A spectroscopic study of NaI containing europium and manganese

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Abstract. NaI crystals containing different concentrations of divalent europium and manganese ions were investigated using the photoluminescence technique. Excitation spectra and decay times of observed Eu^{2+} and Mn^{2+} emissions were analysed in the temperature range 80–300 K. The experimental data from the slightly doped, quenched crystals suggest the preferential pairing of Eu^{2+} and Mn^{2+} ions. At these centres an efficient energy transfer from Eu to Mn takes place. A model is proposed to explain the kinetics of $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer in NaI based on experimental observations. It is established that a short-range interaction mechanism such as an electric dipole–quadrupole interaction or exchange is active between the impurity pairs in which the energy transfer occurs. The results obtained substantiate the ionic radius criterion proposed by Rubio and co-workers to predict impurity pairing in a solid material.

1. Introduction

The study of the transfer of excitation energy among impurity ions in inorganic phosphors has been an area of intense research for over 40 years, mainly because of its importance in a wide variety of physical applications such as the development of solid state lasers and efficient phosphor materials.

It is well known that several kinds of interactions between two ions are responsible for the energy transfer: electric dipole–dipole, electric dipole–quadrupole, electric quadrupole–quadrupole interactions and exchange interactions. The theory of energy transfer due to these interactions has been developed by several workers (Förster 1949, Dexter 1953, Galanin 1955, Eisenthal and Siegel 1964, Inokuti and Hirayama 1965, Blumen and Manz 1979, Chow and Powell 1980, Yaaniso and Varmaa 1987, Sienicik and Winnik 1988). A prime assumption in these theories is that there is random arrangement of sensitisers and activators throughout the solid material; accordingly, this assumption has been used to explain large amounts of experimentally determined data.

In a series of papers, Rubio *et al* (1985, 1987, 1988) and Rubio (1989) reported on the Eu-sensitised Mn fluorescence in single crystals of NaCl, NaBr and KCl. It was ascertained in these studies that $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer occurs in the sodium halide lattices even for very low concentrations of either sensitiser and/or activator ions. From this fact and other experimental observations, it was inferred that the $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer in this type of crystals could not take place between randomly distributed

donor and acceptor ions, but rather occurred in the Eu–Mn close pairs that were formed in the lattice. These pairs are, however, more numerous in the sodium than in any of the potassium halide lattices. To explain this uncommon situation, Rubio *et al* suggested that the marked tendency for the formation of donor (Eu)–acceptor (Mn) pairs might be due to the reduction of strain in the lattice induced by the presence of each impurity alone. If the average radius of the donor and acceptor ions is almost identical to that of the host cations they substitute, then the formation of impurity pairs appears to be favoured in the crystalline matrix. This finding is quite relevant and may lead to more efficient phosphor and laser systems.

Taking into account the importance of continuing this research field, in the present paper we report on further investigations of the $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer in mono-crystalline NaI. The results obtained suggest the preferential pairing of Mn and Eu ions, thus supporting the ionic radius criterion proposed by Rubio *et al* to predict the pairing between two impurity ions in a solid material.

2. Experimental procedure

The doubly doped samples of $NaI:Eu^{2+}:Mn^{2+}$ employed in this investigation were grown by the Czochralski method by R Guerrero at the Crystal Growth Facility of the Institute of Physics, UNAM. In order to prevent the presence of OH^- ions in the crystals the starting materials were first dried and grown under a controlled atmosphere of dry argon. The concentration of Eu and Mn in the samples employed was determined by atomic absorption spectrophotometry. Before any measurements were made, the crystals with dimensions of $0.3 \times 0.3 \times 0.05$ cm^3 were heated for at least 1 h at 800 K and then fast-quenched into acetone in order to dissolve impurity aggregates and precipitates that might be present in the as-grown crystals. This procedure provides fast enough cooling rates to prevent impurity clustering as has been demonstrated by Taylor *et al* (1981) in several alkali halides doped with divalent impurity ions. In view of the high hygroscopic nature of the NaI crystals, all measurements were carried out under a vacuum atmosphere.

Steady state fluorescence and excitation spectra were obtained with a Perkin Elmer 650–10S spectrofluorimeter equipped with a 150 W xenon lamp and a red-sensitive Hamamatsu R928 photomultiplier tube. All the emission and excitation data reported in this paper were corrected for the energy response of the excitation source using an anthracene crystal and for the energy response of the emission detector using a calibrated light source.

For fluorescence kinetics studies, radiation from a PAR Dyscan nitrogen laser was applied to pump the ions into selected states; the resulting transient fluorescence signal was analysed with a 0.45 m Czerny–Turner monochromator, detected with a cooled Hamamatsu R943-03 photomultiplier tube and processed by a PAR 162 boxcar averager in combination with a PAR 165 gated integrator before it was presented on a strip chart recorder. Some of the decay fluorescence data were also taken, connecting the output of the photomultiplier tube to a Tektronix 485 oscilloscope from which the luminescence decay was photographed.

3. Results

Figure 1 shows the emission spectrum of a quenched $NaI:Eu^{2+}$ (10 ppm); Mn^{2+} (50 ppm) phosphor material for excitation in the 3.67 eV absorption band corresponding to the
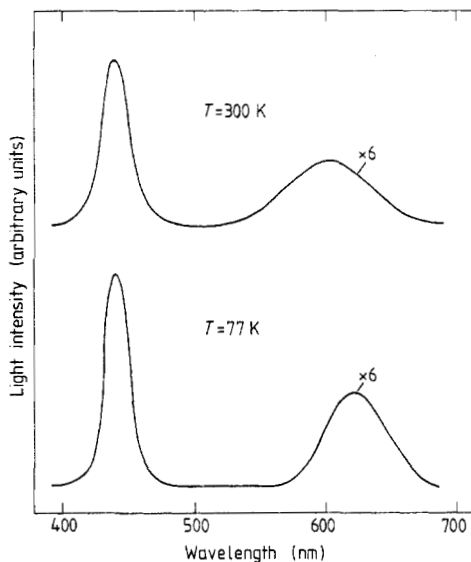
Figure 1. Emission spectrum for an acetone-quenched NaI crystal doubly doped with Mn^{2-} (50 ppm) and Eu^{2+} (10 ppm) ions when the excitation is performed at 338 nm.
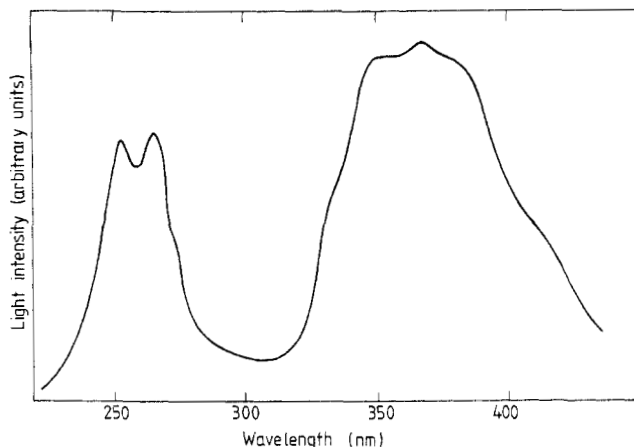

Figure 2. Liquid nitrogen excitation spectrum for Mn emission observed in slightly doped crystals. $\lambda_0 = 620$ nm, $T = 80$ K.

electronic transition $4f^7(^8S) \rightarrow 4f^65d(T_{2g})$ in the Eu^{2+} ion. Two broad bands are evident in the emission spectrum. The blue emission had the same characteristics, i.e., peak position (440 nm) and width (0.16 eV), as the Eu emission band observed in NaI slightly doped with Eu^{2+} ions. It was therefore related to the electronic transition $4f^65d(T_{2g}) \rightarrow 4f^7$ in the Eu^{2+} ions taking place in our doubly doped samples. The orange band appears only after the Eu-doped NaI crystals were simultaneously contaminated with Mn ions and corresponds to the de-excitation of the Mn^{2+} ions from the excited state $^4T_{1g}(G)$ to the ground state $^6A_1$. The peak position of this band moves from 610 to 630 nm when the sample temperature is lowered from 300 to 80 K.

The liquid nitrogen excitation spectrum of the Mn^{2+} emission observed in the slightly doubly doped, acetone-quenched crystals is given in figure 2. It consists of two broad
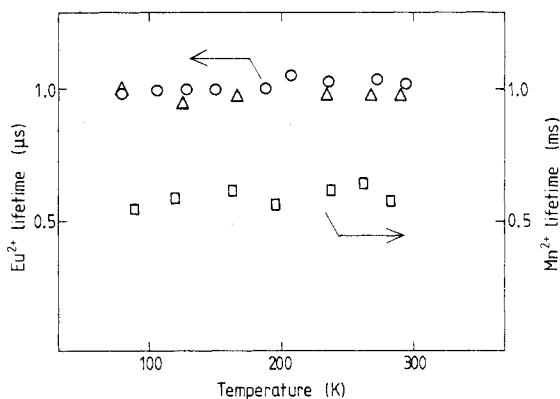
Figure 3. Lifetime data for the Eu^{2+} ($\bigcirc$) and Mn ($\square$) emissions in slightly doped, acetone-quenched crystals as a function of sample temperature. Lifetime data for the Eu emission ($\triangle$) in NaI:Eu (10 ppm) are included for comparison.

absorption bands which are due to the dipole-allowed $4f^7 \rightarrow 4f^6 5d$ (E_g; T_{2g}) transitions of the Eu^{2+} ions. A similar excitation spectrum was obtained for the Eu^{2+} emission. Mn fluorescence is therefore excited by pumping in either of the high (E_g) and low (T_{2g}) energy absorption bands of the Eu^{2+} ions. This indicates that the $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer takes place in our doubly doped samples.

Lifetime measurements performed on the observed emission transitions were carried out in the temperature range 80–300 K. The results obtained are shown in figure 3. For each datum point in the figure the spread in the data is within the size of the representative symbols. In the temperature range investigated, the Mn relaxation signals appeared as pure exponential decays with no measured initial rise times. On the other hand, the Eu fluorescence decay exhibited a pure exponential time dependence with a time constant nearly identical to that measured in NaI:Eu (10 ppm), unlike the non-exponential decays usually observed when donor–acceptor energy transfer occurs.

The emission spectra of some heavily doped crystals (i.e., 48 ppm Eu^{2+}, 150 ppm Mn^{2+} and 48 ppm Eu^{2+}, 320 ppm Mn^{2+}) obtained after quenching into acetone were found to be nearly identical to those in figure 1 for slightly doped samples. Minor differences were found in the widths and peak positions of the Eu^{2+} and Mn^{2+} emissions compared with those determined in the slightly doped samples.

The existence of the $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer in these crystals was also explicitly demonstrated by the excitation spectrum of the Mn emission, which showed the presence of the two broad UV absorption bands typical of the divalent Eu^{2+} ions.

Pulse excitation measurements revealed that the Eu emission in these crystals consisted of two pure exponential decays with time constants of $0.5 \pm 0.05\,\mu s$ and $0.95 \pm 0.05\,\mu s$. On the other hand, although the Mn relaxation signal appeared as a pure exponential decay, as in the slightly doped samples, the associated time constant was found to be smaller (~ 0.40 ms).

The ratio for the intensities of the Mn and Eu emission bands (I_{Mn}/I_{Eu}) in these more heavily doped crystals was determined using various cooling methods. The results are shown in figure 4 for natural cooling in air, placing on a massive copper block and into acetone. All of these, apart from the acetone quench, are relatively slow quenches. The fluorescence spectra portrayed in this figure were taken on several twin samples containing 48 ppm of Eu^{2+} and 350 ppm of Mn^{2+}. It is clearly observed that I_{Mn}/I_{Eu} is larger in the acetone-quenched crystals and decreases when the samples are quenched
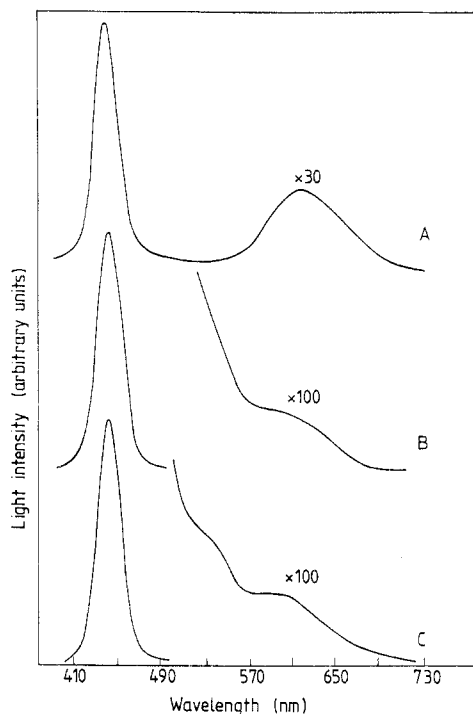
Figure 4. Emission spectrum of a NaI:Eu (48 ppm); Mn (350 ppm) crystal as a function of different methods of cooling: (A) into acetone; (B) onto a massive copper block; and (C) in air. $\lambda_{ex} = 338$ nm.

in air or into a massive copper block. Simultaneously with this effect, the amplitude of the fast Eu fluorescence decay increased. Moreover, an additional band peaking at ~530 nm appeared in the fluorescence spectrum when the less efficient quenches were employed. This latter band was found to be quite prominent in the emission spectrum of the as-grown crystals, as well as in those that were well aged at room temperature. The lifetime of this emission was found to be ~0.15 ms and was constant, within experimental error, in the range of temperatures investigated.

The behaviour described above contrasts with that found in our slightly doubly doped crystals. In the case of samples quenched onto a massive copper block, the ratio I_{Mn}/I_{Eu} was ~20% larger than that found in the acetone-quenched crystals. Moreover, the green emission was not detected in either the fluorescence spectrum of the as-grown crystals or in the spectrum of those samples that were inefficiently quenched. Also, single exponential decays for the Eu luminescence, characterised by a lifetime value of 0.95 ± 0.05 μs, were obtained in all of these crystals independently of the quenching procedure.

4. Discussion

The more significant data described above for slightly doped acetone-quenched crystals can be summarised as follows.

(*a*) Excitation of Eu^{2+} ions produces two broad emission bands in the blue and in the red regions of the electromagnetic spectrum. The former band is due to the de-excitation of the Eu^{2+} ions while the latter is due to the ${}^4T_1 \rightarrow {}^6A_1$ transition of the Mn^{2+} ions.
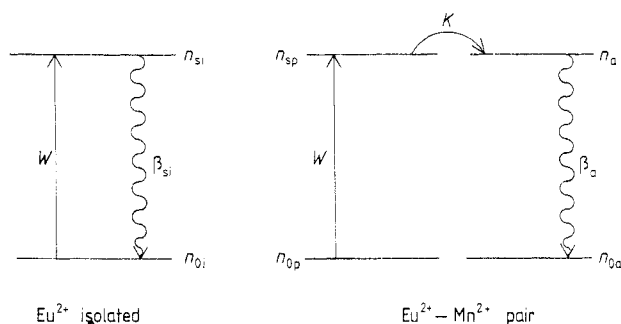
Figure 5. Energy level system used to describe the kinetics of Eu–Mn energy transfer in the NaI lattice.

(b) The excitation spectrum of the Mn^{2+} luminescence reveals the presence of the two $4f^7 \to 4f^6 5d(E_g, T_{2g})$ absorption transitions of Eu^{2+} ions. This result clearly indicates that the $Eu^{2+} \to Mn^{2+}$ energy transfer takes place in our NaI crystals even for the very low concentrations of the donor and acceptor ions employed.

(c) Pulse excitation of Eu^{2+} resulted in a Mn^{2+} luminescence with no observable rise time. Considering the sensitivity and the overall time response of our experimental set-up, this result indicated that the rise time of the Mn fluorescence should be shorter than 25 ns.

(d) The decay pattern of the Eu^{2+} luminescence in NaI:Eu is not affected by the presence of the Mn^{2+} ions in the doubly doped crystals.

If one assumes that the Eu and Mn ions were randomly distributed in the NaI lattice, then the process of $Eu^{2+} \to Mn^{2+}$ energy transfer should not have occurred in our slightly doubly doped, quenched crystals. In fact, the rate of Eu $\to$ Mn energy transfer calculated from Dexter's (1953) theory of energy transfer, using a random distribution of donor and acceptor ions, is lower than the experimentally determined decay rate of the Eu^{2+} ions. The observation of Eu-sensitised Mn fluorescence in our slightly doped samples therefore suggests that impurities are not randomly distributed in the lattice; rather, they occur as pairs of Eu^{2+}–Mn^{2+} in the crystal even after a severe quench into acetone. A nearest-neighbour cation separation distance ($\sim$6.46 Å) in the NaI lattice along the $\langle 100 \rangle$ direction predicts a very efficient energy transfer, as will be shown below.

On the basis of these observations a model describing the essential features of the kinetics of Eu $\to$ Mn energy transfer in the NaI lattice can be built up. In this model (figure 5) both Eu^{2+} and Mn^{2+} ions are treated as two energy level systems. This model considers that in the Eu–Mn pairs the Eu^{2+} emission is completely quenched by energy transfer to the Mn^{2+} ions and that the observed Eu^{2+} luminescence in the slightly doubly doped crystals originates exclusively from the Eu^{2+} ions that are not interacting with Mn^{2+}. The rate equations describing the time evolution of the excited state populations for both the isolated and paired Eu–Mn ions are given by:

$$\mathrm{d}n_{\mathrm{si}}/\mathrm{d}t = Wn_{0\mathrm{i}} - \beta_{\mathrm{si}}n_{\mathrm{si}} \qquad \mathrm{d}n_{\mathrm{sp}}/\mathrm{d}t = Wn_{0\mathrm{p}} - Kn_{\mathrm{sp}} \qquad \mathrm{d}n_{\mathrm{a}}/\mathrm{d}t = Kn_{\mathrm{sp}} - \beta_{\mathrm{a}}n_{\mathrm{a}} \qquad (1)$$

where n_{si} and n_{sp} are the concentrations of excited states of the sensitiser Eu ion in the isolated and coupled forms, respectively, $n_{0\mathrm{i}}$ and $n_{0\mathrm{p}}$ are the corresponding ground state populations, n_{a} is the concentration of excited state Mn ions forming the impurity pairs, β_{si} and β_{a} are the fluorescence decay rates of the isolated Eu^{2+} and coupled Mn^{2+} ions, K is the rate of energy transfer and W is the absorption probability, which is assumed to be the same for both isolated and coupled Eu ions. Direct excitation of Mn^{2+} was considered to be negligible in view of the forbidden nature of the d $\to$ d Mn transitions.

Equations (1) can be easily solved for continuous excitation to give the ratio for the emission intensities of the activator Mn^{2+} ions (I_a) and the isolated Eu^{2+} ions (I_{si}) in the limit of weak pumping where $n_{0i} \simeq N_{si}$ and $n_{0p} \simeq N_{sp}$, where N_{si} and N_{sp} are the total concentrations of isolated and coupled Eu ions:

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

The ratio for the number of paired Eu and Mn ions (N_{sp}) and the total concentration of Eu ($N_{st} = N_{si} + N_{sp}$) in the crystal can be obtained from equation (2) after some minor manipulations:

$$N_{sp}/N_{st} = [1 + (I_{si}/I_a)(\beta_{si}^r/\beta_{si})(\beta_a/\beta_a^r)]^{-1}. \tag{3}$$

Considering that the radiative decay rate for Eu and Mn emissions are equal to the inverse of the low-temperature (80 K) lifetime values, N_{sp}/N_{st} was found to be ~0.1 when our experimentally determined room-temperature data for the acetone-quenched crystals, i.e., $\beta_{si} = 1 \times 10^6\ s^{-1}$, $\beta_a = 192\ s^{-1}$ and $I_{si}/I_a = 0.1$ were employed in equation (3). Thus about 10% of the total Eu^{2+} ion concentration in these crystals are paired with Mn ions. This result supports the ionic radius criterion proposed by Rubio *et al* to predict impurity pairing in an alkali halide crystal. According to this criterion, it is expected that Eu^{2+} and Mn^{2+} ions form close pairs in the NaI lattice in view of the ionic radii of the Eu^{2+} (1.12 Å), Mn^{2+} (0.80 Å) and Na^+ (0.99 Å) ions. In fact, the average radius of Eu^{2+} and Mn^{2+} ions is nearly identical to that of the host cation Na ions that they substitute. Moreover, if these two ions couple through an I^- ion along a $\langle 100 \rangle$ direction forming a $\langle 100 \rangle$ dimer, then they fit quite well in the allotted space in the lattice.

At this point it is important to mention that the percentage of Eu ions coupled to Mn ions in quenched crystals of NaCl and NaBr was previously estimated to be $\sim90\%$ in both cases (Rubio *et al* 1985, 1987), although this appears to be an overestimate. A recent re-examination (Rubio 1989) of the kinetics of the $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer taking place in these two crystals, using the model depicted in figure 5 and the rate equations (1), gave the result that $\sim30\%$ of the Eu^{2+} ions were paired with the Mn ions after quenching. Although this percentage is smaller than previous estimates, it still points out that the Eu and Mn ions have a strong tendency to form close pairs in the sodium halide lattices.

Let us now discuss the possible mechanism for the $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer taking place in the samples of NaI. Taking into account that the isolated pair transfer rate is time-independent, solutions to the rate equations (1) can be obtained under the assumption that w represents a delta function excitation pulse:

$$n_s(t) = n_s(0) \exp(-Kt)$$

$$n_a(t) = \frac{Kn_s(0)}{(\beta_a - K)} [\exp(-Kt) - \exp(-\beta_a t)]. \tag{4}$$

The time at which the activator fluorescence intensity reaches its maximum value (t_{max}) can be found by setting the first time derivative of $n_a(t)$ equal to zero, giving

$$t_{max} = [1/(K - \beta_a)] \ln(K/\beta_a). \tag{5}$$

When $t_{max} < 25$ ns and the experimentally determined decay time of the Mn emission in the slightly doped crystals are employed in equation (5), then the rate of $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer is found to be $>5 \times 10^8\ s^{-1}$ at 300 K.

The forbidden nature of the $3d \rightarrow 3d\ Mn^{2+}$ absorption transitions suggests that the $Eu^{2+} \rightarrow Mn^{2+}$ energy transfer mechanism is either an electric dipole–quadrupole
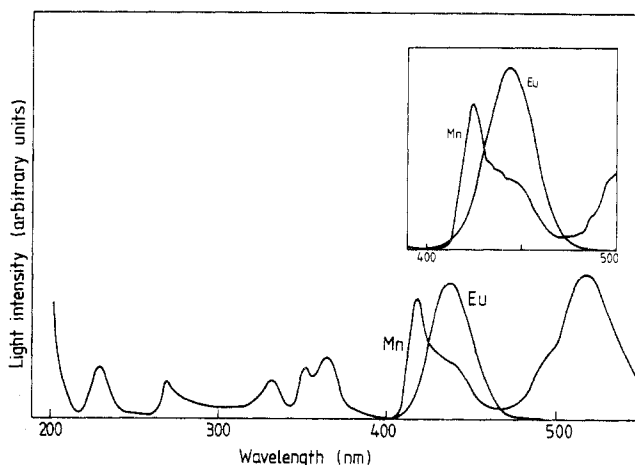
Figure 6. Room-temperature overlap region of Eu emission and Mn absorption. The latter spectrum was taken from Rodriguez *et al* (1983) for $NaCl:Mn^{2+}$. The inset shows the normalised shape functions.

interaction or exchange. According to Dexter's theory of energy transfer (Dexter 1953), the transfer rate for an electric dipole–quadrupole interaction mechanism is given by:

$$W_{sa}^{DQ} = \frac{3\hbar^4 c^4 Q_a}{4\pi n^4 \tau_s^0} \frac{f_q}{f_d} \frac{(\lambda_s)^2}{(R_{sa})^8} \int \frac{f_s(E)F_a(E)}{E^4} \, dE \tag{6}$$

where τ_s^0 and λ_s are the intrinsic lifetime (in the absence of energy transfer) and the wavelength position of the donor emission, R_{sa} is the interaction distance between the ions involved in the transfer. Q_a is the integrated absorbency of the acceptor ion,

$$\Omega = \int [f_s(E)F_a(E)/E^4] \, dE$$

represents the spectral overlap between the normalised shapes of the Eu emission $f_s(E)$ and Mn absorption $F_a(E)$, and f_q and f_d are the oscillator strengths of the activator quadrupole and dipole electrical transitions. The other symbols in equation (6) have their usual meanings. Since the absorption coefficient of Mn is quite difficult to measure, Q_a was estimated using the expression derived by Blasse (1969) i.e., $Q_a = 4.8 \times 10^{-16} f_d$ where $f_d \simeq 10^{-7}$ for Mn^{2+} ions. To obtain $F_a(E)$ we employed the absorption spectrum of Mn^{2+} in NaCl given by Rodriguez *et al* (1983). This was done because we were unable to obtain the absorption spectrum of the Mn ion in the overlap region of the Eu emission because of its low concentration. Moreover, this spectrum has not been reported in the literature, as far as we know. This approximation is, however, a reasonable one since the absorption spectra of Mn^{2+} in several alkali halides are very similar, as has been shown by Rodriguez *et al* (1983). The normalised lineshape functions for the Eu emission and Mn absorption in the overlap region are shown in figure 6. With this approximation Ω was found to be $3.39 \times 10^{-2} \, eV^{-5}$.

Since the exact nature of the Eu–Mn pair complex can not be inferred from our experimentally determined data, the rate of energy transfer via a dipole–quadrupole
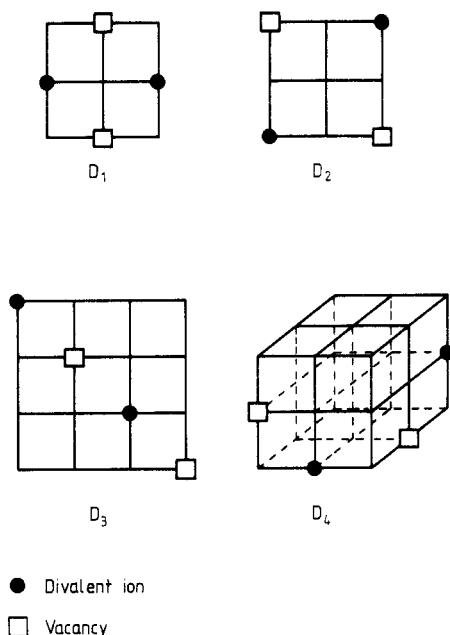
● Divalent ion

□ Vacancy

Figure 7. Possible configurations for the Eu–Mn dimer complex in the NaI lattice that were considered in the calculation of the energy transfer rate via multipolar or exchange interaction mechanisms.

Table 1. Theoretical calculated values for the rate of energy transfer from Eu to Mn ions in NaI at 300 K using the dimer configurations shown in figure 7.

Dimer configuration	Sensitiser–activator distance (Å)	Energy transfer rate	
		W_{sa}^{DD} (s^{-1})	W_{sa}^{DQ} (s^{-1})
D_1	6.46	8.6×10^4	4.0×10^7
D_2, D_3	9.14	1.1×10^4	2.5×10^6
D_4	7.92	2.6×10^4	7.9×10^6

interaction mechanism was calculated using different configurations for the Eu–Mn dimer such as those given in figure 7. Defect and binding energies for these types of dimers have been calculated for different kinds of divalent impurity ions in the alkali halides by Bannon *et al* (1985). The obtained values for W_{sa}^{DQ} for each considered dimer complex are given in table 1. In this table the energy transfer rate calculated using an electric dipole–dipole interaction mechanism is also included for comparison. Closer agreement between calculated and experimental values for W_{sa}^{DQ} is achieved when the $\langle 100 \rangle$ dimer configuration (D_1) is employed to perform the calculations. The calculated value appears smaller than that estimated from our experimental data, however, suggesting that an exchange (superexchange) interaction mechanism may be responsible for the energy transfer from the Eu to Mn ions in the NaI lattice. Such interactions can lead to much higher energy transfer rates than those predicted from equation (6). In fact, magnetic studies have shown that cation exchange can be relatively strong for 180° interactions involving one p-orbital of an anion intermediary, as is the case in the D_1 dimer configuration (Anderson 1963).

Unfortunately, only a rough estimate for the energy transfer rate using a super-exchange interaction mechanism is possible at the present time. This is because the wavefunction overlap integral of the sensitiser and activator electrons involved in the interaction can not be calculated since accurate expressions for the wavefunctions are not known. The estimate can be obtained from the expression derived by Dornauf and Heber (1980) for the transfer probability in the case of superexchange:

$$W_{sa}^{exch} = (1/\tau_s^0)\exp[\gamma(R_0 - R_{sa})]$$ (7)

where τ_s^0 and R_{sa} have the same meaning as above, R_0 is the critical interaction distance and γ is the exchange constant. According to Dexter $\gamma = 2/L$, where L is an 'effective average Bohr radius' for the excited and unexcited states of the paired complex. Using the D_1 dimer configuration, a value for R_0 similar to that found for the dipole–quadrupole interaction mechanism (~ 10 Å) and a typical value for the effective Bohr radius of ~ 1.4 Å, which is about half of the Mn–I separation, a rate of 1.5×10^8 s^{-1} is obtained. If we juxtapose this result to the W_{sa}^{DQ} calculated above, we may conclude that Eu $\rightarrow$ Mn energy transfer via a superexchange interaction mechanism appears to have a higher probability than Eu $\rightarrow$ Mn energy transfer via a multipolar interaction mechanism. On the other hand, the large distances between donor and acceptor ions, as well as their locations in other types of dimer complexes such as those given in figure 7, appear to be less appropriate for the occurrence of this type of interaction.

Although it is recognised that these calculations are phenomenological they suggest that the possible nature of the Eu–Mn complex could be that of the D_1 dimer. They also indicate that the experimentally determined data can only be explained if a short-range interaction mechanism such as an electric dipole–quadrupole or exchange is active between the Eu and Mn ions forming the impurity pairs.

Finally, several comments can be made about the data taken from our more heavily doped crystals. The fluorescence and decay kinetics studies performed in such crystals suggest that impurity aggregates (precipitates), which were already present in the as-grown crystals, could not be completely dissolved even after quenching. Moreover, their formation appeared to be favoured when inefficient quenches were employed. Unfortunately, the nature of these aggregates (precipitates) can not be inferred from our optical data, but it is reasonable to think that they could be composed of both Eu^{2+} and Mn^{2+} ions.

The data shown in our figure 4 may suggest that Eu–Mn pairs and probably small Eu–Mn aggregates were the complexes mainly present in our heavily doped crystals after they were quenched into acetone. However, when less efficient quenches were employed impurity clustering is favoured. The pairs and the small aggregates might act as efficient nucleation centres for the formation of large aggregates and even second phase precipitates in which Eu^{2+} $\rightarrow$ Mn^{2+} energy transfer also occurs.

In these impurity aggregates (precipitates) one may think of a process in which the excitation migrates fast enough through the donor (Eu) system until it comes into the neighbourhood of an acceptor (Mn) ion where direct relaxation by donor–acceptor energy transfer can occur. In this fast-diffusion limit, single exponential donor decays are predicted with a lifetime value shorter than the intrinsic one. According to this scheme, the fast Eu fluorescence decay ($\tau = 0.50 \pm 0.05$ μs) observed in these crystals may be associated with the de-excitation of the Eu^{2+} ions forming aggregates (precipitates) in which the process described above takes place. On the other hand, the Eu fluorescence decay associated with a lifetime value of 0.95 ± 0.05 μs might be associated with the Eu ions that were still in solution in the NaI lattice and were therefore not interacting with any Mn ions.

The long lifetime of the 530 nm band suggests that this emission is due to the de-excitation of the Mn ions that are excited by energy transfer by Eu^{2+} ions. A similar band has been observed in as-grown or room-temperature-annealed crystals of NaCl:Eu:Mn and NaBr:Eu:Mn doped with similar concentrations of Eu^{2+} and Mn^{2+} ions as those employed in our heavily doped NaI crystals. One may ascribe this band to Mn ions forming aggregates (precipitates) in which a few Eu ions are incorporated.

In order to get a better understanding of the physical processes taking place in these more heavily doped crystals, especially in the impurity aggregates, their optical properties as a function of different annealing treatments are under study at the present time.

In summary, we have used optical (emission and excitation) spectroscopy to analyse energy transfer from Eu to Mn ions in monocrystalline NaI. The most important conclusion from the results of this work is the strong tendency for Eu^{2+} and Mn^{2+} ions to form close pairs in this host. This finding is in agreement with the ionic radius criterion proposed by Rubio and co-workers to predict pairing between two impurity ions in an alkali halide crystal.

Acknowledgments

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