

NONRADIATIVE TRANSITIONS BETWEEN LEVELS OF TRIVALENT RARE-EARTH IONS  
IN YTTRIUM-ALUMINUM GARNET CRYSTALS

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Nonradiative transitions between levels of  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Ho}^{3+}$ , and  $\text{Tm}^{3+}$  ions in yttrium-aluminum garnet crystals are studied. The temperature dependences of the probabilities for nonradiative transitions are studied and it is shown that in the single-frequency model approximation the optical phonons with energy  $\sim 700 \text{ cm}^{-1}$  play the predominant role. The spontaneous nonradiative transition probabilities for various energy gaps between the levels and the dependence of the nonradiative transition probability on the energy gap are determined by measuring the quantum yield, lifetime, and kinetics of luminescence at  $77^\circ\text{K}$ . For gaps lying between  $1200$  and  $5000 \text{ cm}^{-1}$ , the dependence can be satisfactorily approximated by an exponential law. The relaxation times from the major excitation levels to the  ${}^4\text{F}_{3/2}$  level are measured for  $\text{Nd}^{3+}$  ions excited by radiation from a ruby or rhodamine-6G laser or by the second harmonic from a neodymium laser. The measurements are based on the kinetics of the luminescence emitted by the  $\text{Nd}^{3+}$  ions from the  ${}^4\text{F}_{3/2}$  level. The relaxation time from levels with an energy  $\sim 18\,800 \text{ cm}^{-1}$  is  $5 \times 10^{-7}$  sec. For levels lower than  $18\,800 \text{ cm}^{-1}$ , the time does not exceed  $5 \times 10^{-8}$  sec. On the basis of the dependence of the nonradiative transition probabilities on the energy gap between the levels, the relaxation time between the  ${}^4\text{I}_{11/2}$  and  ${}^4\text{I}_{9/2}$  levels of the  $\text{Nd}^{3+}$  ions is estimated at  $5 \times 10^{-7}$  sec.

NONRADIATIVE transitions between levels of impurity ions in crystals are one of the manifestations of the interaction between the ion and the crystal lattice. Such transitions can lead to a decrease of the intensity and to a reduction of the lifetime of the luminescence of the ions, and can also exert a noticeable influence on the operation of a laser using activated crystals.

The theory of nonradiative transitions between levels of impurity ions in crystals was developed in<sup>[1,2]</sup>. Nonradiative transitions between levels of trivalent rare-earth ions (TR-ions) were investigated experimentally in detail for the crystals  $\text{LaBr}_3$ ,  $\text{LaCl}_3$ ,  $\text{LaF}_3$ ,  $\text{SrF}_2$ , and  $\text{Y}_3\text{O}_3$ <sup>[3-10]</sup>. It was shown<sup>[10]</sup> that for TR ions the rates of nonradiative transitions are determined by the structure of the phonon spectrum, namely, by the limiting frequencies of the optical phonons in the vibration spectrum of the crystals. It turned out that in the region of low temperatures ( $4.2\text{--}77^\circ\text{K}$ ) in a given crystal lattice the dependence of the probability of nonradiative transitions on the energy gap between the levels can be well approximated by an exponential law and the value of the probability for the given energy gap remains practically unchanged when the TR ion is replaced. It should be noted that the crystal having the highest-frequency oscillations was  $\text{Y}_2\text{O}_3$  ( $550 \text{ cm}^{-1}$ )<sup>[7]</sup>. For these crystals, the values of the probabilities of nonradiative transitions between the levels of TR ions turned out to be higher than in  $\text{LaCl}_3$ ,  $\text{LaBr}_3$ ,  $\text{LaF}_3$ , and  $\text{SrF}_2$ <sup>[10]</sup>.

We have investigated the nonradiative transitions between levels of the ions  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Ho}^{3+}$ , and  $\text{Tm}^{3+}$  in crystals of yttrium aluminum garnet  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG), which is widely used as a laser active material<sup>[11]</sup>: Experiments on the temperature quenching of luminescence of the TR ions yielded the temperature dependence of the nonradiative transition probabilities and showed that optical phonons with energy  $\sim 700 \text{ cm}^{-1}$

play the decisive role in processes of nonradiative transitions between the levels of the TR ions in the YAG crystals in the single-particle-model approximation.

From measurements of the quantum yield, lifetime, and the flareup of the luminescence, we determined the values of the probabilities of nonradiative transitions of TR ions for different energy gaps between the levels. In the time measurements, the luminescence was excited by a ruby laser, the second harmonic of a neodymium laser, and by lasers based on organic-dye solutions operating in the Q-switched regime. Using excitation of the  $\text{Nd}^{3+}$  ions by the second harmonic of a neodymium laser at levels with energy  $\sim 18\,800 \text{ cm}^{-1}$ , the flare-up of the luminescence from the  ${}^4\text{F}_{3/2}$  level was used to measure the relaxation time from one of the pump ground levels to the upper laser level, which amounts to  $5 \times 10^{-7}$  sec. The times of relaxation from other pump levels lying below  $\sim 18\,800 \text{ cm}^{-1}$  turned out to be shorter than  $5 \times 10^{-8}$  sec.

The investigations yielded the dependence of the probability of nonradiative transitions on the energy gap between the levels of the TR ions in the YAG crystals. For gaps in the interval  $1200\text{--}5000 \text{ cm}^{-1}$ , this dependence is well approximated by an exponential law. The obtained dependence has made it possible to estimate the time of relaxation between the levels  ${}^4\text{I}_{11/2}$  (the lower laser level) and  ${}^4\text{I}_{9/2}$  (the ground state) of the  $\text{Nd}^{3+}$  at  $\sim 5 \times 10^{-7}$  sec.

#### INVESTIGATION PROCEDURE AND EXPERIMENTAL RESULTS

The measurements of the probabilities of the nonradiative transitions and the investigation of the temperature quenching of the luminescence were carried out on YAG crystals activated with the ions  $\text{Er}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Ho}^{3+}$ , and  $\text{Tm}^{3+}$ , grown by spontaneous crystallization



0.25. In the case of luminescence of the  $\text{Er}^{3+}$  ions in the  $0.54 \mu$  region, the comparison was made with rhodamine-6G, the quantum yield of which is close to unity. As shown by estimates, the total quantum yield of the luminescence of the  $\text{Er}^{3+}$  ions from the  ${}^4\text{S}_{3/2}$  level in YAG crystals does not exceed 0.1. From the level  ${}^4\text{S}_{3/2}$  of the  $\text{Er}^{3+}$  ions there is observed also luminescence to the level  ${}^4\text{I}_{13/2}$  ( $1.2 \mu$ ). In YAG crystals, however, the intensity of this luminescence is much lower than the intensity of the luminescence in the regions of  $0.54$  and  $0.86 \mu$ .

The probability of nonradiative transitions, determined from the values of the lifetimes and from the quantum yield of the luminescence from the  ${}^4\text{S}_{3/2}$  level, is  $(9 \pm 2) \times 10^3 \text{ sec}^{-1}$ .

The ions  $\text{Nd}^{3+}$  in YAG (transition  ${}^4\text{G}_{7/2} - {}^2\text{G}_{7/2} + {}^4\text{G}_{5/2} \Delta E = 1200 \text{ cm}^{-1}$ )

In the case of  $\text{Nd}^{3+}$  in YAG, radiative transitions are observed from the level  ${}^4\text{F}_{3/2}$  to the levels  ${}^4\text{I}_{9/2-15/2}$  (luminescence in the region  $0.9-1.8 \mu$ )<sup>[16]</sup>. When excited to levels lying above  ${}^4\text{F}_{3/2}$ , the neodymium ions experience nonradiative relaxation to the level  ${}^4\text{F}_{3/2}$ .

At temperatures 77 and 300°K, we measured the times of relaxation from the levels  ${}^4\text{G}_{7/2}$  ( $\sim 18\,800 \text{ cm}^{-1}$ ),  ${}^2\text{G}_{7/2} + {}^4\text{G}_{5/2}$  ( $\sim 17\,300 \text{ cm}^{-1}$ ), and  ${}^4\text{F}_{9/2}$  ( $\sim 14\,400 \text{ cm}^{-1}$ ) to the level  ${}^4\text{F}_{3/2}$  on the basis of the flare-up of luminescence from the level  ${}^4\text{F}_{3/2}$  (Fig. 1).

The luminescence of the  $\text{Nd}^{3+}$  ions at the indicated level was excited by the second harmonic of a neodymium laser ( ${}^4\text{G}_{7/2}$ ), by a rhodamine-6G laser ( ${}^2\text{G}_{7/2} + {}^4\text{G}_{5/2}$ ), and by a ruby laser ( ${}^4\text{F}_{9/2}$ ) with a pulse duration not exceeding 20 nsec. The luminescence signal in the region of  $0.9 \mu$  was registered with a photo-multiplier on an oscilloscope screen. The time resolution of the receiving apparatus was 50 nsec. The luminescence decay of the level  ${}^4\text{F}_{3/2}$  of  $\text{Nd}^{3+}$  introduced no errors in the measurement of the luminescence flare-up time, since the lifetime of the  ${}^4\text{F}_{3/2}$  level is  $240 \mu\text{sec}$ .

Measurements of the relaxation time were carried out on YAG crystals with a neodymium content 0.5 at.%, length 20 mm, and thickness 3 mm. When the  $\text{Nd}^{3+}$  ions were excited to the  ${}^4\text{G}_{4/7}$  level, flare-up of luminescence was observed from the  ${}^4\text{F}_{3/2}$  level (Fig. 3). The flare-up time was  $5 \times 10^{-7} \text{ sec}^{-1}$ .

To verify the reproducibility of the results on going from sample to sample, similar measurements were performed on YAG containing, besides the  $\text{Nd}^{3+}$  ions, also 0.5 at.%  $\text{Cr}^{3+}$  or 1 at.%  $\text{Ce}^{3+}$ . The time of luminescence flare-up from the level  ${}^4\text{F}_{3/2}$  when excited to the  ${}^4\text{G}_{7/2}$  level remained unchanged.

When the  $\text{Nd}^{3+}$  ions were excited to the levels  ${}^2\text{G}_{7/2} + {}^4\text{G}_{5/2}$  and  ${}^4\text{F}_{9/2}$ , no flare-up of luminescence from the  ${}^4\text{F}_{3/2}$  level was observed within the limits of the time resolution of the receiving apparatus. This indicates that the time of relaxation from these levels does not exceed 50 nsec. Thus, when  $\text{Nd}^{3+}$  ions are excited to the  ${}^4\text{G}_{7/2}$  level, the time of luminescence flare-up from

the level  ${}^4\text{F}_{3/2}$ , which equals  $5 \times 10^{-7} \text{ sec}$  at room and nitrogen temperatures, is determined by the time of relaxation between the levels  ${}^4\text{G}_{7/2}$  and  ${}^2\text{G}_{7/2} + {}^4\text{G}_{5/2} (\Delta E = 1200 \text{ cm}^{-1})$ <sup>[18]</sup>.

The maximum energy gap in the group of levels lying below  ${}^4\text{G}_{7/2}$  is  $\sim 1000 \text{ cm}^{-1}$ . The probability of spontaneous nonradiative transitions is in this case not less than  $2 \times 10^7 \text{ sec}^{-1}$ .

## DISCUSSION OF RESULTS

### 1. Temperature Quenching of the Luminescence of the Ions $\text{Nd}^{3+}$ , $\text{Er}^{3+}$ , $\text{Ho}^{3+}$ , and $\text{Tm}^{3+}$

When the temperature is raised from 300 to 900°K, a shortening of the lifetime of the luminescence of the ions  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  is observed. This shortening can be due to the change in the probability of the radiative transitions or to the increase of the probability of the non-radiative transitions. However, the fact that no reduction in the lifetime of the luminescence of the ions  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  is observed in this temperature interval indicates that the observed reduction of the lifetime of the luminescence of the  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  ions is not connected with a change in the probability of the radiative transitions and is due to the increase of the probability of nonradiative transitions with increasing temperature. This increase is due to an increase in the contribution of the stimulated nonradiative transitions.

From the shortening of the luminescence lifetimes of the ions  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  we calculated the probabilities of the temperature quenching  $W(T)$ . Figure 4 shows the obtained  $W(T)$  plots. According to<sup>[10]</sup>, the temperature dependence of the probability of nonradiative transitions, which are realized with emission of phonons of one frequency, can be represented in the form

$$W(T) = W_0(1 + \bar{n})^p, \quad (3)$$

where  $\bar{n} = (e^{\hbar\omega/kT} - 1)^{-1}$  are the occupation numbers of the phonons,  $p$  is the number of phonons with energy  $\hbar\omega$  participating in the process, and  $W_0$  the probability of spontaneous nonradiative transitions.

At a given energy gap between the levels, the value of  $W_0$  in (3) is larger the higher the frequency of the

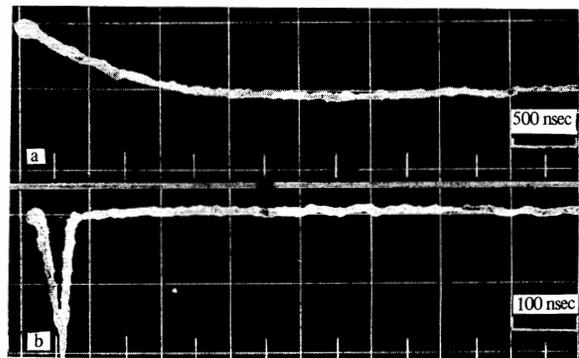


FIG. 3. Oscilloscope of the flare-up of luminescence of the  $\text{Nd}^{3+}$  ions from the  ${}^4\text{F}_{3/2}$  level when excited by the second harmonic of a neodymium laser: a—flare-up of luminescence, b—generation pulse.

<sup>1)</sup>No flare-up of luminescence of the  $\text{Nd}^{3+}$  ions from the  ${}^4\text{F}_{3/2}$  level was observed in [17] for YAG crystals excited to the  ${}^4\text{G}_{7/2}$  level.

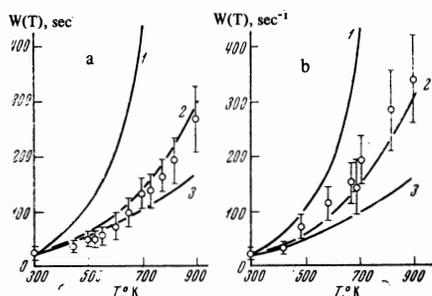


FIG. 4. Plots of the probability of nonradiative transitions between the levels  $5I_7$  and  $5I_8$  of the  $\text{Ho}^{3+}$  ions (a) and between the levels  $3H_4$  and  $3H_6$  of  $\text{Tm}^{3+}$  (b). Points—experimental results, curves—calculated for phonons with energies 600 (1), 700 (2), and 800  $\text{cm}^{-1}$  (3).

phonons participating in the process, for in this case the order of the process is lowered.

To calculate  $W(T)$  in (3) it is necessary to know the probability of spontaneous nonradiative transitions  $W_0$  and the frequencies of the optical vibrations of the YAG lattice. The values of  $W_0$  for the transitions  ${}^3H_4$ — ${}^3H_6$  of the  $\text{Tm}^{3+}$  ions and of the transitions  ${}^5I_7$ — ${}^5I_8$  of the  $\text{Ho}^{3+}$  ions was determined by us and amounts to  $\sim 20 \text{ sec}^{-1}$  for both ions. The frequencies of the optical oscillations for the YAG crystals were obtained in<sup>[19]</sup>. According to these data, in the phonon spectrum of the YAG crystals there is a whole series of optical vibrations with frequencies up to 860  $\text{cm}^{-1}$ .

Comparing the experimentally-observed temperature dependences of the nonradiative-transition probabilities with the calculated ones obtained from expression (3), we can estimate the frequencies of the optical vibrations, which play the principal role in the processes of temperature quenching of the luminescence of  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$ . Figure 4 shows, besides the experimental data, also calculated curves of the probabilities of temperature quenching of luminescence for photons with frequencies 600, 700, and 800  $\text{cm}^{-1}$ . The best agreement with experiment is obtained for the curves describing the process with emission of seven phonons of frequency  $\sim 700 \text{ cm}^{-1}$ .

Our investigations of the electron-vibrational spectra of the ions  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Cr}^{3+}$  in YAG crystals have shown that the intensity of the oscillations with frequencies 800–860  $\text{cm}^{-1}$  is very low, whereas those with frequency  $\sim 700 \text{ cm}^{-1}$  are quite intense. Apparently, oscillations with frequencies 800–860  $\text{cm}^{-1}$  are weakly coupled with the active TR ion and exert no significant influence on the nonradiative transitions between the levels of the TR ions in the YAG crystals.

In the case of the ions  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$  in YAG crystals, the lifetimes of the luminescence from the level  ${}^4F_{3/2}(\text{Nd}^{3+})$  and  ${}^4I_{13/2}(\text{Er}^{3+})$  do not change with increasing temperature from 77 to 900°K (Fig. 2). For the  $\text{Nd}^{3+}$  ions the distance from the level  ${}^4F_{3/2}$  to the next-lower-lying level  ${}^4I_{15/2}$  is 4360  $\text{cm}^{-1}$ <sup>[16]</sup> and is close to the analogous distances for the ions  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$ . It should be expected that the value of the probability of the temperature quenching of the luminescence of the  $\text{Nd}^{3+}$  ions will be close to those observed in the case of  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$ . However, the probability of the radiative transition for the ions  $\text{Nd}^{3+}$  amounts to  $\sim 4 \times 10^3 \text{ sec}^{-1}$  and is much higher than the probability of the temperature quenching (300  $\text{sec}^{-1}$  at maximum

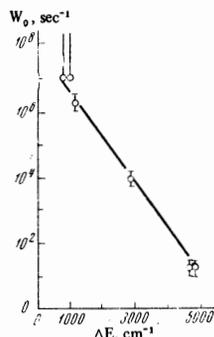


FIG. 5. Dependence of the probability of spontaneous nonradiative transitions on the energy gap between the levels.

temperature), whereas in the case of the ions  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  these probabilities are comparable in magnitude. Therefore no shortening of the lifetime of the  ${}^4F_{3/2}$  level of the  $\text{Nd}^{3+}$  ion is observed in the investigated temperature interval.

In the case of the  $\text{Er}^{3+}$  ions there is likewise no shortening of the lifetime of the  ${}^4I_{13/2}$  level in this temperature interval, although the probability of the radiative transition in the case of  $\text{Er}^{3+}$  is close to the probabilities for  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$ . This is connected with the much larger distance ( $\sim 6000 \text{ cm}^{-1}$ ) between the radiative level  ${}^4I_{13/2}$  and the ground state  ${}^4I_{15/2}$  than in the case of the  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  ions<sup>[13]</sup>. An increase of the energy gap between the levels leads to an increase in the number of the phonons participating in the process and to a decrease of the probability of the temperature quenching of the luminescence.

## 2. Dependence of the Probability of Nonradiative Transitions Between the Levels of the Ions $\text{Nd}^{3+}$ , $\text{Er}^{3+}$ , $\text{Ho}^{3+}$ , and $\text{Tm}^{3+}$ on the Energy Gap Between the Levels

As a result of our investigations we obtained the probabilities of the spontaneous nonradiative transitions for different energy gaps between the levels of a number of TR ions in YAG crystals (Fig. 5). This dependence is well approximated by an exponential law, just as for other crystals<sup>[5-10]</sup>. The values of the probabilities of the nonradiative transitions between the levels of the TR ions in the YAG crystals slightly exceed the values of these probabilities in  $\text{Y}_2\text{O}_3$  crystals<sup>[10]</sup>. Thus, for the energy gap 2750  $\text{cm}^{-1}$  in  $\text{Y}_2\text{O}_3$  crystals<sup>[10]</sup> the value of  $W_0$  is  $6.5 \times 10^3 \text{ sec}^{-1}$ , whereas in YAG crystals for  $\Delta E = 2870 \text{ cm}^{-1}$  it is equal to  $W_0 = 9 \times 10^3 \text{ sec}^{-1}$ . This is apparently due to the larger spread of the phonon spectrum in YAG crystals.

The obtained dependence of  $W_0$  on the energy gap between the levels makes it possible to estimate the probability of nonradiative relaxation between the levels  ${}^4I_{11/2}$  (lower laser level) and  ${}^4I_{9/2}$  (ground state) of the ions  $\text{Nd}^{3+}$  in YAG crystals. The minimum energy gap between these levels is 1200  $\text{cm}^{-1}$ <sup>[16]</sup>. The probability of the spontaneous nonradiative transitions corresponding to this gap (Fig. 5) is equal to  $2 \times 10^5 \text{ sec}^{-1}$ . This value coincides with the value of the probability of the nonradiative transitions between the levels  ${}^4G_{7/2}$  and  ${}^2G_{7/2} + {}^4G_{5/2}$  of the  $\text{Nd}^{3+}$  ions. The relaxation time between these levels does not depend on the temperature in the interval 77–300°K. One can expect the probability of the nonradiative relaxation between the

levels  ${}^4I_{11/2}$  and  ${}^4I_{9/2}$  of the  $Nd^{3+}$  ions likewise not to change strongly on going from 77 to 300°K.

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