

Up-conversion and excitation energy transfer between impurity ions in $\text{Pr}^{3+} : \text{Y}_2\text{SiO}_5$, $\text{Pr}^{3+} : \text{Lu}_2\text{SiO}_5$, and $\text{Pr}^{3+} : \text{Gd}_2\text{SiO}_5$ crystals

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Abstract. Anti-Stokes fluorescence from the 3P_0 level of impurity ions was detected in $\text{Pr}^{3+} : \text{Y}_2\text{SiO}_5$, $\text{Pr}^{3+} : \text{Lu}_2\text{SiO}_5$, and $\text{Pr}^{3+} : \text{Gd}_2\text{SiO}_5$ crystals non-resonantly pumped by laser radiation with a certain power density. The integrated intensity of the anti-Stokes fluorescence depends nonlinearly on the pump power density. As the atomic concentration of impurity ions was increased from 0.3% to 0.6% and 1.8%, the anti-Stokes fluorescence intensity was saturated due to the concentration quenching of the 1D_2 term of the impurity Pr^{3+} ions. The anti-Stokes fluorescence and quenching of the 1D_2 term occur due to the cross relaxation of the electronic energy of excited terms of the Pr^{3+} ions.

Keywords: up-conversion, impurity rare-earth ions.

1. Introduction

The study of mechanisms of excitation of high energy levels of impurity rare-earth ions (REIs) upon their multiphoton pumping or due to summation of electronic excitations in an ensemble of interacting ions is a very important field of investigations closely related to the development of IR-pumped solid lasers [1–3]. Excitation of the energy levels of REIs due to summation of photons of substantially lower energies has been called the frequency up-conversion [4]. A high efficiency of various up-conversion schemes using the energy levels of REIs is related to the peculiarities of their electronic spectra and, first of all, to the presence of several metastable states and the relatively slow nonradiative relaxation of intermediate electronic levels [5, 6].

At present, a great number of up-conversion experiments have been performed with many REIs [2–4]. It is important to note that several schemes can be realised for one REI, which provide excitation of high energy levels by summing photons of substantially lower energies. This can be demonstrated by the example of the trivalent Pr^{3+} ion [7–10]. Because the position of the energy levels of impurity

REIs changes insignificantly with changing a crystal matrix, we will use the generalised energy level diagram of the Pr^{3+} ion shown in Fig. 1.

In Ref. [7], the 3P_0 term of the Pr^{3+} ion was excited due to up-conversion through the intermediate 1G_4 term using two pump photons at wavelengths 1.01 and 0.93 μm . The first photon at 1.01 μm resonantly excited the $^3H_4 \rightarrow ^1G_4$ transition (3H_4 is the ground-state term), while the second photon excited the $^1G_4 \rightarrow ^3P_0$ transition [7]. It was shown in Ref. [7] that the 3P_0 term can be also excited due to two-photon absorption of the 0.93- μm radiation at the $^3H_4 \rightarrow ^1G_6$ transition. In Ref. [8], other methods of excitation of the 3P_0 term of the Pr^{3+} ions were realised. In the first case, one-frequency pumping at 0.576 μm was used, when the first photon excited resonantly the $^3H_4 \rightarrow ^1D_2$ transition, while the second photon excited the $^3H_6 \rightarrow ^3P_0$ transition. The 3H_6

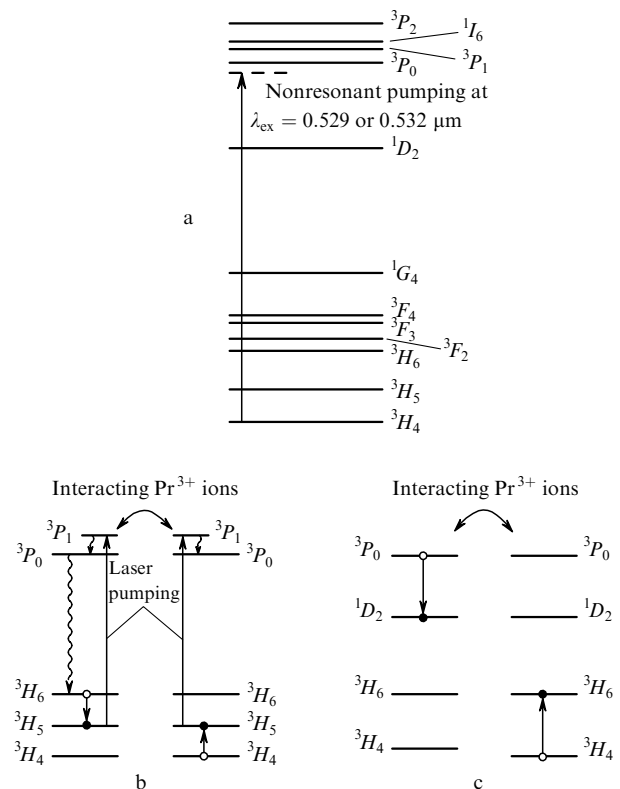


Figure 1. Energy level diagram of the impurity Pr^{3+} ion (a) and the schemes of cross relaxation of the excited 3H_6 (b) and 3P_0 (c) terms upon interaction between two Pr^{3+} ions.

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term was populated due to the radiative ${}^1D_2 \rightarrow {}^3H_6$ relaxation. In the second case, two-stage excitation was used: the first photon at 2.18 μm excited the ${}^3H_4 \rightarrow {}^3H_6$ transition, while the second photon at 0.579 μm excited the ${}^3H_6 \rightarrow {}^3P_1$ transition. The 3P_0 state was populated due to the subsequent intracentre nonradiative ${}^3P_1 \rightarrow {}^3P_0$ relaxation.

A substantially different up-conversion scheme was used to pump a $\text{Pr}^{3+} : \text{LaCl}_3$ crystal [11]. In this case, the 3P_0 state of the impurity Pr^{3+} ions was excited by the non-resonant cw 0.529- μm laser radiation when the pump power density exceeded a certain threshold value. The difference between the pump photon and nearest 3P_0 term energies was $\sim 1146 \text{ cm}^{-1}$ (see Fig. 1), i.e., the crystal was transparent at the pump frequency below the threshold. This effect was explained in paper [11] in the following way. Despite the absence of an exact resonance, the impurity Pr^{3+} ions are nevertheless excited to the 3P_0 state upon intense laser pumping, probably, due to a weak absorption at the wings of the ${}^3H_4 \rightarrow {}^3P_0$ transition. Due to the subsequent intracentre nonradiative and radiative relaxations of the 3P_0 term, one of the Pr^{3+} ions can transfer to the excited 3H_6 state. It is important that then, after cross relaxation caused by the interaction between two adjacent Pr^{3+} ions (one of them in the excited 3H_6 state), both these ions find themselves in the excited 3H_5 state (Fig. 1b). However, now the 0.529- μm pump radiation is resonant with the ${}^3H_5 \rightarrow {}^3P_1$ transition, and therefore both these ions can be excited by this radiation to the 3P_1 state and can again return to the excited 3P_0 state due to nonradiative relaxation (Fig. 1b). Excitation occurs nonlinearly, and the intensity of fluorescence from the 3P_0 level exhibits an avalanche increase when the pump power density exceeds the threshold [11].

It is important to note that the cross relaxation of the excitation energy of impurity REIs is one of the mechanisms of fluorescence quenching in an ensemble of interaction ions [12, 13]. Cross relaxation causes the quenching of fluorescence of impurity ions from the 3P_0 level in a $\text{LaF}_3 : \text{Pr}^{3+}$ crystal [14]. Therefore, cross relaxation can be behind various effects [12]. However, as a rule, it is difficult to determine the intermediate terms of REIs involved in cross relaxation.

The Y_2SiO_5 , Lu_2SiO_5 , and Gd_2SiO_5 crystals belonging to the family of oxyorthosilicates with the general formula $\text{RE}_2(\text{SiO}_4)\text{O}$ ($\text{RE} = \text{Y}, \text{La}, \text{Gd}, \dots, \text{Lu}$) have a high optical quality, they are transparent in a broad spectral range, and allow a sufficiently high-concentration doping with ions without deterioration of their optical quality. Oxyorthosilicate crystals are used for the extensive search for new laser and scintillation materials. In this paper, we studied the influence of the detuning from the resonance on the excitation efficiency of the anti-Stokes fluorescence of Pr^{3+} ions in Y_2SiO_5 ($\text{Pr} : \text{YSO}$), Lu_2SiO_5 ($\text{Pr} : \text{LSO}$) and Gd_2SiO_5 ($\text{Pr} : \text{GSO}$) matrices pumped by the nonresonant 0.532- μm laser radiation. The relative positions of the terms and their crystal-splitting parameters in these crystals vary weakly [15–18]. We measured the temperature and concentration dependences of the fluorescence intensity at the ${}^3P_0 \rightarrow {}^3H_4$ and ${}^1D_2 \rightarrow {}^3H_4$ transitions in impurity Pr^{3+} ions and showed that the saturation of the anti-Stokes fluorescence intensity with increasing the concentration of Pr^{3+} in the $\text{Pr} : \text{YSO}$ crystal is caused by the quenching of the 1D_2 term. Depending on the method of excitation of the 1D_2 term, there exist two mechanisms of its concentration quenching.

2. Experimental

The $\text{Pr} : \text{YSO}$, $\text{Pr} : \text{LSO}$, and $\text{Pr} : \text{GSO}$ crystals were grown by the Czochralski technique from iridium crucibles. The atomic concentration of praseodymium in the $\text{Pr} : \text{YSO}$ crystals was 0.3 %, 0.6 %, and 1.8 %, and in the $\text{Pr} : \text{LSO}$ and $\text{Pr} : \text{GSO}$ crystals, it was 0.3 %. The $\text{Pr} : \text{YSO}$, $\text{Pr} : \text{LSO}$ crystals and the $\text{Pr} : \text{GSO}$ crystal belong to different structural types [19, 20]. This is reflected first of all by the parameters of their unit cells: $a = 14.43 \text{ \AA}$, $b = 10.41 \text{ \AA}$, $c = 6.733 \text{ \AA}$, $\beta = 122.13$ degree of arc, $V = 856.1 \text{ \AA}^3$ (YSO); $a = 14.33 \text{ \AA}$, $b = 10.32 \text{ \AA}$, $c = 6.671 \text{ \AA}$, $\beta = 122.3$ degree of arc, $V = 833.8 \text{ \AA}^3$ (LSO); and $a = 9.16 \text{ \AA}$, $b = 7.09 \text{ \AA}$, $c = 6.83 \text{ \AA}$, $\beta = 107.58$ degree of arc, $V = 422.9 \text{ \AA}^3$ (GSO) [19, 20]. The unit cell of these crystals has two types of non-equivalent cationic sites with a specific structure of the ligand crystal field [15–18]. For this reason, two types of the optical Pr^{3+} centres with differently split terms are observed in the $\text{Pr} : \text{YSO}$, $\text{Pr} : \text{LSO}$, and $\text{Pr} : \text{GSO}$ crystals [15–18].

In experiments with nonresonant pumping, we used the second harmonic of a single-mode Q -switched cw $\text{Nd} : \text{YAG}$ laser. The laser pulse repetition rate was 6 kHz and the average second-harmonic radiation power was 0.4 W. The laser radiation was focused on a crystal by a lens with a focal distance of 15 cm. Low-temperature measurements were performed using a standard nitrogen optical cryostat, and measurements above 300 K were carried out by means of a stabilised Joule heating of crystals. The system of Joule heating was mounted inside the nitrogen optical cryostat, so that the measurements were performed over the entire temperature range without any additional adjustment of the detection scheme.

The absorption and fluorescence spectra of the crystals were recorded with an MDR-24 grating monochromator equipped with a FEU-100 photomultiplier operating in the photon counting mode. The fluorescence decay curves were measured by the method of single-photon correlation counting [21]. The Pr^{3+} optical centres of the first type with the split term were selectively excited at the ${}^3H_4 \rightarrow {}^3P_0$ transition by a cw Ar^+ laser with an external acousto-optic modulator.

3. Experimental results and discussion

The relative positions of the 3H_4 , 1D_2 , 3P_0 , and 3P_1 terms and their crystal-field splittings for the two Pr^{3+} optical centres in the $\text{Pr} : \text{YSO}$, $\text{Pr} : \text{LSO}$, and $\text{Pr} : \text{GSO}$ crystals are well known [15–18]. The 3H_4 level is the ground-state term of Pr^{3+} ions. The terms 1D_2 , 3P_0 , and 3P_1 determine the absorption by the Pr^{3+} ions in the optical range [5, 6, 15–17]. The 0.532- μm laser pump radiation falls into the transparency region of the crystals under study (Fig. 2). The difference of the energies of laser photons and the nearest 3P_0 term of optical Pr^{3+} centres of the first and second type in the three crystals under study is, respectively, 1745 and 1914 cm^{-1} (YSO), 1688 and 1878 cm^{-1} (LSO), and 1877 and 1974 cm^{-1} (GSO) (Fig. 2). These energies exceed the corresponding energy for a $\text{Pr}^{3+} : \text{LaCl}_3$ crystal [11]. The energy interval between the 1D_2 and 3P_0 terms for the two optical Pr^{3+} centres is $\sim 5000 \text{ cm}^{-1}$ on average [15–18]. The crystal-field splitting of the ground-state 3H_4 term is $\sim 400 \text{ cm}^{-1}$ [15–17]. Therefore, even taking the Stark components of the term into account, the crystals under study cannot absorb light at a wavelength of

0.532 μm . Unlike the case described in Ref. [11], the frequency of the 0.532- μm laser radiation is resonant with the ${}^3H_5 \rightarrow {}^3P_0$ transition in the Pr : YSO and Pr : LSO crystals (Fig. 1). Therefore, the impurity Pr^{3+} ions in the 3H_5 state can be efficiently excited by this laser radiation (Fig. 1b).

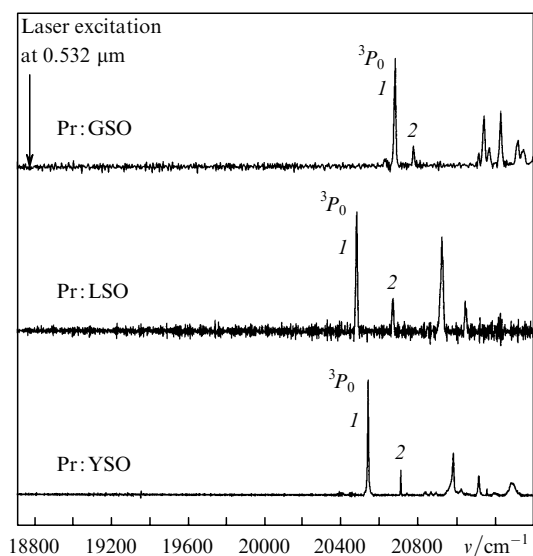


Figure 2. Absorption spectra of crystals in the region of the ${}^3H_4 \rightarrow {}^3P_0$ transition for Pr^{3+} centres of the first (1) and second (2) types. The arrow shows the position of the laser line.

Despite the facts presented above, the absorption in crystals at 0.532 μm drastically increased when the pump power density achieved a certain threshold value ($\sim 10 \text{ W cm}^{-2}$), which was almost the same for all the crystals. This was accompanied by the appearance of fluorescence of impurity Pr^{3+} ions in the Stokes and anti-Stokes regions with respect to the laser line (Fig. 3). This fluorescence can be easily identified using the data [15–18]. The anti-Stokes fluorescence is caused by optical transitions from the excited 3P_0 term to the ground-state 3H_4 term of the impurity Pr^{3+} ions (Fig. 1a). The ${}^3P_0 \rightarrow {}^3H_5$ optical transitions give rise to fluorescence in the anti-Stokes region with respect to the laser line (Fig. 3). The Stokes fluorescence is determined by the ${}^1D_2 \rightarrow {}^3H_4$ transitions (Fig. 1a).

The Pr : YSO, Pr : LSO, and Pr : GSO crystals excited by nonresonant laser radiation exhibited fluorescence of only Pr^{3+} optical centres of the first type [15–18]. This is explained by the fact that the resonance condition for the 3P_0 term of optical Pr^{3+} centres of the first type are better fulfilled and the concentration of optical Pr^{3+} centres of the first type is substantially higher [18]. Due to the nonuniform population of non-equivalent cationic sites in the unit cell of oxyorthosilicates [18], 70 % of the total number of impurity ions belongs to optical centres of the first type.

Therefore, similarly to Ref. [11], the up-conversion of laser pump photons takes place in the Pr : YSO, Pr : LSO, and Pr : GSO crystals due to the population of the 3P_0 state of impurity ions. The efficiency of this process is almost identical for all the crystals under study and is independent

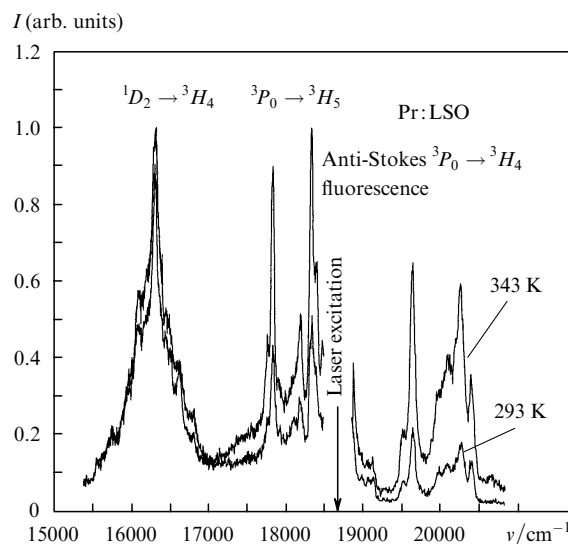


Figure 3. Fluorescence of impurity Pr^{3+} ions in the Pr : LSO crystal pumped by nonresonant laser radiation with the power density above the threshold.

of the pump–frequency detuning from the ${}^3H_4 \rightarrow {}^3P_0$ transition frequency (Figs 1a and 2).

The intensity of the ${}^1D_2 \rightarrow {}^3H_4$ fluorescence of impurity Pr^{3+} ions weakly depends on temperature (Fig. 3). At the same time, the anti-Stokes fluorescence strongly depends on temperature. As the temperature of the Pr : YSO and Pr : LSO crystals was increased, the intensity of the ${}^3P_0 \rightarrow {}^3H_4$ fluorescence increased stronger than that of the ${}^3P_0 \rightarrow {}^3H_5$ fluorescence (Fig. 3). This effect was substantially weaker in the Pr : GSO crystal. Unlike Ref. [11], we have failed to detect this effect at liquid nitrogen temperature. The anti-Stokes fluorescence from the 3P_0 level disappeared at temperature 250 K. Probably, this is explained by a large detuning of the pump laser frequency from the ${}^3H_4 \rightarrow {}^3P_0$ transition frequency. As the crystal temperature was decreased from 300 to 250 K, the integrated intensity of the anti-Stokes fluorescence decreased exponentially as $I \sim \exp[-\Delta/(kT)]$, where the activation energy is $\Delta = 1941 \text{ cm}^{-1}$ (Pr : YSO), 2581 cm^{-1} (Pr : LSO), and 1310 cm^{-1} (Pr : GSO). We cannot explain these values of the activation energies at present. One can attempt to relate the activation energy with the thermal population of the 3H_5 level. However, this contradicts to the experimental data because the position of the 3H_5 term with respect to the ground-state 3H_4 term of impurity Pr^{3+} ions is almost the same for all crystals under study [15]. The energy gap between the 3H_4 and 3H_5 levels is sufficiently large ($\sim 2000 \text{ cm}^{-1}$) for the change of temperature from 250 to 300 K to affect substantially the 3H_5 term population. The activation energies obtained above also cannot be related to the thermal activation of the Stark components of the 3H_5 and 3H_6 terms because their crystal-field splitting is substantially lower [15–18].

The integrated intensity of anti-Stokes fluorescence of crystals nonlinearly depends on the laser power density (Fig. 4a). This is observed most distinctly for the Pr : YSO crystal containing 0.3 % of impurity ions. The dependence presented in Fig. 4a was obtained by focusing laser radiation on the crystal surface. In this case, the laser power density exceeded the threshold. Then, laser radiation was

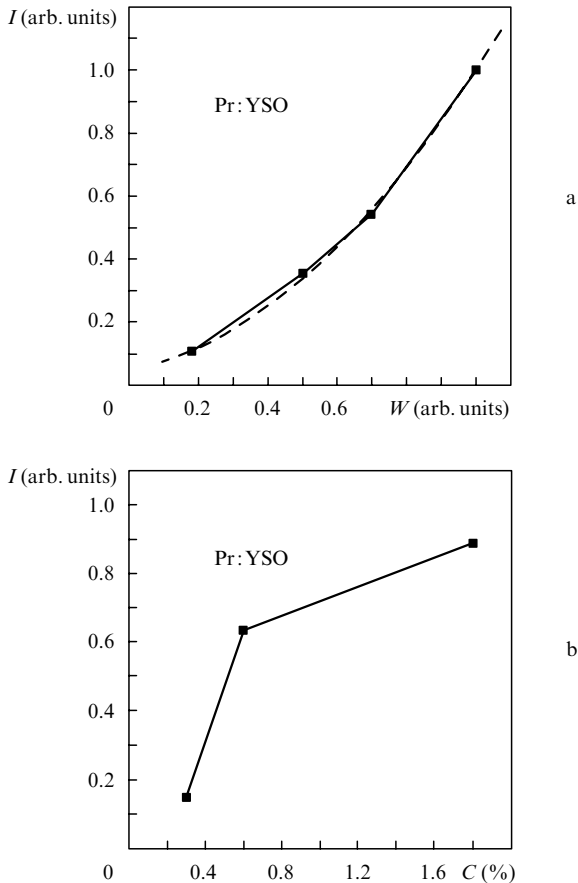


Figure 4. Dependences of the integrated intensity I of the anti-Stokes 3P_0 fluorescence of impurity Pr^{3+} ions in the Pr : YSO crystal on the pump laser power density W (a) and the atomic concentration C of impurity ions (b). The dashed curve is the quadratic approximation of the experimental data.

attenuated by means of calibrated neutral filters with known optical densities. One can see that the experimental data presented in Fig. 4a can be well approximated by a quadratic dependence.

The authors of paper [11] did not specify the concentration of impurity Pr^{3+} ions used in experiments. However, they interpreted the experimental data by the cross relaxation of excited ions, which should interact with each other. Therefore, the observed effect should exhibit the concentration dependence. To verify this, the integrated intensity of anti-Stokes fluorescence was studied for Pr : YSO crystals with the praseodymium concentrations of 0.3 %, 0.6 %, and 1.8 %. The crystals were excited at a fixed laser power density. We did not obtain a quadratic dependence of the anti-Stokes fluorescence intensity on the concentration of impurity ions (Fig. 4b). Figure 4b distinctly demonstrates the saturation of the fluorescence intensity, which can be explained by the concentration quenching [12, 22].

To confirm or reject this assumption, we measured the decay curves of fluorescence from the 3P_0 level for the selectively excited Pr^{3+} optical centres of the first type. At any concentration of Pr^{3+} (0.3 %, 0.6 %, and 1.8 %) in the Pr : YSO crystal, the decay curves of the $^3P_0 \rightarrow ^3H_4$ fluorescence were well described by one exponential with the decay constant equal to 2.1 μs in a broad temperature range from 80 to 300 K. Therefore, the concentration quenching

of the 3P_0 state of impurity Pr^{3+} ions is absent in the concentration range studied [14, 22].

The concentration quenching of the 3P_0 state in the $\text{Pr}^{3+} : \text{LaF}_3$ crystal was observed at a higher concentration (20%) of the Pr^{3+} ions [14]. The scheme of cross relaxation proposed in Ref. [14], which causes fluorescence quenching, is shown in Fig. 1c. According to this scheme, the 3H_6 state of Pr^{3+} ions is efficiently populated. After the subsequent cross relaxation of the 3H_6 term, two excited Pr^{3+} ions in the 3H_5 state can appear, as assumed in Ref. [11].

As mentioned above, both these ions can be excited by pump radiation to the 3P_0 state [11]. However, according to our data, the 3P_0 state in the Pr : YSO crystal is not quenched over the entire concentration range studied. Therefore, it is interesting to study and analyse the quenching of the 1D_2 state of impurity Pr^{3+} ions. The 1D_2 state can be one of the intermediate electronic states involved in the process of nonradiative relaxation and multistage excitation of the 3P_0 term.

Indeed, the 1D_2 state in the Pr : YSO crystal is quenched when the concentration of Pr^{3+} ions exceeds 0.3 % [23]. We also found that, depending on the excitation method and concentration of Pr^{3+} ions, two different quenching mechanisms for the 1D_2 state exist. Under certain conditions, both mechanisms act simultaneously, but it is possible to realise conditions when only one of them will be involved. The latter case takes place upon selective excitation of optical Pr^{3+} centres at the $^3H_4 \rightarrow ^1D_2$ transition [23]. In this case, only the intrinsic fluorescence of Pr^{3+} ions is observed [23]. In the temperature range from 1.5 to 80 K and the Pr^{3+} concentration equal to 0.3%, quenching of the $^1D_2 \rightarrow ^3H_4$ fluorescence of Pr^{3+} ions of both types is exponential, with the decay constants $\tau_1 = 108$ and 145 μs [23]. However, the decay curves gradually deviate from the exponential dependence as the concentration is increased to 0.6 % and 1.8 % [23]. In Ref. [23], the mechanism of quenching of the 1D_2 -fluorescence due to energy transfer to dimers was considered; however, no dimer fluorescence was observed. It is not inconceivable that quenching occurs due to cross relaxation of the 1D_2 term of the impurity Pr^{3+} ions [12–14]. However, the lower Stark component of the 1D_2 term (16507 cm^{-1}) cannot be excited by two photons, which is caused by the positions of the intermediate terms of Pr^{3+} lying below the 1D_2 term [15–18]. Therefore, the quenching mechanism for the 1D_2 fluorescence of Pr^{3+} in the Pr : YSO crystal excited at the $^3H_4 \rightarrow ^1D_2$ transition remains unclear.

Another quenching mechanism for the 1D_2 fluorescence of optical Pr^{3+} centres of the first type in the Pr : YSO crystal is realised if the 1D_2 state is populated due to the intracentre nonradiative $^3P_0 \rightarrow ^1D_2$ relaxation, i.e., after excitation of the 3P_0 term. Thus, upon selective excitation of the 3P_0 term of optical Pr^{3+} centres of the first type at 80 K (Fig. 1a), the 1D_2 fluorescence of the optical Pr^{3+} centres of the second type was observed (Fig. 5) even at the total concentration of impurity ions of 0.3 %. Fluorescence from the 1D_2 level of optical centres of the second type disappeared when the crystal was cooled down to 1.5 K. Therefore, the spectra in Fig. 5 demonstrate energy transfer from optical Pr^{3+} centres of the first type (donors) to optical centres of the second type serving as electronic energy acceptors. This is also confirmed by the decay curves of the 1D_2 fluorescence for optical centres of both types. The fluorescence decay curve for optical centres of the first type strongly deviates from the exponential dependence, while

the decay curve for optical centres of the second type has a gentler ascending slope (Fig. 6).

To determine the type of multipole interaction between non-equivalent optical Pr^{3+} centres, we approximated the fluorescence decay curve of optical centres of the first type by the equation [14, 24]

$$\ln I_d + \frac{t}{\tau_0} = \ln I_0 - \frac{4\pi}{3} n_a R_{\min}^3 (w_{\text{da}} t)^{3/S} \Gamma\left(1 - \frac{3}{S}\right), \quad (1)$$

where I_d is the donor fluorescence intensity; τ_0 is the decay time of the 1D_2 fluorescence; I_0 is the emission intensity at the initial moment $t = 0$; n_a is the number of acceptors per unit volume, which is equivalent to the number of optical Pr^{3+} centres of the second type; R_{\min} is the minimum distance between non-equivalent Pr^{3+} ions in the crystal lattice; w_{da} is the rate constant of energy transfer; Γ is the gamma function; and S takes the values 6, 8 or 10, depending on the type of multipole interaction (dipole–dipole, dipole–quadrupole or quadrupole–quadrupole, respectively).

It follows from (1) that the dependence of $\ln I_d + t/\tau_0$ on $t^{3/S}$ should be linear if the value of S is appropriately chosen. The best fit of the donor emission curve was achieved for $S = 6$ for the dipole–dipole interaction [curve (4) in Fig. 6]. The slope of the straight line gives the rate constant of energy transfer. For the total concentration of the Pr^{3+} ions equal to 0.3%, the concentration of optical centres of the second type amounts to $6.8 \times 10^{18} \text{ cm}^{-3}$, which is equivalent to n_a . The minimum distance between non-equivalent Pr^{3+} ions in the Pr:YSO crystal is 3.403 Å. Therefore, by using the slope of a straight line approximating experimental points (4), we estimate the rate constant of energy transfer as $w_{\text{da}} = 2.5 \times 10^4 \text{ s}^{-1}$. On the other hand, the region of the rise in the emission intensity of acceptors [curve (3) in Fig. 6] also reflects excitation energy transfer, and its characteristic time scale is related to w_{da} . The maximum of curve (3) is achieved at $t \sim 10^{-5} \text{ s}$, and the inverse value of this time gives the estimate of the energy transfer rate $w_{\text{da}} \sim 10^5 \text{ s}^{-1}$. Taking into account that the exact value of n_a used in (1) to estimate w_{da} is unknown, the two numerical values of w_{da} obtained above are in satisfactory agreement.

Therefore, quenching of the 1D_2 state of impurity Pr^{3+} centres of the first type leads to saturation of the anti-Stokes fluorescence when the concentration of impurity ions is increased (Fig. 4b). According to the mechanism proposed in Ref. [11], to excite efficiently the 3P_0 term by nonresonant laser radiation, two excited Pr^{3+} ions in the 3H_5 state should appear during the term relaxation (Fig. 1b). This is possible due to cross relaxation of the 3H_6 term of one of the interacting Pr^{3+} ions. In this case, the condition $E_{3H_6} \sim 2E_{3H_5}$ is well fulfilled.

The authors of paper [11] did not specify the population channel of the 3H_6 term. This can be either the ${}^3P_0 \rightarrow {}^3H_6$ fluorescence or multistage nonradiative relaxation through the intermediate 1D_2 , 1G_4 , 3F_4 , 3F_3 , and 3F_2 terms (Fig. 1a). The influence of quenching of the 1D_2 term on the intensity of the anti-Stokes 3P_0 -fluorescence of optical centres of the first type in the Pr:YSO crystal means that the 1D_2 term is involved in the population channel of the 3H_5 term. Indeed, in the case of excitation energy transfer between non-equivalent optical centres (Fig. 6), the electronic excitation of the 1D_2 term of optical Pr^{3+} centres of the first type disappears, and the lower 3H_6 and 3H_5 terms can no longer be excited. At present, we cannot specify the intermediate terms of the Pr^{3+} ions involved in the cross relaxation of the 1D_2 term. Also, unknown is the population channel of the 3H_5 term of optical Pr^{3+} centres of the first type, which can take part in excitation of the anti-Stokes 3P_0 fluorescence.

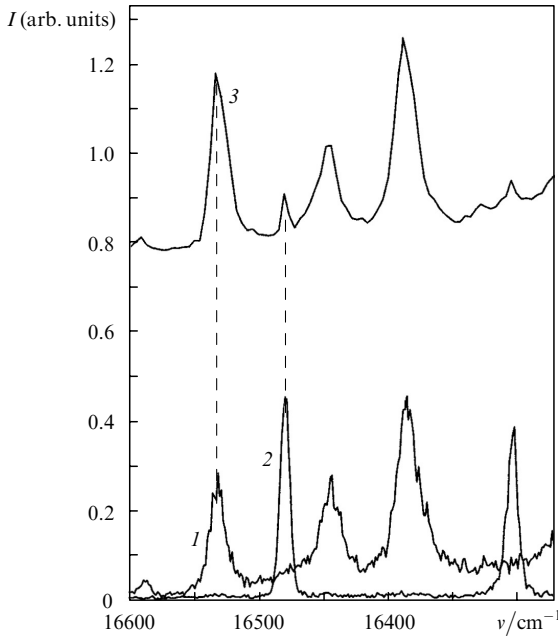


Figure 5. Fluorescence spectra of the Pr:YSO crystal observed upon selective excitation of non-equivalent optical centres of the first type at the ${}^3H_4 \rightarrow {}^1D_2$ transition (1), the second type at the ${}^3H_4 \rightarrow {}^1D_2$ transition (2), and the first type at the ${}^3H_4 \rightarrow {}^3P_0$ transition (3).

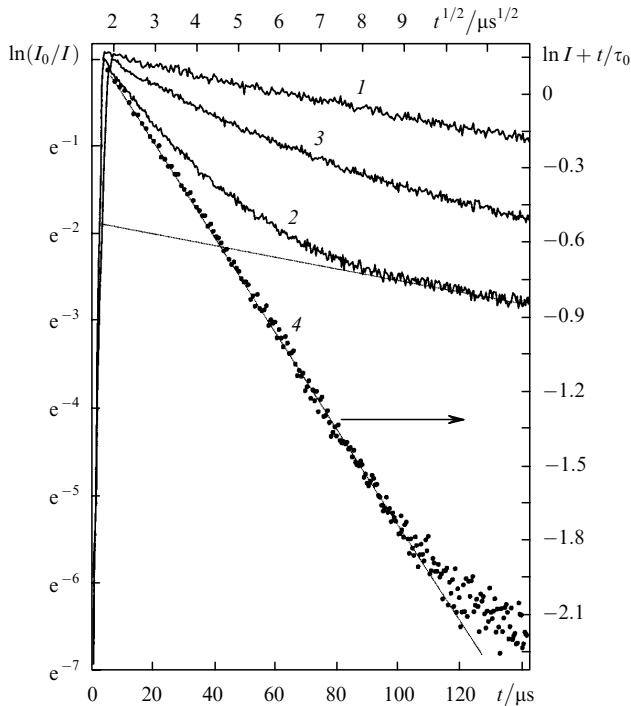


Figure 6. The 1D_2 -fluorescence decay curves for two types of optical centres in the Pr:YSO crystal (0.3% Pr): the first type at $T = 1.5$ (1) and 80 K (2); the second type at $T = 80$ K (3); and the approximation of curve (2) (4).

4. Conclusions

We have observed nonresonant excitation of the anti-Stokes 3P_0 fluorescence of impurity Pr^{3+} ions in the $\text{Pr} : \text{YSO}$, $\text{Pr} : \text{LSO}$, and $\text{Pr} : \text{GSO}$ crystals when the pump power density at $0.532 \mu\text{m}$ has achieved a certain threshold ($\sim 10 \text{ W cm}^{-2}$). The integrated intensity of the anti-Stokes fluorescence is a nonlinear function of the pump power density. An exact quadratic dependence is not observed due to quenching of the 1D_2 term of optical Pr^{3+} centres of the first type. The excitation efficiency of anti-Stokes fluorescence of the crystals is independent of the detuning of the pump laser frequency from the $^3H_4 \rightarrow ^3P_0$ transition frequency of impurity Pr^{3+} ions.

It is unclear why the intensity of the anti-Stokes fluorescence of impurity ions in these crystals strongly depends on temperature in a narrow temperature range from 250 to 300 K and, moreover, why the intensity of the $^3P_0 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3H_5$ fluorescence depends on temperature, whereas the $^1D_2 \rightarrow ^3H_4$ fluorescence intensity changes with temperature only weakly (Fig. 3). The saturation of the anti-Stokes 3P_0 fluorescence intensity is related to quenching of the 1D_2 term of optical Pr^{3+} centres of the first type. The concentration quenching of this term is caused by two mechanisms: the Förster energy transfer from the 1D_2 term to optical Pr^{3+} centres of the second type and presumably cross relaxation of the 1D_2 term involving optical Pr^{3+} centres of the first type only.

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