THE EXCITATION DENSITY EFFECT ON THE FLUORESCENT DECAY TIMES OF Nd PENTAPHOSPHATE SINGLE CRYSTAL*

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The dependence of the decay times of the NdP_5O_{14} single crystal on the excitation density was studied in a region of small excitation of a sample. The lengthening of the decay times with decrease of the excited molecule number has been observed. The implication of the obtained results for the concept of energy migration in highly concentrated crystal is discussed.

1. Introduction

In the last few years the Nd stoichiometric laser materials characterizing a small concentration quenching of fluorescence were a subject to intensive experimental and theoretical investigations [1–6]. In general the knowledge of the Stark structure of the Nd^{3+} levels ($^4F_{3/2}$, $^4I_{15/2}$ and $^4I_{13/2}$) allows [1] to anticipate the fluorescence behaviour of the different neodymium doped crystals. Nevertheless, the concentration quenching of the fluorescence in highly concentrated Nd crystals characterizes a different (linear) dependence [2–4], $k \sim N$, contrary to the other Nd materials described by the well known Förster relation, $k \sim N^2$. It was suggested [4] that in the Nd crystals with unusually weak cross-relaxation the quenching constant $k \sim p(1-p)N^2$, where $p = N_d/N$ is a number characterizing the ratio of the excited ions to the total number of Nd ions. In a small excitation limit, $p \ll 1$, the linear dependence, $k \sim N_d \cdot N$, should be observed.

In this paper we present the results of the decay time measurements of the single NdP_5O_{14} crystal in dependence on the excitation density. The obtained results throw the new light on the mechanism of energy migration in highly concentrated Nd materials.

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2. Experimental part

The NdP_5O_{14} crystals were grown from the phosphoric acid solution according to the method described by Danielmayer et al. [6]. The fluorescence decay times of the crystals for the crystal powder sample were determined to be 80 μsec. In the experiment we have used a single crystal of thickness 0.03 cm and area 0.03 cm^2. A single crystal was pumped by the Q-switched ruby laser pulse ($\lambda = 0.694$ μm, pulse duration 40 nsec). The crystal absorption for the laser line was determined to be $\alpha = 0.09$. The experimental setup is shown in Fig. 1. The laser beam with energy of 0.01 J was focused on a crystal sample. The density of the excited ions was calculated from relation $D = E(Vh\nu_L)^{-1}$, where E is the energy absorbed by crystal, determined in our experiment to be 1.8 μJ, $h\nu_L$ is the energy

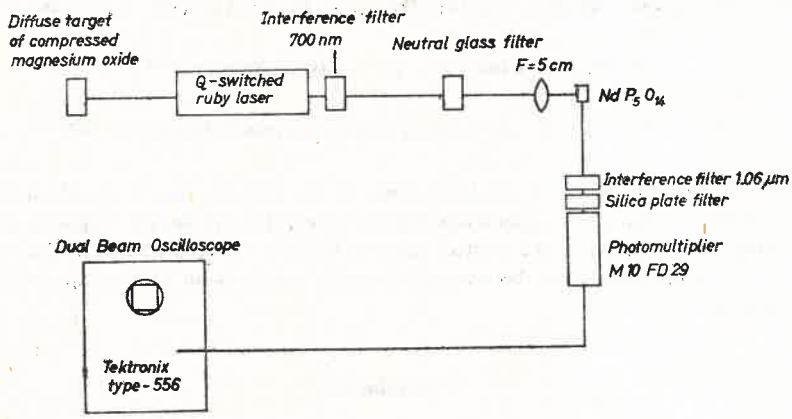

Fig. 1. Experimental setup

of laser photon, $h\nu_L = 2.87 \cdot 10^{-19}$J, and V is the absorbing volume. With this excitation we have estimated $D = 2.7 \cdot 10^{19}$ ions/cm^3. It means that less than 1% Nd ions were excited during the experiment. The concentration of the Nd ions in crystal is $4.1 \cdot 10^{21}$ cm^{-3}. The intensity of the laser beam exciting a crystal sample was lowered by means of the neutral glass filters. The neodymium fluorescence of the NdP_5O_{14} sample induced by the laser pulse was measured with the photomultiplier M10 FD29 C. Zeiss Jena and recorded on a Tektronix 556 oscilloscope and next photographed. The intensities of the fluorescent decay curves in peaks ($t = 0$) are assumed to be proportional to the excitation density. Figure 2 shows the variation of the fluorescent decay curves of the NdP_5O_{14} crystal on the relative intensities of the excitation.

3. Discussion

The dependence of the measured decay times on the excitation density have been reported for the first time for the NdP_5O_{14} crystal by Blätte et al. [7] who have pumped the crystal using a pulsed dye laser tuned to 5810 Å. For the excitation density about $2 \cdot 10^{20}$ cm^{-3} the measured lifetime was 66 μsec. At the excitation density $2 \cdot 10^{21}$ cm^{-3}

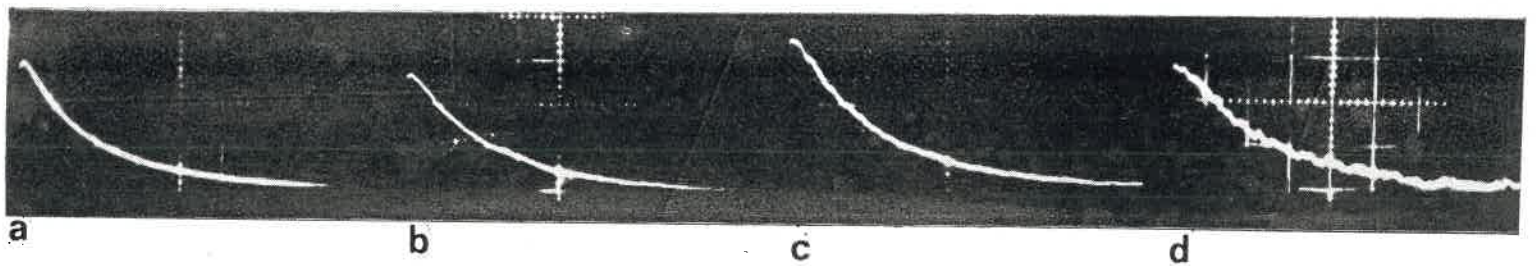

Fig. 2. The fluorescent decay curves of NdP_5O_{14}. The time scale is 50 μsec/division. A. $I_R = 14, \tau = 80$ μsec; B. $I_R = 5.2$, $\tau = 100$ μsec; C. $I_R = 2.4$, $\tau = 110$ μsec; D. $I_R = 0.14$, $\tau = 130$ μsec

the measured decay time was shortened to 25 μsec. A similar phenomenon was observed in ruby by Neeland and Evtuhov [8] and in $PrCl_3$ by German and Kiel [9]. In these experiments the lifetime shortening was explained by the competitive stimulated emission.

The dependence of the decay time on the excitation density in small excitation limit, where the stimulated emission can be excluded, was reported for the first time for the NdP_5O_{14} by Stręk et al. [10]. The dependence of the observed decay rates for the NdP_5O_{14} sample on the relative excitation intensity is plotted in Fig. 3. The relative intensity in our experiment was changed from $I_R = 14$ corresponding to $\tau = 80$ μsec to $I_R = 0.14$ corresponding to $\tau = 130$ μsec. From the experimental conditions we have estimated the upper limit of the excitation density to be $D = 2.7 \cdot 10^{19}$ cm^{-3}, exciting less than 1% neodymium

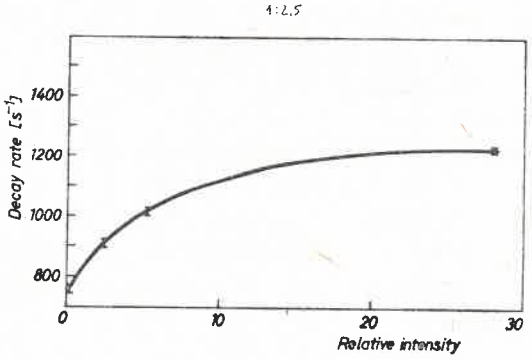

Fig. 3. The dependence of the decay rate constants on the relative excitation intensities

ions in a sample. At a relative intensity $I_R = 0.14$ we have excited less than 0.01% ions. That estimation allows us to exclude the competitive stimulated emission to be responsible for the lifetime shortening for the NdP_5O_{14} crystal.

Recently also Flaherty and Powell [11] have reported the dependence of the fluorescence decay time for the NdP_5O_{14} crystal on the laser excitation wavelength. The fluorescence lifetime of the $^4F_{3/2}$ level was measured pumping selectively into various parts of the $^4G_{5/2,7/2}$ absorption band. The fluorescent lifetime was 67 μsec for $\lambda_{exc} = 5784.5$ Å whereas $\lambda_{exc} = 5837$ Å it was 77 μsec. It is obvious that their results could be also interpreted in terms of the excitation density effect.

To understand the observed dependence of the fluorescent decay time on the excitation density we first refer to our model of the concentration quenching of fluorescence in highly concentrated Nd crystal [1, 4, 10]. In the diffusion model of fluorescence quenching it is assumed that the probability of excitation $\varphi(r, t)$ is described by diffusion equation

$$\partial\varphi(r, t)/\partial t = D\nabla^2\varphi(r, t) - \sum_i C_{da}/r_i^6 \varphi(r, t) - 1/\tau_0 \varphi(r, t), \tag{1}$$

where D is the diffusion constant, τ_0 a relaxation time due to the spontaneous emission and nonradiative relaxation, and C_{da} the donor–acceptor interaction constant. For a large diffusion constant when $DC_{da}^{-1/3}t^{2/3} \gg 1$ the fluorescent decay curve may be approximated

by an exponential function [1] with the decay time

$$\frac{1}{\tau} = \frac{1}{\tau_0} + 31.4p(1-p)\,(C_{da}C_{dd}^3)^{1/4}N^2, \tag{2}$$

where C_{dd} is the donor–donor interaction constant. This equation revealed that in the region of small excitation density, $p(1-p) \sim p$, the decay rate should vary linearly from p. However, it was not confirmed by the nonlinear dependence observed in experiment (Fig. 3). Moreover, the shortening of the measured decay times is the process slower than it should be expected from Eq. (2).

In seeking an explanation for this unusual results, we would like to point out the possibility of a greater role of the radiative spatial energy transfer in energy migration in the NdP_5O_{14} crystal, than it was assumed. Recently, Selzer, Yen and Hamilton [12, 13] have discovered a new kind of the radiative concentration independent of spectral energy transfer in ruby. The lifetime measured in the experiment was dependent on the geometry and varied between 3.8–20 msec.

Referring to our experiment, the excitation density effect may also be interpreted as the excitation geometry variation. One can expect, therefore, that a systematic experimental studies of the spatially-spectral energy transfer in the highly concentrated Nd crystal are indispensable. A proper theoretical description of the phenomenon of the excitation density effect on the fluorescent decay rates should be based upon solution of the spatially dependent diffusion equation.

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