$Eu^{2+} \rightarrow Mn^{2+}$ energy transfer in monocrystalline NaCl and NaBr

Julio Rubio O.
Departamento de Física, Universidad Autónoma Metroplitana–Iztapalapa, Apartado Postal 55-534, 09340 México, Distrito Federal, Mexico
(Received 24 May 1988; revised manuscript received 25 August 1988)

In the present paper the essential features of the kinetics of $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer in NaCl, NaBr, and KCl have been reexamined in terms of a model in which both the europium and manganese ions are treated as two-energy-level systems. The rate equations describing the time evolution of the excited-state populations of the Eu^{2+} and Mn^{2+} ions were solved for continuous excitation to give the ratio for the number of europium ions which are paired with the manganese ions and the total concentration of europium in the crystal. The result obtained is smaller than that previously reported although it still indicates the strong tendency for the Eu and Mn ions to form close pairs in the sodium halide lattices.

The Eu→Mn energy transfer in alkali halides reported previously[1,2] has been reexamined and found to take place in terms of the following rate equations for the ground-state and excited-state population of Eu^{2+} and Eu^{2+}-Mn^{2+} pairs:

$$\begin{aligned} \frac{dn_{si}}{dt} &= Wn_{0i} - \beta_{si} n_{si} \ , \\ \frac{dn_{sp}}{dt} &= Wn_{0p} - Kn_{sp} \ , \\ \frac{dn_a}{dt} &= Kn_{sp} - \beta_a n_a \ , \end{aligned} \tag{1}$$

with the steady-state solutions $n_{si} = Wn_{0i}/\beta_{si}$ and $n_a = Wn_{0p}/\beta_a$, where the population n and fluorescence decay rates β are defined on the energy-level scheme of Fig. 1. According to the experimental observations, this model considers that in the Eu-Mn complexes the energy transfer from the europium to the manganese ions proceeds at a rapid rate that quenches the sensitizer emission completely. On the other hand, the unpaired europium ions are, on the average, at a distance from the manganese ions such that no energy transfer can take place, leaving, therefore, the lifetime of the donor ions unchanged.

Let us now consider the model predictions for the relative fluorescence intensities of the europium and manganese ions. Since the fluorescence intensity of a specific level is equal to the product of the population and the radiative decay rate (β^r) of the level, the ratio for the emission intensities of the activator manganese ions (I_a) and the isolated Eu ions (I_{si}), in the limit of weak pumping where $n_{0i} \approx N_{si}$ and $N_{0p} \approx N_{sp}$, is given by

$$\frac{I_a}{I_{si}} = [(\beta_a^r/\beta_a)N_{sp}]/[(\beta_{si}^r/\beta_{si})N_{si}] \ , \tag{2}$$

where N_{si} and N_{sp} are the total concentrations of isolated and coupled europium ions.

From this expression, the ratio for the number of europium ions which are paired with manganese ions (N_{sp}) and the total concentration of Eu^{2+} ($N_{st} = N_{si} + N_{sp}$) in the crystal can be obtained after some minor manipulations:

$$\frac{N_{sp}}{N_{st}} = \frac{I_a(\beta_{si}^r/\beta_{si})}{I_{si}\left[\frac{\beta_a^r}{\beta_a} + \left[\frac{I_a}{I_{si}}\right]\left[\frac{\beta_{si}^r}{\beta_{si}}\right]\right]} \ . \tag{3}$$

Now, considering the experimentally determined data reported in our previous papers, it is found from Eq. (3) that

$$\left[\frac{N_{\text{Eu-Mn}}}{N_{\text{Eu(tot)}}}\right]_{\text{NaCl:Eu,Mn}} = 0.35$$

and

$$\left[\frac{N_{\text{Eu-Mn}}}{N_{\text{Eu(tot)}}}\right]_{\text{NaBr:Eu,Mn}} = 0.27 \ .$$

Thus, about 30% of the total concentration of the europium ions are paired with the manganese ions in the doubly doped quenched crystals of NaCl and NaBr. If a similar calculation is performed for the KCl:Eu,Mn system,[3] the percentage of associated europium ions is found

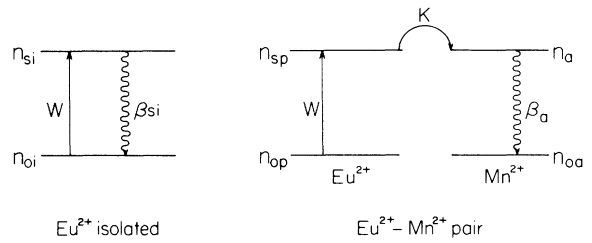

FIG. 1. Every-level system employed to describe the kinetics of Eu→Mn energy transfer in the lattices of NaCl, NaBr, and KCl.

to be only about 0.2%. Although these percentages are smaller than those previously estimated using an unappropriate procedure, they still point to the strong tendency of the europium and manganese ions to form close pairs in the sodium-halide lattices. Therefore, the main conclusions of our previous papers based on the ionic radius criterion are still preserved. In particular, the expectation that the number of Eu-Mn pairs in the sodium halide lattices should be greater than in the potassium halides is well obeyed.

[1]J. Rubio O., H. Murrieta S., R. C. Powell, and W. A. Sibley, Phys. Rev. B **31**, 59 (1985).

[2]J. Rubio O., A. Muñoz F., and J. García M., Phys. Rev. B **36**, 8115 (1987).

[3]J. Rubio O., A. Muñoz F., C. Zaldo, and H. Murrieta S., Solid State Commun. **65**, 251 (1988).