

Nonradiative transfer of excitation energy in crystals with the interaction of three optically active centers

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It is shown that in oxide and fluoride crystals activated by Er^{3+} ions, there are different mechanisms of energy transfer, which are associated with the interactions of two and three optically active centers.

We consider the mechanisms of nonradiative transfer of excitation energy from the ${}^4\text{S}_{3/2}$ level of the Er^{3+} ion in the crystal $\text{Y}_3\text{Al}_5\text{O}_{12}$, YAlO_3 , $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, and YLiF_4 .

A quantum-mechanical description of the processes of energy transfer in crystals in the case of interactions of two and three optically active centers, using first and second-order perturbation theory, was considered in Refs. 1 and 2.

In the case of sudden excitation of donors, the kinetics of the luminescence of the donors is a complicated, multistage process³ because of the random distribution of acceptors throughout the crystal (assuming the multipole order of the interaction between ions remains constant). The kinetic curves can be broken up into three segments corresponding to the stages of ordered and disordered static decay and migration of excitations via the ions of the activator.⁴ In the stage of ordered static decay, excitation energy is transferred by acceptors in the immediate neighborhood of the donors (the most rapid transfer occurs for acceptors in the first coordinate sphere). In the case of interaction of two optically active centers the macroscopic rate of transfer is given by $W_0 = C_{da}c\sum_j R_j^{-6}$ and this stage is limited to times $t_r = R_{\min}^6/C_{da}$ (c is the concentration of acceptors, R_j is the distance between the donor and the j th acceptor, R_{\min} is the radius of the first coordinate sphere, and C_{da} is the microscopic parameter of donor–acceptor transfer).⁴ We note that in the case of interaction of two centers the velocity parameter W_0 is proportional to the concentration of acceptors. The probability of static transfer of excitation energy for interaction of three centers is

proportional to the square of the acceptor concentration.⁵ Hence for the ordered stage we have in this case $W_0 \sim c^2$.

The probability of interaction depends on the overlap integrals, the widths of transitions between Stark levels, the photon spectrum of the crystal, and on other factors. Under certain conditions and concentrations, transfer of excitation energy via interaction of three optically active centers (three-particle interaction) can compete with transfer via the interaction of two centers. This competition should show up in the concentration dependence of the parameter W_0 of ordered static transfer.

The mechanism of concentration quenching of luminescence from the level ${}^4S_{3/2}$

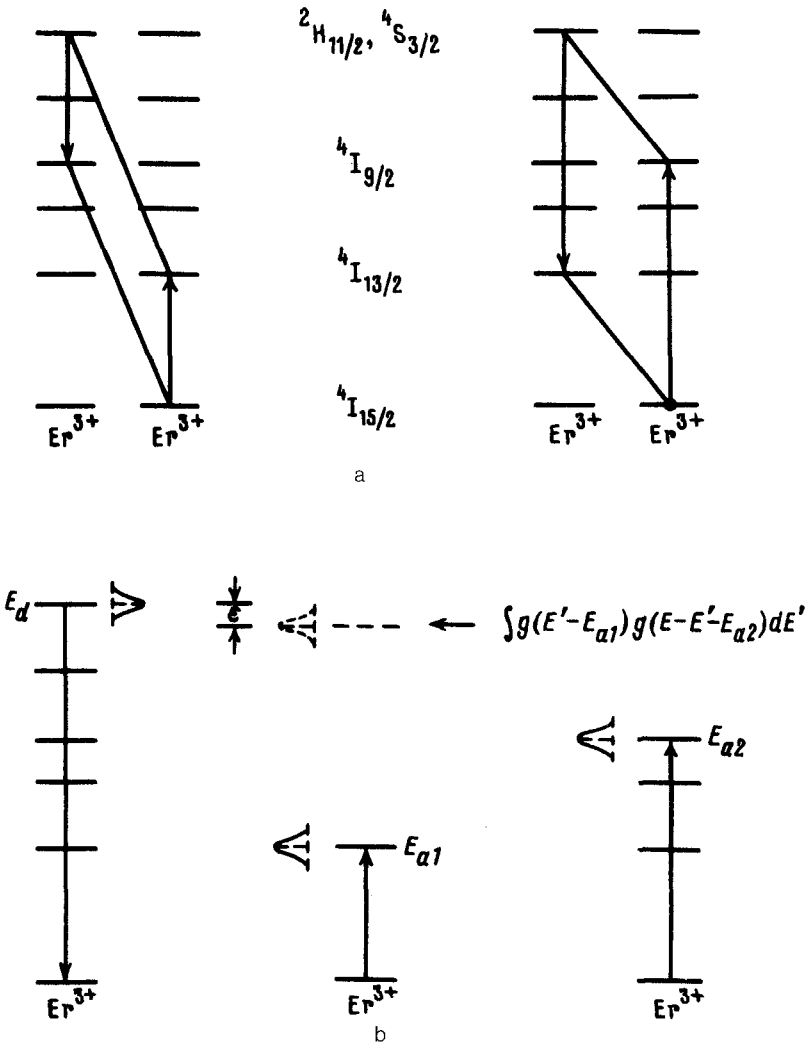


FIG. 1. Nonradiative transfer of excitation energy from the ${}^4S_{3/2}$ level of Er^{3+} by the cross-relaxation mechanism for the interaction of (a) two or (b) three optically active centers.

of the Er^{3+} ion (Fig. 1a) was discussed in Refs. 6 and 7. This phenomenon is typical of the interaction of two centers (two-particle interaction). A detailed study by the present authors of the mechanism of transfer of energy from the $^4S_{3/2}$ level of Er^{3+} in $(\text{YEr})_3\text{Al}_5\text{O}_{12}$ crystals showed that at high concentrations the kinetics of luminescence is not consistent with the description obtained in the framework of the two-particle interaction $\text{Er}^{3+}-\text{Er}^{3+}$ using only the parameters C_{da} and C_{dd} .⁸⁻¹⁰ Beginning with concentrations $\sim 10\%$ and $\sim 25\%$ for temperatures 300 K and 77 K, respectively, the experimental kinetics is more rapid than predicted by the theory. The disagreement between the experimental and theoretical curves increases in proportion to the square of the concentration of acceptors. Therefore, it was assumed in Ref. 10 that the transfer of excitation energy from the $^4S_{3/2}$ level of Er^{3+} in $(\text{YEr})_3\text{Al}_5\text{O}_{12}$ is due to both two-particle and three-particle interactions of the ions.

The experimental dependence of the parameter W_0 on the concentration of Er^{3+} ions is shown in Fig. 2 for the crystals $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, YAlO_3 , and YLiF_4 at temperature 300 K in logarithmic coordinates. The method of measuring W_0 was described in Refs. 8 and 9. We see that for $\text{YLiF}_4-\text{Er}^{3+}$ crystals the dependence

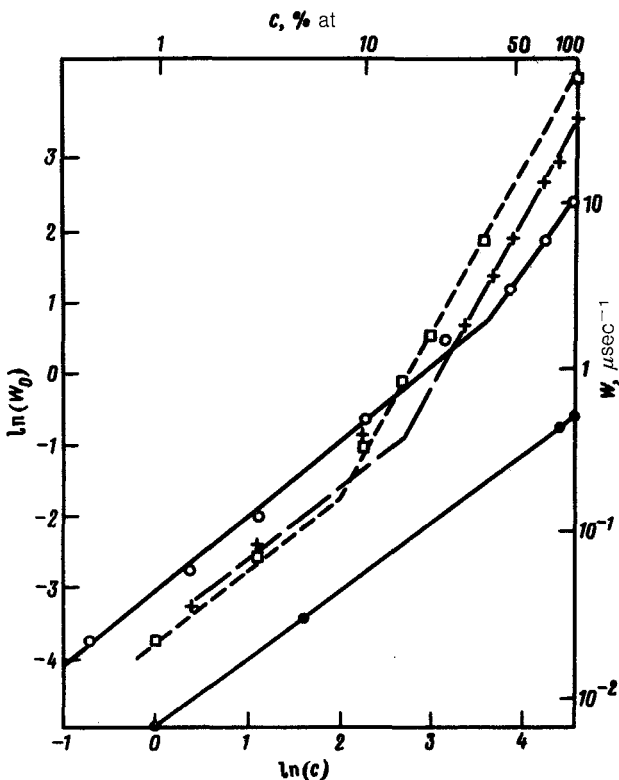


FIG. 2. Concentration dependence of the parameter W_0 of ordered static decay in logarithmic coordinates for the transfer of excitation energy from the $^4S_{3/2}$ level of Er^{3+} in the crystals $\text{Y}_3\text{Al}_5\text{O}_{12}-\text{Er}^{3+}$ (+), $\text{YAlO}_3-\text{Er}^{3+}$ (\square), $\text{Gd}_3\text{Ga}_5\text{O}_{12}-\text{Er}^{3+}$ (\circ), and $\text{YLiF}_4-\text{Er}^{3+}$ (\bullet).

between $\ln(W_0)$ and $\ln(c)$ is linear for the entire concentration series, which corresponds to quenching of luminescence due to the interaction of only two centers. For the crystals $Y_3Al_5O_{12}$ and $YAlO_3-Er^{3+}$ a deviation from linearity is observed for concentrations of 5–10%, and for concentrations greater than 30% the ratio $\ln(W_0)/\ln(c) = 2$. Therefore, at low concentrations quenching of the luminescence occurs because of interactions between two ions, and at higher concentrations two-particle interactions are replaced with three-particle interactions.

The probability of transfer of excitation energy from the $^4S_{3/2}$ level of Er^{3+} in the case of three-particle interactions depends on the overlap integral for transitions between Stark levels of the corresponding multiplets (Fig. 1b)

$$S = \int g_1(E_1 - E) \int g_2(E_2 - E') g_3(E_3 - E' - E) dE dE' . \quad (1)$$

An analysis of the energy-level diagrams of Er^{3+} ions in the crystal studied here^{11–14} shows that the overlap integral is largest for $Y_3Al_5O_{12}$ and $YAlO_3$ and smallest for $YLiF_4$.

For the crystal $Gd_3Ga_5O_{12}-Er^{3+}$ a slight deviation from linearity is observed at the end of the concentration series (70–80%). This may be caused by the fact that the probability of nonradiative transfer of excitation energy depends on the relation between the uniform (Γ_i) and nonuniform ($\tilde{\epsilon}$) components of the width of the transitions between Stark levels, i.e., on the shape of the line contour $g_i(E)$. The probability of interaction of two centers in the transfer of excitation energy is

$$W_{da} \sim [\Gamma_d + \Gamma_a] / [\epsilon^2 + (\Gamma_d + \Gamma_a)^2];$$

and for three centers

$$W_{daa} \sim [\Gamma_d + \Gamma_a + \Gamma_a] / [\epsilon^2 + (\Gamma_d + \Gamma_a + \Gamma_a)^2].$$

Since in a $Gd_3Ga_5O_{12}-Er^{3+}$ crystal the quantity ϵ is much larger than in the crystals $Y_3Al_5O_{12}-Er^{3+}$ and $YAlO_3-Er^{3+}$ (Ref. 10), transfer via the mechanism of Fig. 1b is less favorable in $Gd_3Ga_5O_{12}-Er^{3+}$ than in $Y_3Al_5O_{12}-Er^{3+}$ and $YAlO_3-Er^{3+}$ crystals, which was also observed in the experiment.

Hence, we have shown that the ordered decay stage of nonradiative transfer of excitation energy from the $^4S_{3/2}$ level of Er^{3+} in the crystals $Y_3Al_5O_{12}$, $Gd_3Ga_5O_{12}$, $YAlO_3$, and $YLiF_4$ and occurs because of interactions of two and three optically active centers.

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