

## Nonradiative energy transfer from $\text{Cu}^+$ to $\text{Mn}^{2+}$ ions in monocrystalline NaCl

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The optical emission and excitation spectra of NaCl slightly doped with both  $\text{Cu}^+$  and  $\text{Mn}^{2+}$  ions have been analyzed. Our spectroscopic data indicate that energy transfer from the donor  $\text{Cu}^+$  to the acceptor  $\text{Mn}^{2+}$  ions takes place in this material even at very low concentrations of the dopants and after the crystals are subjected to severe quenching treatments. This result suggested that the impurities are not randomly distributed but rather are forming small clusters of Cu-Mn. Some insight into the nature of these clusters, as well as of the possible mechanism of  $\text{Cu}^+ \rightarrow \text{Mn}^{2+}$  energy transfer taking place inside them, was gathered with the help of the Dexter theory for energy transfer.

### INTRODUCTION

About four years ago, Rubio and co-workers<sup>1</sup> reported the observation of an efficient energy-transfer process from the donor  $\text{Eu}^{2+}$  ions to the acceptor  $\text{Mn}^{2+}$  ions in single crystals of NaCl. This process was found to occur in the Eu-Mn close pairs which were preferentially formed in the lattice of NaCl even after the crystals were slightly contaminated with both kind of ions and subjected to severe quenching treatments.<sup>2</sup> In order to explain the strong tendency for the formation of Eu-Mn pairs in the lattice of NaCl, these authors considered a criterion which is based on the ionic radii of the donor and acceptor impurities. It appears that if the average ionic radius of the two ions is nearly identical to that of the host cation ion that they substitute in the lattice, then impurity-pair formation is probably favored to reduce the strain in the lattice introduced by the presence of each impurity alone.

Since this discovery, extensive work has been performed in our laboratory trying to obtain experimental evidence which might give support to the ionic-radius criterion mentioned above. The optical properties of the systems NaBr:Eu,Mn, NaI:Eu,Mn,  $\text{CaF}_2$ :Eu,Mn, KCl:Eu,Mn and KBr:Eu,Mn have been analyzed<sup>3-7</sup> with this purpose. It was found that in all the sodium and calcium systems investigated,  $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$  pairs are formed even at very low concentrations of the donor and acceptor ions and after the crystalline samples are subjected to severe quenching treatments. In contrast with this situation, europium-manganese pairs are not produced in the potassium halides under very similar experimental conditions; all these results being in very good agreement with the expectations of the ionic-radius criterion.

Since this ionic-radius criterion appears to be quite useful for selecting host crystals and divalent impurity ions between which an efficient energy-transfer process is expected, it is rather interesting to explore its validity in other kinds of doubly doped crystals.

With this main objective in mind, the optical properties of the NaCl: $\text{Cu}^+$ , $\text{Mn}^{2+}$  system were investigated and the results obtained are described in this paper. This system was selected to perform this investigation since: (a) the optical properties of NaCl:Cu and NaCl:Mn have been analyzed by several workers.<sup>8-11</sup> This available information is very useful for carrying out an interpretation of the spectroscopic data which may be obtained in the NaCl:Cu,Mn system. It has been established in these studies that both  $\text{Cu}^+$  and  $\text{Mn}^{2+}$  ions enter the lattice of NaCl substitutionally for the sodium ions and, (b) energy transfer from  $\text{Cu}^+$  to  $\text{Mn}^{2+}$  is expected to take place in this host crystal since copper emission overlaps  $\text{Mn}^{2+}$  absorption. Moreover, since the average ionic radius (0.90 Å) of the  $\text{Cu}^+$  and  $\text{Mn}^{2+}$  ions is similar to that of the  $\text{Na}^+$  (0.99 Å) ions, it is expected that small Cu-Mn complexes will be formed in the lattice of NaCl according to the expectation of the ionic radius criterion.

### EXPERIMENT

The single crystals of NaCl doubly doped with copper and manganese ions were all grown in our laboratory in evacuated quartz tubes using a modified Bridgman technique. The dopants were CuCl and  $\text{MnCl}_2$ . The content of copper in the freshly quenched crystals was determined from the intensity of the  $\text{Cu}^+$  characteristic absorption band peaking at 4.8 eV using Smakula's equation with a value for the oscillator strength of 0.006.<sup>12</sup> Manganese concentration was determined by atomic absorption spectrophotometry.

Emission and excitation data were obtained using the same equipment as that described previously.<sup>3-7</sup> All the emission and excitation spectra were corrected for the energy response of the excitation source and for the energy response of the emission detector.

Pulse excitation measurements were obtained by exciting the samples at 266 nm with a quadrupled Nd:YAG (Neodymium-doped Yttrium aluminum garnet) laser at the laboratory of Powell at Oklahoma State University.

The sample fluorescence was processed by either a PAR model 4400 boxcar averager or by a Tektronix model 7104 storage oscilloscope.

### SPECTROSCOPIC RESULTS

Figure 1 shows the 300-K emission spectra of several NaCl:Cu(28 ppm),Mn(120 ppm) twin samples after they were heated for 1 h at 873 K and then cooled to room temperature using various methods of cooling; such as natural cooling in air, placing onto a massive copper block, and into acetone. The band peaking at 355 nm is due<sup>10</sup> to the deexcitation of the  $\text{Cu}^+$  ions from the lowest triplet level of the  $3d^9 4s$  configuration to the ground state  $3d^{10}$ . The orange-red band peaking at 590 nm appears after the NaCl:Cu<sup>+</sup> crystals are simultaneously contaminated with  $\text{Mn}^{2+}$  ions. The peak position of this band moves to longer wavelengths when the sample temperature is decreased. This band was attributed to the transition  ${}^4T_1(G) \rightarrow {}^6A_1$  of the  $\text{Mn}^{2+}$  ions.

Reference to Fig. 1 shows that the ratio of the intensities of the manganese and copper emission bands is critically dependent on the procedure which is employed to quench the samples and increases with the use of the less efficient ones.

The 10-K excitation spectra of the  $\text{Cu}^+$  and  $\text{Mn}^{2+}$  emissions taken after a crystal was quenched into acetone are portrayed in Fig. 2. In both cases, the spectrum consists of several absorption bands which are typical of the  $\text{Cu}^+$  ions.<sup>8-10</sup> Manganese emission is, therefore, produced by exciting into the  $\text{Cu}^+$  absorption bands. This fact clearly demonstrates that  $\text{Cu}^+ \rightarrow \text{Mn}^{2+}$  energy transfer occurs in our slightly doubly doped crystals. The differences which can be appreciated in the excitation spectra of the copper and manganese emissions (Fig. 2) may suggest that the nature of the complex center in which the emission peaking at 355 nm is produced, is different to that in which the orange-red luminescence

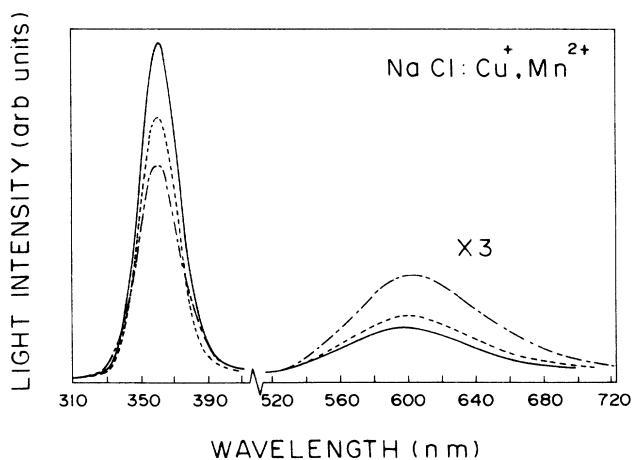


FIG. 1. Room-temperature emission spectra of several twin samples of NaCl:Cu (28 ppm), Mn (120 ppm) after they were heated for 1 h at 873 K and then quenched in natural air (— · — · —), onto a massive copper block (— — —), and into acetone (— — —).

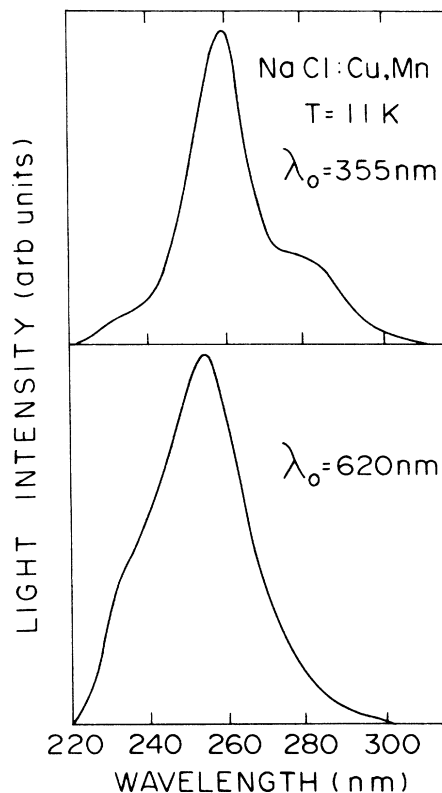


FIG. 2. Liquid-helium excitation spectra for the  $\text{Cu}^+$  and  $\text{Mn}^{2+}$  emission bands observed in our slightly doped crystals of NaCl.

originates as a consequence of a  $\text{Cu} \rightarrow \text{Mn}$  energy-transfer process.

Lifetime measurements performed in the acetone-quenched crystals revealed that the decay scheme of the  $\text{Cu}^+$  emission consists of a pure exponential decay with an associated lifetime value of  $38 \mu\text{s}$  at 300 K and  $310 \mu\text{s}$  at 10 K. These data are nearly identical to that previously reported<sup>9</sup> for  $\text{Cu}^+$  emission in NaCl. On the other hand, the manganese emission was characterized by a pure exponential decay with a time constant of 26 ms at 300 K and  $\sim 50$  ms at 10 K.

Similar results to those described above were obtained in crystals which were contaminated with copper and manganese ions in the range of concentrations (28–40 ppm) of  $\text{Cu}^+$  and (120–280 ppm) of  $\text{Mn}^{2+}$ .

$\text{Cu}^+ \rightarrow \text{Mn}^{2+}$  energy transfer is expected to take place in NaCl since the  $\text{Cu}^+$   $3d^9 4s \rightarrow 3d^{10}$  emission strongly overlaps the  $\text{Mn}^{2+}$   ${}^6A_1 \rightarrow {}^4E$  absorption. This phenomenon occurred in our slightly doubly doped crystals even after they were heated near to the melting point and subjected to a severe quench into acetone. This treatment has been reported<sup>13</sup> to be a fully efficient one to retain a random dispersion of impurities in the alkali halides and to prevent impurity clustering during the quenching treatment.

### $\text{Cu}^+$ AND $\text{Mn}^{2+}$ CLUSTERS

For the low concentrations of donor and acceptor ions in our crystals, it is not possible that the  $\text{Cu}^+ \rightarrow \text{Mn}^{2+}$

energy-transfer process which is observed in our acetone-quenched samples would take place between copper and manganese ions randomly distributed in the lattice of NaCl. Rather, it must arise from small clusters of Cu-Mn such as dimers, trimers, etc., which are formed in the crystal. In these small aggregates of  $\text{Cu}^+\text{-Mn}^{2+}$  the energy transfer from copper to manganese is so efficient that it quenches the donor emission completely. Therefore, the  $\text{Cu}^+$  luminescence observed in our quenched samples is due to those  $\text{Cu}^+$  ions which are not interacting with any manganese ions. Under these circumstances the overall decay scheme of the  $\text{Cu}^+$  luminescence in quenched NaCl:Cu,Mn crystals should be the same as that in NaCl slightly doped with copper ions. This expectation is confirmed by our data.

The ratio for the number of  $\text{Cu}^+$  ions which were associated with the manganese ions ( $N_p$ ) to the total concentration of copper ( $N_T$ ) in our acetone-quenched crystals could be roughly estimated using a simple model in which both the donor and acceptor ions are treated as two-energy-level systems. This model is only applicable at very low temperatures where the copper ion can be described by two energy levels, i.e., the ground state and the metastable  $^3T_{2g}$  excited level from which the luminescence originates. The basic assumptions of this model have been described elsewhere.<sup>14</sup> According to them, it is found that  $N_p/N_T$ , in the limit of weak pumping, is given by<sup>14</sup>

$$\frac{N_p}{N_T} = \frac{I_{\text{Mn}}\beta'_{\text{Cu}}/\beta_{\text{Cu}}}{I_{\text{Cu}}[\beta'_{\text{Mn}}/\beta_{\text{Mn}} + (I_{\text{Mn}}/I_{\text{Cu}})(\beta'_{\text{Cu}}/\beta_{\text{Cu}})]}, \quad (1)$$

where  $\beta'$  and  $\beta$  are the radiative and fluorescence decay rates, respectively. If our liquid-helium data, i.e.,  $\beta_{\text{Cu}} \approx \beta'_{\text{Cu}} \approx 3.3 \times 10^2 \text{ s}^{-1}$  and  $I_{\text{Mn}}/I_{\text{Cu}} \approx 0.18$  are employed in Eq. (1), then  $N_p/N_T$  is found to be  $\sim 0.15$ . Thus, about 15% of the total concentration of copper ions in our slightly doped NaCl:Cu,Mn specimens appeared to be associated with the manganese ions. This percentage is larger when the slower cooling rates such as those characterized by quenching in natural air or onto a massive copper block are employed in view of the enhanced probability for impurity cluster formation. These findings along with those previously reported in the sodium halides<sup>1-5</sup> doped with  $\text{Eu}^{2+}$  and  $\text{Mn}^{2+}$  ions, and in the systems  $\text{RbMgF}_3\text{:Eu,Mn}$ ,<sup>15</sup>  $\text{CaF}_2\text{:Ce,Mn}$ ,<sup>16</sup>  $\text{CaF}_2\text{:Ce,Eu}$ ,<sup>17</sup> and  $\text{CaF}_2\text{:Eu,Mn}$  (Ref. 6) indicate that some kind of ions when they are introduced into "appropriate" crystalline matrixes tend to form impurity clusters even at very low impurity concentrations. They might also give support to the ionic radius criterion proposed by Rubio and co-workers<sup>1</sup> to explain this uncommon phenomenon.

From the model depicted above, and the fact that the rise time of the manganese emission was determined to be shorter than 25 ns, the rate of  $\text{Cu}^+ \rightarrow \text{Mn}^{2+}$  energy transfer was estimated to be  $> 1.1 \times 10^8 \text{ s}^{-1}$  at 10 K.

#### ENERGY-TRANSFER MECHANISMS

Since the  $\text{Cu}^+$  absorption transitions may be partially allowed in crystals and those of the  $\text{Mn}^{2+}$  ions are forbid-

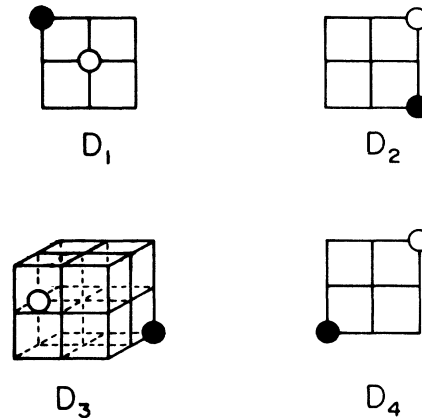


FIG. 3. Four of the simplest configurations for the Cu-Mn complex in the lattice of NaCl which were considered to calculate the rate of energy transfer via electric multipolar interaction mechanisms.

den, it might be expected that the  $\text{Cu}^+ \rightarrow \text{Mn}^{2+}$  energy-transfer mechanism taking place in NaCl is of the electric quadrupole-quadrupole type. The transfer rate for such a mechanism is given by<sup>18</sup>

$$W_{SA}^{QQ} = \frac{3\hbar^4 c^4}{4\pi n^4 \tau_s^0} Q_a \frac{\lambda_s^4}{R_{SA}^{10}} \frac{f_Q^2}{f_D^2} \Omega(f_s, F_A), \quad (2)$$

where  $\Omega(f_s, F_A) = \int [f_s(E)F_A(E)/E^4]dE$ . The meaning of the other symbols in Eq. (2) has been described elsewhere.<sup>14</sup> The magnitude of the overlap integral  $\Omega$  was calculated using the normalized line-shape functions for the Cu emission and Mn absorption in the overlap region. The result was  $1.3 \times 10^{-2} \text{ eV}^{-5}$ . On the other hand,  $Q_A$  was estimated following the procedure employed previously,<sup>14</sup> the result being  $4.8 \times 10^{-23} \text{ eV cm}^2$ . Now, taking into account that  $f_D \sim 10^{-7}$ ,  $f_Q \sim 10^{-10}$ , and the values mentioned above for  $\Omega$  and  $Q_A$ , the critical interaction distance for energy transfer was found to be  $\sim 15 \text{ \AA}$  at 300 K. Hence, within the lifetime of the copper excitation only those manganese ions within a radius of around  $15 \text{ \AA}$  will be sensitized.

Although the nature of the Cu-Mn clusters which were present in our acetone-quenched samples could not be inferred from our data, different kinds of small aggregates in which the Cu and Mn ions are separated by at most  $15 \text{ \AA}$  can be imagined in the lattice of NaCl. Some of the simplest ones are illustrated in Fig. 3. In these complexes, the position of the cation vacancy, created by the introduction of the  $\text{Mn}^{2+}$  ion into the alkali-halide lattice, has not been drawn for simplicity. However, it is well known<sup>19</sup> that sodium vacancies are mainly associated with the  $\text{Mn}^{2+}$  ions forming nearest neighbor (NN) or next-nearest-neighbor (NNN) dipolar complexes in the lattice of NaCl.

#### CALCULATED RATE OF ENERGY TRANSFER

The rate of  $\text{Cu} \rightarrow \text{Mn}$  energy transfer via an electric quadrupole-quadrupole interaction mechanism was calculated using the dimer configurations shown in Fig. 3.

TABLE I. Calculated rates of  $\text{Cu}^+ \rightarrow \text{Mn}^{2+}$  energy transfer using electric multipolar interaction mechanisms and the complexes shown in Fig. 3.

Complex	Interaction Distance ( $\text{\AA}$ )	$W_{SA}^{DP}$ ( $\text{s}^{-1}$ )	$W_{SA}^{DQ}$ ( $\text{s}^{-1}$ )	$W_{SA}^{QQ}$ ( $\text{s}^{-1}$ )
$D_1$	3.98	$3.2 \times 10^2$	$2.5 \times 10^5$	$2.0 \times 10^8$
$D_2$	5.62	$4.0 \times 10^1$	$1.6 \times 10^4$	$6.2 \times 10^6$
$D_3$	6.89	$1.2 \times 10^1$	$3.1 \times 10^3$	$8.1 \times 10^5$
$D_4$	7.95	$5.1 \times 10^0$	$9.9 \times 10^2$	$1.9 \times 10^5$

The results obtained are given in Table I along with those found from the use of either an electric dipole-dipole or an electric dipole-quadrupole interaction mechanism. As expected, more reasonable values are obtained when an electric quadrupole-quadrupole interaction mechanism is employed to perform the calculations. At this point, it should be mentioned that an exchange (superexchange) interaction mechanism might be also responsible for the  $\text{Cu} \rightarrow \text{Mn}$  energy transfer taking place in the small impurity aggregates. However, a calculation of the energy-transfer rate using this interaction mechanism was not attempted since only a very rough estimate can be obtained. In fact, the calculation is strongly dependent on the wave-function overlap integral of the donor and acceptor electrons involved in the exchange interaction. This makes it important to use accurate expressions for the wave functions which are not known at the present time.

Although it is recognized that the calculations above are phenomenological they may suggest that in order to account for the estimated rate of  $\text{Cu}^+ \rightarrow \text{Mn}^{2+}$  energy transfer, the copper and manganese ions in our acetone-quenched samples should be separated by at most 4  $\text{\AA}$  in the lattice of NaCl. This condition is fulfilled by the complex  $D_1$ . However, other small aggregate complexes in which a copper ion is surrounded by several manganese ions occupying the positions of first neighbors to the copper ion could be also appropriate to account for the rate of  $\text{Cu} \rightarrow \text{Mn}$  energy transfer. In addition to the complexes which are portrayed in Fig. 3, higher-order ag-

gregates are expected to exist in the crystals when they are subjected to relatively slow quenches.

### ANNEALING EXPERIMENTS

Impurity clustering was enhanced when the quenched crystals were stored at room temperature. It was ascertained that the intensity of the  $\text{Cu}^+$  emission decreased to the benefit of the  $\text{Mn}^{2+}$  emission as the elapsed time at room temperature between quench and measurement increased. The detailed kinetics for both emission bands is given in Fig. 4 for a crystal which was previously heated for 1 h at 873 K and then fast quenched into acetone.

The pulse excitation measurements performed at different times during the room-temperature annealing showed that the decay scheme of the Cu fluorescence consisted of a pure exponential decay with an associated lifetime value of 38  $\mu\text{s}$  for annealing times up to  $\sim 6$  h. At longer annealing times, however, an initial nonexponential portion followed by the intrinsic decay (38  $\mu\text{s}$ ) was observed.

All these data together may be explained considering that isolated  $\text{Cu}^+$  ions,  $\text{Mn}^{2+}$ -cation vacancy dipoles and small Cu-Mn aggregates were mainly the complexes which existed in our crystals after they were quenched into acetone. Impurity clustering was enhanced during the room-temperature annealing. Moreover, the small Cu-Mn aggregates acted as efficient nucleation centers for the manganese ions inducing, therefore, the formation of more complex aggregates and even second phase precipitates in which some copper ions were embedded. In these more complex aggregates a larger fraction of the excited  $\text{Cu}^+$  ions were within the effective interaction sphere of the  $\text{Mn}^{2+}$  energy sinks and a nonexponential portion at short times in the  $\text{Cu}^+$  fluorescence decay was expected due to different copper-manganese interaction distances. It cannot be ignored however, that manganese aggregates and even second phase precipitates without any incorporated copper ions, may be formed during the annealing process in view of the higher concentration of manganese as compared to that of copper in our samples.

### FINAL CONSIDERATIONS

It should be mentioned that the emission and excitation spectra of the NaCl:Cu,Mn system have been previously examined,<sup>20</sup> but for the case in which the  $\text{Cu}^+$  concentration is higher than that of  $\text{Mn}^{2+}$ ; this situation is opposite to the one we are reporting. Moreover, the

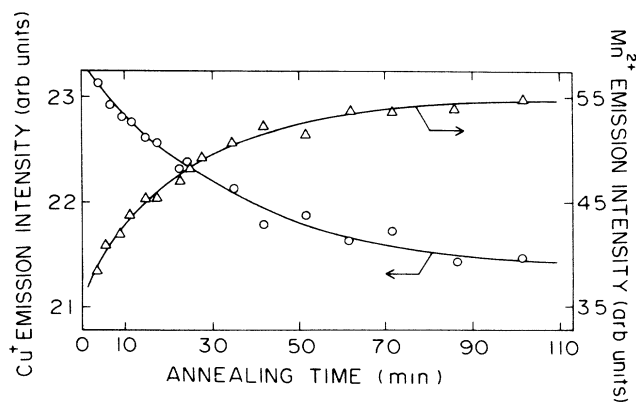


FIG. 4. Evolution of the intensities of the  $\text{Cu}^+$  and  $\text{Mn}^{2+}$  emissions observed in an acetone-quenched crystal as a function of the annealing time at room temperature.

available spectroscopic data were obtained in "as-grown" and well-aged crystals. It was inferred that  $Mn^{2+}$  ions were embedded in the  $Cu^+$  aggregates (precipitates) which were present in both kind of samples. The very efficient energy-transfer process from  $Cu^+$  to  $Mn^{2+}$  observed in this previous work was accounted for by considering the proximity of both ions in the aggregates. All this information along with that given in the present paper might give a quite complete characterization of the optical properties of the NaCl:Cu,Mn system under very different experimental conditions.

### CONCLUSIONS

Finally, one may conclude that the spectroscopic data presented in this paper suggest that small Cu-Mn clusters are formed in the lattice of NaCl even at very low concentrations of the dopants, and after the crystals are subjected to severe quenching treatments. This preferential

impurity clustering which has been considered to be infrequent in most previous studies of energy transfer between impurities in solids, appears to be quite helpful to those working on the design of more efficient phosphor and laser systems.

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