SOVIET PHYSICS JETP VOLUME 30, NUMBER 3 MARCH, 1970

RESONANT AND NONRESONANT PROCESSES OF EXCITATION ENERGY TRANSFER FROM Tu^{3+} *OR* Ho^{3+} *IONS TO THE* Er^{3+} *IONS IN* $(Y, Er)_3Al_5O_{12}$ *CRYSTALS*

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Submitted April 21, 1969

Zh. Eksp. Teor. Fiz. **57**, 794–805 (September, 1969)

Transfer of excitation energy from Tu^{3+} or Ho^{3+} ions to Er^{3+} ions in $(Y, Er)_3Al_5O_{12}$ crystals doped with Tu^{3+} or Ho^{3+} was observed and studied at temperatures between 77 and 500°K. It is shown that for the Tu^{3+}—Er^{3+} system the transfer may result from resonant interaction processes. For Ho^{3+}—Er^{3+} the energy transfer can be attributed to nonresonant processes in which high energy optical phonons of $\sim$790 cm^{-1} energy are absorbed. A comparison of the experimental and theoretical values for the transfer probabilities in the two systems shows that at high temperatures nonresonant transfer processes between ions in crystals possess a probability which is close to that for resonant ones.

NONRADIATIVE transfer of excitation energy between ions and crystals can result from the processes of resonant and nonresonant interaction. The former of these processes pertains to the case when there is at least partial overlap of the donor luminescence lines and the acceptor absorption lines. In the second case, no such overlap exists and phonons must take part in the energy transfer.

It is assumed in the literature[1,2] that the effective energy transfer occurs only in resonant transitions of the donor and acceptor ions.

Nontheless, some investigations (see, for example[3]) have revealed cases of energy transfer between ions even without overlap of the transitions. Moreover, investigations of the temperature dependence of the energy transfer between the rare-earth ions in crystals in the temperature interval 2—77°K, when the lines in the spectra of these ions are inhomogeneously broadened, have established that the principal role in the transfer is played by nonresonant processes in which phonons take part.

It is of interest to compare the efficiencies of the two processes of high temperatures, when the lines of the rare-earth ions in the crystals are homogeneously broadened[1)][6].

To this end, we investigated the transfer of excitation energy from the Tu^{3+} and Ho^{3+} ions to the Er^{3+} ions in crystals based on yttrium-erbium aluminum garnet $(Y, Er)_3Al_5O_{12}$, where both resonant and nonresonant interaction processes are possible. The efficiencies were compared in crystals of erbium-aluminum garnet $Er_3Al_5O_{12}$(EAG) activated with Tu^{3+} or Ho^{3+}. In theoretical estimates of the transfer probability it is customary to use the mean value of the distance between the ions, obtained under the assumption that the ions have a statistical distribution in the crystals. This assumption is a rather crude approximation and can lead to errors that hinder the comparison of the theoretical data with the experimental ones. In the EAG crystals investigated by us, the Tu^{3+} (Ho^{3+}) ions are located at equal and exactly known distances 3.7 Å from the Er^{3+} ions[7], thereby making the comparison of theory with experiment more reliable.

The transfer of excitation energy from the $^4I_{11/2}$ level of the Er^{3+} ions to the ions Ho^{3+} or Tu^{3+} (direct transfer) was observed in a number of crystals[1,3-5,8,9]. In the crystal $(Y_{1.5}Er_{1.44}Tu_{0.06})Al_5O_{12}$ at room temperature, energy transfer was also observed from the $^3H_4$ level of the Tu^{3+} ions to the Er^{3+} ions (inverse transfer)[1]. The inverse transfer of energy from the $^5I_7$ level of the Ho^{3+} in the same crystals was not observed before.

We have observed in the present investigation also a reverse energy transfer from the Ho^{3+} ions to the Er^{3+} ions in $(Y, Er)_3Al_5O_{12}$ crystals. The temperature dependence of the reverse energy transfer from the Tu^{3+} and Ho^{3+} ions to the Er^{3+} ions was investigated in detail in a wide temperature interval (77—500°K) and in a wide interval of the Er^{3+} concentration. We show that in the Tu—Er case, the transfer can be due to resonant interaction processes, and the observed transfer probabilities are close to those calculated for the dipole-dipole interaction mechanism. In the Ho—Er case, the temperature dependence of the transfer can be attributed to nonresonant processes, in which high-frequency optical phonons with energy $\sim$790 cm^{-1} are absorbed. A comparison of the observed probabilities in these systems makes it possible to conclude that the nonresonant interaction processes have a high efficiency, close to that of the resonant processes.

THEORETICAL QUESTIONS

A theory of resonant nonradiative energy transfer between ions was developed for the multipole interaction mechanism in[10,11]. For the case of dipole-dipole interaction, the transfer probability is connected with experimentally measured quantities, viz., the overlap integral of the spectra of the donor and acceptor ions, and also with the transition probabilities of these ions and the distances between them. According to[11,12], the expression for the transfer probability W_1 can be written in the form

$$W_1 = \frac{3\pi\hbar e^4 f_1 f_2}{n^4 m^2 \omega^2 R^6} \int g_1(E) g_2(E) dE,$$

[1)] We do not consider cases of "disordered" crystals and glasses, in which the lines are apparently not homogeneously broadened even at high temperatures.

where n is the refractive index of the medium, m and e are the mass and charge of the electron, and R is the distance between ions; $\int g_1(E)g_2(E)dE$ is the overlap integral of the absorption spectrum $g_1(E)$ of the donor ion and of the luminescence spectrum $g_2(E)$ of the acceptor ion under the normalization conditions $\int g_1(E)dE = 1$ and $\int g_2(E)dE = 1$, ω is the average overlap frequency, and $f_{1,2}$ are the donor and acceptor ion oscillator strengths.

The processes of nonresonant interaction between two different ions were considered, for the multipole interaction mechanism, in[13,14]. A nonzero transfer probability is obtained in second order of perturbation theory.

Let us denote the wave functions of the ions in the ground and in the excited states respectively by $\psi^0_{1,2}$ and $\psi^*_{1,2}$, and let us write the perturbation in the form

$$H' = H_{12} + V_1' + V_2',$$

where H_{12} is the Hamiltonian of the multipole interaction of two ions, and $V'_{1,2}$ is the interaction of the first and second ions with the lattice.

The operator $V'_{1,2}$ can be represented in the form[14]

$$V'_{1,2} = V_{1,2}\,\varepsilon,$$

where $V_{1,2}$ is the dynamic part of the lattice-orbit interaction, which acts only on the electronic wave functions of the ions, and ϵ is the thermal deformation.

We can then obtain[14] for the process of nonresonant energy transfer with emission (absorption) of a phonon of frequency ω_p in the Debye model:

$$W_2 = \frac{2\pi}{\hbar^2}|\langle\psi_1{}^*\psi_2{}^0|H_{12}|\psi_1{}^0\psi_2{}^*\rangle|^2\left\{\frac{3\omega_p}{4\pi^2v^3n\rho}|[\langle\psi_2{}^*|V_2|\psi_2{}^*\rangle\right. \tag{2}$$

$$\left.-\langle\psi_2{}^0|V_2|\psi_2{}^0\rangle+\langle\psi_1{}^0|V_1|\psi_1{}^0\rangle-\langle\psi_1{}^*|V_1|\psi_1{}^*\rangle]|^2\begin{pmatrix}n_p+1\\ n_p\end{pmatrix}\right\},$$

where v is the speed of sound in the crystal, ρ is the density of the crystal, and n_p are the occupation numbers of the phonons. In expression (2), the factor $(n_p + 1)$ corresponds to processes with emission of a phonon, and n_p to processes with absorption of a phonon of frequency ω_p.

An analysis of expression (2) shows that the transfer probability depends on the matrix elements of the multipole interaction, which are determined, as usual, by the transition probabilities (oscillator strength) of the individual ions. In addition, W_2 depends on the difference between the matrix elements of the dynamic part of the lattice-orbit interaction between the excited and ground states of the acceptor ion, and between the ground and excited states of the donor ion. The temperature dependence of W_2 is determined mainly by the dependence of n_p on the temperature. In the case of processes of nonresonant transfer with participation of optical phonons, the structure of the matrix elements and the temperature dependence part remain the same, and only the coefficients in expression (2) change.

We note that expressions (1) and (2) were obtained for the case when the transfer is effected between a pair of levels of one ion and a pair of levels of another ion. In the case of rare-earth ions in crystals, each of the levels consists of several Stark components. In estimating the transfer probability, it is necessary to take into account the probability of populating the Stark sublevels, the transitions between which make the main contribution to the transfer. To this end, it is necessary to multiply expressions (1) and (2) by the product of the probabilities of finding the ions of the corresponding Stark sublevels.

INVESTIGATED CRYSTALS

The inverse transfer of excitation energy from the Tu^{3+} and Ho^{3+} ions to the Er^{3+} ions was investigated in series of crystals based on yttrium aluminum garnet (YAG) with a constant content of Tu or Ho (1%) and with variable Er concentration. The crystals were grown by spontaneous crystallization from the solution in the melt from raw material of a high degree of purity. The content of other rare earth's in the oxide of Er, Tu, and Ho used to grow the crystals was less than 5×10^{-4}%.

INVESTIGATION PROCEDURE

We measured the lifetime (τ) and the luminescence intensity (J) of the Tu^{3+} at the $^3H_4$ level and of the Ho^{3+} ions at the $^5I_7$ level in the investigated crystals as functions of the Er concentration. The measurements of τ and J were made with continuous variation of the temperature from 77 to 500°K, using a procedure described in[5]. The sample temperature was monitored with a copper-constantan thermocouple.

In the measurement of τ, the excitation of the luminescence was at the levels of the Er^{3+}, Tu^{3+}, and Ho^{3+} ions with energy 10,000–25,000 cm^{-1}. However, owing to nonradiative transitions, the ions experience rapid relaxation to the levels $^4I_{13/2}$(Er), $^3H_4$(Tu), or $^5I_7$(Ho).

In the investigation of the concentration dependences of J for the onis Tu^{3+} from the $^3H_4$ level and Ho^{3+} from the $^5I_7$ level, the excitation was produced by a mercury lamp (DRSh-500) combined with an SZS-14 filter, which eliminated the radiation of wavelength larger than 1.2 μ. The spectra were registered with a diffraction monochromator (MDR-2) with a grating of 300 lines/mm and a dispersion of 80Å/mm. The luminescence intensity in relative units was estimated from the area under the $J(\lambda)$ curve, where λ is the radiation wavelength.

To compare the experimental data with the theoretical values of the transfer probability, we measured the oscillator strengths of the ions Er^{3+} and Tu^{3+}, and also the overlap integral of the spectra that enter in formula (1). The oscillator strengths $f_{1,2}$ were calculated from the formula

$$f_{1,2} = \frac{c^2m}{\pi Ne^2}\int k\left(\frac{\nu}{c}\right)d\left(\frac{\nu}{c}\right), \tag{3}$$

where $k(\nu/c)$ is the absorption coefficient and N is the activated concentration.

The magnitude of the integral in (3) was estimated from the absorption spectra obtained with the aid of a two-beam spectra photometer (SP-700) at room temperature. The resolution in the registration of the spectra was not worse than 10 cm^{-1}.

The overlap integral was determined at room and nitrogen temperatures from the absorption and luminescence spectra. The spectra were recorded with

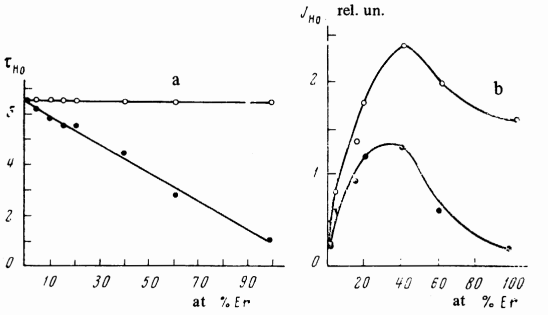

FIG. 1. Lifetime (msec) (a) and luminescence intensity (b) of Ho^{3+} ions at the $^5I_7$ level vs. the Er concentration in $(Y, Er)_3Al_5O_{12}$ crystals: ○ – 293° K, ○ – 77° K.

an MDR-2 monochromator with resolution not worse than 2 cm^{-1}.

EXPERIMENTAL RESULTS

Figure 1 shows plots of the luminescence lifetime and intensity of the Ho^{3+} ions at the $^5I_7$ level against the erbium concentration at room and nitrogen temperatures. At 293°K, a rapid decrease of τ of Ho is observed with increasing Er^{3+} concentration, from 6.5 msec for pure YAG to 1.1 msec for EAG crystals. At 77°K, the lifetime of the luminescence of the Ho^{3+} ions does not depend on the Er^{3+} concentration and amounts to 6.5 msec. We note that τ of Ho^{3+} ions in the YAG crystal (Fig. 1a) does not depend on the temperature. Thus, the increase of the erbium concentration leads to a strong temperature quenching of the holmium luminescence.

This is also evidenced by the dependence of the Ho^{3+} luminescence on the Er^{3+} concentration (Fig. 1b). The Ho^{3+} luminescence intensity curve lies much higher at 77°K than at 293°K. In the EAG crystal with 1% Ho, the luminescence intensity of the Ho^{3+} ions decreases by a factor of 8 on going from 77 to 293°K.

The lifetime of the Ho^{3+} of the same crystal was plotted as a continuous function of the temperature (2). In the temperature interval 77–180°K, τ remains unchanged, and then the lifetime decreases and ceases to depend on the temperature at T ≈ 370°K.

The same investigations were performed with YAG crystals activated with Er^{3+} and Tu^{3+}. It turned out that with increasing erbium temperature, at 293°K, a sharp decrease of τ of the Tu^{3+} ions is observed, from 8.5 msec for pure YAG with 1% Tu to 0.65 msec for an EAG crystal with 1% Tu. At nitrogen temperature, the lifetime of the Tu^{3+} ions in the investigated series of crystals does not depend on the erbium concentration and amounts to 10.5 msec. We note that τ of the Tu^{3+} ions in the YAG crystals (without erbium) remains practically unchanged on going from 293 to 77°K (it changes from 8.5 to 10.5 msec).

A plot of $\tau(T)$ for an EAG crystal with 1% Tu is shown in Fig. 2. We see that at 77–100°K the lifetime τ remains unchanged, after which it starts to decrease and becomes independent of the temperature at 280°K. It is interesting to note that τ has the same value, 0.65 msec, for the Tu^{3+} and Ho^{3+} ions in EAG crystals at high temperatures.

Thus, in both investigated systems (Fig. 2) a temperature quenching of the luminescence of the Tu^{3+} and Ho^{3+} ions takes place with increasing temperature, accompanied by a decrease of the lifetime and by a decrease of the luminescence intensity.

DISCUSSION OF RESULTS

As indicated in the preceding part, at T = 77°K the lifetime of the luminescence of Ho (or Tu) does not depend on the Er concentration (Fig. 1a). It follows therefore that the decrease of τ and J with increasing Er concentration, observed with increasing temperature, cannot be connected with a change in the crystal field at the location of the Ho^{3+} (Tu^{3+}) ions. The independence of the lifetimes of the Tu^{3+} and Ho^{3+} ions of the temperature in YAG crystals without erbium shows that the temperature quenching of luminescence by multiphoton relaxation from the levels $^5I_7$(Ho) or $^3H_4$(Tu) is ineffective[15,16].

An examination of Fig. 2 shows that the temperature quenching of the luminescence can be connected only with energy transfer from the Ho^{3+} (Tu^{3+}) ions to the Er^{3+} ion2). Since the experimentally observed luminescence damping curves of Ho and Tu in EAG crystals were singly-exponential, the probability of such a transfer W can be calculated from the relation

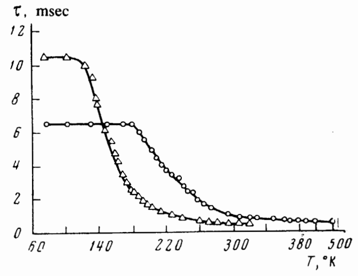

FIG. 2. Temperature dependence of the lifetime of Tu^{3+} ions at the $^3H_4$ level and of Ho^{3+} at the $^5I_7$ level in EAG crystals activated with 1% Tu (△) or 1% Ho (○).

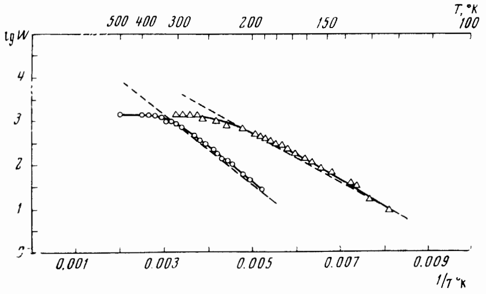

FIG. 3. Dependence of the transfer probability W on the temperature in EAG crystals activated with 1% Tu (△) and 1% Ho (○). The dashed lines show the theoretical relations.

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2) We note that energy transfer from the Ho^{3+}(Tu^{3+}) ions to Er^{3+} ions with subsequent rapid migration over the Er^{3+} ions and with transfer of excitation energy to the Ho^{3+}(Tu^{3+}) ions cannot lead to a reduction of the lifetimes of Ho^{3+}(Tu^{3+}), The decrease of the lifetime τ of the Ho^{3+} (Tu^{3+}) ions is due to transfer of energy from these ions to the Er^{3+} ions with subsequent migration over the ER^{3+} ions and extinction by the quenching impurities.

$$\frac{1}{\tau(T)} - \frac{1}{\tau_0} = W(T),$$

where $\tau(T)$ are the experimental dependences (Fig. 2) and τ_0 is the radiation lifetime of the Ho^{3+} (Tu^{3+}) ions in the EAG crystals at 77°K.

The obtained temperature dependences of the transfer probability are plotted in a semi-log scale in Fig. 3. For EAG crystals with Ho at low temperatures (200–280°K), the curve has an exponential form

$$W \sim \exp(-\Delta_1 / kT), \tag{4}$$

where $\Delta_1 = 1350 \pm 50\ \text{cm}^{-1}$. In the case of crystals activated with Tu, in the temperature range 120–200°K the dependence is also exponential

$$W \sim \exp(-\Delta_2 / kT), \tag{5}$$

with $\Delta_2 = 1030 \pm 50\ \text{cm}^{-1}$.

Let us discuss the possible mechanisms of excitation-energy transfer from the Tu^{3+} (Ho^{3+}) ions to the Er^{3+} ions in EAG crystals. Earlier, in the investigation of direct transfer in YAG crystals, it was shown that in the Er–Tu pair there is an overlap of the spectra corresponding to the transitions $^4I_{13/2} \longleftrightarrow {}^4I_{15/2}$(Er) and $^3H_4 \longleftrightarrow {}^3H_6$(Tu)[1,5,17]. Figures 4 and 5 show the spectra obtained by us for the Er^{3+} and Tu^{3+} ions, and also the energy level scheme of the terms $^4I_{13/2,15/2}$(Er) and $^3H_{4,6}$(Tu) in YAG crystals[3)] [17]. We see that resonance actually takes place in this system for several transitions, viz., $(6177 \rightarrow 0)\ \text{cm}^{-1}$ of the Tu^{3+} ions and $(426 \rightarrow 6603)\ \text{cm}^{-1}$ of the Er^{3+} ions. Thus, the temperature dependence of the reverse energy transfer from Tu^{3+} to Er^{3+} (Fig. 3) can be obtained from relations that are characteristic of resonant-interaction processes.

Let us attempt to estimate the transfer efficiency for the dipole-dipole interaction mechanism. In order to obtain the theoretical dependence of the transfer efficiency as the temperature, it is necessary to multiply the right side of (1) by the probability of finding the Tu^{3+} ion at the $6177\ \text{cm}^{-1}$ level (w_{6177}) and the ion Er^{3+} at the $426\ \text{cm}^{-1}$ level (w_{426}) (Fig. 5). The values of w_{6177} and w_{426} can be calculated from the relations

$$w_{6177} = \exp\left(-\frac{620}{kT}\right) \Big/ \sum_i \exp(-\Delta_i/kT), \tag{6}$$

$$w_{426} = \exp\left(-\frac{426}{kT}\right) \Big/ \sum_j \exp(-\Delta_j/kT), \tag{7}$$

where the $620\ \text{cm}^{-1}$ is the distance to the lower level of the $^3H_4$ term of the Tu^{3+} ions (Fig. 5), and $\Delta_{i,j}$ is equal respectively to the difference between the energies of each level of the $^3H_4$ and $^4I_{15/2}$ terms and the energies of the levels 5557 and $0\ \text{cm}^{-1}$.

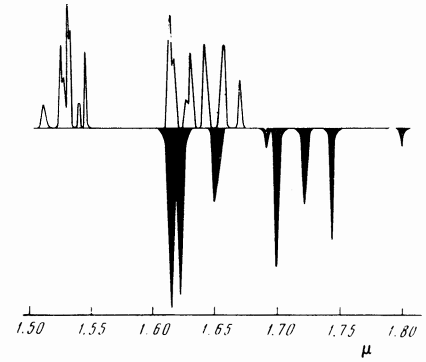

FIG. 4. Luminescence spectra of Er^{3+} ions (top) (transition $^4I_{13/2} - {}^4I_{15/2}$) and absorption spectra of Tu^{3+} ions (transition $^3H_6 - {}^3H_4$) in YAG crystals. T = 77° K.

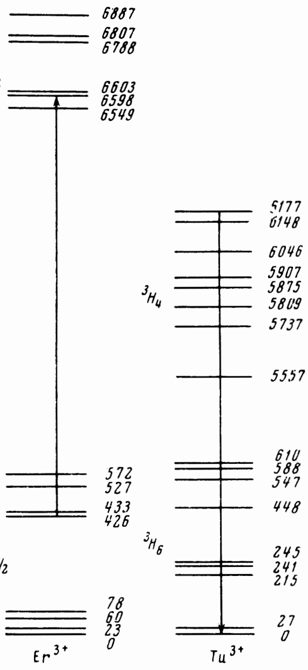

FIG. 5. Energy level scheme of the terms $^4I_{13/2,\ 15/2}$ of the Er^{3+} ions and $^3H_{4,\ 6}$ of the Tu^{3+} ions in YAG crystals at 77° K.

The transfer probability can then increase with increasing temperature as a result of the increase of w_{6177} and w_{426}, and also as a result of the increase of the overlap integral. Estimates of the overlap integral at 77°K from the spectra of Fig. 4 yield a value $4 \times 10^{14}\ \text{erg}^{-1}$. With increasing temperature, as shown by the measurements, the overlap integral remains practically unchanged and the observed increase of the efficiency of the inverse transfer W_1' with increasing temperature is proportional to the increase of w_{6177} and w_{426}:

$$W_1' = W_1 w_{6177} w_{426}, \tag{8}$$

where W_1 is determined by formula (1) and does not depend on the temperature.

Let us substitute in (1) the values $\omega = 1.2 \times 10^{15}$ ($6177\ \text{cm}^{-1}$), the measured oscillator strengths f_1 and f_2 for the transitions indicated by the arrows in Fig. 5, equal to 9×10^{-7} (Er) and 7×10^{-7} (Tu), and also $n = 1.8$[19] and the distance R for the garnet structure, equal to 3.7 Å[7]. We calculate the values of w_{6177} and w_{426} in (8) from relations (6) and (7). Then the temperature dependence of the probability of energy transfer

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[3)] In EAG crystals, the character and mutual positions of the lines in the Er^{3+}, Tu^{3+}, and Ho^{3+} spectra remained essentially unchanged compared with the YAG crystals. In particular, the scheme obtained in [18] for the Stark components of the ground state of erbium in the EAG crystal coincides within $3\ \text{cm}^{-1}$ with the scheme shown in Fig. 5 for the YAG crystals.

from the Tu^{3+} ions to the Er^{3+} ions in EAG crystals will have the form shown by the dashed line in Fig. 3. We see that the theoretical curve coincides with the experimental one in the entire investigated temperature interval, with the exception of high temperatures (>250°K). The obtained experimental value of Δ_2, namely 1030 cm^{-1}, is close to the value $\delta_1 + \delta_2$ at $426 + 620 = 1046^{-1}$ obtained from 8) at temperatures such that $kT < \delta_{1,2}$. Thus, in crystals of EAG with 1% Tu the temperature luminescence quenching of the Tu^{3+} ions at the $^3H_4$ level can be attributed to resonant interaction processes that lead to the transfer of excitation energy from the Tu^{3+} ions to the Er^{3+} ions.

Let us stop to discuss in greater detail the transfer processes in EAG crystals activated with holmium. As was established earlier[1,5,17], there is no overlap of the spectra corresponding to the transitions $^4I_{13/2} \longleftrightarrow {}^4I_{15/2}$(Er) and $^5I_7 \longleftrightarrow {}^5I_8$(Ho) in YAG crystals. Figures 6 and 7 show the luminescence spectra of the Er^{3+} and Ho^{3+} ions and the level scheme obtained by us for the terms $^4I_{13/2,\,15/2}$ and $^5I_{7,8}$ in YAG crystals.

The frequency of the line with the longest wavelength in the emission spectrum of Er^{3+} is 5977 cm^{-1}. The uppermost level of the $^5I_7$ term of Ho^{3+} has an energy 5450 cm^{-1}, and to effect the excitation-energy transfer from the ions Ho^{3+} to the Er^{3+} ions it is necessary to absorb phonons with energy $\hbar\omega_p \geq$ 527 cm^{-1}. Thus, inverse energy transfer from Ho^{3+} to Er^{3+} can occur only as a result of nonresonant-interaction processes.

Since the Debye temperature for YAG crystals amounts to $\sim$500 cm^{-1}[20–22], nonresonant transfer in which phonons from the acoustic branch takes part has apparently a low probability. The experimentally observed reverse transfer is accomplished by absorption of phonons of higher frequency, corresponding to the optical branch of the dispersion curve. An investigation of the reflection in the infrared region and of Raman scattering of YAG crystals[23] shows that oscillation frequencies up to $\sim$850 cm^{-1} appear in the spectra. Thus, optical phonons with frequencies 527–850 cm^{-1} can participate in the excitation-energy transfer from the Ho^{3+} ions to the Er^{3+} ions.

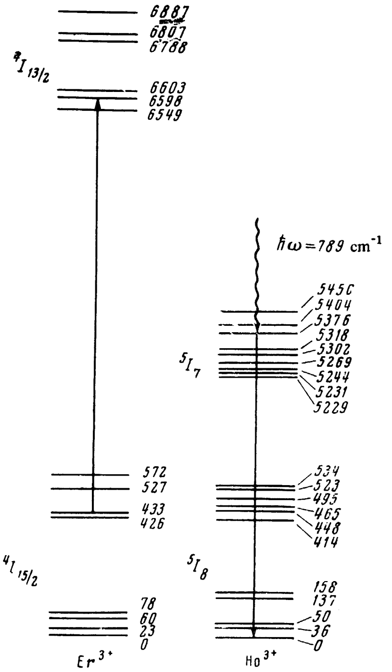

FIG. 7. Energy level scheme of the terms $^4I_{13/2,\ 15/2}$ of Er^{3+} and $^5I_{7,\ 8}$ of Ho^{3+} in YAG crystals at 77° K. The arrows designate the transitions that make the main contribution to the observed nonresonant transfer.

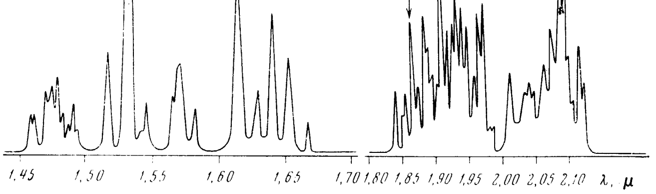

FIG. 6. Luminescence spectra of Er^{3+} ions (left) (transition $^4I_{13/2} - {}^4I_{15/2}$ and Ho^{3+}(transition $^5I_7 - {}^5I_8$) in YAG crystals; T = 293° K.

We have attempted to estimate more accurately the frequencies of the phonons that make the main contribution to the observed nonresonant transfer. Multiplying the right side of (2) by the probabilities w_1 and w_2 of finding the ions Ho^{3+} and Er^{3+} at one of the sublevels of the terms $^5I_7$ and $^4I_{15/2}$, and separating the temperature-dependence part, we obtain[4] for the nonresonant interaction with absorption of a phonon of frequency ω_p

$$W_2' = W_2^0 w_1 w_2 (e^{\hbar\omega_p/kT} - 1)^{-1}, \tag{9}$$

where w_2^0 is a temperature-independent constant.

Since W_2^0 depends on the matrix elements of the multipole interaction, which are determined by the values of the oscillator strengths of the transitions Ho^{3+} and Er^{3+} ions, the main contribution to the transfer is made by the most intense transitions in the spectra of these ions. In addition, the difference between the transition energies should coincide with the frequency of the optical phonons in the oscillation spectrum of the YAG crystal. An additional verification of the correctness of the choice of the transitions of the Ho^{3+} and Er^{3+} ions and of the frequency of the phonon participating in the process is the best agreement between the theoretical temperature dependence and that observed in experiment (Fig. 3).

We have chosen the transitions designated by the arrows in Figs. 6 and 7. The difference between the energies of these transitions is 789 cm^{-1}. In the oscillation spectrum of the YAG crystal there is a close frequency, 783 cm^{-1}[23][5]. Substituting in (9) in lieu of w_1 and w_2 respectively the probability of finding the Ho^{3+} ion at the 5376 cm^{-1} level (w_{5376}) and of the Er^{3+} ion at the 433 cm^{-1} level (w_{433}) and neglecting unity in the denominator of (9), we obtain

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[4] Expression (9) was obtained for acoustic phonons. However, the structure of the matrix elements and the temperature-dependent part remain the same on going over to optical phonons.

[5] An oscillation with frequency 790 cm^{-1} was observed by us also in the electron-vibrational spectra of the ions Nd^{3+}, Er^{3+}, and Cr^{3+} in YAG crystals.

$$W_2' = W_2^0 \frac{\exp(-147/kT)}{\sum_m \exp(-\Delta_m/kT)} \cdot \frac{\exp(-433/kT)}{\sum_j \exp(-\Delta_j/kT)} e^{-789/kT} \qquad (10)$$

where 147 cm^{-1} is the distance to the lower level of the $^5I_7$ term (Fig. 7), and the expressions in the denominator are similar to those used in (6) and (7).

The temperature dependence of the probability of energy transfer from the Ho^{3+} ions to the Er^{3+} ions in the EAG crystals will then have the form represented by the dashed line in Fig. 3. We see that in the temperature interval 200–280°K this dependence agrees well with the experimental one, and the slope of the experimental curve Δ_1, which equals 1350 cm^{-1}, is close to that obtained from (10), which amounts to 1369 cm^{-1} at low temperatures.

The independence of the lifetime of the temperature, observed at high temperatures in both pairs (Fig. 2), is connected with the fact that the lifetime of the Tu^{3+} or Ho^{3+} ions in the EAG crystals becomes comparable at these temperatures with the lifetime of Er^{3+}. This is confirmed by the fact that the lifetimes of the Tu^{3+} and Ho^{3+} ions in the EAG crystals coincide at high temperatures (Fig. 2).

It is of considerable interest to compare the coefficients W_1 and W_2^0 in (8) and (10); these coefficients determine the matrix elements of the resonant and nonresonant interactions. Substituting the experimentally obtained values of the probability in (8) and (10), we get $W_1 = (7 \pm 2) \times 10^6\ \text{sec}^{-1}$ and $W_2^0 = (9 \pm 2) \times 10^6\ \text{sec}^{-1}$, i.e., the temperature-independent constants are close in magnitude for both processes. Consequently, the experimentally observed difference in the probability for resonant and nonresonant processes (Fig. 3) is connected with the fact that the factor $n_p = (e^{789/kT} - 1)^{-1}$ is small in the investigated temperature interval.

In the case of nonresonant transfer with phonon emission, when the transfer probability is $W(T) \sim n_p + 1$, the probabilities of the resonant and nonresonant transfers become comparable. This was indeed observed in an investigation[5] of the energy transfer from Er^{3+} to Tu^{3+} or Ho^{3+} ions in YAG crystals, where it was established that the probabilities of interaction of the Er^{3+} and Tu^{3+} ions (overlap of the spectra is present) and of Er^{3+} and Ho^{3+} ions (there is no overlap) are close in magnitude.

The foregoing indicates the high efficiency of the processes of nonresonant interaction with participation of phonons in crystals activated with trivalent rare-earth ions.

In conclusion, the authors are grateful to K. K. Pukhov for valuable discussions.

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Translated by J. G. Adashko
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