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Energy transfer mechanisms between Ce^{3+} and Nd^{3+} in YAG : Nd, Ce at low temperature

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Résumé. — On étudie, à basse température, les mécanismes de transfert d'énergie entre les ions Ce^{3+} et Nd^{3+} incorporés dans des cristaux de grenat d'aluminium-yttrium (YAG) en utilisant comme source d'excitation sélective un laser à colorant à impulsion et accordable permettant de pomper dans la première bande d'absorption de Ce^{3+} . On observe des transferts d'énergie aussi bien radiatifs que non radiatifs. Les courbes de déclin de la fluorescence des ions Ce^{3+} sont enregistrées pour diverses concentrations en Ce^{3+} allant de 0,003 à 0,02 at. % et des concentrations en Nd^{3+} habituellement utilisées dans les barreaux laser YAG : Nd ($\approx 0,73$ et 0,88 at. %). Etant donné qu'aucune diffusion n'a lieu parmi les ions Ce^{3+} , il est possible de décrire les courbes de déclin à l'aide de la théorie d'Inokuti-Hirayama. Le meilleur accord est obtenu pour une distance critique moyenne $R_0 \approx 1,1$ nm aussi bien pour des couplages du type dipôle-dipôle que dipôle-quadrupôle. Ceci signifie que ces deux couplages contribuent au transfert d'énergie non radiatif $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ dans les cristaux YAG : Nd, Ce pour les concentrations considérées.

Abstract. — The energy transfer mechanisms between Ce^{3+} and Nd^{3+} are studied at low temperature ($T = 4.4$ K) in Ce codoped YAG : Nd crystals using selective pulsed dye laser excitation to pump into the first Ce^{3+} absorption band. Both radiative and nonradiative energy transfers are observed. Ce^{3+} fluorescence decay curves are measured for various Ce^{3+} concentrations ranging from 0.003 to 0.02 at. % and typical Nd^{3+} concentrations used in YAG : Nd laser rods (≈ 0.73 and 0.88 at. %). Since no diffusion occurs among Ce^{3+} ions, the Ce^{3+} decay curves are fitted according to Inokuti-Hirayama's theory. The best agreement is obtained for a average critical distance $R_0 \approx 1.1$ nm for dipole-dipole as well as quadrupole-dipole couplings. This means that both couplings contribute to nonradiative $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer in YAG : Nd, Ce crystals for the used concentrations.

1. Introduction.

A number of applications of a variety of options YAG : Nd lasers and laser systems has increased considerably during last years [1]. Although the YAG : Nd crystal is studied for more than 20 years, unresolved problems subsist and the importance of YAG : Nd lasers for their applications justify to continue studies of this classical laser crystal [1-3]. Improved parameters of these lasers result from refinements in design and in optical pumping efficiency. The later improvement can be provided either by using codoped YAG : Nd laser rods [4, 5] or by doping the glass envelope with cerium together with a fluorescent dye in a cooling liquid system [6]. Both these methods can lead up to 40 %

increase in output power [4, 7]. Jacobs *et al.* [4] have studied the usefulness of $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer in the laser glass ED2 while Kvapil *et al.* [7, 8] have reported for the first time an increase of output powers of YAG : Nd, Ce laser rods in comparison with those noncoactivated by Ce. Now, the most YAG : Nd laser rods made by Monokrystal Turnov (Czechoslovakia) are codoped by Ce [9].

The detailed study of $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer in YAG : Nd, Ce crystals was reported by one of us (Marès) in a previous paper [10]. This paper shows that radiative $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer plays a major role in this crystal at temperatures from liquid nitrogen to higher ones. The contribution of the radiative $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer to improvement of laser rod pumping is roughly three times greater than expected from concentration differences between Nd and Ce [10]. A reason of this favourable behaviour results from overlapping between wide Ce^{3+} emission

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band (ranging from 480 to 700 nm) and some high absorbing Nd^{3+} lines, especially in the yellow range [10-13] together with high Ce^{3+} fluorescence quantum yield approaching to 1 [12] and high Ce^{3+} absorption cross section ($\sigma_A(\text{Ce}^{3+}) \approx 10^{-18} \text{ cm}^2$ [13]) which is more than ten times higher in comparison with Nd^{3+} one ($\sigma_A(\text{Nd}^{3+}) \approx 2.6 \times 10^{-20} \text{ cm}^2$) [14]. The detailed calculations of improvement of the pumping efficiency in YAG:Nd, Ce by $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ radiative transfer are given in [10].

A question arises what is the contribution of nonradiative energy transfer to the radiative $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ one. This problem can be studied from shortening of fluorescence decays of donor ions (Ce^{3+}) if various acceptor (Nd^{3+}) concentrations are present [15-18]. The Ce^{3+} fluorescence lifetimes of YAG:Ce or YAG:Nd, Ce crystals are in the range 47-120 ns [10, 13, 19-24] but the intrinsic Ce^{3+} fluorescence lifetime is most probably ≈ 60 ns [22, 24]. The Ce^{3+} lifetimes exceeding 60 ns are caused by migration of excitation energy among Ce^{3+} ions or by their interaction with defect centres [22, 24], especially if Ce concentrations are high. Also, a way of excitation (by photons or by electron beam) may influence the Ce^{3+} decays in YAG [21, 23].

The presented paper brings new results on the study of energy transfer mechanisms between Ce^{3+} and Nd^{3+} in YAG:Nd, Ce crystals at low temperature. In section 2, we make a brief summary of the theory of energy transfer mechanisms between two impurity ions (donors and acceptors) in crystals. Section 3 is devoted to a presentation of the experimental Ce^{3+} decays obtained at low temperature which exhibit a shortening up to 32 ns. The various possibilities of energy transfer mechanisms, distribution of impurities and fitting procedures are discussed and calculated.

2. Energy transfer mechanisms between two impurity (donors and acceptors) ions in crystals.

Various energy transfer mechanisms between two impurity ions have been treated extensively by a lot of researchers since the early works of Förster and Dexter [15, 16]. The results of their treatments are summarized in several significant papers [15-18, 25-30]. The donor-acceptor transfer mechanisms are resonant radiative and non-radiative, nonresonant radiative or non-radiative [27, 28, 31].

The resonant radiative energy transfer between donor and acceptor ions depends on size and shape of the crystal. The structure of donor fluorescence depends on acceptor concentration but the donor lifetime does not change with acceptor concentration [29]. The probability W_{DA} of this transfer is given by formula

$$W_{\text{DA}} = \frac{\sigma_A}{4\pi R^2 \tau_0} \int f_D(E) F_A(E) dE \quad (1)$$

where σ_A is integrated absorption cross section of

acceptor (A) ion, R the distance between D and A ions, τ_0 the intrinsic lifetime of donor (D) ion, $f_D(E)$ and $F_A(E)$ are normalized fluorescence spectrum of donor ion and normalized absorption spectrum of acceptor ion, respectively.

The resonant nonradiative energy transfer between donor and acceptor ions arises *via* multipolar or exchange couplings [15, 16]. Intrinsic decay processes of donor and acceptor ions can be accompanied by direct transfer of excitation energy from donor to nearby acceptor or by more complicated processes including migration of excitation energy between donor ions. Both these transfer processes do not result in fluorescence of donor ions but shorten donor fluorescence decays. They can be investigated from donor fluorescence decay curves under pulsed laser excitation or from quantum efficiency measurements [27, 30].

The case without diffusion between donor ions was treated by Inokuti and Hirayama [23] which used Förster and Dexter's results for multipolar or exchange interactions [15, 16]. For multipolar electric interaction the intensity of donor fluorescence $\phi(t)$ is given by

$$\phi(t) = \phi(0) \exp\left(-\frac{t}{\tau_0}\right) \times \exp\left[-\frac{4\pi}{3} N_A R_0^3 \Gamma\left(1 - \frac{3}{s}\right) \left(\frac{t}{\tau_0}\right)^{3/s}\right] \quad (2)$$

where $\phi(0)$ is the intensity at $t = 0$ when excitation is stopped, τ_0 the intrinsic donor fluorescence lifetime if no acceptor ions are present, N_A the concentration of acceptor ions, R_0 the critical distance, $\Gamma\left(1 - \frac{3}{s}\right)$ the Euler's function, $s = 6, 8$ or 10 the coefficient for dipole-dipole, quadrupole-dipole and quadrupole-quadrupole interaction, respectively. The critical distance R_0 (equal donor-acceptor separation where the probability of transfer $P_{\text{DA}} = \frac{1}{\tau_0}$) can be written as [17]

$$R_0^6 = \frac{3\hbar^4 c^4}{4\pi} Q_A \frac{1}{n^4} \int \frac{f_D(E) F_A(E)}{E^4} dE \quad (3)$$

where $Q_A = k^{(s)}$, f is constant of multipolar interaction, f the oscillator strength and n the index of refraction.

The case when energy diffusion between donor ions is not negligible was treated by Yokota and Tanimoto [26] from diffusion equation. For random distribution of acceptors and for small diffusion constant D between donor ions, the donor excitation density is

$$\phi(t) = \phi(0) \exp\left(-\frac{t}{\tau_0}\right) \times \exp\left[-\frac{4}{3} \pi^{3/2} N_A (\alpha t)^{1/2}\right] \times \left(\frac{1 + 10.87x + 15.5x^2}{1 + 8.74x}\right)^{3/4} \quad (4)$$

when $x = D\alpha^{-1/3}t^{2/3}$ and $\alpha = \frac{R_0^s}{\tau_0}$. At early times ($x \ll 1$) diffusion is not important and only donors with nearby acceptors are decaying. The opposite case is long time limit where only donors that are still excited are those far away from any acceptor. Then, donor lifetime is expressed by

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_D}$$

where τ_D is decay rate *via* donor diffusion. This equation means that the diffusion between donor ions can be neglected if final parts of decays tend to the same slope (to intrinsic lifetime τ_0).

The last case of energy transfer mechanisms are nonresonant radiative or nonradiative energy transfers [31]. The excitation energy is transferred with the assistance of one or two phonons. These transfer mechanisms depend on ion concentrations because at very low concentrations the phonon-assisted radiative transfer prevails while at high concentrations nonradiative couplings are dominant.

3. Experiments.

The fluorescence decays and spectra measurements were made at liquid helium temperature in order to complete the previous investigation of $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer in YAG : Nd, Ce at liquid nitrogen and room temperatures [10] and to exclude any phonon assistance or influence of photoionisation processes between Ce^{3+} ions and lattice traps [32, 33]. The Ce^{3+} fluorescence ($\lambda_p \approx 555$ nm) was excited by tunable dye laser Quantel pumped by 3rd harmonic of YAG : Nd pulsed laser (repetition rate 10 pps, pulsewidth ≈ 10 ns). The outcoming fluorescence was detected by cooled photomultiplier C31034A and processed by Ortec photon counting system. The experiments were piloted by Tektronix 4051 computer and the decays were measured by an H-P 1980 B Oscilloscope Measurement System (fast Ce^{3+} decays) and by an IN90 Intertechnique multichannel analyser (long Nd^{3+} decays). The fitting of the decay curves was made by computer Tektronix 4051.

The Ce^{3+} and Nd^{3+} fluorescence (emission, decay) have been studied on three doped and codoped YAG single crystal (activated by Nd^{3+} and coactivated by Ce^{3+} and Cr^{3+}). The concentrations were calculated from expression $N = \alpha_{\text{Peak}} / \sigma_{\text{Peak}}$ where α_{Peak} and σ_{Peak} are peak absorption coefficient and cross section, respectively. α_{Peak} were determined from absorption spectra (performed on Cary 17 spectrophotometer) and the used peak absorption cross sections were

$$\sigma_{\text{Peak}}(\text{Nd}^{3+}) \approx 2.6 \times 10^{-20} \text{ cm}^2 \quad [14]$$

and

$$\sigma_{\text{Peak}}(\text{Ce}^{3+}) \approx 1.8 \times 10^{-18} \text{ cm}^2 \quad [13, 20].$$

All concentrations are related to Y^{3+} content in YAG (in atomic percent) and are summarized in table I. All

measured samples were cut from central parts of YAG crystals (facette free parts). The detail measurements of concentrations of various impurities on similar YAG : Nd crystals performed by neutron activation analysis [34] shown agreement with our determination of concentrations described above. Cr concentrations were too weak (below 50 ppm) to be measured accurately.

YAG : Ce (n° (1)) and YAG : Nd, Ce (n° (2) and n° (3)) samples were selected from various crystals having Nd^{3+} concentrations in the range 0.75-1.0 at. % and Ce^{3+} concentrations from 0.002 to 0.19 at. %. The usual dimensions of the samples were roughly 5×5 mm but their thickness varied from ≈ 0.15 to 3 mm in order to exclude the surface excitation, especially for YAG : Ce crystal with higher concentration. The measured concentrations are typical for YAG : Nd, Ce laser rods and their selection was performed also from further reason because of elimination of Nd^{3+} fluorescence quenching by cross relaxation [32] which appears if Nd^{3+} concentrations exceeds 1 at. % and which could alter the efficiency of $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer mechanisms. The presented results and the previous ones [10] show that $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ transfer in YAG : Nd, Ce crystals is *via* both radiative and nonradiative mechanisms. The radiative mechanism was clearly detected from dips in Ce^{3+} fluorescence spectrum (see Fig. 1) observed both at low and higher temperatures [10].

The nonradiative resonant $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer has been detected from shortening of Ce^{3+} fluorescence decays at liquid helium temperature (see Table I and Fig. 2). The Ce^{3+} fluorescence lifetimes shorten from intrinsic value $\tau_0 \approx 60$ ns (evaluated from Ce^{3+} fluorescence decay of YAG : Ce sample (1), Fig. 3) to ≈ 32 ns if Nd concentration increases. No longer

Fig. 1. — Part of Ce^{3+} fluorescence spectrum of YAG : Nd, Ce crystal for two different pathways of Ce^{3+} emission through the crystal at room temperature (dips correspond with Nd^{3+} absorption levels in YAG : Nd, Ce).

Table I. — Concentration of Nd^{3+} and Ce^{3+} ions in the studied YAG : Ce, YAG : Nd, Ce and YAG : Nd, Ce, Cr crystal samples. $R(N_A)$ and $R(N_D)$ are the average distances between ions calculated according to equation (6), $R(C_i)$ combined density of both ions and $\tau_{1/e}$ experimental Ce^{3+} lifetime (equal time at which the intensity decreases to I_0/e).

n°	Sample	$N_A(\text{Nd}^{3+})$ [at. %]	$N_D(\text{Ce}^{3+})$ [at. %]	$R(N_A)$ [nm] (6)	$R(N_D)$ [nm] (6)	$R(C_i)$ [nm] [36]	$\tau_{1/e}(\text{Ce}^{3+})$ [ns]
(1)	YAG : Ce	—	0.19	—	2.09	—	61.1
(2)	YAG : Nd, Ce	0.73	0.003	1.33	8.32	2.66	39.0
(3)	YAG : Nd, Ce, Cr	0.88	0.02	1.25	4.42	2.48	32.0

Fig. 2. — Semilogarithmic plot of the Ce^{3+} fluorescence decays in single doped YAG (curve (1), sample (1) and in double doped YAG by Nd^{3+} and Ce^{3+} , curves (2) and (3), samples (2) and (3), respectively) at 4.4 K. The dashed lines indicate slopes of final parts of decay curves.

Fig. 3. — Semilogarithmic plot of the Ce^{3+} fluorescence decay of YAG : Ce crystal (1) at 4.4 K.

Ce^{3+} lifetimes exceeding 60 ns have been observed on the studied samples. The Ce^{3+} fluorescence decay curves at low temperature (if Nd^{3+} ions are present) exhibit deviations from single exponential at short time but their tails return to exponential shape approaching nearly the shape of Ce^{3+} intrinsic decay. This nonexponential behaviour of Ce^{3+} decays at low temperature in YAG : Nd, Ce crystals starts from very low Ce^{3+} concentrations (≈ 0.003 at. % Ce^{3+}).

4. Discussion.

4.1 Ce^{3+} AND Nd^{3+} ENERGY LEVELS AND TRANSITIONS IN YAG : Nd, Ce. — The energy transfer mechanisms between Ce^{3+} and Nd^{3+} in YAG : Nd, Ce can be discussed on the basis of the knowledge of the nature of Ce^{3+} and Nd^{3+} energy levels and transitions. Energy level diagrams of these ions in YAG are given in figure 4. $4f^1 \leftrightarrow 4f^05d^1$ transitions of Ce^{3+} are allowed transitions of electric dipole character [11]. Radiationless transitions of Ce^{3+} ion in YAG are not important at low and room temperatures because increase substantially at temperatures above 600 K

Fig. 4. — The configurational coordinate model of Ce^{3+} and Nd^{3+} energy levels in YAG : Nd, Ce crystal. Vertical lines represent radiative transitions.

[12]. We can see from figure 4 that there is resonance between Ce^{3+} absorption transition $^2\text{F}_{5/2} \rightarrow$ first 5d excited state and one of the transition $^4\text{I}_{9/2} \rightarrow$ higher lying Nd^{3+} levels. But exact determination of Nd^{3+} level participating to the resonance is not possible due to the richness of Nd^{3+} levels and the lack of information about exact positions of Nd^{3+} levels in YAG. The position of Ce^{3+} levels in YAG was roughly determined from photoconductivity measurements (the ground Ce^{3+} state $^2\text{F}_{5/2}$ is approximatively $30\,600\text{ cm}^{-1}$ below the bottom of YAG conduction band [33]).

Nd^{3+} energy levels arise from $4f^3$ electronic configuration and higher lying $4f^25d$ states but the later states are too high and probably completely in the conduction band. The transitions among $4f^3$ electronic levels are forbidden in a free ion but are forced by the odd parity terms of the crystal field arising from point charges of the ligands [35]. These perturbations induce electric-quadrupole and magnetic-quadrupole transitions. The electric dipole transitions may arise as consequence of interaction between electronic and vibrational states. For $\text{Nd}^{3+}4f^3$ configuration some transitions are spin-allowed ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}, \dots$) but this is not valid for the remaining ones. All these data are evidences that various dipole or quadrupole transitions arise among Nd^{3+} levels in YAG.

4.2 DIFFUSION PROBLEM IN YAG:Nd, Ce. — The nonradiative energy transfers may be influenced by diffusion among donor ions [26, 27, 36]. Owing to that donor Ce^{3+} concentrations are weak and the long time parts of Ce^{3+} decay curves have nearly exponential shape with roughly the same slope (in log scale) as the decay curve of YAG:Ce sample, the diffusion between Ce^{3+} ions can be considered as very weak (according to expression $\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_D}$ below equation (4) in the second part of this paper). In order to check this assumption we have calculated the diffusion constant D from Yokota and Tanimoto's theory [26] with the formula given in [30, 36]

$$\frac{1}{\tau_D} = 11.4 N_A \alpha^{1/4} D^{3/4}. \quad (5)$$

The evaluation of diffusion constant gives value $D \approx 9.2 \times 10^{-11} \text{ cm}^2/\text{s}$ which is smaller than typical values D ($10^{-11} \leq D \leq 10^{-5} \text{ cm}^2/\text{s}$) [36]. Also the calculated diffusion length for our samples according to equation $l = (6 D \tau_0)^{1/2}$ [37] is about $5.8 \times 10^{-2} \text{ nm}$ and much smaller than average distance between Ce^{3+} ions. This weak diffusion may be explained by the Stokes shift occurring in Ce^{3+} centre (see Fig. 4) and leading to the absence of resonance condition between various Ce^{3+} donors; the situation can change at higher temperatures and at high concentrations where strong excited-state absorption and photoionization are observed [13, 20, 33].

4.3 CONDITIONS OF $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ DONOR-ACCEPTOR TRANSFER IN YAG:Nd, Ce. — Brief review theories of energy transfer mechanisms was given in part 2. Discussion of conditions in our YAG:Nd, Ce crystals allow us to select the best procedure to fit the experimentally observed data. The preceding part shows that we can neglect the diffusion among Ce^{3+} ions for our samples. Some other ideas can be obtained from calculations of average distances between Ce and Nd in YAG lattice. The average distances between donor or acceptors are given by formula [5]

$$R = \left(\frac{3}{4\pi} \right) N_{D(A)}^{-1/3} \quad (6)$$

where $N_{D(A)}$ is donor or acceptor concentration. For combined density of both ions the similar formula was derived with exception of a multiplication factor 2 [36]. The average distances between donors, acceptors and for combined density are given in table I. In our case, the average distance between Nd^{3+} and Ce^{3+} is determined mainly by the distance between Nd^{3+} acceptor ions (Ce^{3+} ions are embedded into « sublattice » of much more Nd^{3+} ions). It means that variously distant Ce^{3+} - Nd^{3+} donor-acceptor pairs arise.

The distribution of Nd^{3+} ions in the studied crystals will be probably rather random character as results, for example, from the measurements of Nd^{3+} fluorescence spectra at low temperatures. The Nd^{3+} fluorescence spectra of our samples do not exhibit inhomogeneous splitting due to significant local changes around Nd^{3+} ions which arises if pairs are present or other ions replace the nearest neighbours of Nd^{3+} ions [2, 10, 18, 37]. The fluorescence of one $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ emission lines at low temperature is presented in figure 5. This spectrum consists of only one peak and very weak peaks could be identified in the wings of the main peak (they arise probably due to deviations in statistical distribution of both ions in YAG). Figure 6 shows a part of tight YAG structure [38]. One can see that all metal or rare earth ions are bound *via* oxygen

Fig. 5. — $^4\text{F}_{3/2}(a) \rightarrow ^4\text{I}_{9/2}(1)$ fluorescence of Nd^{3+} of YAG:Nd, Ce sample (2) at 4.4 K excited by tunable laser wavelength $\lambda = 444 \text{ nm}$.

Fig. 6. — Part of the tight garnet structure with dodecahedral, octahedral and tetrahedral sites of the metal and rare earth ions. Average distances are : $\bar{r}_1 = 0.2328$ or 0.2434 nm, $\bar{r}_2 = 0.1954$ nm, $\bar{r}_3 = 0.1807$ nm and $\bar{r}_{Y^{3+}-Y^{3+}} \leq 0.4762$ nm [38].

(O²⁻) ions. This should exclude an exchange interaction between Ce³⁺ and Nd³⁺ and also a presence of Ce³⁺ near Nd³⁺ ions. The later can also be excluded from ionic radii of ions. The ionic radii of both Ce³⁺ and Nd³⁺ ($r_i(\text{Ce}^{3+}) \approx 0.114$ nm, $r_i(\text{Nd}^{3+}) \approx 0.112$ nm) exceed that of Y³⁺ ($r_i(\text{Y}^{3+}) \approx 0.102$ nm) ions which replace mainly. This substitution building of Ce³⁺ and Nd³⁺ ions into YAG lattice does not need charge compensation and no or a small amount of charge compensation defects arise. The above given conditions lead to conclusion that the measured crystals exhibit rather random distribution of Nd³⁺ ions and variously distant Ce³⁺-Nd³⁺ donor-acceptor pairs. This and no diffusion between Ce³⁺ ions (see preceding part 4.3) show that we can use Inokuti-Hirayama's model (Eq. (2)) to fit the experimentally observed Ce³⁺ decays at low temperature.

4.4 RESULTS OF FITTINGS FOR VARIOUS MULTIPO-LAR INTERACTION. — Ce³⁺ decay curve of YAG : Ce sample (1) is purely exponential (Fig. 3) with time constant of $\tau_0 \approx 60$ ns which represents the Ce³⁺ intrinsic lifetime. Figures 7-10 show the results of fittings according to equation (2) for dipole-dipole and quadrupole-dipole couplings for the given donor-acceptor concentrations (see Table I) of the samples (2) and (3). The standard least square method was used for these fittings with parameter R_0 (critical distance). Reasonably good agreement with the experimental

Fig. 7. — Fluorescence decay of Ce³⁺ of the sample (2) in the presence of Nd³⁺ ions fitted to Inokuti-Hirayama's equation for dipole-dipole interaction (—) at $T = 4.4$ K; ... are experimental points.

Fig. 8. — Fluorescence decay of Ce³⁺ of the sample (3) in the presence Nd³⁺ ions fitted to Inokuti-Hirayama's equation for dipole-dipole interaction (—) at $T = 4.4$ K; ... are experimental points.

curves were obtained for an average critical distance $R_0 \approx 1.1$ nm which reflects the situation that variously distant Ce³⁺-Nd³⁺ donor-acceptor pairs participate in both couplings.

Table II. — Critical distances R_0 of Ce³⁺ → Nd³⁺ nonradiative energy transfer at low temperature for D-D and Q-D interactions and their average values.

n°	Sample	$R_0(\text{D-D})$ [nm]	$R_0(\text{Q-D})$ [nm]	$R_0(\text{ave})$ [nm]
(2)	YAG : Nd, Ce	0.99	1.18	1.09
(3)	YAG : Nd, Ce, Cr	1.01	1.21	1.11
$R_0(\text{D-D}) \cong 1$ nm ; $R_0(\text{Q-D}) \cong 1.2$ nm

Fig. 9. — Fluorescence decay of Ce^{3+} of the sample (2) in the presence of Nd^{3+} ions fitted to Inokuti-Hirayama's equation for quadrupole-dipole interaction (—) at $T = 4.4$ K; ... are experimental points.

Fig. 10. — Fluorescence decay of Ce^{3+} of the sample (3) in the presence of Nd^{3+} ions fitted to Inokuti-Hirayama's equation for quadrupole-dipole interaction (—) at $T = 4.4$ K; ... are experimental points.

The summary of the best fittings for both interaction is given in table II. Generally, the dipole-dipole couplings is effective through greater distances while the quadrupole-dipole one prevails if donor-acceptor distances decrease. The good fittings for both dipole-dipole and quadrupole-dipole couplings mean that at least one type of interaction and may be even both couplings contribute(s) to $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ nonradiative energy transfer in YAG : Nd, Ce for the concentrations used. Similar behaviour was observed by one of us (Boulon [30, 36]) for nonradiative transfer $\text{Bi}^{3+} \rightarrow \text{Eu}^{3+}$ in germanate glass where the contribution of quadrupole-dipole coupling increases with the increase of acceptor Eu^{3+} concentration above 1 at. % ($R_0 \approx 0.9$ nm at low temperature).

The average critical distance R_0 for nonradiative $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer has been calculated from equation (3) for dipole-dipole interaction. This calculated value $R_0 \approx 0.3$ nm is too small in comparison with the average fitted value $R_0 \approx 1.1$ nm. Calculation of R_0 can be affected by the fact that there is radiative $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ transfer which makes the evaluation of overlap integral very inappropriate and also the coefficient of dipole-dipole interaction was roughly estimated.

5. Conclusion.

In conclusion, the main results of this study can be summarized by the following :

(1) $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer in YAG : Nd, Ce crystals occurs by both radiative and nonradiative mechanisms at low temperature.

(2) The diffusion among Ce^{3+} donor ions is negligible for the used weak Ce^{3+} concentrations.

(3) Nonradiative resonant $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer is *via* dipole-dipole and quadrupole-dipole couplings for the concentrations used (0.003-0.02 at % Ce^{3+} and below 1.0 at. % for Nd^{3+}). Contribution of quadrupole-dipole coupling appears by those donor-acceptor Ce^{3+} - Nd^{3+} pairs with shorter distances.

(4) The average critical distance $R_0 \approx 1.1$ nm for $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ nonradiative transfer was determined from equation (2).

Further investigations are underway to get the knowledge about the excited states close to the conduction band by using both photoconductivity and two-photon Nd^{3+} absorption.

From application point of view the codoping of YAG : Nd by Ce is advantageous and now is used in wide scale for improving of YAG : Nd laser rods [7, 9]. The $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ radiative and nonradiative energy transfers lead to the increase of the Nd^{3+} pumping efficiency by using UV and blue part of radiation of conventional Xe flashlamp where is a lack of efficient Nd^{3+} absorption lines (some of Xe flashlamps have considerable distribution in the near UV and blue ranges). Until now, with except of YAG : Nd, Ce crystals [7, 8, 10], the only another application of $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer is its use in laser glass ED2 [4]. The estimation how $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfers improve pumping efficiency of Nd lasers was given by one of us (Mares) in [10] for radiative $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ transfer in YAG : Nd, Ce and by Jacobs *et al.* [4] for $\text{Ce}^{3+} \rightarrow \text{Nd}^{3+}$ transfer in laser glass ED2. Both these applications give evidence that the Ce^{3+} - Nd^{3+} impurity system could also be used in similar garnet or solid state laser crystals, glasses and materials for transfer of UV and blue parts of radiation into green, yellow and red ranges or even into near infrared (*via* Nd^{3+} emission peaking around 870 and 1 064 nm).

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