TEMPERATURE DEPENDENCE OF ENERGY TRANSFER BETWEEN RARE EARTH IONS IN CRYSTALS

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The temperature dependence of energy transfer between rare earth ions in $Y_3Al_5O_{12}$, $Y_3Ga_5O_{12}$, and LaF_3 crystals is investigated at temperatures between 4.2° and 77°K. A sharp exponential decrease of the interaction probability is observed near helium temperatures. The decrease is explained as being due to a decline in the excitation energy migration between the same ions. It is shown that population of the first excited state of the donor ion plays an important role in improving the migration at the higher temperatures.

RECENTLY[1,2] there has been reported a decrease in the effectiveness of energy transfer between Eu^{3+} and Nd^{3+} ions in $NaY(WO_4)_2$ and Nd^{3+} and Yb^{3+} ions in glasses at low temperatures. In both cases this decrease is associated with processes of migration of excitation energy between the donor ions. Feofilov et al.[2] attribute this effect to the decline of migration at temperatures when $kT < \Gamma$, where Γ is the width of the donor line. We note that both these systems are characterized by wide spectral lines (several tens of cm^{-1}). These investigations were carried out at fixed temperatures: 77° and 4.2°K.

We have found a sharp decrease in energy transfer at T = 4.2°K in systems with narrow lines ($kT > \Gamma$), for which the interpretation proposed in[2] is inapplicable. We investigated the transfer of energy between Er^{3+} and Tu^{3+} in crystals of $Y_3Al_5O_{12}$ (YAG), as well as the concentration quenching of the luminescence of Er^{3+} in YAG and Nd^{3+} in crystals of $Y_3Ga_5O_{12}$ (YGG) and LaF_3 during a continuous variation of temperature from 4.2° to 77°K. In the investigation of transfer, the probability of interaction W_{int} of the ions Er^{3+} and Tu^{3+} was calculated from the relation

$$W_{int} = \tau_{int}^{-1} = \tau_{meas}^{-1} - \tau_{rad}^{-1},$$

where τ_{meas} is the measured lifetime of Er^{3+} ions in the $^4I_{13/2}$ level, shortened by interaction with Tu^{3+} ions, and τ_{rad} is the radiation lifetime of Er^{3+} ions. In the case of the concentration quenching of the luminescence of Er^{3+} ions from the $^4I_{13/2}$ level, the probability W_{int} was calculated analogously from the change in lifetime in crystals with different activator concentrations.

The measurements of the luminescence lifetime were made on samples placed in a copper block cooled by vapors of liquid helium. The temperature of the sample was monitored with a carbon resistor. The luminescence was excited by short light pulses (~15 μsec). The radiation detectors were PbS photoresistors in the case of Er (1.6 μ) and an FÉU-28 for Nd (0.9 μ).

The experimental results are given in Fig. 1. As can be seen, $\tau(T)$ has a markedly different character in different temperature intervals. Shortening of the τ of luminescence and consequently growth of W_{int} for the studied systems begins at different temperatures: for crystals with Er at 4.2°K (Fig. 1a), for Nd in LaF_3 at 7°K, and for Nd in YGG at 12°K (Fig. 1b). A comparison of the temperature dependence of transfer of energy

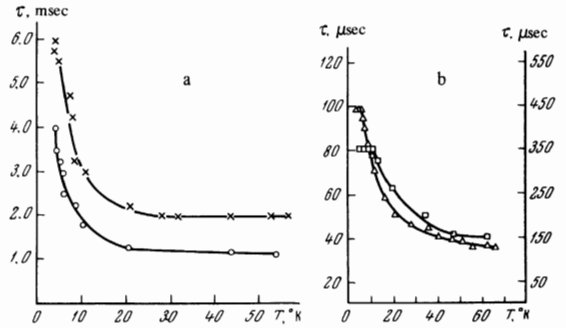

FIG. 1. Temperature dependence of τ of luminescence in the crystals: a–X–YAG: 1% Er, 0.2% Tu; O–YAG: 20% Er; b–Δ–LaF_3: 8% Nd (right scale), □–YGG: 7% Nd.

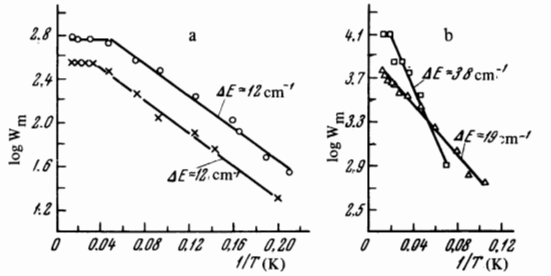

FIG. 2. Temperature dependence of W_m in the crystals: a–X–YAG: 1% Er, 0.2% Tu: O–YAG: 20% Er; b–Δ–LaF_3: 8% Nd, □–YGG: 7% Nd.

from Er to Tu and the concentration quenching of Er luminescence in YAG crystals (Fig. 1a) shows that this dependence is similar to and associated with the migration of excitation energy between Er^{3+} ions. Migration of excitation energy also plays an important role in the concentration quenching of Nd^{3+} ions.

At very low temperatures the energy transfer and quenching processes take place because of the temperature-independent process of direct multipole interaction (Fig. 1b). Subtraction of this interaction permits construction of the dependence of the probability of energy migration W_m on temperature for these systems (Fig. 2). These dependences have the form $W_m \sim \exp(-\Delta E/kt)$, and ΔE turns out to be approximately equal to half the distance to the first excited level of the donor ion. This distance is: for Er^{3+} in YAG, 24 cm^{-1},[3] for Nd^{3+} in YGG, 80 cm^{-1}[4], and for Nd^{3+} in LaF_3,

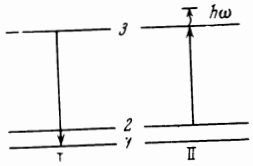

FIG. 3

40 cm^{-1}.[5] Thus, the improvement of migration is directly associated with the population of the first excited state in these systems. This improvement may be brought about by the following two effects.

1. At helium temperature the line of rare earth ions in a crystal corresponding to the transition 3—1 (or 1—3, Fig. 3) is inhomogeneously broadened.[6] Migration between ions is thereby more difficult, since the lines of neighboring ions do not overlap, and non-resonant transfer (with phonon emission) for low phonon frequencies (~ 1 cm^{-1}) is ineffective because of the low density of phonon states. As temperature is increased, the homogeneous width $\Delta\nu_1$ of level 1 will increase as $A_{21}\exp(-\Delta E_{12}/kT)$, where A_{21} is the probability of the radiationless transition 2—1; thus, the overlap of the lines of neighboring ions will improve and with it the migration of energy between them due to resonant transfer.

2. As the temperature is increased level 2 (Fig. 3) becomes populated, and the process of nonresonant migration of energy to donor ions with phonon emission can occur: ion I goes from level 3 to level 1, evoking the transition of Ion II from level 2 to level 3; a phonon with frequency $\hbar\omega \sim h\nu_{21}$ is released. This process is independent of the character of the line broadening, and its probability is markedly higher than the probability of processes of nonresonant transfer within the limits of the width of the 3—1 line because of the higher density of states of high-frequency phonons. The importance of nonresonant transfer is indicated, for example, by the fact that the interaction probability of Er^{3+} and Tu^{3+} ions in YAG (where the spectra overlap) has the same order of magnitude as that of Er^{3+} and Ho^{3+} in YAG (where the spectra do not overlap).[7] The investigation of energy migration processes in systems with strongly different line widths may allow making a choice between these two effects.

We also observed a weakening of the interactions at low temperatures in a large number of other crystals: YAG with Nd, YAG with Er and Ho, $SrMoO_4$ with Nd, $SrMoO_4$ with Er, etc. Evidently, these effects are characteristic of all crystals with rare earth impurities.

In conclusion, we express thanks to R. V. Bakradze and G. P. Kuznetsova, as well as to M. V. Dmitruk for making the single crystals available.

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4