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Emission Spectra of NaCl:Mg Crystals

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Introduction It has been established that in NaCl crystals four different magnesium centers were produced by X-irradiation and subsequent F- and thermal bleaching. The center in NaCl:Mg which absorbs at about 3.9 eV (designated as  $Mg_1$  /1/) was formed by illumination in the F-band at 300 K of X-irradiated crystals. Optical and thermal properties of this center have been investigated by Watterich et al. /1, 2/. The main results are the following: a) the center is not paramagnetic, b) optical bleaching of these centers at room temperature leads to an increase of the F-band absorption, c) the  $Mg_1$  center decays around 100 °C and other Mg centers are formed. The authors suggested a model of the  $Mg_1$  center. It consists of a dimer which has captured two electrons and two anion vacancies.

The afore mentioned investigations have been carried out at room temperature, in our previous paper /3/ we studied the optical and thermal properties of the  $Mg_1$  center in the temperature region from 80 to 300 K.

It was observed that the  $Mg_1$  center associated with the absorption band at 3.9 eV optically decays at 80 K and another center, which has two absorption bands at 2.6 and 3.2 eV is formed. At room temperature these bands could not be resolved. The latter center is thermally destroyed above 300 K and the F-absorption band, which is originally present, recovers. From these results we found that the model for the  $Mg_1$  center proposed by Watterich and Raksányi /2/ is unacceptable. A new model has been suggested in which the absorption bands at 2.6 and 3.2 eV are due to an electronic transition of the F-center perturbed by the  $Mg_c^+$  ion ( $F_A(Mg_c^+)$ ) and the  $Mg_1$  center is a substitutional atom  $M_c^0$  attached to an anion vacancy ( $Mg_c^0 V_a^+$ ).

The optical conversion  $Mg_c^0 V_a^+ \rightarrow F_A(Mg_c^+)$  takes place at 80 K and this process is optically reversible.

In this note we intend to confirm these results by emission measurements.

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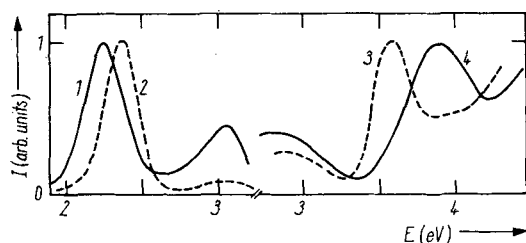


Fig.1

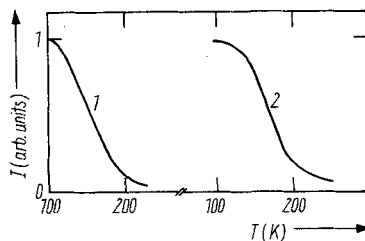


Fig.2

Fig. 1. Corrected emission (1), (2) and excitation (3), (4) spectra at 80 K. The emission spectra are measured with (1) 3.9 and (2) 3.6 eV excitation light. Excitation spectra are measured for (3) 2.4 and (4) 2.1 eV emission light

Fig. 2. Temperature dependence of the (1) 2.4 and 2.2 eV emission intensities under excitation with light at (1) 3.6 and (2) 3.9 eV

**Experimental procedure** NaCl crystals with 0.2 to 0.5 wt%  $\text{MgCl}_2$  ( $\text{MgCl}_2$  added to the melt) used in this note were grown in helium atmosphere with the Stockbarger method. Crystals were X-rayed at room temperature for 5 min at 40 kV and 50 mA. Excitation of luminescence was carried out using light from deuterium, tungsten, and mercury lamps passing through a grating monochromator MDR-4. Luminescence light was detected with a FEU-79 photomultiplier in the photon counting regime or a PbS detector through suitable filters or a grating monochromator MDR-2.

**Experimental results**  $\text{Mg}_c^0\text{V}_a^+(\text{Mg}_1)$  centers are produced by X-irradiation and subsequent F-bleaching at a temperature above 250 K and have an absorption band with peak energy of 3.9 eV at 80 K /1 to 3/. Excitation in this absorption band leads to two emission bands at 2.25 eV with halfwidth of 0.3 eV and at about 3.1 eV at 80 K (Fig. 1, curve 1). Similar emission bands at 2.25 and 2.6 eV have been also observed in NaF:Mg crystals and ascribed to the  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  (A-band) and  $^1\text{P}_1 \rightarrow ^1\text{S}_0$  (C-band) transitions of the  $\text{Mg}^0$  atom, respectively /4/. It is therefore likely that in NaCl:Mg the observed emission bands at 2.25 and 3.1 eV are due to these transitions.

Aside from these emissions, two emission bands at 2.35 and about 3.0 eV are observed just after X-irradiation at 300 K. Thermal annealing above 400 K leads to the disappearance of these emissions. The model for the center responsible for these emissions is not clear at present, however, it is likely that the latter emission bands are also associated with transitions of the  $\text{Mg}^0$  atom (Fig. 1, curve 2).

The excitation spectra for both emission bands at 2.25 and 2.35 eV are shown in Fig. 1. As in the case of NaF:Mg, the excitation band at about 2.7 eV is due to the  $^1S_0 \rightarrow ^3P_1$  transition (A-band) and the corresponding absorption band is very weak because the spin-orbit coupling is very small and cannot be observed by absorption measurements /4/. In contrast to the NaF:Mg crystals, in which the  $Mg^0$  related emission is observed at room temperature /4/, the emission of the  $Mg^0$  center cannot be detected above 230 K in NaCl:Mg samples as shown in Fig. 2.

As mentioned above, the optical bleaching of  $Mg_c^0V_a^+$  centers at 80 K leads to formation of the  $F_A(Mg_c^+)$  centers. Therefore, it is expected that the emission of these centers can be observed at 80 K. Since the process  $Mg_c^0V_a^+ \rightarrow F_A(Mg_c^+)$  is optically reversible, luminescence is excited by light with energy which lies in the region between  $Mg_c^0V_a^+$  and  $F_A(Mg_c^+)$  absorption bands. In X-irradiated NaCl:Mg crystals after F-bleaching at room temperature the emission band at 1.04 eV with halfwidth 0.12 eV is observed at 80 K as shown in Fig. 3. This emission decays after thermal treatment at 350 K. The maximum position of this emission is not very different from that of the F-emission band /5/. From its behavior the observed emission is likely due to  $F_A(Mg_c^+)$  centers.

Upon prolonged F-bleaching at 300 K of the X-irradiated crystals, the additional absorption band centered at about 1.85 eV appears at the shorter wavelength side of the M absorption band. The same shift of the M absorption band is observed in NaCl doped with divalent cations, such as Mg, Mn, Ni, Cd, and Pb. This absorption band has been interpreted as arising from the  $Z_4$  center /6/.

However, a formation of the  $Z_1$  centers in these samples is not established and it is generally considered that  $Mg^{++}$  (as well as Mn, Ni, Cd, and Pb) changed its valence state during irradiation and subsequent optical and thermal bleaching. Furthermore, since  $F_A(Mg_c^+)$  centers are formed in NaCl:Mg crystals /3/, it is believed that the observed absorption is associated with  $M_A(Mg_c^+)$  (M center perturbed by  $Mg_c^+$ ).

Excitation into this absorption band leads to the emission band at 1.24 eV with halfwidth 0.16 eV at 80 K. The excitation and emission spectra for M and  $M_A$  centers are shown in Fig. 4. The third emission band at about 1.42 eV at 80 K is also observed in undoped NaCl samples and according to /7/ is associated with emission of  $F_2^+$  centers.

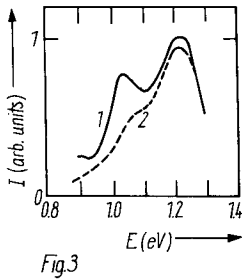


Fig.3

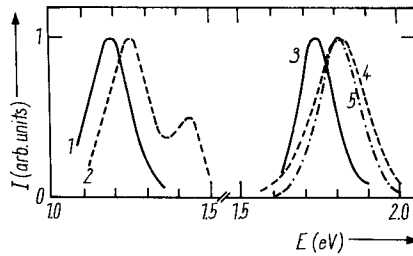


Fig.4

Fig. 3. Corrected emission spectra at 80 K for excitation with light at 3.4 eV of NaCl:Mg crystals after (1) X-irradiation and F-bleaching at 300 K and (2) subsequent thermal bleaching at 350 K

Fig. 4. Corrected emission spectra (1), (2) and excitation (3) to (5) spectra at 80 K. The emission spectra are measured with (1) 1.65 and (2) 1.85 eV excitation light. The excitation spectra are measured for (3) 1.1, (4) 1.24, and (5) 1.45 eV emission light

**Conclusion** It has been well established that Z-type centers are formed in alkali halides doped with divalent cations like  $\text{Ca}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$  and rare earths  $\text{Sm}^{++}$ ,  $\text{Eu}^{++}$ , and  $\text{Yb}^{++}$ , which have a low second-ionization potential. However, in the last years in alkali halides doped by Mg, Mn, Pb, Ni, and Cd (with higher values of second-ionization potential) F-type perturbed centers have been observed and in the opinion of some authors the perturbative effect is due to divalent cations (Z-type centers) /6, 8 to 10/.

In previous paper /3/ and this one we show, in contrast to the latter assumption, that the perturbative effect in NaCl:Mg crystals is likely due to the presence of the  $\text{Mg}_c^+$  ion in the vicinity of the F-type center ( $\text{F}_A(\text{Mg}_c^+)$  type center).

This interpretation is supported by the observed emission of the  $\text{Mg}_c^0\text{V}_a^+$  center which optically converts to the  $\text{F}_A(\text{Mg}_c^+)$  center.

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