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Energy transfer in $\text{CaCl}_2\text{:Eu:Mn}$ crystals

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Abstract. An investigation was made of the energy transfer between Eu^{2+} and Mn^{2+} ions in CaCl_2 single crystals under photoexcitation. The studies performed at several impurity concentrations and the measurements of the excitation spectra and lifetimes of the observed europium and manganese emissions in the temperature range 11–300 K suggest that the $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ energy transfer process taking place in our slightly doubly doped crystals of $\text{CaCl}_2\text{:Eu:Mn}$ occurs in small complexes of Eu–Mn which are formed in the lattice. The spectroscopic data obtained substantiate the ionic radius criterion proposed by Rubio *et al* to predict pairing between two impurity ions in a solid material between which energy transfer is desired. For the complex system studied in the present investigation, it was not possible to identify unambiguously the nature of the ion–ion interaction producing the energy transfer. However, calculations based on the Dexter model of energy transfer indicate that the rate of $\text{Eu} \rightarrow \text{Mn}$ energy transfer, estimated from our experimentally determined data, can only be explained if a short-range interaction mechanism such as dipole–quadrupole interaction or exchange in nature is active. In order to obtain a better understanding of the $\text{Eu} \rightarrow \text{Mn}$ energy transfer process occurring in two-activator $\text{CaCl}_2\text{:Eu:Mn}$, we also obtained emission, excitation and lifetime data for one-activator $\text{CaCl}_2\text{:Eu}$ and $\text{CaCl}_2\text{:Mn}$ phosphor materials.

1. Introduction

Several years ago, Rubio *et al* (1985) proposed an ionic radius criterion to predict pairing between two doubly valent impurity ions in an alkali-halide host. It appears that this criterion provides a reasonable basis for selecting impurity ions and host crystals which may lead to the development of efficient phosphor materials and solid state lasers. In particular, according to this criterion, compounds containing sodium, calcium or cadmium ions as host cations might be good candidates for the preferential formation of small complexes of Eu–Mn that gives rise to effective energy transfer and the promise of very efficient devices for optical wavelength conversion.

With this expectation at hand, $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ energy transfer in CaCl_2 slightly contaminated with both europium and manganese ions has been investigated, and the results obtained are presented in this paper. Research on the optical characteristics of this phosphor material can help to determine whether the impurities are randomly distributed or clustered.

2. Experimental details

The single crystals of $\text{CaCl}_2\text{:Eu}$, $\text{CaCl}_2\text{:Mn}$ and $\text{CaCl}_2\text{:Eu:Mn}$ employed in this

investigation were grown in our laboratory by the Bridgman technique. The impurity concentration was determined by atomic absorption spectrophotometry.

Emission, excitation and lifetime data were obtained with the same experimental equipment as described elsewhere (Camarillo and Rubio 1989, Caldiño *et al* 1990). All the emission and excitation spectra were corrected for lamp intensity, photomultiplier sensitivity and monochromator response. All measurements were carried out under a vacuum atmosphere with the sample mounted in the cold finger of an Air Products model CS-202 cryogenic refrigerator with a temperature controller capable of temperature variation between 11 and 300 K.

3. Results

In the photoluminescence spectra of one-activator $\text{CaCl}_2:\text{Eu}^{2+}$ (60 ppm) crystals, we observed an intense broad-band emission centred at about 429 nm with a width at half-maximum of 0.15 eV at 300 K and 0.11 eV at 11 K. The 11 K excitation spectrum of this emission exhibited two broad absorption bands whose centres of gravity (first moment) peaked at about 40550 and 27415 cm^{-1} . These bands are due to the dipole-allowed $4f^7 \rightarrow 4f^65d(e_g, t_{2g})$ transitions of the doubly valent europium ion.

The photoluminescence spectra of single-crystal CaCl_2 doped with Mn^{2+} ions in the concentration range 2000–5000 ppm consist of an asymmetric orange–red band peaking at about 580 nm with a width at half-maximum of 0.28 eV at 300 K. Upon lowering the sample temperature to 11 K, the peak position of the emission shifts to longer wavelengths (about 596 nm) and its width at half-maximum is reduced to 0.20 eV. This band was attributed to the ${}^4T_1({}^4G) \rightarrow {}^6A_{1g}({}^6S)$ spin-forbidden transition in the Mn^{2+} ions occupying Ca sites in the lattice of CaCl_2 . The appearance of the excitation spectrum corresponding to this emission is much the same as that exhibited by Mn^{2+} ions in octahedral coordination for other hosts (Mehra 1968, Regis and Farge 1976, Ghosh and Mukherjee 1981, Rodríguez *et al* 1983). At 11 K, it consists of bands in the regions 20 080, 23 175, 24 201, 27 701, 28 653, 30 066, 37 495 and 40 323 cm^{-1} , corresponding to transitions from the ${}^6A_{1g}({}^6S)$ ground state to the excited states ${}^4T_1({}^4G)$, ${}^4T_{2g}({}^4G)$, [${}^4A_{1g}({}^4G)$, ${}^4E_g({}^4G)$], ${}^4T_{2g}({}^4D)$, ${}^4E_g({}^4D)$, ${}^4T_1({}^4P)$, ${}^4A_{2g}({}^4F)$ and ${}^4T_{2g}({}^4F)$, respectively, of the $3d^5$ configuration.

As is evident from the foregoing data on the excitation and luminescence spectra of one-activator $\text{CaCl}_2:\text{Eu}$ and $\text{CaCl}_2:\text{Mn}$, there exists an overlap region between the Eu^{2+} emission and the Mn^{2+} ${}^6A_{1g}({}^6S) \rightarrow {}^4T_{2g}({}^4G)$ and ${}^6A_{1g}({}^6S) \rightarrow {}^4A_{1g}, E_g({}^4G)$ absorptions. This overlap region is portrayed in figure 1. Therefore, the existence of processes of energy transfer between Eu^{2+} and Mn^{2+} ions in $\text{CaCl}_2:\text{Eu}:\text{Mn}$ crystals is expected. The data that we have obtained for a series of two-activator phosphors corroborate this expectation. In fact, when divalent europium is excited in either the $4f^65d(e_g)$ or the $4f^65d(t_{2g})$ absorption bands, both manganese and europium emission are observed as can be appreciated in figure 2 for a $\text{CaCl}_2:\text{Eu}(40 \text{ ppm}):\text{Mn}(400 \text{ ppm})$ crystal at 11 K. Moreover, the excitation spectrum corresponding to the Mn^{2+} emission exhibits the Eu^{2+} absorption bands as can be seen in figure 3. At this point, it should be mentioned that direct excitation of the manganese ions could not be produced in our slightly doubly doped crystals even under excitation at 24 201 cm^{-1} (413 nm) which is in the wavelength region of the prominent ${}^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$ absorption transition of Mn^{2+} in this material. This is explained by the fact that the transitions within the d^5 Mn^{2+} configuration are forbidden in spin and parity.

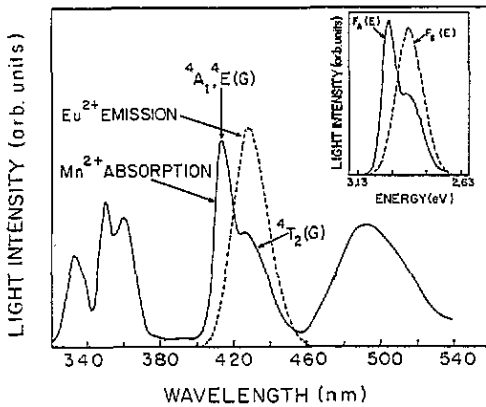


Figure 1. Room-temperature overlap region between europium emission (---) and manganese absorption (—). The inset shows the normalized shape functions.

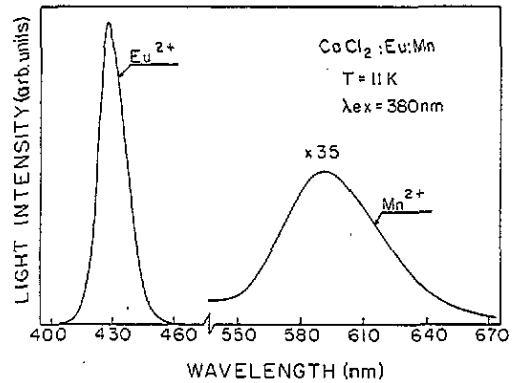


Figure 2. 11 K emission spectrum of a $\text{CaCl}_2:\text{Eu};\text{Mn}$ crystal doubly doped with europium (40 ppm) and manganese (400 ppm) ions under excitation at 380 nm.

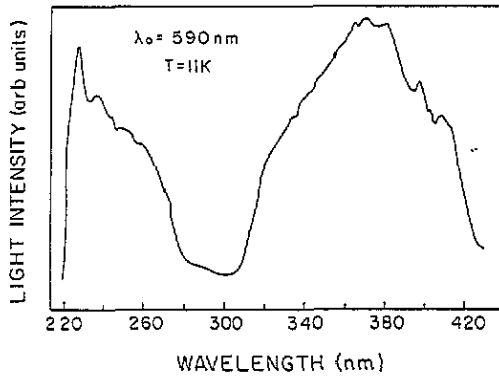


Figure 3. 11 K excitation spectrum for the Mn^{2+} emission obtained in the same $\text{CaCl}_2:\text{Eu}(40 \text{ ppm});\text{Mn}(400 \text{ ppm})$ crystal which was employed to record the emission spectrum portrayed in figure 1.

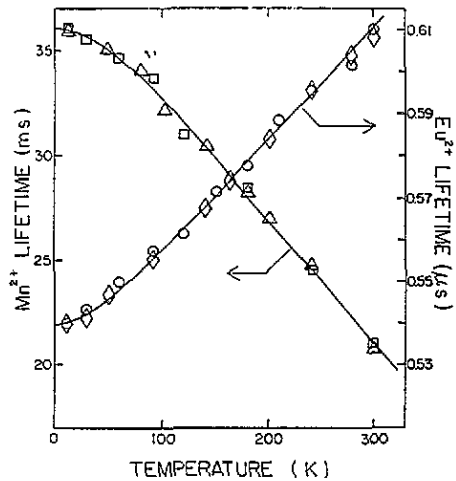


Figure 4. Lifetime data for Eu^{2+} (O) and Mn^{2+} (□) emissions in the $\text{CaCl}_2:\text{Eu}(40 \text{ ppm});\text{Mn}(400 \text{ ppm})$ phosphor material. Lifetime data for the Eu emission (◇) in one-activator $\text{CaCl}_2:\text{Eu}(60 \text{ ppm})$ and for the Mn emission (Δ) in $\text{CaCl}_2:\text{Mn}(2000 \text{ ppm})$ are included for comparison.

Lifetime measurements performed on the emission transitions observed in our $\text{CaCl}_2:\text{Eu}(60 \text{ ppm})$, $\text{CaCl}_2:\text{Mn}(2000 \text{ ppm})$ and $\text{CaCl}_2:\text{Eu}(40 \text{ ppm});\text{Mn}(400 \text{ ppm})$ crystals were carried out in the temperature range 11–300 K. The results obtained are shown in figure 4. In the temperature range investigated, the manganese fluorescence decay in the doubly doped samples, after pulse excitation of Eu^{2+} , exhibited a purely exponential time dependence with no observable rise time. Taking into account the sensitivity and the overall time response of our experimental set-up, this result

indicated that the rise time of the manganese fluorescence was shorter than 25 ns. The time constant of the decay decreases from 36 ± 3 ms at 11 K to 21 ± 3 ms at 300 K. This decrease in the lifetime of the emission when the sample temperature is increased may be explained considering that the probabilities for the phonon-assisted and non-radiative processes are enhanced with the increase in temperature (Caldiño and Rubio 1992). The decay scheme of the Mn^{2+} emission in one-activator $\text{CaCl}_2:\text{Mn}$ was found to be very similar to that measured in the doubly doped crystals.

The Eu^{2+} fluorescence decay in the doubly doped samples was found to consist, in all the temperature range investigated, of a single-exponential decay, unlike the non-exponential decays usually observed when donor-acceptor energy transfer occurs. The value for the decay constant slightly decreased as the sample temperature was lowered, i.e. 0.61 ± 0.03 μs at 300 K and 0.54 ± 0.02 μs at 11 K. The Eu^{2+} fluorescence in a $\text{CaCl}_2:\text{Eu}$ (60 ppm) sample having no manganese present also exhibited a pure exponential decay in the temperature range 11–300 K with a time constant which was determined to be equal, within experimental error, to that measured for the Eu fluorescence decay in the doubly doped crystals, as can be appreciated from the data portrayed in figure 4. These results indicate that the decay pattern of the Eu^{2+} luminescence in $\text{CaCl}_2:\text{Eu}$ is not affected by the presence of the manganese ions in our doubly doped crystals.

Similar results to those described above were obtained in crystals which were simultaneously contaminated with both europium and manganese ions in the concentration range 10–60 ppm Eu^{2+} , 40–400 ppm Mn^{2+} . They also showed little change with thermal treatment of the sample at 873 K for several hours.

4. Discussion

The spectroscopic results described above clearly indicate that $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ energy transfer occurs in our doubly doped crystals of CaCl_2 . This is most easily seen in figure 3 where it is apparent that Eu^{2+} -ion absorption produces Mn^{2+} emission. However, for the low concentrations of sensitizer and activator impurity ions in our samples, the interaction distance between them (greater than 50 Å) is so large for statistically distributed impurities that no effects of energy transfer would be observed. In fact, the rates of $\text{Eu} \rightarrow \text{Mn}$ energy transfer calculated from Dexter's (1953) theory of energy transfer at a distance of about 50 Å, using both dipole-dipole and dipole-quadrupole interaction mechanisms, are quite small compared with the experimentally determined decay rate of the Eu^{2+} ions.

On the other hand, it is well recognized that, regardless of the non-radiative energy transfer process between sensitizer and activator ions in solids, the decay pattern of the sensitizer ions should be affected by the presence of the acceptor ions. Our spectroscopic data revealed, however, that in our $\text{CaCl}_2:\text{Eu}:\text{Mn}$ crystals this is not the case.

This latter fact and the observation of europium-sensitized manganese fluorescence in our slightly doubly doped crystals of $\text{CaCl}_2:\text{Eu}:\text{Mn}$ may suggest that the impurities are not randomly distributed in the lattice of calcium chloride but rather occur as impurity complexes of Eu-Mn. The presence of small clusters of Eu-Mn in the calcium chloride lattice is not unexpected since the Mn^{2+} ions (radius, 0.8 Å) are smaller than the Ca^{2+} ions for which they substitute (0.99 Å) and the Eu^{2+} (1.12 Å) ions are larger. The elastic strain induced when the Eu^{2+} ions enter the lattice of

CaCl_2 can be reduced by clustering with Mn^{2+} ions. In the $\text{Eu}^{2+}-\text{Mn}^{2+}$ complexes, the energy transfer from the europium to the manganese ions may proceed at a rapid rate which quenches the sensitizer luminescence completely. This conclusion is supported by our lifetime data portrayed in figure 4 which show that the Eu^{2+} lifetimes in $\text{CaCl}_2:\text{Eu:Mn}$ and in $\text{CaCl}_2:\text{Eu}$ are the same within experimental error ($\pm 5\%$). On the other hand, the unassociated 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 Eu^{2+} ions unchanged. According to this situation, the europium ions which are forming the $\text{Eu}-\text{Mn}$ complexes do not exhibit any fluorescence and the observed europium emission in our $\text{CaCl}_2:\text{Eu:Mn}$ crystals originates exclusively from the Eu^{2+} ions which are not interacting with Mn^{2+} .

The ratio of the number N_p of Eu^{2+} ions which were associated with the manganese ions to the total concentration N_T of europium in our $\text{CaCl}_2:\text{Eu}(40 \text{ ppm}):\text{Mn}(400 \text{ ppm})$ samples could be roughly estimated using a simple model in which both the sensitizer and the activator ions are treated as two-energy-level systems. The basic assumptions of this model have been described elsewhere (Muñoz and Rubio 1988). According to them, N_p/N_T in the limit of weak pumping is given by

$$N_p/N_T = I_{\text{Mn}}(\beta_{\text{Eu}}^r/\beta_{\text{Eu}})/I_{\text{Eu}}[\beta_{\text{Mn}}^r/\beta_{\text{Mn}} + (I_{\text{Mn}}/I_{\text{Eu}})(\beta_{\text{Eu}}^r/\beta_{\text{Eu}})] \quad (1)$$

where β^r and β are the radiative and fluorescence decay rates, respectively. Considering that the radiative decay rates are equal to the inverse of the low-temperature (11 K) lifetime values, i.e. $\beta_{\text{Eu}}^r = 1.85 \times 10^6 \text{ s}^{-1}$, $\beta_{\text{Mn}}^r = 27.8 \text{ s}^{-1}$, N_p/N_T is found to be about 0.06 when our spectroscopic room-temperature data i.e. $\beta_{\text{Eu}} = 1.64 \times 10^6 \text{ s}^{-1}$, $\beta_{\text{Mn}} = 47.6 \text{ s}^{-1}$ and $I_{\text{Mn}}/I_{\text{Eu}} \approx 0.03$ are employed in equation (1). Thus, about 6% of the total concentration of Eu^{2+} ions in our $\text{CaCl}_2:\text{Eu}(40 \text{ ppm}):\text{Mn}(400 \text{ ppm})$ crystals appeared to be associated with Mn^{2+} ions. This finding together with those previously reported in the sodium halides doubly doped with Eu^{2+} and Mn^{2+} ions (Rubio *et al* 1985, 1987, 1988, Cywinski *et al* 1987, Camarillo and Rubio 1989, Muñoz and Rubio 1989, Rubio 1989), and in the systems $\text{NaCl}:\text{Pb,Mn}$ (Jaque *et al* 1982, Capelletti *et al* 1985), $\text{RbMgF}_3:\text{Eu:Mn}$ (Shinn and Sibley 1984), $\text{CaF}_2:\text{Ce,Mn}$ (McKeever *et al* 1986), $\text{CaF}_2:\text{Ce,Eu}$ (Caldino *et al* 1989) and $\text{CaF}_2:\text{Eu:Mn}$ (Caldino *et al* 1990) indicate that some kinds of ion when they are introduced into 'appropriate' crystalline matrixes tend to form impurity complexes even at very low impurity concentrations. It is also in agreement with the expectation of the ionic radius criterion proposed by Rubio *et al* (1985) to predict preferential impurity pairing in a solid material.

The energy transfer process in the small clusters of $\text{Eu}-\text{Mn}$ can be strongly enhanced because of the small interionic distances. From the model mentioned above, it can also be obtained that the intensity of the activator ion reaches a maximum value after pulse excitation of the donor ions at a time t_{max} given by (Muñoz and Rubio 1988)

$$t_{\text{max}} = [1/(W - \beta_a)] \ln(W/\beta_a) \quad (2)$$

where W is the rate of energy transfer and β_a the fluorescence lifetime of the activator ion. From this equation and our experimentally determined data, i.e. $t_{\text{max}} < 25 \text{ ns}$ and $\beta_a = 47.6 \text{ s}^{-1}$, the rate of $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ energy transfer was estimated to be greater than $6 \times 10^8 \text{ s}^{-1}$ at 300 K.

Unfortunately, our experimental techniques cannot provide positive identification of the nature of the Eu–Mn complexes. However, some information about them can be obtained using Dexter's (1953) theory of energy transfer. This worker showed that dipole–dipole interactions can generally be expected to dominate the energy transfer mechanism when both the sensitizer and the activator ions are characterized by dipole-allowed transitions. The long lifetime measured for the manganese emission, however, is indicative of the forbidden nature of the $3d \rightarrow 3d$ transitions. Therefore, it is reasonable to assume that, for Eu \rightarrow Mn energy transfer in CaCl_2 , the mechanism which takes place is of either the electric dipole–quadrupole type or exchange in nature.

The transfer rate W_{SA}^{DQ} for the electric dipole–quadrupole interaction is related to the transfer rate W_{SA}^{DD} for the electric dipole–dipole interaction through the relation

$$W_{SA}^{DQ} = (\lambda_S/R_{SA})^2(f_q/f_d)W_{SA}^{DD} \quad (3)$$

where λ_S is the wavelength position of the sensitizer's emission, R_{SA} is the distance between the ions involved in the transfer, and f_q and f_d are the oscillator strengths of the activator quadrupole and dipole electrical transitions, respectively. The expression for the electric dipole–dipole transfer probability W_{SA}^{DD} is given by (Dexter 1953)

$$W_{SA}^{DD} = \frac{3\hbar^4 c^4}{4\pi n^4 \tau_S^0} \left(\frac{1}{R_{SA}}\right)^6 Q_A \int \frac{F_S(E)F_A(E)}{E^4} dE \quad (4)$$

where τ_S^0 is the sensitizer intrinsic lifetime (in the absence of energy transfer), Q_A is the integrated absorbancy of the acceptor ion, and $\Omega(F_S, F_A) = \int [F_S(E)F_A(E)/E^4] dE$ represents the spectral overlap between the normalized shapes of the Eu emission $F_S(E)$ and Mn absorption $F_A(E)$. The other symbols in equation (4) have their usual meanings.

The critical distance R_c of energy transfer from sensitizer (S) to activator (A) is defined as the distance for which the probability of transfer equals the probability of radiative emission of the sensitizer, i.e. the distance for which $W_{SA}\tau_S^0 = 1$.

From equations (3) and (4) we have

$$R_c^6 = (3\hbar^4 c^4 / 4\pi n^4) Q_A \Omega(F_S, F_A) \quad (5)$$

for a dipole–dipole interaction and

$$R_c^8 = (3\hbar^4 c^4 f_q \lambda_S^2 / 4\pi n^4 f_d) Q_A \Omega(F_S, F_A) \quad (6)$$

for a dipole–quadrupole interaction. The overlap integral $\Omega(F_S, F_A)$ was calculated using the normalized lineshape functions for the 300 K Eu^{2+} emission and Mn^{2+} absorption in the overlap region, which are shown in the inset of figure 1. The result was about $4.5 \times 10^{-2} \text{ eV}^{-5}$. On the other hand, since the absorption coefficient of manganese is quite difficult to measure, Q_A was estimated using the relationship $Q_A = 4.8 \times 10^{-16} f_d$ given by Blasse (1969) where f_d is the oscillator strength of the dipole electrical absorption transition of the activator ion. If we assume for f_d a value of 10^{-7} , Q_A was found to be $4.8 \times 10^{-23} \text{ eV cm}^2$. Now, using the values for Q_A and Ω in equation (5), the critical interaction distance for a dipole–dipole interaction mechanism was found to be about 5 Å. Hence, within the lifetime of the donor excitation, only those acceptor ions within a radius of around 5 Å will be sensitized. The shortest distance for an Eu–Mn dimer complex in the lattice of CaCl_2

is about 4.2 Å. The rate of energy transfer calculated from equation (4) at a distance of 4.2 Å ($5.6 \times 10^6 \text{ s}^{-1}$) is quite small in comparison with that estimated (greater than $6 \times 10^8 \text{ s}^{-1}$) from our spectroscopic data. This allowed the conclusion that the assumption of an electric dipole-dipole interaction as a mechanism for $\text{Eu} \rightarrow \text{Mn}$ energy transfer in CaCl_2 is not consistent with the experimental observations. Let us now, therefore, consider an electric dipole-quadrupole interaction as a possible mechanism for energy transfer. If equation (6) is employed with $\lambda_s = 4290 \text{ Å}$, $f_d = 10^{-7}$ and $f_q = 10^{-10}$, then the value for R_c was found to be about 11 Å.

Different kinds of small complex in which the Eu and Mn ions are separated by at most 11 Å can be imagined in the lattice of CaCl_2 . Four of the simplest are those dimers in which the Eu and Mn ions are separated by 4.2 Å (configuration D_1), 4.95 Å (configuration D_2), 6.24 Å (configuration D_3) and 6.43 Å (configuration D_4). The rate of $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ energy transfer via an electric dipole-quadrupole interaction mechanism was calculated for each of these dimer configurations and the results obtained are given in table 1 together with those calculated from the use of an electric dipole-dipole interaction mechanism for comparison. As expected, more reasonable values are obtained when a dipole-quadrupole interaction mechanism is employed rather than an electric dipole-dipole mechanism to perform the calculations. Although these calculations are phenomenological, they may suggest that, in order to account for the estimated rate of $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ energy transfer, the europium and manganese ions should be separated by at most 5 Å in the lattice of CaCl_2 . This condition is fulfilled by the Eu-Mn dimer possessing the configuration of either D_1 or D_2 . However, other small aggregate complexes in which the europium ion is surrounded by several manganese ions occupying Ca positions at first or second neighbours to the europium ion might also be appropriate to account for the estimated rate of $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ energy transfer.

Table 1. Theoretical calculated values for the rate of energy transfer from europium to manganese ions in CaCl_2 at 300 K using both dipole-dipole and dipole-quadrupole interaction mechanisms.

Complex configuration	Sensitizer-activator distance (Å)	Energy transfer rate (s^{-1})	
		W_{SA}^{DD}	W_{SA}^{DQ}
D_1	4.20	5.6×10^6	5.8×10^9
D_2	4.95	2.1×10^6	1.6×10^9
D_3	6.24	5.2×10^5	2.4×10^8
D_4	6.43	4.3×10^4	1.9×10^8

An exchange (superexchange) interaction mechanism might be also responsible for the $\text{Eu} \rightarrow \text{Mn}$ energy transfer in the small impurity aggregates. The probability (W_{SA}^{EX}) for the transfer from Eu^{2+} to Mn^{2+} in this case can be written as the product of two terms, i.e. one connected with the wavefunction-overlap integral of sensitizer and activator electrons and another with the energy transfer overlap of the emission of Eu^{2+} and the absorption of Mn^{2+} . Unfortunately, expressions for the wavefunctions involved in the calculation of the overlap integral are not available at the present time. This prevents a calculation of the energy transfer rate using this interaction mechanism. However, Dexter (1953) estimated W_{SA}^{EX} to be in the range 10^{10} – 10^{11} s^{-1} for distances of about 4 Å between sensitizer and activator ions. At distances of about

4–5 Å as in the Eu–Mn complexes D₁ and D₂, this probability is expected to be in the range 10^9 – 10^{11} s⁻¹ which is also close to the experimental value.

Although for the complex system investigated here it is not possible to identify unambiguously the nature of the Eu–Mn interaction producing the energy transfer, the calculations based on the Dexter model of energy transfer indicate that the fast rise time of the manganese fluorescence after Eu²⁺ excitation can be explained only if a short-range interaction mechanism such as electric dipole–quadrupole or exchange in nature is active. These calculations also substantiate the conclusions above in the sense that energy transfer from Eu²⁺ to Mn²⁺ ions in our slightly doubly doped crystals of CaCl₂:Eu:Mn takes place in the small complexes of Eu²⁺–Mn²⁺ which are formed in this material.

In summary, we have analysed the optical properties of CaCl₂ slightly doped with both europium and manganese ions. The spectroscopic data obtained indicate that the Eu²⁺ → Mn²⁺ energy transfer process which takes place in this system occurs in the small complexes of Eu–Mn which are preferentially formed in the crystal. This preferential impurity clustering, which has been considered to be infrequent in most studies of energy transfer between impurities in solids, appears to be quite a relevant finding which may help us to design more efficient phosphor and laser systems. It is also in agreement with the expectation of the ionic radius criterion, which then appears to be valid not only for alkali halides doubly doped with divalent impurities but also for compounds possessing a more complicated structure.

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