the fast drop at beginning of decay indicates the presence of superexchange coupling to the four acceptors from the first coordination sphere, the subsequent exponential part corresponds to the linear approximation of the transfer function at early times, with the first four acceptor sites, whose emission was already consumed in the fast initial drop, excluded from summation. The observed subsequent interval of non-linear decay corresponds to the continuous uniform approximation for d-d interaction: this portion enables evaluation of the dipole-dipole transfer microparameter $C_{DA} = 1.85 \times 10^{-40} \text{ cm}^6 \text{ s}^{-1}$. This analysis shows the donor and acceptor ions in the down-conversion energy transfer in Nd:YAG are coupled by mixed superexchange and d-d interactions, the first being dominating for the n.n. acceptor ions. The validity of the parameters determined from the behavior of decay over definite temporal intervals was checked by the global description of decay with the transfer function (11) and it shows that the discrete distribution model distribution mode has definite superiority over the other models. The migration-assisted transfer can be easily accommodated in the random distribution model. The migration-assisted transfer is responsible for the quasi-exponential decay at very long times: in YAG this corresponds to a d-d transfer rate $\bar{W} = \bar{W}_0 C_{Nd}^2$, with $\bar{W}_0 = 240 \text{ s}^{-1} (\text{at.}\% \text{ Nd})^{-2}$.

The emission quantum efficiency can be calculated with the decay laws (2) and (4), with the energy transfer parameters inferred from the emission decay. Thus, at low Nd concentrations (to $\sim 1.2 \text{ at.}\%$), where the direct D-A transfer dominates, the emission quantum efficiency is given by

$$\eta_{qe} \cong \exp(-bC_A), \quad (12)$$

with

$$b = \sum_i \frac{W_i}{\tau_D^{-1} + W_i}. \quad (13)$$

In case of Nd:YAG, $b = 0.223$ (at.% Nd)⁻¹ and the emission quantum efficiency at 1 at.% Nd equals 0.80. At higher Nd concentrations, where the migration-assisted transfer gains strength, the emission quantum efficiency becomes

$$\eta_{qe} \cong \frac{1}{1 + \tau_D \bar{W}} \exp\left(-\sum_i \frac{W_i}{\tau_D^{-1} + W_i + \bar{W}} C_A\right). \quad (14)$$

The values calculated with these equations describe well those measured for Nd:YAG at various Nd concentrations by various methods based on the effects of the heat generated by non-radiative processes [20-24]. From comparison of the description of the experimental data with the predictions based on the various models of distribution of the Nd ions it is obvious that the discrete random placement model is the unique model that provides correctly the observed facts.

3.3. THE SELF-QUENCHING OF EMISSION AT HIGH PUMP INTENSITIES.

The accelerated emission decay at higher pump intensities was observed in many Nd-doped materials, including Nd:YAG single crystals and thin films. The only cause for this was considered the upconversion self-quenching by interaction between two excited Nd ions, without a proper account of the simultaneous presence of down-conversion, which was accounted for only as a constant reduction of the donor lifetime [12-14]. Moreover, the upconversion was characterized by a constant transfer rate W^{up} , with the Bernoulli-type rate equation

$$\frac{dn_D}{dt} = -\frac{t}{\tau_D} - W^{up} n_D^2, \quad (15)$$

which has simple analytical solution. The transfer rate for 1 at.% Nd in case of the thin films [14] was about six times smaller than for single crystals [12], and thus the transfer rates could be 5 to 30 times larger than the down-conversion rates.

Although very convenient for analysis, the assumption of unique (global) upconversion transfer rate would correspond physically to the artificial model of average distance than to the more realistic model of random discrete distribution. Moreover, this model does not account for the evolution of the relative importance of the upconversion and down-conversion due to the modification of the concentrations of the acceptors specific to each of these processes.

Preliminary discussion of the self-quenching in Nd laser materials at high excitation intensities under joint action of upconversion and down-conversion was presented in Refs. [30, 36] and this model is developed in this work. Since the unexcited and excited Nd ions that can serve as acceptors in down- and respectively upconversion, with relative concentrations $(1 - r(t))C_{Nd}$ and $r(t)C_{Nd}$ can occupy the same type of sites i around donor, the energy transfer function for the direct donor-acceptor transfer can be written

$$P(t) = \sum_i \ln \left\{ 1 - C_{Nd} + [1 - r(t)] C_{Nd} \exp(-W_i^{dw} t) + r(t) C_{Nd} \exp(-W_i^{up} t) \right\}, \quad (16)$$

where W_i^{dw} and W_i^{up} are the transfer rates for the down-conversion, respectively upconversion. The transfer function (16) depends both on Nd concentration and on pump intensity, as well as on the ratio between the upconversion and down-conversion rates, $R_i = W_i^{up} / W_i^{dw}$. At low Nd concentrations the transfer function (16) can be written as the sum of the transfer function for down-conversion and for upconversion, $P(t) \approx P^{dw}(t) + P^{up}(t)$, with

$$P^{dw}(t) = \sum_i \ln \left\{ 1 - [1 - r(t)] C_{Nd} + [1 - r(t)] C_{Nd} \exp(-W_i^{dw} t) \right\}, \quad (17)$$

$$P^{up}(t) = \sum_i \ln \left\{ 1 - r(t) C_{Nd} + r(t) C_{Nd} \exp(-W_i^{up} t) \right\}. \quad (18)$$

However, these two transfer function are not independent, since the relative concentrations of donors are determined by the same fraction $r(t)$; since the fraction $r(t)$ decreases during decay, the contribution of upconversion to quenching decreases in time, whereas that of down-conversion increases. Since the acceptor concentrations for these processes depend on the pump intensity, the transfer functions will show corresponding pump dependence. For instance, the transfer function $P^{dw}(t)$ has small value and quite weak dependence on time at the beginning of decay, then increases steadily, whereas $P^{up}(t)$ increases strongly at early times, reaches a maximum value, then drops asymptotically to zero. However, the global transfer function $P(t)$, equation (16) increases permanently in time, in a manner dependent on the ratio R . By using these equations for the transfer function it was found the decays reported in literature for 1 at.% Nd:YAG can be well described assuming $R \approx 20 - 30$.

The fraction $r(t)$ influences also the acceptor concentrations for both steps (migration and quenching) in case on the migration-assisted transfer and thus the transfer rates: $\bar{W}^{dw} = \bar{W}_0^{dw} [1 - r(t)]^2 C_{Nd}^2$ for down-conversion and $\bar{W}^{up} = \bar{W}_0^{up} r(t) [1 - r(t)] C_{Nd}^2$ for upconversion. Thus, by difference from the migration-assisted down-conversion at weak pump intensities, where the acceptor concentration for the migration and quenching act is almost constant at any moment of decay and practically equal to the Nd concentration, making the migration rate constant, in case of high excitation intensities the concentration of acceptors for both these acts can be low at the beginning of decay but increase during decay and thus the migration-assisted transfer rate starts from a low, but increases steadily in time. However, in case of migration-assisted upconversion the concentration of acceptors for the quenching act decreases during decay and thus

the transfer rate starts with a low value, increases to the moment when $r(t) = 0.5r(0)$, then decreases again.

The quite complex form of the transfer function for the joint action of upconversion and down-conversion precludes an analytical solution for the emission quantum efficiency. However, this can be calculated numerically. Figure 2 shows the calculated emission quantum efficiency for down-conversion only, up-conversion only and joint down-and up-conversion for 1 at.% Nd:YAG at various pump intensities (fractions $r(0)$) and ratios R . The energy transfer parameters for down-conversion are those inferred from experiments on emission decay.

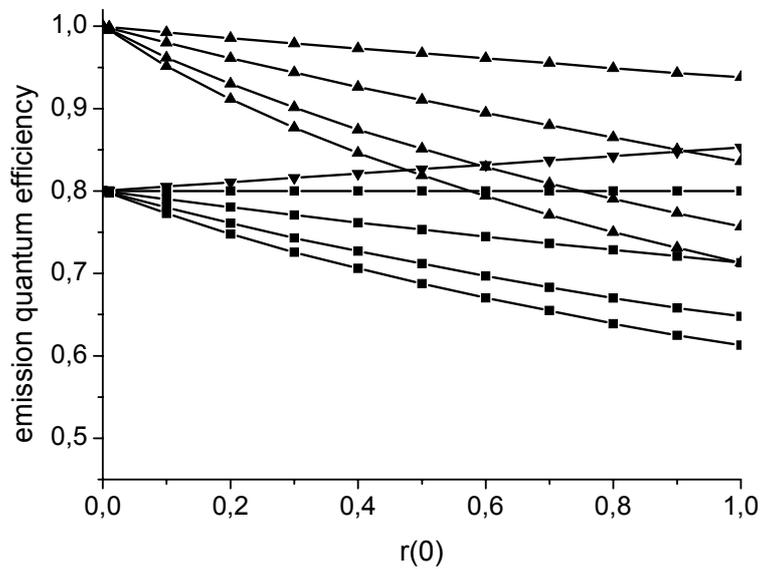


Fig. 2 – The calculated emission quantum efficiency for 1 at.% Nd:YAG for various initial fractions of excitation $r(0)$: up-pointing triangles, upconversion only, in descending order $R = 1, 10, 30, 50$; down-pointing triangles, down-conversion only; squares, joint down-conversion and upconversion, descending order $R = 1, 10, 30, 50$.

Figure 2 illustrates several major features of the emission quantum efficiency in Nd:YAG at high excitation intensities:

- the quantum efficiency for down-conversion-only starts from the value corresponding to weak pump intensity (0.8) and increases linearly with the initial fraction of excitation. Such behavior is normal, since high excitation reduces the concentration of acceptors for down-conversion.

- the emission quantum efficiency for upconversion-only starts from the value 1 at low inversion and decreases with increasing $r(0)$; this behavior is connected with the low concentration of the acceptors for upconversion at low excitation and with its increase with excitation intensity. The process is enhanced

at higher transfer rates. It is also obvious that the emission quantum efficiency for upconversion-only transfer becomes smaller than for down-conversion-only even for very high rates only for quite large (in region of 0.5) initial excitation. This shows that the quite low values of emission quantum efficiency inferred from various experiments under high intensity pumping cannot be explained by upconversion-only energy transfer even for very high transfer rates.

– the emission quantum efficiency under joint action of upconversion and down-conversion is practically equal to the product of the efficiencies of these two processes when acting alone. Thus, the emission quantum efficiency under joint action of these processes is considerably lower than when only the upconversion is active;

– when the upconversion and down-conversion rates are equal, the emission quantum efficiency under the joint action of these processes is independent on the initial excitation $r(0)$, although the efficiencies of these processes when acting alone depend on $r(0)$.

4. CONCLUSION

Theoretical modeling of the emission quantum efficiency in the Nd laser materials at high pump intensities evidences the need for accurate account of all energy transfer processes and of their competition in de-excitation of the emitting level. It is thus shown that consideration of upconversion-only energy transfer cannot account for the reduction of emission quantum efficiency and consideration of the joint action of upconversion and down-conversion would be necessary.

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