Spectral migration of electronic excitation between Nd^{3+} ions in CaF$_2$–YF$_3$ crystals under selective laser excitation conditions

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(Submitted 24 January 1978)
Zh. Eksp. Teor. Fiz. 75, 66–74 (July 1978)

A study was made of the structure of inhomogeneously broadened spectra and of migration of electronic excitation between neodymium ions in disordered CaF$_2$–YF$_3$ crystals. The method of selective laser excitation of time-resolved luminescence spectra was used. The contribution of the homogeneous component to the spectral line broadening was determined. Two groups of activator centers were found and a Stark splitting scheme of some states was obtained for them. A study of the time evolution of the luminescence spectra of selectively excited particles made it possible to detect and investigate spectral migration of the excitation energy within the inhomogeneous luminescence line profile. The kinetics of spectral migration was described satisfactorily by the dipole–dipole interaction of the Nd^{3+} ions. The characteristic time of energy transfer between two types of center was determined.

PACS numbers: 71.55.Jv, 33.70.Jg, 33.55.+c

There are several methods for the direct observation of the migration of the electronic excitation energy between rare-earth ions: these methods can be divided into stimulated emission and spectroscopic. The stimulated emission methods are usually employed in studies of the migration in disordered condensed media doped with Nd^{3+} ions and are based on a study of the kinetics of the relaxation of a narrow dip "burnt" in the inhomogeneously broadened $^4F_{3/2} \to {}^4I_{11/2}$ neodymium band by selective stimulated release of the stored energy.[1-4] Spectroscopic methods include those based on the red shift of the luminescence lines of various rare-earth ions observed as a result of cooling to helium temperature[5,6] and the currently very popular method of selective laser excitation of activator ions in disordered matrices (for details see Alimov *et al.*,[7] Dianov *et al.*,[8] Alimov *et al.*,[9] and the literature cited in these papers). This method is based on narrowing of inhomogeneously broadened luminescence lines under monochromatic laser excitation ($\Delta\lambda_{st} \ll \Delta\lambda_{inh}$) of specific optical centers and it can be used to study the kinetics of relaxation of the line profile of the preferentially excited centers resulting from the migration of energy between the active centers.

The selective laser excitation method was first used in the Soviet Union to study Eu^{3+} ions in a glass matrix.[7] It was found that the application of the method to media with a strong inhomogeneous line broadening can give such important characteristics as the energies of the Stark splitting of multiplets of specific groups of centers, homogeneous line widths, lifetimes, transition probabilities, and changes in these parameters from one center to another.

Later the selective laser excitation method was used to detect spectral migration of energy between Nd^{3+} ions in yttrium fluorite crystals[8] and to study variation of the Stark splitting energies, lifetimes, and radiative transition probability of various optical Nd^{3+} centers in silicate glass.[9] It should be noted that in the case of the Nd^{3+} ion a study of the relaxation kinetics of the luminescence line profile of centers excited by monochromatic laser and radiation yields very important results, such as the rates and channels of the relaxation of the energy stored in the $^4F_{3/2}$ metastable level in lasers and light amplifiers.

We investigated CaF$_2$–YF$_3$–NdF$_3$ yttrium fluorite crystals containing 12 wt. % YF$_3$ and variable amounts of NdF$_3$ from 0.1 to 3 wt. %. The selective excitation method was applied using the apparatus described earlier,[9] in which the selective excitation source was a 6G rhodamine laser emitting 550–625 nm radiation in the form of pulses of 12.5 Hz repetition frequency and ~15 nsec duration. The dye was excited by the second harmonic ($\lambda = 0.532\ \mu$) of a commercial (LTIPCh-7) YAG:Nd^{3+} laser. The apparatus described earlier[9] was modified by replacing a dispersive prism resonator with a resonator which contained a diffraction grating and a prism beam expander; this made it possible to reduce the width of the stimulated emission line to <0.1 nm. A high-luminosity MDR-2 grating monochromator with 4 nm/mm dispersion was used as the spectroscopic instrument. The photorecording system comprised an FÉU-83 photomultiplier and a PAR-162 gate integrator, whose technical capabilities were described earlier.[8,9] As before,[9] the kinetics of luminescence decay was recorded by photographing traces on the screen of a TR-4401 oscilloscope.

We first investigated the structure of inhomogeneously broadened Nd^{3+} bands of yttrium fluorite. It was important to compare the nature of the inhomogeneous broadening of the spectra of mixed CaF$_2$–YF$_3$ crystals, which—in spite of their disorder—had a definite type of crystal structure and symmetry of the immediate anion environment, with the results obtained for glasses in which the angular and radial distributions of anions relative to the activator ion varied enormously from one center to another.

Figure 1 shows the absorption spectra of Nd^{3+} of an yttrium fluorite crystal obtained in the regions of 0.35

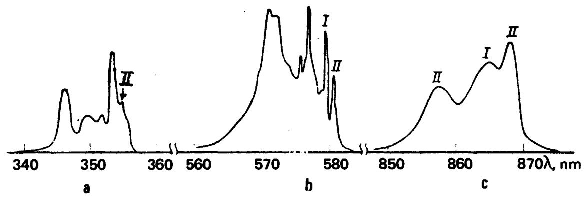

FIG. 1. Absorption spectra of Nd^{3+} in CaF_2–YF_3 crystals at $T = 77$ °K (I and II denote two types of activator center).

(a), 0.58 (b), and 0.87 μ (c) recorded at $T = 77$°K using an SF-8 spectrophotometer. The absorption spectrum in the 0.58 μ region (corresponding to the $^4I_{9/2} \to {}^4G_{5/2}$, $^2G_{7/2}$ transition) coincided with the intensity maximum of the radiation emitted by the tunable rhodamine 6G laser and had several relatively narrow long-wavelength peaks. These peaks probably corresponded to transitions between the various Stark sublevels within one center and in different optical centers in the matrix. Neodymium was excited in the absorption band of this transition and it rapidly relaxed to the $^4F_{3/2}$ metastable level. The luminescence due to transitions from this level to $^4I_{9/2}$ and $^4I_{11/2}$ was recorded by the gating method with a delay time $t_d = 30$ μsec (the recording lasted $\Delta t = 5$ μsec). This short delay time was selected to avoid the influence of the relatively slow processes of the ion–ion interaction on the form of the spectra. The measurements were carried out on samples (with 0.1 wt. % NdF_3) whose optical density excluded the influence of reabsorption of the luminescence of the $^4F_{3/2} \to {}^4I_{9/2}$ resonance transition on the form of the spectra (for a spectral slit width less than 0.8 nm). The laser excitation wavelengths λ_e corresponded to the positions of the intensity maxima of the narrow components in the long-wavelength part of the absorption spectrum (560–585 nm).

Figure 2 shows the luminescence spectra of the $^4F_{3/2} \to {}^4I_{11/2}$ transitions obtained using excitation wavelengths $\lambda_e = 576.7$, 579, and 580.2 nm. Clearly, the spectra of both transitions were quite different for different excitation wavelengths λ_e, which indicated that the 579 and 580.1 nm absorption lines were associated with different optical centers.

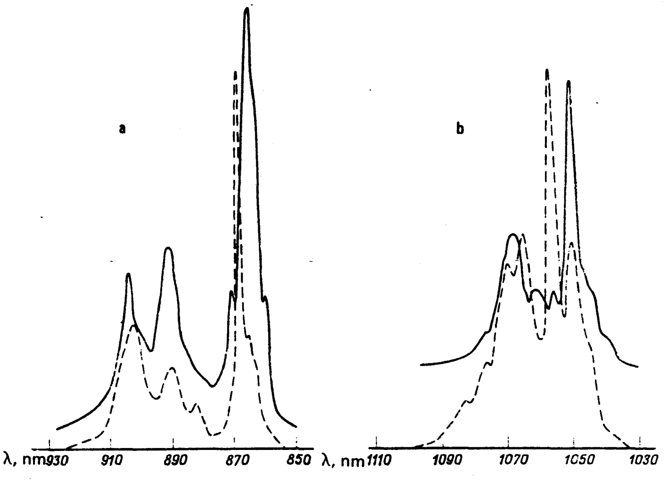

FIG. 2. Luminescence spectra of Nd^{3+}: a) due to the $^4F_{3/2} \to {}^4I_{9/2}$ transition ($\lambda_e = 579$ nm); b) due to the $^4F_{3/2} \to {}^4I_{11/2}$ transition ($\lambda_e = 576.7$ nm) in a CaF_2—YF_3 crystal subjected to selective laser excitation ($T = 77$ °K); the dashed curves represent the spectra obtained for $\lambda_e = 580.2$ nm.

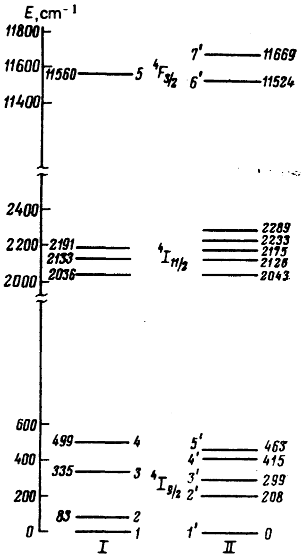

FIG. 3. Stark level schemes for two types of Nd^{3+} center in CaF_2–YF_3 crystals.

The existence of two types of center in yttrium fluorite crystals was discovered earlier in stimulated emission investigations[10] and also in a study[11] of the luminescence spectra of Nd^{3+} under $^4I_{9/2} \to {}^4F_{3/2}$ resonance excitation.

An analysis of the luminescence (Fig. 2) and absorption (Fig. 1c) spectra enabled us to construct an approximate Stark splitting scheme of the $^4I_{9/2}$, $^4I_{11/2}$, and $^4F_{3/2}$ multiplets for the two types of activator center (Fig. 3), which we called I and II centers; one should remember that each of these centers clearly represented a group of centers and was characterized by inhomogeneous line broadening. The indeterminacy of the level positions was <20 cm⁻¹.

The results indicated that, in contrast to silicate glass,[9] a CaF_2–YF_3 crystal does not exhibit a continuous and smooth variation of the structure of the centers with a corresponding smooth variation of the energies of the Stark splitting from one center to another. In this crystal the neodymium ions occupy mainly two specific positions with different environments but in each position there are certain fluctuations of the crystal field that result in the observed inhomogeneous broadening of the spectra of the group of centers in question.

We cannot exclude the possibility that our luminescence spectra do not contain peaks corresponding to transitions to all the Stark levels. In the case of the type II centers the $^4F_{3/2}$ and $^4I_{9/2}$ multiplets split into the maximum possible number of the Stark components (two and five, respectively) and the large value of the splitting of the $^4F_{3/2}$ level ($\Delta E = 145$ cm⁻¹) is evidence of the low symmetry of these centers. The $^4I_{11/2}$ multiplet of the II centers consists, in our scheme, of five Stark components although the maximum number of the splitting components in a low-symmetry electric field is six.

Clearly, the luminescence peak corresponding to the sixth Stark component is not resolved because of the residual inhomogeneous broadening of the spectra.

The selective excitation method was used also to study the nature of the broadening of the spectral lines of yttrium fluorite crystals. This was done by selective laser excitation of the ${}^4I_{9/2} \to {}^4D$ transition in the type II centers by the third harmonic of the LTIPCh-7 neodymium laser of wavelength $\lambda_e = 354.7$ nm (identified by an arrow in Fig. 1a). The observed positions of the luminescence peaks in the ${}^4F_{3/2} \to {}^4I_{9/2}$, ${}^4I_{11/2}$ spectra are in agreement with the spectra recorded using $\lambda_e = 580.2$ nm (type II centers, Fig. 2) but in the case of $\lambda_e = 354.7$ nm there is a better spectral selection of the type II centers, as manifested (for example) by an increase in the ratio of the intensities of the luminescence lines at $\lambda_l = 867.7$ nm (type II centers) and $\lambda_l = 865$ nm (type I centers), corresponding to the $6' \to 1'$ and $5 \to 1$ transitions (Fig. 3).

Excitation at $T = 77$°K with wide-band (lamp) radiation produced the line at $\lambda_l = 867.7$ nm, which had an inhomogeneous width of $\Delta = 22$ cm^{-1}. Laser excitation with $\lambda_e = 354.7$ nm at the same temperature reduced the inhomogeneous width to 15.3 cm^{-1} because of partial correlation between the energies of the ${}^4I_{9/2} \to {}^4D$ and ${}^4F_{3/2} \to {}^4I_{9/2}$ transitions (curve I in Fig. 4). Increase of temperature to $T = 194$°K produced a homogeneous broadening component of the line ($\lambda_l = 867.7$ nm) because of an increase in the probability of relaxational transitions, accompanied by phonon absorption, to higher Stark levels of the ${}^4I_{9/2}$ and ${}^4F_{3/2}$ states (curve 2 in Fig. 4).

The homogeneous component δ was determined by separation from a complex Voigt profile using tables in Posener's paper.[12] At $T = 194$°K this component was $\delta \approx 17$ cm^{-1}, whereas at $T = 300$°K it increased to $\delta \approx 23$ cm^{-1}. It was interesting to note that at room temperature the ratio Δ/δ was ≈ 1.

The spectrum corresponding to the transition between the ${}^4F_{3/2}$ level and the lowest component ${}^4I_{9/2}$ ($\lambda_{\max} = 865$ nm) of the type I centers was inhomogeneously broadened and its width was 85 cm^{-1}, which remained constant up to 300°K, Such a large inhomogeneous width could be explained by superposition of a considerable number of lines belonging to the *L*, *M*, or *N* centers[13] deformed by variations of the composition in the nearest coordination spheres on increase of the YF_3 concentration.

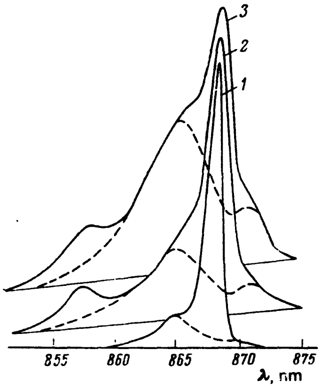

FIG. 4. Parts of the luminescence spectra (due to the ${}^4F_{3/2} \to {}^4I_{9/2}$ transition) of a CaF_2–YF_3 crystal (3 wt. % NdF_3), recorded subject to various time delays after selective laser excitation ($\lambda_e = 354.7$ nm): 1) $T = 77$°K, $t_d = 3\times10^{-5} - 1.5\times10^{-3}$ sec; 2) $T = 194$°K, $t_d = 3\times10^{-5}$ sec; 3) $T = 194$°K, $t_d = 1\times10^{-3}$ sec. The dashed curves represent the luminescence spectra of the type I centers.

We also studied the decay kinetics of the luminescence emitted from the two groups of centers I and II under selective excitation conditions. With this in mind we separated the spectral lines at $\lambda_{\max} = 865$ and 867.7 nm, representing the luminescence of the I and II centers, by means of a monochromator with 0.8 nm resolution. In the case of the crystal with 0.1 wt. % NdF_3, which did not exhibit concentration quenching at room temperature, the lifetime τ of the group I centers was 630 μsec, whereas for the group II centers it was 525 μsec. Cooling to 77°K did not alter the lifetime of the type I centers, whereas the lifetime τ of the II centers decreased to 400 μsec. These temperature dependences of the lifetimes of the two groups of centers could be explained by the smallness of the Stark splitting of the ${}^4F_{3/2}$ level of the group I centers ($\Delta E < 85$ cm^{-1}) compared with the splitting in the case of the group II centers ($\Delta E = 145$ cm^{-1}); this is shown in Fig. 4. A reduction in the population of the upper Stark component of the ${}^4F_{3/2}$ state of the type II centers increased the average probability of radiative transitions to levels of the ${}^4I$ term, in accordance with the expression[14]

$$A_{av} = (n_{6'} A_{6'} + n_{7'} A_{7'})/(n_{6'} + n_{7'}). \quad (1)$$

Here, $A_{6'}$ and $A_{7'}$ are the total intensities of the spontaneous transitions from the lower and upper components of ${}^4F_{3/2}$ to the levels of the ${}^4I$ term; $n_{6'}$ and $n_{7'}$ are the corresponding populations of the lower and upper Stark components of the ${}^4F_{3/2}$ level. Substituting in Eq. (1) the populations $n_{6'}$ and $n_{7'}$, as well as the value of A_{av} at temperatures of 300 and 77°K, we found the radiative transition probabilities for the two components of the ${}^4F_{3/2}$ level: $A_{6'} = 2.64\times10^3$ sec^{-1} and $A_{7'} = 0.42\times10^3$ sec^{-1}.

An increase in the neodymium concentration in yttrium fluorite resulted in a gradual reduction of the lifetime τ of the ${}^4F_{3/2}$ level because of an increase of the quenching interaction between the Nd^{3+} ions. The change in τ of the type I centers was greater than the change in τ of the type II centers. When the concentration of NdF_3 reached 3 wt.%, the lifetimes of both types of center became equal and amounted to 320 μsec at 194°K.

Our study of the spectral properties of the two types of center under selective excitation and recording of their luminescence demonstrated the possibility of determining the parameters of the ion–ion interaction and of the spectral migration of energy between the centers of the same and different (II → I) types by the selective excitation method.

The nature of the kinetics of the spectral migration and its rate were known to govern the energy and spectral properties of a given material when used as the active medium in a laser.

We studied the spectral migration by combining selective excitation of the type II centers with recording of the luminescence in the 850–875 nm range ($\lambda_{max} = 867.7$ nm for the type II centers and $\lambda_{max} = 865$ nm for the type I centers) after various delays t_d from the moment of excitation. As reported above, the highest selectivity was observed for the type II centers excited by the third harmonic of a YAG:Nd^{3+} laser ($\lambda_e = 354.7$ nm). The luminescence recording time was 5 μsec, whereas the delay time t_d was varied from 30 μsec to 1.5 msec. Such delayed measurements of the luminescence spectra were carried out on a crystal with 3 wt.% NdF_3, when the lifetimes of the types I and II centers were identical, which simplified greatly the subsequent analysis of the spectral migration kinetics.

A change in the delay time from 30 μsec to 1.5 msec in recording the luminescence of a sample kept at 77°K did not alter the spectrum (curve I in Fig. 4), indicating that there was no spectral migration at this temperature. Increase of temperature to 194°K resulted in a considerable change in the spectra on increase of t_d (curves 2 and 3 in Fig. 4). Clearly, an increase in the delay time increased the intensity of the line at $\lambda_{max} = 865$ nm, compared with the intensity of the line at $\lambda_{max} = 867.7$ nm. This was due to nonradiative energy transfer from the metastable level of the type II centers to the metastable level of the type I centers because of the interaction between these centers. The absence of the interaction between the type II and I centers at a low temperature (77°K) and its appearance at a higher temperature (194°K) was not unexpected because an increase in temperature (as reported above) resulted in a rapid increase of the homogeneous line widths of the resonance transitions and, moreover, gave rise to a larger number of transitions involving the excited Stark levels, which facilitated energy resonances in the ion–ion interactions.

An analysis of the spectral migration effect (transfer of energy from the type II to type I centers) was made using the theory of the static donor–acceptor energy transfer,[15] similar to that used by us earlier.[7] The decay kinetics of the excited state of donors (group II centers) in the case of irreversible energy transfer to acceptors (group I centers) can be described by the following expression in the case of the dipole–dipole interaction[15]:

$$n_{II}(t) = n_{II}(0) \exp\left[-t/\tau_{II}\right] \exp\left[-(t/\tau_R)^{1/2}\right], \tag{2}$$

where τ_{II} is the lifetime of the type II centers and τ_R is the characteristic energy-transfer time in which the population of the excited donor level decreases by a factor of e because of the spectral energy migration. This energy transfer (relaxation) time is

$$\tau_R = \frac{\tau_{II}}{\left[\Gamma(^1/_2)\, n_I/c_0\right]^2}, \tag{3}$$

where n_I is the concentration of the type I centers; c_0 is the critical concentration of the type I centers at which the energy transfer time is equal to the spontaneous deactivation time of the $^4F_{3/2}$ level in the II centers; Γ is the gamma function.

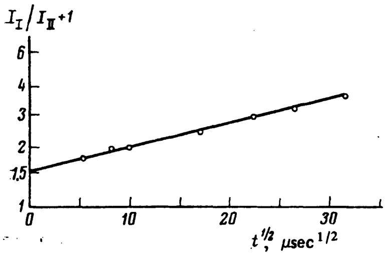

FIG. 5. Analysis of the kinetics of the spectral migration in a CaF_2–YF_3 crystal (3 wt. % NdF_2).

When the lifetimes are equal, $\tau_I = \tau_{II}$, Eq. (2) can be written in the form

$$\ln\left[\frac{I_I(t)}{I_{II}(t)} + 1\right] - \ln\left[\frac{I_I(0)}{I_{II}(0)} + 1\right] = \left(\frac{t}{\tau_R}\right)^{1/2}. \tag{4}$$

We shall assume that the ratio of the intensities deduced from the area under the spectra bounded by the continuous and dashed lines (Fig. 4) is equal to the ratio of the populations of the excited levels n_I/n_{II}.

This method was used to analyze the spectra recorded after the following delay times t_d: 30, 75, 100, 300, 500, 700, 1000, and 1500 μsec. Figure 5 shows the dependence obtained by substitution of the values of $I_I(t_d)$, $I_{II}(t_d)$, $I_I(0)$, and $I_{II}(0)$, and t_d in Eq. (4). This dependence is described satisfactorily by the square-root law ($\sqrt{t}$) corresponding to the dipole–dipole Nd^{3+}(II)–Nd^{3+} (I) interaction. In the range of short delay times ($t_d \to 0$) at $T = 194$°K we find that $I_I/I_{II} + 1 = 1.52$, which agrees with the value of $I_I/I_{II} + 1$ obtained at $T = 77$°K and represents the degree of selectivity of the radiation employed. In the range of long delay times ($t_d > 1$ msec) the ratio of the line intensities I_{II} and I_I reaches its maximum value and ceases to depend on t_d. This range of t_d demonstrates saturation of the spectral migration of the excitation energy.

A comparison of such spectra with $t_d > 1$ msec with the spectrum obtained as a result of wide-band excitation (using a tungsten lamp) showed that they were identical. This indicated that the migration of electronic excitation was reversible, i.e., that energy was transferred not only from the type II centers to the type I centers but also for I to II. Soon after the excitation the energy flux from the type II to the type I centers predominated because of the selective population of the type II centers, but after some time the reverse energy flux I → II became comparable with the forward flux II → I, which resulted in establishment of an equilibrium of the populations of the metastable levels in both centers. This equality of the populations resulting from the migration was the reason for the identity of the spectra obtained as a result of monochromatic ($t_d > 1$ msec) and wide-band excitation, and it indicated complete disappearance of the "memory" of the selective excitation of the neodymium ion system.

It is clear from Eq. (4) that the slope of the line in

Fig. 5 during the intital stages (before the reverse transfer processes became significant) could be used to determine the characteristic time of the energy transfer from the type II to the type I centers, which was found to be $\tau_R = 1.2$ msec. Knowing this value, we were able to find the probability of energy transfer from the type II to the type I centers over an average distance:

$$P_{\rm ct} = \frac{1}{\tau_{II}[\Gamma(^1/_2)]^2} = 270 \text{ sec}^{-1}. \qquad (5)$$

An analysis of our energy level schemes of the Nd^{3+} ions in the I and II centers and the knowledge of the homogeneous line broadening at 194°K demonstrated a possibility of a resonant dipole-dipole interaction between these centers due to the overlap of the homogeneous line widths of the various transitions.

In addition to the spectral migration of the excitation energy from the II to the I centers, we discovered that spectral migration occurred also in a group of similar II centers (curves 2 and 3 in Fig. 4). The luminescence line of the type II centers at $\lambda_{\max} = 867.7$ nm at $T = 194$°K had a homogeneous line width of $\delta \approx 17$ cm^{-1} during the first moments after monochromatic excitation and this width was 1.3 times less than the inhomogeneous broadening of this line. The subsequent increase in the delay time t_d broadened the line to 21 cm^{-1} because of energy migration to spectroscopically similar ions belonging to the same type (II) of center. This process involved only the 6′–1′ resonant transition to ions separated from the excited ions by an energy of the order of the homogeneous line width.

We shall conclude by stressing that our results have revealed considerable differences between the nature of the inhomogeneous broadening of bands in two types of structurally disordered solids: randomly disordered solid-solution crystals and glasses with spatially disordered structures.

The authors are grateful to V. A. Myzina for determining the composition of the crystals.

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Translated by A. Tybulewicz