

Energy transfer between europium and manganese close pairs in monocrystalline sodium bromide

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In the present paper fluorescence intensity and lifetime measurements of the Eu^{2+} and Mn^{2+} emissions have been carried out in the range of temperatures 10–300 K in single crystals of NaBr doubly doped with europium and manganese ions. The data obtained indicate that an efficient sensitized luminescence with the Eu^{2+} ions as sensitizers and the Mn^{2+} ions as activators occurs between the numerous Eu-Mn pairs which are preferentially formed in this material. The calculations based on the Förster-Dexter model of energy transfer indicate that the experimentally determined fast rise time of the manganese fluorescence after pulse excitation of Eu^{2+} can only be explained if a short-range interaction mechanism, such as an electric dipole-quadrupole interaction or exchange in nature, is active. These calculations also substantiate the ionic-radius criterion proposed by Rubio and co-workers to predict pairing between two impurity ions in a solid material.

INTRODUCTION

Energy transfer from europium or lead to manganese ions in single crystals of sodium chloride has been recently studied by Rubio and co-workers.^{1,2} It was ascertained that in both cases $\text{Eu} \rightarrow \text{Mn}$ and $\text{Pb} \rightarrow \text{Mn}$ energy transfer occurs even for very low concentrations of either the sensitizer and/or the activator ions. From analyses of the experimentally determined data, these authors arrived at the conclusion that Eu-Mn and Pb-Mn pairs are preferentially formed in the crystalline matrix; the percentage of total sensitizer ions forming these pairs being $\sim 99\%$ in the former case and $\sim 70\%$ in the latter. This is an uncommon situation and is in contrast to most impurity-sensitized luminescence situations where a statistical distribution of sensitizers and activators through the solid material is found. To explain this situation, Rubio and co-workers proposed an ionic-radius criterion. If one takes into account the ionic radii of Eu^{2+} (1.12 Å) and Mn^{2+} (0.80 Å), it is inferred that if these two ions couple through a Cl^- ion along a $\langle 100 \rangle$ direction, then they must fit into a space of 5.6 Å. Since Mn^{2+} is smaller than Na^+ ($R=0.98$ Å) and Eu^{2+} is larger, the two ions together fit perfectly in the allotted space in the lattice. The same argument applies to the case of lead and manganese ions in NaCl, although in this case, since the ionic radius of Pb^{2+} (1.24 Å) is larger than that of Eu^{2+} , the $\langle 100 \rangle$ Pb-Cl-Mn complex does not fit as perfectly as in the europium-manganese case. As a consequence of this fact, the number of impurity pairs which are formed in the sodium chloride matrix is expected to be smaller.

In order to get a better insight into the validity of the ionic-radius criterion to predict pairing between two impurity ions between which energy transfer is desired, in

the present investigation the phenomenon of Eu^{2+} -sensitized Mn^{2+} fluorescence in monocrystalline NaBr has been studied. It is shown that the efficient energy transfer from europium to manganese ions observed in this crystal is due to the presence of numerous Eu-Mn pairs which are preferentially formed in the lattice, this result being in very good agreement with the ionic-radius criterion.

EXPERIMENT

The doubly doped samples of NaBr:Eu,Mn employed in this investigation were grown by R. Guerrero at the Crystal Growth Facility of the National University of Mexico by the Czochralski technique. To eliminate the presence of OH^- ions in the crystals, the starting materials were first dried and the growing was carried out under a controlled atmosphere of dry argon. The concentration of europium and manganese was determined by atomic absorption spectrophotometry. Thermal quenching was carried out by heating the samples at 800 K for 1 h and then dropping them, as fast as possible, onto a massive copper block at room temperature.

Continuous fluorescence spectra were obtained with either a Perkin-Elmer 650-10S or a Perkin-Elmer LS-5 spectrofluorimeter; the excitation source in the former being a 150-W xenon lamp while in the latter it was a 10-W pulsed xenon lamp. In all cases, the emission and excitation spectra were corrected for lamp intensity and photomultiplier sensitivity.

Lifetime measurements were performed with an EG&G-PAR Dyscan 2100UV laser as the excitation source. The sample fluorescence was focused on the entrance slit of a Pacific 0.45-m Czerny-Turner monochromator. The transient response was detected on a cooled

Hamamatu R943-03 photomultiplier tube and amplified with a PAR model No. 115 wide-band amplifier. Then, it was displayed and photographed on a Tektronix 466 oscilloscope. Low-temperature measurements were taken with crystals in an Air Products DE-202 cryogenic refrigerator.

In order to get a better insight into the state of the impurities in the crystals, electron-paramagnetic-resonance (EPR) measurements were also performed with a Varian E-4 reflection-type X-band spectrometer with 100-kHz field modulation.

RESULTS

The optical-absorption spectrum of a doubly doped crystal containing 8 ppm of Eu^{2+} and 130 ppm of Mn^{2+} consisted of two broad bands whose centers of gravity peaked at $\sim 40\,000$ and $\sim 28\,900\text{ cm}^{-1}$. It is well known that these two bands are due to the dipole-allowed $4f^7 \rightarrow 4f^65d(t_{2g}, e_g)$ transitions of the doubly valent europium ions.^{3,4} When the crystals were excited with light lying in either of the two broad absorption bands, the fluorescence spectra portrayed in Figs. 1 and 2 for "as-grown" and quenched samples were obtained. The room-temperature emission spectrum of the as-grown crystals consisted of three bands peaking at 428, 510, and 590 nm. Both the 510- and 590-nm emission peaks shift to lower energies (longer wavelengths) as the temperature is lowered, whereas the 428-nm emission peak does not appreciably shift. Both the peak energy and shift with temperature of the 510- and 590-nm bands are consistent with Mn^{2+} emission characteristics.

When the as-grown crystals were heated for 1 h at 800 K and then quenched to room temperature, the recorded emission spectrum was found to be different. In particular, the emission band peaking at 510 nm disappeared after the thermal treatment. Moreover, the intensity of the orange band increased at the expense of the europium emission band peaking at 428 nm, and its wavelength position shifted from 590 to 585 nm. The evolution of the intensities of the emission bands peaking at 428, 510, and ~ 590 nm as a function of the annealing temperature to which the as-grown crystal was subjected is portrayed in Figs. 3(a) and 3(b). In order to obtain these data the crystal was heated for 30 min at the temperatures given in the figure and then quenched to room temperature to record the emission spectrum.

In order to get additional information on the processes taking place during the annealing treatments, EPR measurements were also performed in parallel with the optical ones. Previous to any heat treatment, the spectrum of the as-grown crystal mainly consisted of an isotropic broad line (Fig. 4). A weak Eu^{2+} spectrum due to those europium ions occupying C_{2v} symmetry sites in the lattice of NaBr (Ref. 5) [i.e., associated with sodium cation vacancies along $\langle 110 \rangle$ directions forming impurity ($I-V$) dipolar complexes] was also detected. The broad line had a Lorentzian shape with a full width at half maximum of 300 ± 30 G and a g factor close to 2. This broad line is quite similar to that frequently observed in manganese-doped NaCl and it has been commonly inter-

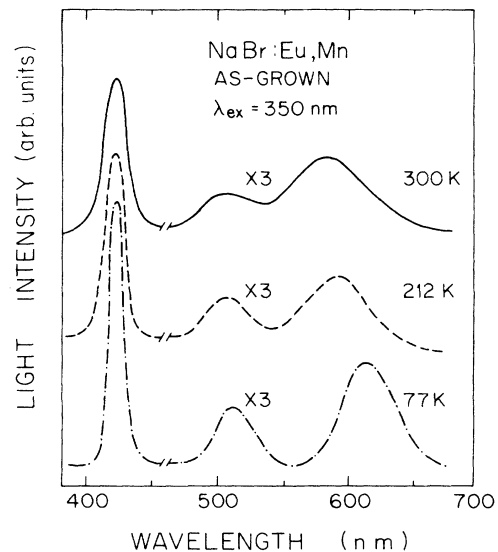


FIG. 1. Emission spectrum of as-grown NaBr single crystals doubly doped with manganese and europium ions as a function of sample temperature.

preted on the basis of a precipitated state of manganese in the crystalline matrix.^{6,7}

When the as-grown crystal was heated, the intensities of the Eu^{2+} EPR spectrum, as well as of the broad manganese line changed as illustrated in Figs. 3(a) and 3(b). At this point, it should be pointed out that the broad line did not disappear even after heating the crystal at 800 K for several hours. This result may give an indication that the solubility limit of Mn^{2+} in the lattice of NaBr is below 130 ppm at 800 K.

Figure 5 portrays the 77-K excitation spectra corresponding to the 428, 510-, and 590-nm bands observed in

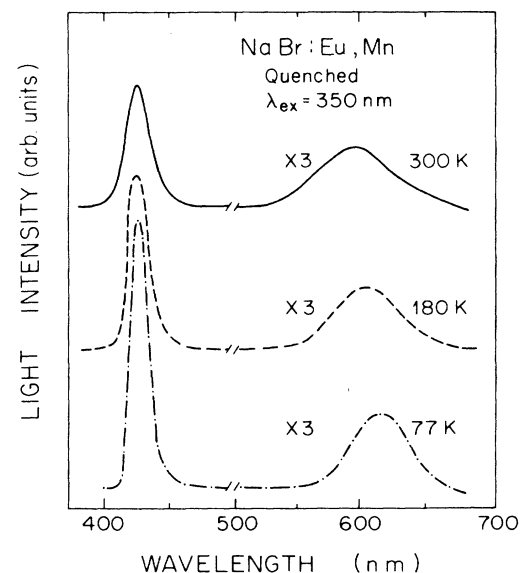


FIG. 2. Emission spectrum for quenched NaBr single crystals doubly doped with manganese and europium ions as a function of sample temperature.

the emission spectrum of the as-grown crystals. In Fig. 6 the excitation spectra for the emission bands peaking at 428 and 585 nm observed in the quenched samples are displayed. In both cases, the intense excitation bands are due to Eu^{2+} transitions. In the excitation spectra of the orange emission, several attempts were made to resolve the Mn^{2+} absorption bands in the overlap region of the Eu^{2+} emission. However, all of them were unsuccessful in view of the presence of the xenon lines of our excitation lamp in this spectral region.

Lifetime measurements were also performed on the emission transitions observed in the as-grown and quenched crystals in the range of temperatures 10–300 K. The results obtained are given in Figs. 7(a) and 7(b) for as-grown and quenched samples, respectively. In this temperature range, the manganese relaxation signal obtained in the quenched crystals appeared as a pure ex-

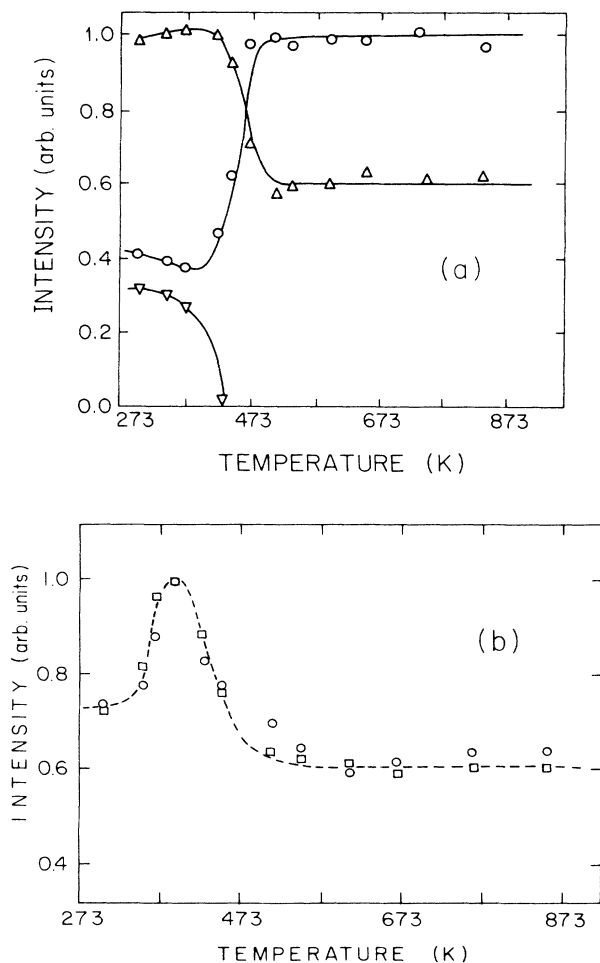


FIG. 3. (a) Evolution of the intensities of the broad manganese EPR line (Δ), the 510 nm emission band (∇), and of the orange manganese emission band peaking at 590 nm (\circ) as a function of the temperature to which the as-grown crystal was subjected. (b) Evolution of the intensities of the Eu^{2+} -EPR spectrum (\square) and of the emission band peaking at 428 nm (\circ).

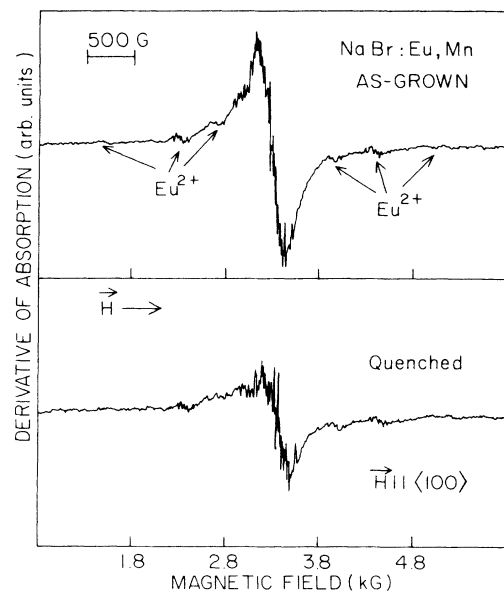


FIG. 4. Room-temperature EPR spectrum observed for as-grown samples and quenched ones.

ponential decay with a time constant which corresponds to the lifetime of the ${}^4T_{1g}(G)$ excited level of Mn^{2+} . The decay time increased continuously as the temperature was lowered from 300 to 10 K. The decay scheme of the Eu^{2+} fluorescence consisted of a unique decay constant the value of which is $1.05 \pm 0.04 \mu\text{s}$ at room temperature and it was practically independent of temperature in the range 10–300 K as can be appreciated from the results portrayed in Fig. 7. The Eu^{2+} fluores-

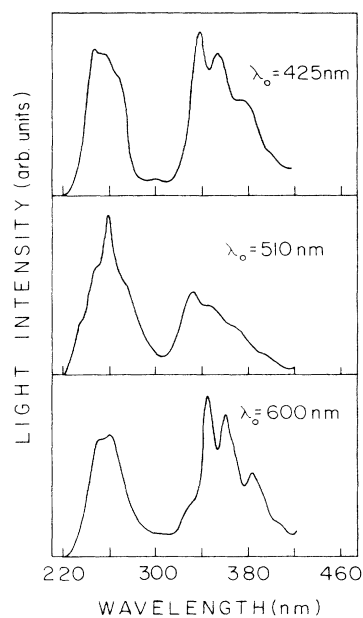


FIG. 5. Liquid nitrogen excitation spectra corresponding to the emission bands peaking at 428, 510, and 590 nm in as-grown crystals.

cence in a sample having no manganese present also exhibited a pure exponential decay in the range of temperature 10–300 K, with a time constant which was determined to be equal, within experimental error, to that measured for the Eu^{2+} emission in the doubly doped crystal. These data are also included in Fig. 7 for the sake of comparison.

The decay scheme of the Eu emission in the as-grown crystals was found to be nearly identical to that found in the quenched samples. However, the Mn^{2+} emission at 590 nm appeared as a nonexponential decay with the first e^{-1} time equal to ~ 4 ms at room temperature. This value increased as the sample temperature was lowered from 300 to 10 K. The luminescence of the emission band peaking at 510 nm also appeared as a nonexponential decay with the first e^{-1} time equal to ~ 0.2 ms; this value being slightly temperature dependent.

DISCUSSION

The presence of the Eu^{2+} absorption bands in the excitation spectrum of the orange manganese emission in as-grown and quenching crystals indicate that energy transfer from europium to manganese ions occurs in both cases. The intensity of the Mn^{2+} emission observed in the quenched samples is much greater than can be explained by energy transfer between statistically distributed impurity ions. In fact, for the low Eu^{2+} concentration in our samples, the interaction distance between the sensitizer europium ions and the activator manganese ions is so large for statistically distributed impurities that energy transfer would have to be extremely efficient over this range since the experimentally determined rise time of the manganese luminescence is quite short (< 50 ns). If a preferential pairing of the Eu and Mn ions in the NaBr lattice occurred, then considerable sensitization would result even at low concentra-

tions of both types of ions. This pairing may be expected in the sodium bromide lattice. In fact, if these two ions couple through a Br^- ion along a $\langle 100 \rangle$ direction, then they must fit quite well into a space of 5.96 Å.

For an interaction distance between europium and manganese ions of 5.96 Å in the NaBr lattice, energy transfer may proceed at a rapid rate which quenches the sensitizer luminescence completely. This conclusion is supported by our lifetime data portrayed in Fig. 7 which show that the Eu^{2+} lifetimes of NaBr:Eu,Mn and NaBr:Eu are the same within experimental error.

From our optical and lifetime data, the number of Eu-Mn pairs which are formed in the lattice may be estimated in the following manner: The intensity of an emission at a frequency ν is related to the number of excited ions N_e by:⁸

$$I(\nu) = N_e P' h \nu, \quad (1)$$

where P' is the radiative rate of the transition and $h\nu$ is the energy of the emitted photon. From this equation we obtain that

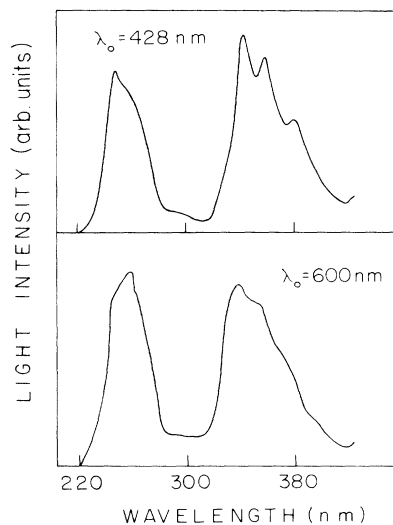


FIG. 6. 77 K excitation spectra of the 428 and 585 nm emission bands observed in quenched crystals.

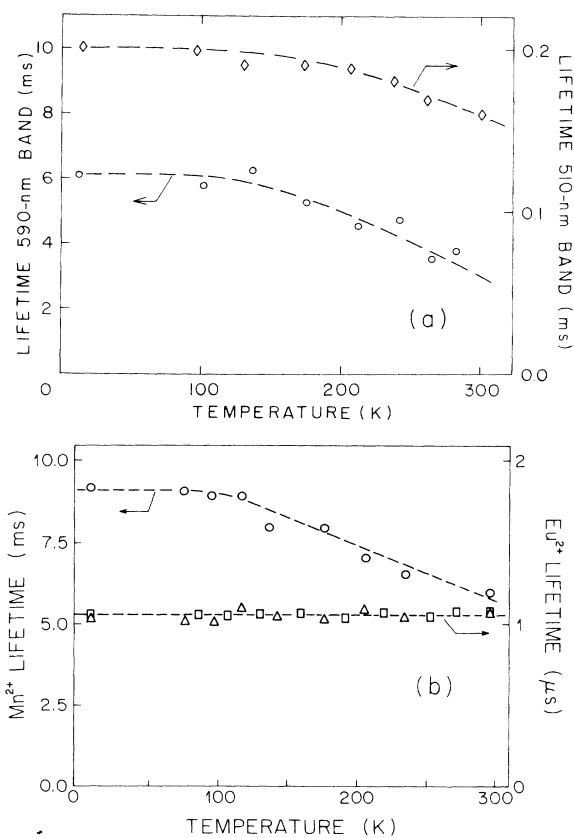


FIG. 7. (a) Lifetime data for the 510 and 590 nm emission bands as a function of sample temperature in as-grown samples. (b) Lifetimes of the 428 nm (Δ) and 585 nm (\circ) emission bands as a function of sample temperature in quenched samples. Lifetime data for the Eu-emission (\square) in NaBr:Eu are also included for the sake of comparison.

$$I_{\text{Mn}} = N_{\text{Eu-Mn}} P_{\text{Mn}}^r (h\nu)_{\text{Mn}}, \quad (2)$$

$$I_{\text{Eu}} = N_{\text{Eu}} P_{\text{Eu}}^r (h\nu)_{\text{Eu}},$$

where N_{Eu} is the number of europium ions which are not paired with the manganese ions and $N_{\text{Eu-Mn}}$ is the number of europium-manganese pairs. By integration of the room-temperature fluorescence spectrum given in Fig. 1 for the quenched sample, it was found that $I_{\text{Mn}} = 0.25 I_{\text{Eu}}$. Now, assuming that P^r is equal to the inverse of the low-temperature lifetime ($P_{\text{Eu}}^r \cong 10^6 \text{ s}^{-1}$; $P_{\text{Mn}}^r \cong 110 \text{ s}^{-1}$) and $(h\nu)_{\text{Mn}} = 2.12 \text{ eV}$, $(h\nu)_{\text{Eu}} = 2.9 \text{ eV}$, it is found from Eq. (2) that

$$\frac{N_{\text{Eu-Mn}}}{N_{\text{Eu}}} = \frac{I_{\text{Mn}} P_{\text{Eu}}^r (h\nu)_{\text{Eu}}}{I_{\text{Eu}} P_{\text{Mn}}^r (h\nu)_{\text{Mn}}} = 3 \times 10^3. \quad (3)$$

Thus almost all of the Eu^{2+} ions are paired with Mn^{2+} ions directly in this material. This result is in very good agreement with the expectation mentioned above and supports the ionic-radius criterion proposed by Rubio *et al.* for the pairing between two impurity ions in an alkali halide matrix.

On the other hand, the simplest way to estimate the rate of energy transfer between sensitizers and activators is by using a system of two energy levels to characterize the ions. If one assumes that the energy transfer rate W_{sa} is time independent, then the number of activators which are excited after the excitation pulse is given by⁹

$$N_a(t) = \frac{W_{sa} N_s(O)}{(P_a^r - P_s^r - W_{sa})} \times \{ \exp[-(P_s^r + W_{sa})t] - \exp(-P_a^r t) \}. \quad (4)$$

In this equation $N_s(O)$ represents the initial population of the excited state of the sensitizer ion immediately after the pulse, and P_s^r and P_a^r are the radiative rates of the sensitizer and the activator ions, respectively. By taking the time derivative of Eq. (4) and setting it to zero, an expression for the time, t_{max} , at which the intensity of the activator is a maximum is obtained:

$$t_{\text{max}} = \frac{1}{(P_s^r - P_a^r + W_{sa})} \ln \left[\frac{P_s^r + W_{sa}}{P_a^r} \right]. \quad (5)$$

Pulse excitation of the low-energy Eu^{2+} absorption band resulted in a Mn^{2+} luminescence with a rise time shorter than 50 ns. Substituting the values for t_{max} , P_s^r , and P_a^r mentioned above in Eq. (5) it is obtained that $W_{sa} > 3 \times 10^8 \text{ s}^{-1}$.

A theory for energy transfer in solids has been formulated many years ago by Förster and Dexter.^{10,11} These authors 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 $3d \rightarrow 3d$ transition. Therefore, it is reasonable to assume that for $\text{Eu} \rightarrow \text{Mn}$ energy transfer the mechanism which takes

place is either of the electric dipole-quadrupole type or exchange in nature.

The transfer rate for the electric dipole-quadrupole interaction is related to the transfer rate for the electric dipole-dipole interaction through the relation

$$W_{sa}^{dq} = \left[\frac{\lambda_s}{R_{sa}} \right]^2 \left[\frac{f_q}{f_d} \right] W_{sa}^{dd}, \quad (6)$$

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, 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

$$W_{sa}^{dd} = \frac{3\hbar^4 c^4}{4\pi n^4 \tau_s} \left[\frac{1}{R_{sa}} \right]^6 Q_A \int \frac{f_s(E) F_a(E)}{E^4} dE, \quad (7)$$

where we have assumed that the field strength in the medium is equal to that in air. τ_s is the radiative lifetime of the sensitizer, Q_A is the integrated absorption coefficient for the activator ion, E is the energy involved in the transfer, R_{sa} has the same meaning as in Eq. (6) and

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

is the overlap between the normalized shape of the luminescence band of the Eu^{2+} ions [$f_s(E)$] and of the absorption bands of Mn^{2+} [$F_a(E)$]. The other symbols in Eq. (7) have their usual meaning.

Because the small absorption coefficient of manganese is difficult to measure, we used the relationship $Q_A = 4.8 \times 10^{-16} f_a$ given by Blasse,¹² where f_a is the oscillator strength of the absorption transition of the activator ion, in order to calculate the integrated absorption coefficient of Mn^{2+} . Assuming for f_a a value of 10^{-7} , Q_A was found to be $4.8 \times 10^{-23} \text{ eV cm}^2$. In order to calculate the overlap integral Ω , the room temperature Eu^{2+} emission shown in Fig. 1 was employed to obtain $f_s(E)$. In order to obtain $F_a(E)$, we used the absorption spectrum of Mn^{2+} in NaCl given by Rodriguez *et al.*¹³ This was done since we were not able to obtain the absorption spectrum of manganese in the overlap region of Eu emission and this spectrum has not been reported in the literature, as far as we know. This approximation, however, appears to be a reasonable one since the reported absorption spectra of Mn^{2+} in several alkali halides are quite similar, as it is shown in the work of Rodriguez *et al.*

Figure 8 displays the normalized line-shape functions for the Eu emission and Mn absorption. From these data, Ω was found to be $4.04 \times 10^{-2} \text{ eV}^{-5}$; this value being only slightly temperature dependent. Now, with the fluorescence data discussed above and the values for Q_A and Ω , the critical interaction distance R_c defined as the distance at which $W_{sa} \tau_s = 1$ and the rate of dipole-dipole energy transfer can be estimated from Eq. (7); the results being 4.9 \AA and $0.3 \times 10^6 \text{ s}^{-1}$, respectively. Hence within the lifetime of the donor excitation only those acceptor ions within a radius of around 5 \AA will be sensi-

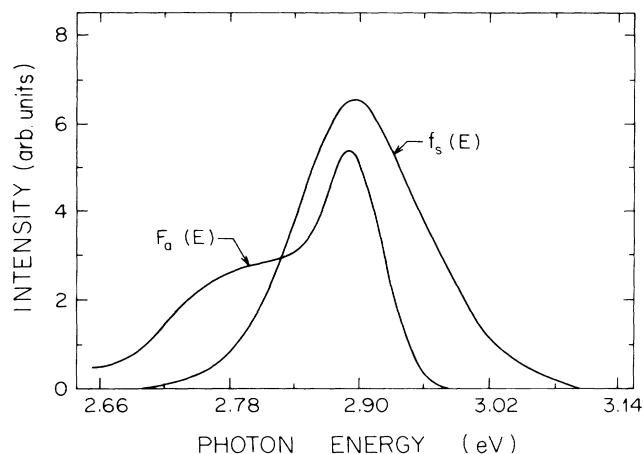


FIG. 8. Normalized line-shape functions for the Eu emission [$f_s(E)$] and Mn absorption [$F_a(E)$].

tized. Since the shortest distance for an Eu-Mn pair in the lattice of NaBr is 5.96 Å, it may be expected that no transfer process should take place between these impurity ions in our doubly doped quenched samples. This conclusion, however, is not in agreement with our experimentally determined data. Moreover, the rate of energy transfer which is obtained considering an electric dipole-dipole interaction mechanism is quite small in comparison with that experimentally determined. These two facts allow the conclusion that the assumption of an electric dipole-dipole interaction as a mechanism for Eu→Mn energy transfer in NaBr 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 Eq. (6) is employed with $\lambda_s = 4280$ Å, $R_{sa} = 5.96$ Å, $f_d = 10^{-7}$, and $f_q = 10^{-10}$, then the values for R_c and W_{sa}^{dq} are found to be 11 Å and 1.5×10^8 s $^{-1}$, respectively; the latter value being close to the experimentally determined one. If we juxtapose this result to the W_{sa}^{dd} energy transfer rate calculated above, we may conclude that Eu→Mn energy transfer in NaBr by a dipole-quadrupole mechanism has a higher probability than Eu→Mn energy transfer by a dipole-dipole interaction. Unfortunately, neither the probability for energy transfer nor the critical interac-

tion distance can be calculated in this case using an exchange-interaction mechanism since both quantities are strongly dependent on the wave-function-overlap integral of the sensitizer and activator electrons involved in the exchange interaction. This makes it important to use expressions for the wave functions which are not known. However, Dexter¹¹ estimated W_{sa}^{ex} to be in the range 10^{10} – 10^{11} s $^{-1}$ for distances of about 4 Å between the sensitizer and the activator ions. At distances of about 6 Å (as in the Eu-Mn pair in NaBr), this probability is expected to be in the range 10^8 – 10^9 s $^{-1}$ which is also close to the experimental value. Thus, the calculations based on the Förster-Dexter model of energy transfer indicate that the fast rise time of the manganese fluorescence after Eu excitation can only be explained if a short-range interaction such as electric dipole-quadrupole or exchange in nature is operative. These calculations also substantiate the conclusions above in the sense that energy transfer from Eu $^{2+}$ to Mn $^{2+}$ in NaBr takes place in the Eu-Mn pairs which are preferentially formed in this material.

Finally, some comments should be made dealing with the data taken in our as-grown samples. First of all, a comparison of the excitation spectra corresponding to the orange emission band observed in as-grown and quenched crystals reveals that the magnitude of the $10Dq$ splitting (Table I) of the $4f^65d$ configuration of the Eu $^{2+}$ ions into its e_g and t_{2g} states is larger in the excitation spectrum of the as-grown crystals. This result indicates that the crystal field acting at the site occupied by the europium ions which transfer their excitation energy to the manganese ions responsible for the emission band peaking at 590 nm in the as-grown samples is larger than at the site occupied by the Eu $^{2+}$ ions which form the Eu-Mn pairs in the quenched crystals.

On the other hand, the data portrayed in Fig. 3 show that there exists a very good correlation between the evolution of the intensities of the Eu $^{2+}$ -EPR spectrum and of the europium emission band peaking at 428 nm as a function of the annealing temperature to which the as-grown crystal was subjected. From this fact, it is inferred that the emission at 428 nm observed in our as-grown crystals was due to those Eu $^{2+}$ -cation-vacancy dipoles which were still isolated in the NaBr lattice, and therefore, not interacting with any manganese ions. It is also seen from the same data that the increase in the

TABLE I. Values for the centers of gravity of the Eu $^{2+}$ absorption bands observed in the excitation spectra of the different emission bands in our doubly doped crystals. Values for the $10Dq$ splitting of the $4f^65d$ configuration into its e_g and t_{2g} levels are also included.

Crystal	Temperature (K)	Emission band (nm)	Center of gravity of the high-energy absorption band (cm $^{-1}$)	Center of gravity of the low-energy absorption band (cm $^{-1}$)	$10Dq$ (cm $^{-1}$)
As-grown	77	428	40 000	28 986	11 014
As-grown	77	510	39 370	29 070	10 300
As-grown	77	590	39 526	28 169	11 357
Quenched	77	428	40 000	28 986	11 014
Quenched	77	585	39 526	28 818	10 708

concentration of europium dipoles which takes place in the range of temperatures (300–450 K) correlates with the thermal resolution of the emission band peaking at 510 nm. At higher annealing temperatures, the concentration of europium dipoles decreased, this decrease being correlated with the decrease in intensity of the broad Mn^{2+} -EPR line. Simultaneously, the intensity of the orange manganese emission peaking at 590 nm was enhanced and slightly shifted to shorter wavelengths (585 nm). This change in the position of the orange emission band due to heating may be explained as due to the dispersion of Mn-ion clusters around the Eu-Mn pairs by the annealing temperature.

The long lifetime of the 510 nm emission band suggests that this band is due to the deexcitation of manganese ions which were excited by energy transfer by Eu^{2+} ions. A similar band has been observed in our as-grown manganese-doped NaCl crystals. It is also destroyed by heating the sample at ~ 400 K for several minutes. It appears from these facts, that the emission band peaking at 510 nm is due to some manganese aggregates (or precipitates) in which the europium ions were embedded. The structure of these aggregates, however, cannot be inferred from our optical data.

The data described above can be summarized as follows: In the range of temperatures 300–450 K the manganese aggregates (precipitates) responsible for the 510 nm emission band are destroyed. As a consequence of this fact some europium and manganese ions were incorporated in the lattice. At higher temperatures (450–520 K), the partial thermal resolution of the manganese precipitates associated with the broad EPR line takes place. This fact produced that some manganese ions and some europium ions which were embedded into the manganese precipitates were put in solution in the crystal and therefore Eu-Mn close pairs were formed in the lattice. As a result of this pairing a more efficient energy transfer from europium to manganese ions occurred and therefore an enhancement in the intensity of the orange emis-

sion band occurred. On the other hand, from our lifetime data it is inferred that the europium ions which were incorporated into the manganese precipitates also transfer their excitation energy so efficiently to the manganese ions that quench the europium emission completely.

In summary, we have used optical and electron paramagnetic resonance spectroscopy to analyze energy transfer from europium to manganese ions in monocrystalline NaBr. The most important conclusion drawn from the results of this work is the strong tendency for the Eu^{2+} and Mn^{2+} ions to form close pairs in this host. The relative number of paired Eu^{2+} ions compared to unpaired ions was found to be of the order of 10^3 . This result is in very good agreement with the ionic-radius criterion proposed by Rubio and co-workers to predict pairing between two impurity ions in an alkali halide matrix. On the other hand, our data suggest that in the as-grown samples several types of complexes are present while in the quenched crystals, mainly Eu^{2+} - Mn^{2+} pairs exist. The impurity ion pairs exhibit extremely efficient energy transfer from Eu^{2+} to Mn^{2+} . Thus the strong tendency for pairing coupled with the efficient energy transfer provides a method for significantly increasing the Mn^{2+} luminescence by enhanced pumping through the Eu^{2+} ions.

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