Vol. 84 (1993) *ACTA PHYSICA POLONICA A* No. 5

Proceedings of the Winter Workshop, Karpacz 1993

RELAXATION OF THE $^4S_{3/2}$ LEVEL OF Er^{3+} IN $Cs_2NaErCl_6$

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Octahedral (O_h) symmetry of the RE^{3+} sites in the $Cs_2NaRECl_6$ crystals removes all of the electric dipole intensity from the $4f$–$4f$ transitions. Thus the decay of luminescence originating in the excited states of RE ions is governed by phonon assisted (vibronic) transitions, multiphonon relaxation and phonon assisted energy transfer (cross relaxation and energy migration to impurities). Contribution of these processes to the decay of the $^4S_{3/2}$ state of erbium in $Cs_2NaErCl_6$ has been studied in the 4.2–300 K temperature region. It has been concluded that at low temperatures the $^4S_{3/2}$ state decays exclusively by vibronic transitions. At about 100 K the cross relaxation via the $^4I_{9/2}$ state becomes operative. Efficiency of this process grows strongly with increasing temperature, reducing the $^4S_{3/2}$ lifetime by almost three orders of magnitude. No evidence has been found that multiphonon relaxations contribute to the decay of the $^4S_{3/2}$ state.

PACS numbers: 78.55.Hx

In our previous work [1] we reported for the first time the absorption properties of $Cs_2NaErCl_6$ and we proposed the assignments of vibronic transitions of Er^{3+}. More extensive study of the compound has been next reported by Hasan and Richardson [2]. Both the studies are very useful for the interpretation of luminescence spectra and lifetimes since they provide the energies of excited states of Er^{3+} as well as the vibrational modes of $ErCl_6^{3-}$ moiety. Preliminary data on Er^{3+} luminescence obtained with broadband excitation into the $^4F_{7/2}$, $^4F_{5/2}$, $^2G_{9/2}$ and $^4G_{11/2}$ group of levels indicated that the $^4F_{9/2}$, $^4I_{9/2}$ and $^4I_{11/2}$ luminescent states are populated by direct vibronic transitions from initially excited levels or by ion–ion interaction [3].

In this work the processes contributing to the relaxation of the $^4S_{3/2}$ state of Er^{3+} are examined. As the Er^{3+} ions in $Cs_2NaErCl_6$ are situated in the sites of octahedral (O_h) symmetry, the electric dipole transition are forbidden. Therefore the excited $^4S_{3/2}$ level may decay by phonon assisted (vibronic) transitions, multiphonon relaxation to the next lower lying level and by ion–ion interaction. In Fig. 1 we present the lifetimes of the $^4S_{3/2}$ level of Er^{3+} in $Cs_2NaErCl_6$ and in $Cs_2NaEr_{0.2}Y_{0.4}Yb_{0.4}Cl_6$ recorded in the 100–300 K temperature region. Temperature influences more strongly the lifetimes measured for diluted sample indicating

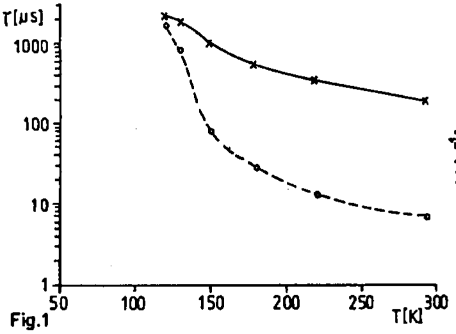

Fig.1

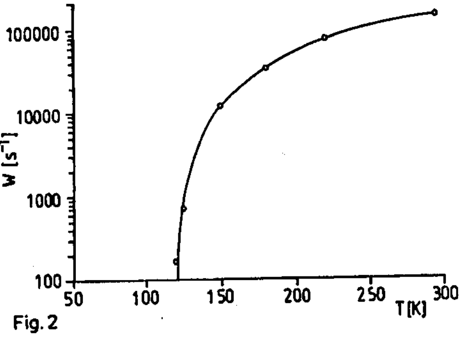

Fig.2

Fig. 1. Influence of temperature on luminescence lifetime of the $^4S_{3/2}$ state of Er^{3+} in $Cs_2NaErCl_6$ (•) and in $Cs_2NaEr_{0.2}Y_{0.4}Yb_{0.4}Cl_6$ (×).

Fig. 2. Influence of temperature on the rate of decay related to Er–Er interaction. Points indicate the values obtained by subtracting the reciprocals of lifetimes shown in Fig. 1.

the presence of ion–ion interactions. The rates of decay related to these interactions determined by subtracting the reciprocals of lifetimes for concentrated and diluted samples are plotted versus temperature in Fig. 2. It can be seen that the process of concentration quenching of luminescence is switched on at about 110 K and that it is very efficient at higher temperatures. Only one cross relaxation scheme may be constructed for the $^4S_{3/2}$ level using the energies of excited states which were derived from absorption spectra. This process involves two simultaneous transitions in which an excited ion makes the $^4S_{3/2} \rightarrow {}^4I_{9/2}$ transition and the coupled unexcited ion makes the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition. As a result, the $^4I_{9/2}$ and $^4I_{13/2}$ levels would be populated. Luminescence spectra recorded in the 775–800 nm spectral region following selective excitation in the $^2H_{11/2}$ level at 519 nm confirm this conclusion. It can be seen in Fig. 3 that at room temperature almost all luminescence intensity is associated with $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transition, whereas at 80 K the luminescence originates exclusively in the $^4S_{3/2}$ level. Particularly strong temperature dependence of cross relaxation efficiency in the 100–200 K temperature region indicates that the resonant condition is fulfilled for upper components of the ground $^4I_{15/2}$ state. The exact positions of the crystal field levels of the $^4I_{9/2}$ state are not known however, and the vibrational modes and crystal field levels involved in the process cannot be identified. Contribution of multiphonon relaxation in the decay of the $^4S_{3/2}$ level may be estimated using the excitation spectra for the luminescence originating in the $^4F_{9/2}$ level which is situated about 3000 cm^{-1} below the $^4S_{3/2}$ level. In Fig. 4 we compare the absorption spectrum of $Cs_2NaErCl_6$ in the 300–800 nm spectral region and the $^4F_{9/2}$ excitation spectra recorded at 300 K for concentrated and diluted samples. It can be seen that the $^4F_{9/2}$ level in concentrated sample is populated mainly from the $^4F_{5/2}$ level by cross relaxation process $^4F_{5/2} \rightarrow {}^4F_{9/2}$: $^4I_{15/2} \rightarrow {}^4I_{13/2}$ which meet the resonant condition with the inclusion of vibrational modes. Efficiency of this process is con-

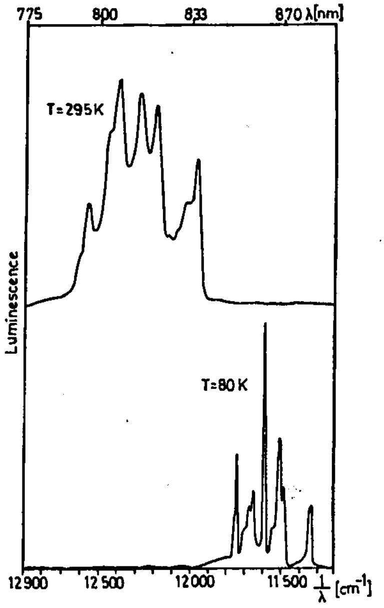

Fig.3

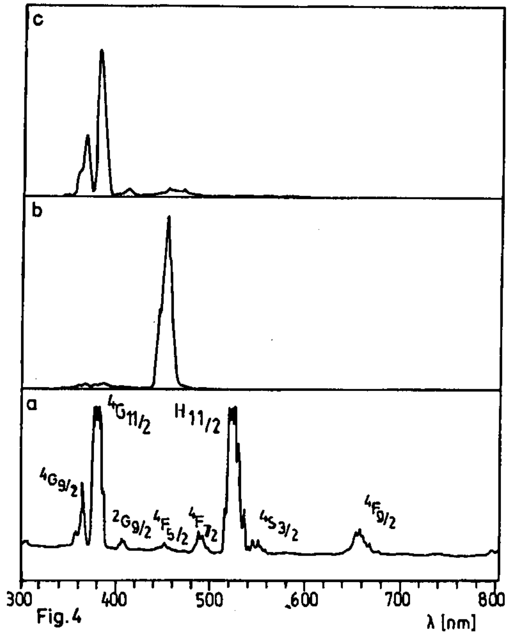

Fig.4

Fig. 3. Luminescence band corresponding to the $^4S_{3/2} \rightarrow {}^4I_{13/2}$ and $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} in $Cs_2NaEr_{0.2}Y_{0.4}Yb_{0.4}Cl_6$ recorded at 295 K and 80 K

Fig. 4. Absorption spectrum of the $Cs_2NaEr_x(Y,Yb)_{1-x}Cl_6$ crystal in the 300–800 nm spectral region (a); excitation spectrum of the luminescence originating in the $^4F_{9/2}$ state, centered at 650 nm for $Cs_2NaErCl_6$ (b) and for $Cs_2NaEr_{0.2}Y_{0.4}Yb_{0.4}Cl_6$ (c).

siderably less important in diluted sample and the $^4F_{9/2}$ luminescence is excited from high energy levels, most probably by direct vibronic transitions. For both the samples the $^2H_{11/2}$ and $^4S_{3/2}$ levels are not present in the excitation spectra, indicating that the multiphonon relaxation of the $^4S_{3/2}$ level is negligibly small.

In conclusion, at room temperature the decay of the $^4S_{3/2}$ level of Er^{3+} in $Cs_2NaErCl_6$ is governed by cross relaxation via the $^4I_{9/2}$ level. Efficiency of this process diminishes with decreasing temperature and becomes negligibly small below about 100 K where the vibronic transitions dominate. Multiphonon relaxation does not contribute significantly to the decay of the $^4S_{3/2}$ level. Occurrence of strong luminescence associated with the $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transition indicates that the cross relaxation process via the $^4I_{13/2}$ level does not remove the excitation out of the $^4I_{9/2}$ level.

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