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INVESTIGATION OF THE ELEMENTARY CROSS-RELAXATION ACT OF THE Nd^{3+} *ION EXCITED STATE IN CRYSTALS*

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The mechanism of Nd^{3+} ion interaction resulting in nonradiative deactivation of the excited state is investigated. It is demonstrated that such a mechanism consists in cross relaxation via the $^4I_{15/2}$ level. The temperature dependence of the process is related to population of excited Stark components. The total energies of the components enter the expression for the populations. Temperature stimulation of nonresonant interaction connected with filling up of the phonon states becomes appreciable on increase of temperature.

AN investigation of the temperature dependences of the excited states of impurity ions in a crystal lattice is an effective tool for the study of the interactions of these ions. In particular, in ionic crystals activated with trivalent rare-earth ions, the nonradiative transfer of excitation energy had been intensively studied. The effects in these objects have not been unambiguously interpreted in the literature, and there is no meeting of minds concerning the mechanisms of the nonradiative transfer. According to one point of view, the temperature dependence of the deactivation of the excited state of the donor (D) is due to the change in the effectiveness of energy migration over the D ions[1,2]. The basis for this assumption is that the temperature dependence of the lifetimes τ of the excited state are given by

$$\tau(T) = \tau_i(1 - Be^{-\Delta E/2kT}),$$

where τ_i is the lifetime measured at low temperatures, when $\tau \neq f(T)$, B is a constant that does not depend on the temperature, and ΔE is the energy of the first excited Stark component of the ground state of D. The factor 2 in the denominator of the argument of the exponential is due, in the opinion of the authors of[1,2], to the essentially nonstationary character of the diffusion over the donor ions during the lifetime of the excited state.

In an earlier paper[3], we have succeeded in eliminating the influence of the migration on the temperature dependence of the deactivation of the excited state. This was made possible because the Nd^{3+} ions tend to form pairs in the fluorite crystals investigated by us, i.e., the Nd^{3+} ions are disposed in neighboring points of the crystal lattice already at sufficiently low activator concentrations[4]. When such a pair is produced, the local crystal field of the ion is altered, and separately standing lines of the paired emission centers are observed in the optical centers. We have investigated the temperature dependence of the relative quantum yield of the luminescence of paired centers in the temperature range 4.2–70°K. It turned out that the quantity directly dependent on the temperature is the elementary act of nonradiative D → A energy transfer. The temperature dependence of the effectiveness of the elementary act of Nd^{3+} ion interaction is illustrated in Fig. 1a. An analysis of this dependence shows that it is not exponential.

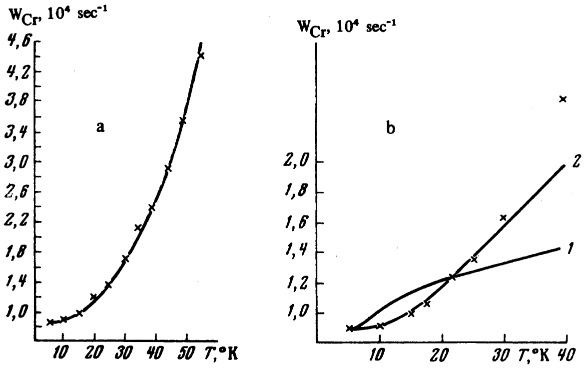

FIG. 1. Temperature dependence of the cross-relaxation probability: a–experimental data from [3], b–present data (points–experiment, curve–calculated from formula (2) at $\Delta E = \frac{1}{2}\Delta E_{ge}$, curve 2–at $\Delta E = \Delta E_{ge}$).

An examination of the crystal splitting scheme of the Nd^{3+} ions in our case (Fig. 2) shows that the most probable channel of nonradiative losses of excited Nd^{3+} ions is cross relaxation via the transitions $^4F_{3/2} \to {^4I_{15/2}}$ and $^4I_{9/2} \to {^4I_{15/2}}$[5-7]. The loss of excitation via the interactions $^4F_{3/2} \to {^4I_{13/2}}$ and $^4I_{9/2} \to {^4I_{15/2}}$ has low probability in our case, for in this case at least two phonons must take part in order to cover the energy deficit. This conclusion is corroborated by experimental data below.

At T = 4.2°K the nonradiative loss of excitation may be due to cross relaxation with participation of the transitions 10 → 3 and 1 → 3. With rising temperature, when the levels 2 and 11 are populated, about 50 transitions can take part in the cross relaxation. Some of them are resonant transitions. We can write for the temperature dependence of the cross relaxation

$$\begin{aligned} W_{cr}(T) = W_g n_g^2 + W_r(n_g n_e + n_e^2) + W_n^-(n_g n_e + n_e^2)\bar{n}_r \\ + W_n^+(n_g n_e + n_e)^2(\bar{n}_r + 1), \end{aligned} \tag{1}$$

where $W_0 = 1/\tau_1 - 1/\tau_0$, τ_1 is the lifetime at low temperatures, where, $\tau \neq f(T)$, and τ_0 is the radiative lifetime. According to the data of[3,8], $\tau_1 \approx 100$ μsec and $\tau_0 = 550$ μsec;

$$W_r = \sum_i \sum_j \sum_k \omega_{ik,jj}^{r}, \qquad W_n^- = \sum_i \sum_j \sum_k \omega_{ik,jj}^{n-},$$

$$W_{n^+} = \sum_i \sum_j \sum_k \omega^{n+}_{ik,jj}.$$

$i = 10, 11$, $j = 3 - 9$, $k = 1, 2$ are the level numbers (see Fig. 2), $\omega^{r}_{ik,jj}$ is the probability of the resonant cross relaxation for the transitions $i \to j$ and $k \to j$ at fixed i, j, and k, and only resonant transitions are taken into account in the summation; $\omega^{n-}_{ik,jj}$ is the probability of nonresonant cross relaxation of the transitions $i \to j$ and $k \to j$ with anti-Stokes deviation at fixed i, j, and k, the summation including only transitions that give an anti-Stokes deviation from resonance; $\omega^{n+}_{ik,jj}$ is the probability of nonresonant cross relaxation of the transitions $i \to j$ and $k \to j$ with Stokes deviation at fixed i, j, and k, the summation including only transitions that give a Stokes deviation from resonance.

Since $\Delta E_{1,2} = 36\ \text{cm}^{-1}$ and $\Delta E_{10,11} = 40\ \text{cm}^{-1}$ (Fig. 2), we assume, without incurring an appreciable error, that $\Delta E_{1,2} = \Delta E_{10,11} = \Delta E_{ge} = 38\ \text{cm}^{-1}$. Then $n_g = 1 - (\exp(\Delta E_{ge}/kT) + 1)^{-1}$ is the population of the ground Stark components of levels $^4F_{3/2}$ and $^4I_{9/2}$, while $n_e = (\exp(\Delta E_{ge}/kT) + 1)^{-1}$ are the populations of the excited Stark component of the $^4F_{3/2}$ level and of the first-excited Stark component of the $^4I_{9/2}$ level, normalized so that $n_g + n_e = 1$. The $^4F_{3/2}$ level splits in our case into two components, and the energy of the second excited Stark component of the $^4I_{9/2}$ level is much higher than ΔE_{ge}. Under these conditions, our normalization is valid at temperatures up to 55°K. The $n_r = [\exp(\Delta E_r/kT) - 1]^{-1}$ are the occupation numbers of the phonon states with energy ΔE_r. The factor $n_r + 1$ corresponds to processes with phonon emission, and n_r to processes with phonon absorption. In our case we are dealing in formula (1) with certain averaged values $\bar{n}_r$, since nonresonant transitions correspond to a large number of deviations from resonance. The combination of transitions 10 – 3 and 1 – 3 is also excluded from the summation over i, j, and k. These transitions account for a cross-relaxation probability W_g.

Thus, the first term in the right-hand side of (1) is the efficiency of cross relaxation with participation of the ground Stark components of the $^4F_{3/2}$ and $^4I_{9/2}$ states. The second term is the efficiency of the resonant cross relaxation with participation of excited Stark components. The third and fourth terms are the effectivenesses of nonresonant cross relaxation with participation of excited Stark components (the third and fourth terms represent processes with phonon absorption and emission, respectively). These processes are accompanied by creation or absorption of acoustic phonons. Indeed, as shown by an analysis of the crystal field splitting scheme, the maximum Stokes deviation from resonance is 82 cm^{-1}. The anti-Stokes cross relaxation can be realized with participation of phonons whose energy is $\Delta E_r \sim kT$ ($k = 0.7\ \text{cm}^{-1}/\text{deg}$, $T = 4.2–55$°K).

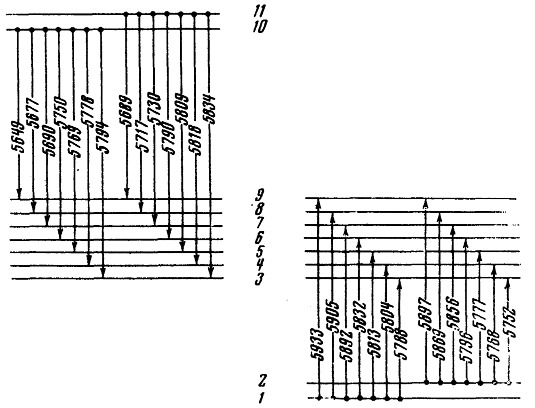

FIG. 2. Scheme of crystal field splitting of the levels of paired emission centers of Nd^{3+} in CaF_2, participating in the cross relaxation (the transition energies are given in cm^{-1}).

An examination of the frequency dependence of the density of the phonon states $\rho(\omega)$[9] shows that in the region of our deviations from resonance $\rho(\omega)$ agrees well with the Debye approximation $\rho(\omega) \sim \omega^2$. It follows from the foregoing that in a certain temperature region the function $W_{cr}(T)$ is determined only by the temperature-dependent variation of the populations n_g and n_e. Indeed, at low frequencies the density of the phonon states is low[9]. No acoustic phonons of high energy ($\Delta E_r > kT$) are excited. Thus, at low temperatures the third term in (1) is small, and the fourth varies with temperature like $n_g n_e + n_e^2$. At low temperatures we then have

$$W_{cr}(T) = W_g n_g^2 + (n_g n_e + n_e^2) W_{\text{int}}, \tag{2}$$

where $W_{\text{int}} = W_r + W_n^+$. Since experiments on many crystals ($Y_3Al_5O_{12}$, $Y_3Ga_5O_{12}$, LaF_3, $SrMoO_4$, $NaLa(MoO_4)$), activated with Nd^{3+} yielded $\overline{W}_{\text{in}}(T) \propto \exp(-\Delta E_{ge}/2kT)$1), where ΔE_{ge} is the energy of the first excited Stark component of the ground state of D,[1] we thought it necessary to attempt to describe the experimental curve by substituting in (2) the expressions for the populations at $\frac{1}{2}\Delta E_{ge}$ and ΔE_{ge}. The only attempt known to us at a description of the temperature dependence of τ by using the total energies of the excited Stark components ended in failure[5]. As already indicated, the experimental results[1,2] yield an activation energy $\frac{1}{2}\Delta E_{ge}$. The authors of[1,2] believe that this is due to the diffusion of the excitation and to the nonstationary character of the process. In our opinion this statement can be regarded only as a hypothesis, since the calculation in[1] was performed under assumptions whose validity is far from obvious.

Our results are shown in Fig. 1b. At T = 20°K, using the experimental results of[3] (Fig. 1a), we obtained from (2) the value of W_{int} at $\Delta E = \frac{1}{2}\Delta E_{ge}$. In the former and latter cases W_{int} is equal to 3×10^4 and $6.7 \times 10^4\ \text{sec}^{-1}$. It turned out further that in the temperature region (up to 30°K) where expression (1) takes the form (2), the experimental curve is correctly described by formula (2) with $\Delta E = \Delta E_{ge}$ and at $W_{\text{int}} = 6.7 \times 10^4\ \text{sec}^{-1} \neq f(T)$ (Fig. 1b). The latter confirms the validity of the assumptions under which expressions (1) and (2) were obtained. At higher temperatures, the temperature stimulation of the cross relaxation, due to the filling of the phonon states, comes into play and it is convenient to represent (1) in the form

$$W_{cr}(T) = W_g n_g^2 + W_{\text{int}}(n_g n_e + n_e^2) + \Delta W_{\text{int}}(T)(n_g n_e + n_e^2), \tag{3}$$

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1) $\overline{W}_{\text{int}}(T)$ is the average probability of excitation-energy migration over the donor ions, followed by transfer to the acceptor.

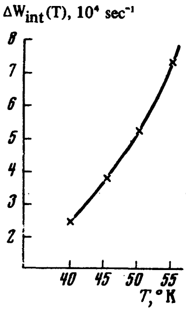

FIG. 3. Function of temperature stimulation of the cross-relaxation effectiveness.

where $\Delta E_{int}(T)$ is the function of temperature stimulation of the cross-relaxation efficiency, due to the filling of the phonon states. Its plot shown in Fig. 3 was obtained from (3) by using the experimental results (see Fig. 1a). The extrapolation of $\Delta E_{int}(T)$ into the region of low temperatures shows that at $T = 30°K$ the value of $\Delta E_{int}(T)$ is lower than W_{int} by about one order of magnitude.

It must be noted that when crystals with high activator concentrations are investigated[2)], when the lifetime τ of the excited state at $T = 4.2°K$ is shorter than the radiative lifetime, the artificial distinction between temperature-dependent and temperature-independent interactions of the Nd^{3+} ions, proposed in[1,2], must be separately justified in each concrete case. Formally this means an estimate of the contribution made to the temperature dependence by the term of the form $W_g n_g^2$ in Eqs. (1)–(3).

Thus, our results allow us to make the following conclusions:

1. The quenching of the luminescence of Nd^{3+} is determined in our case by the cross relaxation through the $^4I_{15/2}$ level, since interaction via the transitions $^4F_{3/2} \rightarrow {}^4I_{13/2}$ and $^4I_{9/2} \rightarrow {}^4I_{15/2}$ could not yield the experimentally observed dependence.

2. At low temperatures (up to 30°K), the temperature dependence of the cross-relaxation effectiveness is determined by the population of the excited Stark components. The expressions for the populations contain in this case the total energies of the excited Stark components[3)].

3. When the temperature is increased ($T > 30°K$), the effectiveness of the nonresonant cross relaxation is stimulated by filling of the phonon states.

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[2)] Precisely such crystals were used in [1].

[3)] The mechanism proposed by us in [3] for temperature activation of nonresonant transfer, connected with population of the phonon state, was used to interpret the temperature dependence of the relative quantum yield of luminescence in the case when the deviation was much larger than kT (the case of interaction of Nd^{3+} and Eu^{3+} ions).

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