

Thermal recovery processes between 80 and 300 K on x-irradiated NaCl:Mn²⁺

F. J. López, M. Aguilar, and F. Agulló-López

*Departamento de Óptica y Estructura de la Materia and Instituto de Física del Estado Sólido,
Consejo Superior de Investigaciones Científicas, Universidad Autónoma de Madrid,
Cantoblanco, Madrid-34, Spain*

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The thermal recovery processes after 80 K irradiation of NaCl:Mn²⁺ have been investigated by using thermoluminescence (TL), optical absorption, and electron paramagnetic resonance (EPR). A main TL glow peak (II) is observed at about 170 K, both in pure and doped samples (the kinetics being, respectively, second and first order). It has been associated to the recombination of mobile V_k centers with electron-trapped centers. For doped samples these electronic centers have been identified as Mn⁰ B centers; whereas for pure samples they are suggested to be F^- centers. The kinetics of the peak as well as the change in the temperature of its maximum with manganese concentration can be accounted for, by using the theory of diffusion-limited reactions. The activation energy for the diffusion of V_k centers has been found to be 0.37 eV. For doped samples, two other glow peaks at 108 K (I) and 222 K (III) are observed. Possible models for them have been advanced; in particular peak III seems to be associated to the thermal release of holes from V_F centers. At variance with the data above room temperature, no correlation has been found between any of the TL peaks and an annihilation step in the F -center concentration.

I. INTRODUCTION

Thermally induced recovery processes can provide detailed information about the defects created by irradiation in alkali-halide crystals.¹⁻³ In particular, thermoluminescence (TL) spectra appear intimately related to those processes⁴⁻¹¹ and they have been extensively used in the past. Unfortunately, the mechanisms operating during the light emission are not completely elucidated yet and this very severely restricts the usefulness of the TL technique. It is not clear whether purely electronic or ionic or both processes are operating, and whether intrinsic or impurity-related color centers are involved. In fact a good correlation has been observed between glow peaks and various annihilation steps of color centers for pure alkali halides.^{7,11-14} For alkali-doped samples a similar correlation appears,^{4,5,10} as well as for other monovalent¹⁵ or divalent¹⁶⁻¹⁸ cationic impurities. However, impurity centers have also been found to correlate with the light emission.^{15,17-25}

In summary, an adequate knowledge of the mechanisms responsible for the light emission are urgently needed before TL measurements could be reliably applied to understand radiation-damage effects. From this mechanistic point of view, the most useful information provided by the TL measurements, is the wavelength spectra of the various glow peaks. Unfortunately these spectra have not been very often reported.

Recently, the TL and thermal recovery of NaCl:Mn²⁺ has been studied by the present au-

thors^{17,18} for samples x-irradiated at room temperature (RT). The glow peaks have been associated to drops in the concentration of F and V centers as well as that of Mn⁺ or Mn⁰ radiation-induced defects. It has been shown that all glow peaks yield the impurity emission band (595 nm) and another wide band at 410 nm, similar to the only one detected in nominally pure samples.¹³ This emission has been attributed to interstitial- F center recombination for both pure¹³ and doped¹⁷ samples. However, more recently the possibility of an V_k -electron recombination has been advanced.^{18,26} The V_k centers were proposed to arise from V_2^m centers (Cl_3^- molecular ions) formed during the RT irradiation,¹⁸ and the electrons were considered to be trapped at the impurities as Mn⁺ or Mn⁰ centers. There is also evidence from x-ray induced luminescence experiments, that the 410-nm emission is related to divalent impurities.²⁶⁻²⁸ On the other hand the interstitial- F center recombination in the perfect lattice should lead to the low-energy intrinsic emission²⁹ [360 nm in NaCl (Ref. 30)] which is severely quenched at or above RT.²⁸

The main objective of this work has been to extend the previous work to low temperatures, in order to clarify the recombination mechanisms responsible for the light emission. To this end, the TL and thermal recovery processes have been studied for NaCl, pure and doped with Mn, x-irradiated at 80 K. On this system EPR spectra are very useful to provide a detailed picture of the defects created by irradiation.

It is expected that the light-emitting processes be the same that above RT, or at least, relevant for

comparison, and that they could be more easily investigated due to the greater simplicity of the defects produced by x-irradiation at low temperature. Furthermore, V_k centers become mobile in that temperature range, so that their role on the light emission, can be more easily elucidated.

II. EXPERIMENTAL DETAILS

The crystals used, were grown in our laboratory from suprapure Merck materials under an inert atmosphere. The impurity content of Mn ions in the different crystals was 1.5, 15, 55, 90, and 150 ppm as determined by atomic absorption spectrophotometry. Quenching treatment was performed by heating the samples at 350 °C for 30 min and dropping them onto a copper block at RT. It was ascertained by EPR measurements that this treatment leaves essentially all the Mn^{2+} in solid solution.

The samples were cooled down to 80 K in a conventional cryostat; x-irradiation was achieved in the cryostat through a 1.5-mm thick aluminium window using a Kristalloflex 2H Siemens apparatus with a tungsten target operating at 50 kV and 30 mA.

For TL measurements an EMI 6256 S photomultiplier tube was chosen due to the low dark current and noise (10^{-12} and 10^{-13} A, respectively). The output current was detected with a Cary 401 vibrating reed electrometer. A Bausch & Lomb high-intensity monochromator was used to analyze the emission spectra in the range 200–650 nm; they were corrected by the spectral efficiency of the photomultiplier.

Heating rate for TL and thermal bleaching experiments was roughly 2 K/min throughout the whole temperature range from 80 to 300 K and completely repetitive from run to run. Moreover it was essentially constant over the region corresponding to each one of the various glow peaks. However, this condition is not essential because glow peaks were analyzed by a peak area method often used in ionic thermocurrent (ITC) experiments. The analysis was performed with an IBM/360 computer in the UAM-IBM research center.

Absorption spectra were performed with a Cary 17 spectrophotometer, and EPR measurements were obtained with a Varian E-12 x-band spectrometer at 100-kHz field modulation, equipped with an E-257 Varian gas-flow temperature controller.

III. EXPERIMENTAL RESULTS

A. TL glow peaks

All TL glow curves were obtained at a fixed wavelength corresponding to the impurity emission (585 nm) except those corresponding to pure NaCl,

where the selected wavelength was 360 nm (intrinsic emission).

Figure 1 shows the TL glow curves for both as-cleaved and quenched NaCl:Mn²⁺ samples (55 ppm) after 30 min of x-irradiation at 80 K. In the spectrum of the quenched sample three glow peaks are observed at 108, 171, and 222 K, although the peak at 108 K is much less intense than the other two. For the as-cleaved sample a main peak appears at 179 K with a shoulder which very likely corresponds to the peak at 171 K occurring in the quenched sample. The peaks at 108 and 222 K are also observed although they have much lower intensity than in the quenched sample as it occurs for the 171 K peak. Furthermore another very weak peak appears at 248 K in the as-cleaved samples.

The TL spectrum for quenched crystals has been studied as a function of manganese concentration. Results are displayed in Fig. 2 for samples x-irradiated during 30 min at 80 K immediately after quenching. It is observed that the peaks at 108 and 222 K appear at the same temperature for all manganese concentrations (from 1.5 to 150 ppm) while the maximum of the central peak shifts to lower temperatures the higher the concentration of Mn; it displaces from 185 K for 1.5 ppm, to 166 K for 150 ppm.

A new peak appears at 210 K for samples containing 1.5-ppm manganese and another one at 191 K for the samples with 90 and 150 ppm. These peaks are of small intensity and have not been further investigated in this work.

From now on, the main peaks near 108, 171, and 222 K will be, respectively, labeled as I, II, and III. It is apparent from Fig. 2 that peak II is always the most intense one, and that the relative intensity of

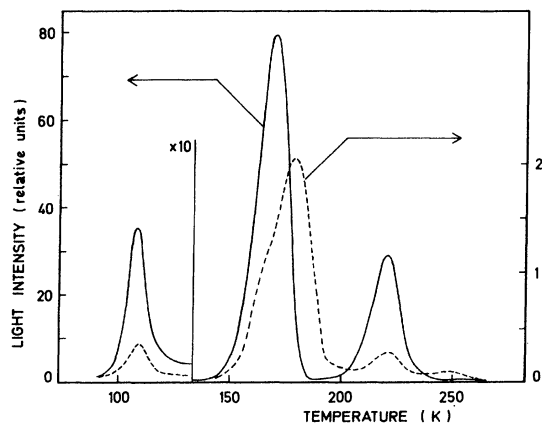


FIG. 1. TL spectra, measured at 585 nm, of NaCl:Mn (55 ppm) x-irradiated during 30 min at 80 K. Continuous line: quenched sample; dashed line: as-cleaved sample.

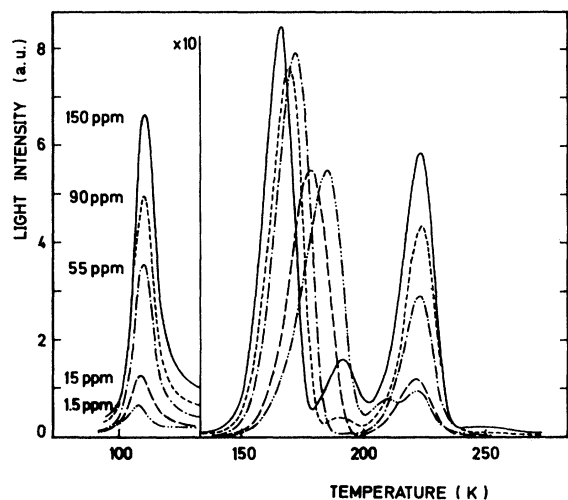


FIG. 2. TL spectra, measured at 585 nm, of NaCl samples doped with various concentrations of Mn as marked on the curves. All samples were x-irradiated during 30 min at 80 K after quenching.

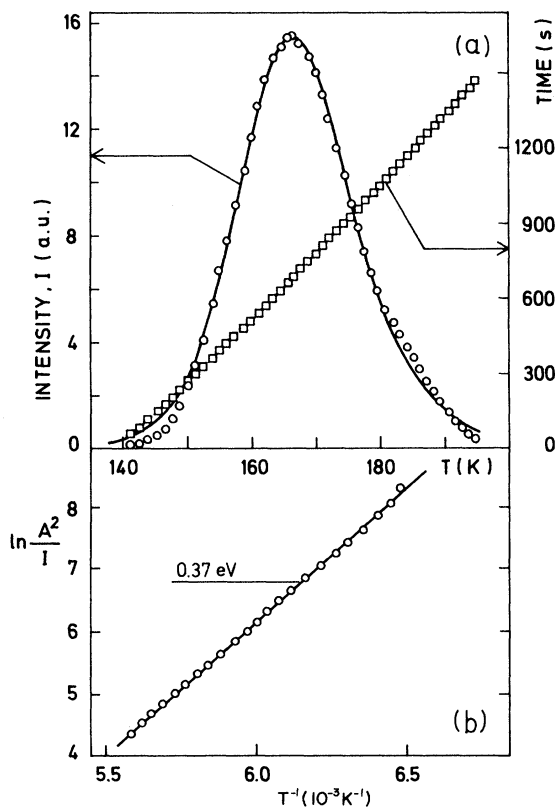


FIG. 3. (a) Experimental (circles) and theoretical (continuous line) glow curve, measured at 360 nm for a pure NaCl sample x-irradiated at 80 K. (b) Analysis of the experimental points by the total glow-peak method (see text).

peaks I and III, with respect to II, grows on increasing the Mn concentration.

The evolution of the glow peaks with the dose of x-irradiation (from 10 min to 8 h) has been also studied for quenched samples with 55 ppm of Mn. The three glow peaks grow up to a saturation level reached after ~ 3 h of x-irradiation for peaks I and II, and ~ 1 h for peak III. It is important to point out that peak II presents its maximum at a constant temperature, regardless of the irradiation dose, although its intensity varies in a wide range (from 17 for 10 min dose to 100 for 8 h in relative units). This is very similar to that observed when its intensity was studied as a function of concentration for a fixed dose of 30 min (from 8 for 1.5 ppm to 100 for 150 ppm, in the former units). Therefore, the shift of peak II to lower temperatures, cannot be attributed to the increase in peak intensity, but to the increasing Mn concentration.

The TL spectrum for a very pure (suprapure) sample of NaCl has been also obtained for comparison purposes. In the temperature range 80–300 K only a weak glow peak at 165 K is observed (Fig. 3).

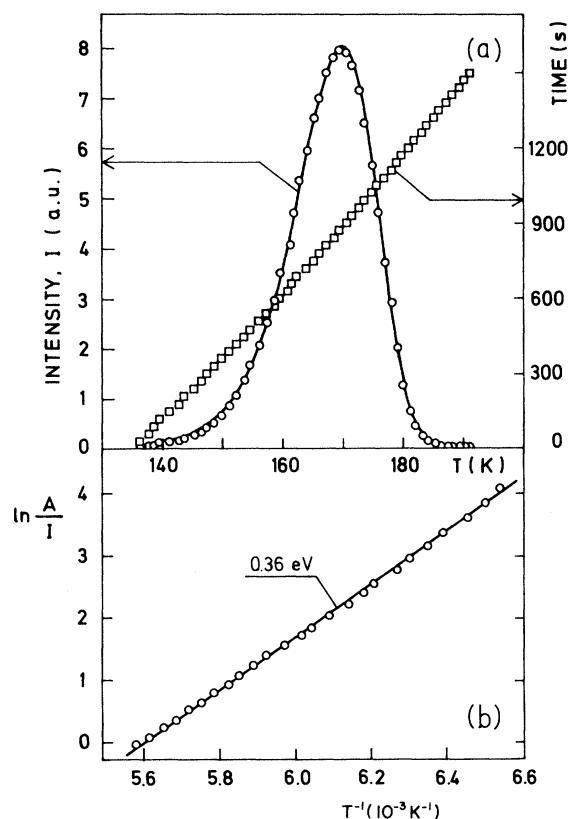


FIG. 4. Experimental (circles) and theoretical (continuous line) glow curve (a); and analysis (b) of peak II for NaCl:Mn (55 ppm) x-irradiated by 30 min at 80 K.

TABLE I. Peak temperatures (T_m), activation energies (E), and preexponential factors (S) of TL glow peaks.

Peak ppm	NaCl			NaCl:Mn				III
	I	1.5	15	II 55	90	150		
T_m (K)	165	108	185	180	171	169	166	222
E (eV)	0.37	0.30	0.37	0.36	0.36	0.37	0.39	0.59
S (s^{-1})	7×10^6	2×10^{10}	3×10^7	5×10^7	3×10^8	7×10^8	5×10^9	1×10^{11}
Kinetics order	2nd	2nd	1st	1st	1st	1st	1st	1st

The TL glow peaks have been analyzed by the total glow-peak method,³¹ which can accept linear as well as nonlinear heating rates. In this method one plots $\ln(A^\alpha/I)$ versus the reciprocal of the temperature, α being the order of the process responsible for the luminescence, I the light intensity at a given time (temperature), and A the area of the glow curve in a linear time scale from that time (temperature) to the end of the peak. The plots should yield straight lines from which the activation energy E and preexponential factor S can be obtained. With both parameters it is possible to reconstruct a theoretical peak and to compare it with the experimental peak.

In all cases it has been possible to obtain an excellent fit between experimental and theoretical peaks. As an illustration, Figs. 3 and 4, respectively, show the experimental and theoretical spectra [3(a) and 4(a)] and the analysis [3(b) and 4(b)] for the peak at 165 K in pure samples, and peak II (171 K) in 55-ppm-doped samples. The activation energies, preexponential factors and kinetics orders for all TL glow peaks, are summarized on Table I.

B. Emission spectra

The wavelength spectra of the emitted light have been measured during heating for each glow peak, they are displayed on Fig. 5. Peak II [Fig. 5(a)] shows the typical emission of the Mn^{2+} at 585 nm,^{17,18,26} as well as a broad band centered at 410–415 nm which has been also observed in the emission spectra of the glow peaks above RT.^{17,18} On the other hand peak III [Fig. 5(b)] presents the emission at 585 nm together with three overlapping bands at 250, 300, and 355 nm and a shoulder near 400 nm.

For peak I which is much less intense than the other two, only the impurity emission at 585 nm has been detected. The emission at 410 nm has not been observed although it has been specifically looked for.

The emission spectrum of the glow peak at 179 K in as-cleaved samples is plotted in Fig. 5(c). A main emission at 585 nm is observed together with two other bands at 310 and 505 nm.

The wavelength spectrum of the glow peak for pure NaCl is given on Fig. 5(d). It consists of a single wide band (~ 1 eV) centered at 360 nm which coincides very well with the low-energy intrinsic emission of NaCl.^{28,30} a very weak hump at 520 nm is also observed.

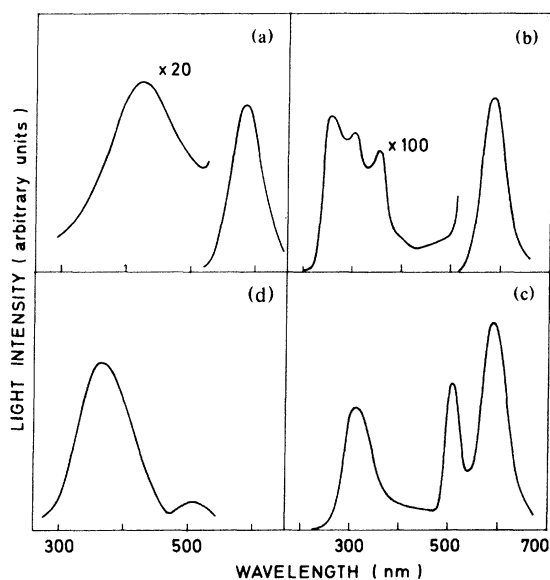


FIG. 5. Emission spectra of TL glow peaks measured during heating for 55-ppm Mn-doped [(a), (b), and (c)] and pure NaCl samples (d). (a) Peak II, quenched sample. (b) Peak III, quenched sample. (c) 179-K peak, as-cleaved sample. (d) 165-K peak, pure sample.

C. Optical absorption and EPR spectra

The optical-absorption spectra of NaCl samples doped with 15, 55, and 90 ppm of Mn, which have been irradiated at 80 K after quenching, present an intense band with two maxima at 405 and 435 nm, and another one at higher energies and showing fine structure (peaks at 215, 225, and 230 nm). All these bands have been attributed by Ikeya and Itoh³² to Mn^0 substituting for Na^+ in off-center position ($Mn^0 B$). On the contrary, in the absorption spectrum of a sample containing 1.5 ppm of Mn x-irradiated at 80 K, the $Mn^0 B$ absorptions are not observed, whereas the F band (450 nm) is apparent.

The EPR spectra have been measured at 85 K on quenched samples with 1.5, 15, and 55 ppm of Mn, before and after x-irradiation at liquid-nitrogen temperature (LNT). In all cases a decrease in the spectrum corresponding to Mn^{2+} , both free or associated to a cation vacancy, was observed after irradiation. Simultaneously, the growth of the spectrum attributed by Ikeya *et al.*³³ to an I_z center (interstitial Cl^- next to Mn^{2+}) was detected. No EPR spectrum associated to $Mn^0 B$ is observed, in agreement with those authors.³²

The spectrum of V_k centers has not been observed, likely due to the masking effect of the very strong spectrum of Mn^{2+} -vacancy dipoles.

The thermal stability of $Mn^0 B$ has been studied, by measuring the intensity of the absorption bands at 405 and 435 nm during heating (55- and 90-ppm samples) or through pulsed thermal annealing (15-ppm samples). Results are displayed on Fig. 6. There appear two strong annealing steps which agree very well in temperature with TL peaks II and III. As for peak I, one cannot reliably conclude from the figure whether it is associated to some annihilation of $Mn^0 B$ centers, particularly if one takes into account its very low intensity.

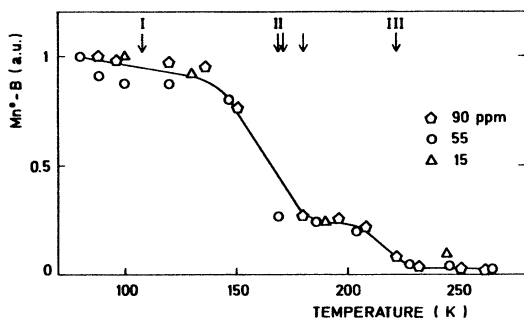


FIG. 6. Thermal annihilation of $Mn^0 B$ measured from the absorption spectra of x-irradiated NaCl:Mn samples; (pentagon) 90 ppm, continuous heating; (O) 55 ppm, continuous heating; (Δ) 15 ppm, pulsed annealing. Arrows indicate the position of TL peaks.

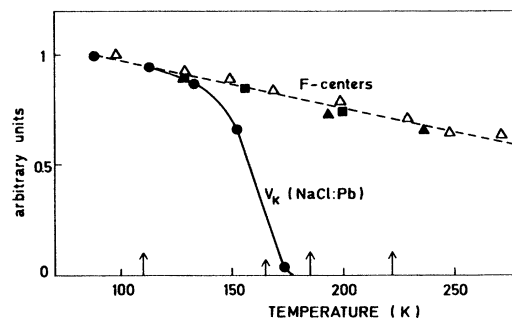


FIG. 7. Thermal annihilation of F centers for: (\blacksquare) pure NaCl, pulsed bleaching; (\blacktriangle) 1.5-ppm Mn-doped, pulsed bleaching; (\triangle) 1.5-ppm Mn-doped, continuous heating; NaCl samples. Full circles show the evolution, measured by EPR, of V_k centers in NaCl:Pb (170-ppm) samples. Long arrows indicate the position of TL peaks in NaCl:Mn (1.5 ppm) and short arrow indicate the position of the glow peak for pure NaCl.

Analogous experiments have been realized with NaCl both pure and doped with 1.5-ppm Mn, where the F band is clearly observed. The two methods: pulsed annealing and continuous heating, have been utilized. For the continuous heating, the drop in the F band has been corrected by the variation on the width of the absorption band. Results plotted in Fig. 7, show that there is not a clear F -center drop associated to any of the TL peaks.

In order to have comparative data on the thermal stability of the V_k centers, the evolution with temperature of the V_k center concentration has been also measured by EPR and optical absorption on NaCl:Pb²⁺ (170 ppm) where the V_k centers are easily observed. Data included in Fig. 7 show that the maximum rate of decay occurs at 160–165 K.

Figure 8 presents the evolution of the EPR spectra

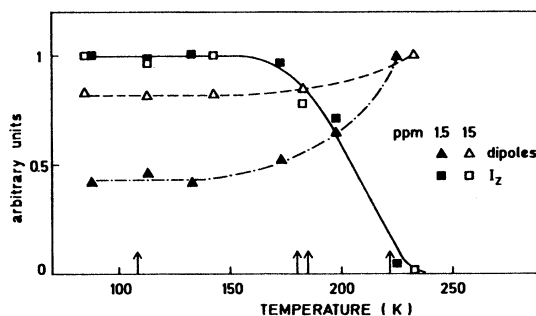


FIG. 8. Evolution with temperature as measured by EPR of dipoles (triangles) and I_z centers (squares) for NaCl:Mn samples x-irradiated at LNT after quenching; (full symbols) 1.5-ppm Mn; (open symbols) 15-ppm Mn. The arrows indicate the position of TL glow peaks.

for samples with 1.5 and 15 ppm of Mn as a function of temperature. The annihilation of the I_2 centers coincides with the greatest regeneration of Mn^{2+} -vacancy dipoles, and the maximum rate of this process occurs at temperatures near peak III.

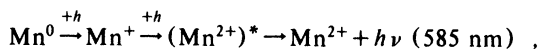
IV. DISCUSSION

First of all, it has been clearly concluded that the main low-temperature recovery processes are essentially different for as-grown and quenched samples, as it was already shown above room temperature.^{17,18} Most data in this paper refer to quenched samples, where the state of aggregation of the impurity is better defined. Therefore the discussion will be essentially concerned with them.

Since no correlation between annihilation of F centers and TL glow peaks has been here found, one has to infer the main general conclusion that F centers do not directly participate in the TL recovery processes. Some other mechanisms, to be described next, have to be invoked to account for the light emission in the various glow peaks.

A. Peak II

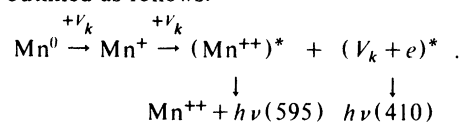
This is the main glow peak occurring in the TL spectra of pure and doped samples. The temperature of the peak very closely agrees with that corresponding to the mobility of the V_k centers (self-trapped holes).³⁴ In fact, similar glow peaks have also been detected in NaCl doped with Cu^+ ,^{24,25} Ag^+ ,³⁵ or Pb^{++} ,³⁶ and ascribed to the motion and recombination of V_k centers. Furthermore, it has been clearly shown for our Mn-doped samples that peak II is associated to the annihilation of $Mn^0 B$ centers. Since the main spectral band of the emitted light lies at 585 nm, which corresponds to the typical Mn^{2+} emission,^{17,18} one would propose the following mechanism:



where h stands for hole and the symbol $*$ applies to an excited state.

The problem is to understand the origin of the 410-nm band accompanying the dominant manganese emission. A F -interstitial (H -center) recombination mechanism, advanced for the high-temperature recovery processes,¹⁷ cannot be maintained on the light of present data, but one must certainly consider hole and impurity processes. A reasonable mechanism, already pointed out in recent papers,^{18,26} is somewhat similar to that proposed by Delbecq *et al.*^{20,21} It involves the tunneling of an electron from the Mn^+ (or Mn^0) ion to a nearby V_k center, to form an excited self-trapped exciton $(V_k + e)^*$ next to the impurity. The radiative decay of this exciton

would yield one of the intrinsic emissions perturbed or made allowed by the impurity.²⁶ This model has been also proposed to account for the occurrence of this 410-nm band observed in the luminescence emission during low-temperature x-irradiation of NaCl doped with divalent cation impurities by Ikeya²⁷ and Aguilar *et al.*²⁸ Therefore the whole process can be outlined as follows:



For the pure samples the corresponding TL glow peak at 165 K contains a single emission band at 360 nm which corresponds to the intrinsic π emission of the self-trapped exciton (STE). Here the V_k centers should recombine with an electron trapped in some intrinsic defect. It appears reasonable to think of an F^- center. In fact, a V_k - F^- tunneling recombination should yield the intrinsic emission, since the extension of the F^- wave function makes plausible that the F center do not perturb appreciably the energy of the STE transition.

Since the reported data for peak II suggest a mechanism involving mobile V_k centers, one should apply the theory of diffusion-limited reactions³⁷ to understand the kinetic behavior of such a peak. According to Waite,³⁷ the rate of a diffusion-limited bimolecular reaction $A + B \rightarrow AB$ is given by

$$\frac{dC_A}{dt} = \frac{dC_B}{dt} = -\chi \left(1 + \frac{r_0}{(\pi Dt)^{1/2}} \right) C_A C_B \quad (1)$$

if the Smoluchowski boundary condition is used and the initial pair density function is taken uniform. In (1), C_A and C_B are the concentrations of species A and B , r_0 stands for the critical interaction distance for the reaction, and $\chi = 4\pi r_0 D$ where $D = D_A + D_B$, D_A and D_B being the diffusion coefficients of the reacting species.

For a luminescent recombination $A + B \rightarrow h\nu$, the kinetics of both species A and B is also governed by Eq. (1). In our case A can be identified with the mobile V_k centers and B should include the electron-trapped centers ($Mn B$ or F^-) labeled L , as well as hole-trapping defects T_{ht} which do not contribute to light emission. It is reasonable to assume that both L and T_{ht} centers are immobile, so that $D_L = D_{T_{ht}} = 0$. Now we can consider two situations:

(i) For *doped-samples* the most efficient traps T_{ht} are, very likely, cation vacancies which after capturing a V_k center are turned into the well established V_F centers.³⁴ It is reasonable to assume that $T_{ht} \gg L$ and then Eq. (1) leads (for annealing times where $\pi Dt \gg r_0^2$) to a first-order reaction for the decay of V_k centers

$$\frac{dC_{V_k}}{dt} = -KC_{V_k} \quad (2)$$

The rate coefficient $K = (C_L + C_{T_{ht}}) \chi \sim C_{T_{ht}} \chi$ is kept essentially constant throughout the reaction, and can be written as $K = S \exp(-E/kT)$. Therefore, in a typical TL experiment a first-order peak should be obtained with a frequency factor $S = 4\pi r_0 D_0 C_{T_{ht}}$ and an activation energy E which corresponds to the activation energy for the diffusion of the V_k centers.

Furthermore one should expect an activation energy independent of Mn concentration and a frequency factor proportional to it.

Experimental data (Table I) yield an activation energy of ~ 0.37 eV essentially constant in a wide range of Mn concentrations and closely in agreement with the value reported by Fabrikant and Kotomin³⁵ for NaCl:Ag. Moreover the frequency factor increases in a roughly linear way with the Mn concentration, in accordance with the theoretical prediction.

On the other hand, one can estimate the value of S in terms of the random walk model. Under the assumption of noncorrelated random jumps of constant length a , the diffusion coefficient can be written

$$D = \frac{1}{6} \Gamma a^2,$$

where Γ is the average jump frequency. It can be expressed as $\Gamma = \nu_0 \exp(-E/kT)$, E being the activation energy for the jump and $\nu_0 \sim 10^{13} \text{ s}^{-1}$. Assuming a rough value of $a = 3 \times 10^{-8} \text{ cm}$ and using the experimental value $E = 0.37 \text{ eV}$ one obtains $D_0 \approx 3 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$. Moreover, r_0 is expected to be $\sim 10^{-7} \text{ cm}$ and $C_{T_{ht}}$ could be estimated as $C_{T_{ht}} \sim 0.02 C_{Mn}$, C_{Mn} being the total concentration of dissolved manganese. Therefore one would predict $S \sim 6 \times 10^{-10} C_{Mn}$, in fair agreement with experimental data in Table I, which yield $S \sim 8 \times 10^{-10} C_{Mn}$. The increase of S with C_{Mn} explains that the temperature for the maximum of the glow peak shifts to lower values, on increasing manganese concentration.

The insensitivity of the position of the glow peak to irradiation dose can be understood considering that in the dose range used, the concentration of V_k and associated electron centers remains lower than that of the hole-trapping centers ($C_L \ll C_{T_{ht}}$). In such conditions, the glow-peak parameters and temperature for the maximum should be dose independent. However, the first-order behavior might fail at much higher irradiation dose.

(ii) For the *pure samples* one is very likely dealing with a concentration of V_k centers similar to that of the electronic centers (F^- centers), whereas that of the competing hole traps is negligible. For such a case ($C_{V_k} \approx C_L$, $C_{T_{ht}} \approx 0$) Eq. (1) becomes

$$\frac{dC_{V_k}}{dt} = -K' C_{V_k}^2; \quad K' = 4\pi r_0 D = 4\pi r_0 D_0 \exp\left(\frac{-E}{kT}\right),$$

which is a second-order reaction, in accordance with the analysis of the TL glow peak. The activation en-

ergy represents, again, the activation energy for V_k diffusion. In fact, the experimental value is in excellent agreement with those inferred from the first-order peaks, in the case of doped samples.

For a second-order peak, the preexponential factor S , as listed in Table I, is given by $S = 4\pi r_0 D_0 C_L(0)$, where $C_L(0)$ is the initial concentration of recombining centers. By comparing to the experimental datum one obtains, after 3-h irradiation at 80 K of pure samples, $C_L(0) \approx 10^{14} \text{ cm}^{-3}$, which is a reasonable value for the F^- or V_k concentration.

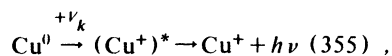
B. Peak III

This peak appearing in the doped samples is also associated to annihilation of $Mn^0 B$ centers. Furthermore the ratio between the area of this peak and that of peak II agrees satisfactorily with the ratio of the heights for the annihilation steps of $Mn^0 B$. Also the spectral composition of the emitted light includes the band at 585 nm as well as some indication of that one at 410 nm [Fig. 5(b)]. Since these emissions are those appearing in peak II, one would propose the same light-emitting process for both peaks. The problem now, is to determine the origin of the V_k centers, since they become thermally unstable at lower temperatures. It is reasonable that holes be thermally released from the V_F centers formed after hole capture by the cation vacancies. In fact, V_F centers are considered to become unstable near 230 K.³⁴ For this case, one is dealing with a process not controlled by diffusion, but by the thermal detrapping of the holes from V_F centers. Consequently the activation energy, $E = 0.59 \text{ eV}$, should correspond to the binding energy of the V_k center to the cation vacancy. Under these conditions, one would not expect any change in the temperature of the peak with Mn concentration as experimentally observed.

The data in Fig. 8 show that annihilation of I_2 centers takes place in correlation with the regeneration of Mn^{++} at temperatures near peak III. Moreover much more Mn^{++} is regenerated near peak III than near peak II. On the contrary, the Mn^{++} -light emission as well as the destruction of $Mn^0 B$ centers are stronger at peak II than at peak III. These results imply that the larger part of Mn^{++} regenerated near peak III must be produced by a nonluminescent mechanism. This process can be visualized as the thermal escape of Cl^- ions of I_2 centers, leaving behind the isolated Mn^{++} . These Cl^- ions probably annihilate through recombination with F^+ centers and are not involved into any light emission. Therefore it must be concluded that I_2 centers are not directly related to peak III.

Finally one should comment on the occurrence of some other bands at 250, 300, and 355 nm in the wavelength spectrum of peak III. They are very likely due to some uncontrolled impurities that contrib-

ute to light emission via the same mechanism invoked for manganese. In particular, the band at 355 nm, which is prominent at long irradiation times, agrees very well in peak position and width (0.29 eV) with the typical emission of Cu^+ in NaCl.^{15,25} The mechanism can be described as



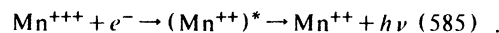
where the Cu^0 has been produced from Cu^+ during irradiation.³⁸ This mechanism has been shown to operate in the recovery processes for Cu-doped NaCl.²⁵

C. Peak I

This peak at 108 K is very weak and only the 585-nm emission has been detected. Due to the dispersion of the data on the evolution of $\text{Mn}^0 B$ centers with temperature in Fig. 6, one cannot definitely ascertain whether or not some $\text{Mn}^0 B$ centers are being destroyed in correlation with that glow peak. In the affirmative case one would suggest the same light-emitting process as that for peaks II and III. However, since V_k centers are stable up to ~ 160 K, one has to think of some mechanism providing the required holes. One possible mechanism recently advanced by Zazubovich and Osminin³⁹ involves recombination of an H center with one F^+ center producing one V_k center. If these V_k centers are formed near the Mn^0 atoms, electron tunneling could be possible and the proposed mechanism would become operative. The H centers could be released from some H_A -type centers that are thermally unstable in the temperature region corresponding to peak I.⁴⁰

Anyhow this proposal is very speculative and it is

difficult to explain why the 410-nm band is not observed as for the other TL glow peaks. In fact, one could also think of an electron-induced process such as



The electron might come from some unknown shallow trap. This mechanism is consistent with the absence of the 410 nm emission. Unfortunately no evidence for the occurrence of Mn^{+++} in irradiated alkali halides is available at present.

D. Peak of untreated samples

This peak is due to the Mn doping since it does not appear in pure samples and emits at 585 nm in addition to 505 and 310 nm [Fig. 5(c)].

It has been ascertained by EPR measurements that in the untreated samples most Mn^{++} ions are in aggregated form.⁴¹ For these aggregated samples, we have observed on the x-ray-induced luminescence at 80 K an emission spectrum involving a band near 500 nm as well as that at 585 nm. It is reasonable to think that the 179-K peak be associated to recombination of V_k centers with Mn^0 or Mn^+ ions forming part of some impurity aggregates.

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