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## Excitonic Processes and Thermoluminescence in NaCl Crystals Doped with Mg or Mn

By

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Processes of defect creation by VUV-excitation are studied by the thermoluminescence method. NaCl crystals doped with Mg or Mn are irradiated at 80 K by monochromatic VUV-light in the region of 7 to 8 eV. Excitation spectra of the glow peaks at 195 K (NaCl-Mg) and 220 K (NaCl-Mn) have maxima at 7.5 and 7.4 eV, respectively. It is concluded that the TL excitation spectra correspond to the formation of an exciton near the divalent metal ( $Mg^{2+}$  or  $Mn^{2+}$ ) of the impurity-vacancy complex. The decay of these excitons leads to formation  $\alpha$ - $I_z$  pairs at 80 K.

Процессы образования дефектов ВУФ-излучением изучались термолюминесцентным методом. Кристаллы NaCl, активированные Mg или Mn, облучались при 80 К светом в спектральной области 7 до 8 эВ. Спектры возбуждения пиков термолюминесценции при 195 К (NaCl-Mg) и 220 К (NaCl-Mn) имеют максимумы при 7,5 и 7,4 эВ, соответственно. Сделан вывод, что спектры возбуждения термолюминесценции соответствуют созданию экситонов около двухвалентного металла ( $Mg^{2+}$  или  $Mn^{2+}$ ), сходящих в состав примесно-вакансионных диполей. Распад этих экситонов при 80 К приводит к образованию  $\alpha$ - $I_z$  пар.

### 1. Introduction

It is now well known that the nonradiative decay of an exciton in the perfect lattice of alkali halide crystals generates an F centre and its complementary interstitial defect, the H centre, which is an interstitial halogen atom [1]. On the other hand, the nonradiative annihilation of the self-trapped exciton near an impurity has been studied in simple cases only. For example, the formation of the exciton perturbed by a Li ion or a  $Sr^{2+}v_c^-$  dipole in KCl crystals leads to the creation  $F_A$ -H or  $Z_1$ -H pairs, respectively [2].

It has been well established that  $Z_1$  centres are formed as reaction products between F centres and complexes of divalent impurity cations like  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$  and rare earths  $Sm^{2+}$ ,  $Eu^{2+}$ , and  $Yb^{2+}$ . No  $Z_1$  centre production has been found in alkali halides doped with electron-trapping divalent impurities, such as  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  [3]. In the latter case, it is not clear whether the F centres are formed near a divalent impurity complex from the perturbed self-trapped excitons or whether another process takes place.

In order to resolve this problem, in our previous paper [4] we studied the nonradiative and radiative annihilation of a self-trapped exciton perturbed by the  $Mg^{2+}v_c^-$  dipole in NaCl by optical absorption and emission measurements. In the present work, the thermoluminescence (TL) method has been applied to study the processes of defect formation near a divalent impurity-vacancy complex in NaCl crystals doped

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with Mg or Mn. In this method the colour centre formation by monochromatic VUV-light irradiation is recorded by the thermoluminescence. The excitation spectra of the glow peaks reveal information concerning colour centres, which is undetectable by other means.

## 2. Experimental Techniques

The NaCl crystals with several concentrations (0.02 to 0.5 wt% in the melt) of  $MgCl_2$  or  $MnCl_2$  used in this work were grown in a helium atmosphere by the Stockbarger method. Absorption and VUV excitation of TL measurements were performed with VMR-2 vacuum grating monochromator. The hydrogen lamp VMF-25 with  $MgF_2$  window was used as the light source. The light was measured with a solar blind photomultiplier FEU-142 for measurements of optical absorption; TL in this measuring system was detected by a FEU-79 photomultiplier operating in the photon counting regime.

For some of the experiments, the crystals were X-rayed using a tungsten tube operating at 50 kV and 50 mA. The crystals were heated from 80 K at a rate of 7 K/min. The photon flux of the exciting light was monitored by a sodium-salicylate screen.

## 3. Experimental Results

TL spectra of NaCl crystals doped with Mg or Mn, X-irradiated at 80 K are shown in Fig. 1. The spectrum of NaCl-Mn induced by X-irradiation at 80 K exhibits glow peaks at about 170, 220, and 245 K. The peak positions of glow peaks agree fairly well with those reported by López et al. [5]. The peak at 245 K has not been further investigated in our work.

The temperature of the glow peak at 170 K agrees with that corresponding to the mobility of the  $V_k$  centres. This is the main glow peak occurring in the TL spectra of pure and Mn-doped crystals and has been attributed to the recombination of mobile  $V_k$  centres with electron-trapped centres [5]. It is known that the  $Mn^{2+}v_c^-$  dipoles act as good electron-trapping centres and in Mn-doped crystals the strong glow peak associated to  $V_k$  centres is observed.

The glow peak at 220 K appears in the Mn-doped samples and its intensity grows with increasing Mn concentration. Therefore, this glow peak is associated to Mn [5].

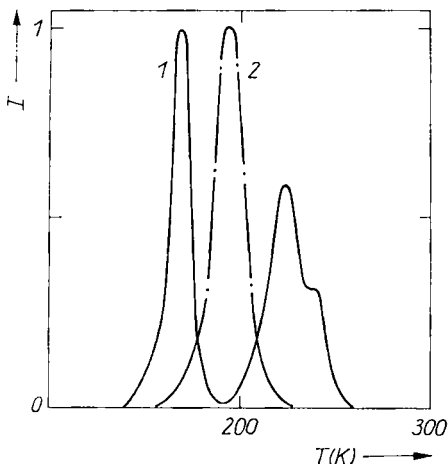


Fig. 1. Thermoluminescence of NaCl doped with (1) Mn and (2) Mg after X-irradiation at 80 K.  $I$  in arb. units

The glow curve of Mg-doped NaCl induced by X-irradiation at 80 K is shown in Fig. 1 (curve 2). The TL spectrum shows a single glow peak at about 195 K. This peak is due to the Mg doping since it does not appear in pure samples. It is also to be noted that no TL glow peak associated to the  $V_k$  centre is observed. The peak at about 170 K is observed after prolonged X-irradiation only and its intensity is the same as in pure NaCl crystals. This result indicates that, in contrast to the  $Mn^{2+}v_c^-$  dipoles, the  $Mg^{2+}v_c^-$  complexes do not act as electron-trapping centres in NaCl crystals. Egranov and Nepomnyachikh [4] have arrived at the same conclusion from absorption measurements.

It has been also shown that the glow peaks at 220 K (NaCl-Mn) and 195 K (NaCl-Mg) are induced by VUV-light excitation with photon energies near the energy of fundamental absorption. Fig. 2 shows the excitation spectra of these glow peaks. The TL excitation spectra are similar in both crystals and have maxima at 7.5 eV for NaCl-Mg and 7.4 eV for NaCl-Mn. These TL excitation bands are distinctly separated from the first exciton band at 7.95 eV [6] and its peak energies are slightly higher than that of the  $\alpha$ -band at 7.2 eV [7].

A recent study by the present authors [4] has shown that the optical creation of an exciton near a cation vacancy associated with the  $Mg^{2+}$  ion has a maximum located on the long-wavelength tail of the first exciton band at about 7.85 eV (Fig. 2, curve 3). These excitons annihilate radiatively and the emission at 2.9 eV can be detected at 80 K (Fig. 2, curve 4).

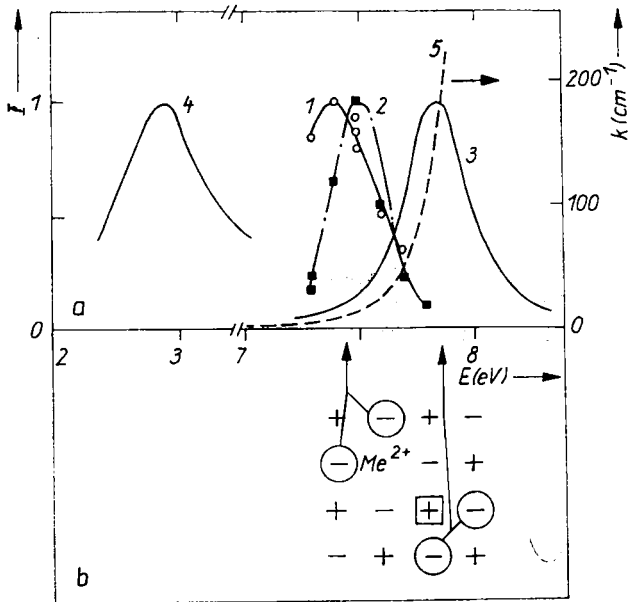


Fig. 2. a) Excitation spectra of VUV-light excited glow peaks at (1)  $T = 220$  and (2) 195 K of NaCl doped with (1) Mn and (2) Mg, excitation spectrum of 2.9 eV emission of NaCl-Mg (3) [4], corrected emission spectrum at 80 K for excitation at 7.8 eV (4) [4], and absorption spectrum of NaCl-Mg used for TL measurements (5). b) The geometric configuration of the divalent metal-vacancy dipole; the vertical arrows show the nonequivalent excitation of halogen ions near impurity-vacancy complex.  $I$  in arb. units

On the other hand, it was shown by Lushchik et al. [8] that the excitation of a halogen ion near a divalent metal ion associated with a cation vacancy occurs at photon energies which are distinctly separated from the energy of the first exciton band and its maximum is located on the short-wavelength tail of the band.

Therefore, it may be concluded that the TL excitation spectra correspond to the formation of an exciton near the divalent metal ion ( $Mg^{2+}$  or  $Mn^{2+}$ ) of the impurity-vacancy complex (Fig. 2b).

The electron-hole pairs produced by X-irradiation are known to be more numerous than excitons created directly by X-irradiation. Thus the substantial part of the perturbed self-trapped excitons near an impurity is formed through migration of self-trapped excitons which are created through trapping of electrons by the self-trapped holes. The efficiency of perturbed self-trapped exciton formation is enhanced with increasing temperature and is small at 80 K.

The fact that the glow peaks appear after X-irradiation and that its intensity was found to be temperature-independent up to 150 K indicates that the glow peaks can be associated with a centre which is formed by the interaction of a migrating intrinsic radiation defect with the divalent metal ion paired with a cation vacancy. In order to study the nature of this defect, the absorption measurements of pure and Mg-doped NaCl after X-irradiated at 80 K were carried out. Since the  $Mg^{2+}v_c^-$  dipoles in NaCl do not act as electron-trapping centres, the optical absorption spectrum in the visible and UV spectral regions of Mg-doped NaCl after X-irradiation at 80 K exhibits only a small F band [9].

The optical absorption change induced by X-irradiation at 80 K in pure and Mg-doped NaCl is shown in Fig. 3. In pure NaCl a small amount of the  $\beta$ -band at 7.35 eV [7] is created. On the other hand, the strong  $\alpha$ -band at 7.2 eV [7] and the weak, broad band at about 6.2 eV are produced in NaCl doped with  $Mg^{2+}$ . In both cases the optical densities of the F band are the same (not shown) and equal at about 0.25 on the scale of Fig. 3.

The enhancement of the  $\alpha$ -centres in crystals doped with divalent cation impurities at 80 K is ascribed to the interstitial halogen ion stabilization by an impurity-vacancy complex. These centres have been called  $I_z$  centres [10]. The interstitial halogen ion which is mobile at 80 K may be trapped by an impurity-vacancy complex to create the  $I_z$  centre. The formation of the  $I_z$  centres in NaCl doped with  $Mn^{2+}$  was studied by Ikeya et al. [11]. EPR experiments by these authors indicate that an interstitial halogen ion is associated with the  $Mn^{2+}$  ion. For the interaction between interstitial ion and divalent cation, the role of Coulomb attraction is important.

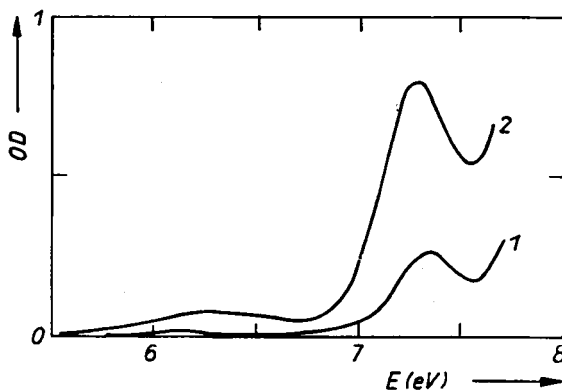


Fig. 3. Optical absorption change of (1) pure and (2) Mg-doped NaCl crystals after X-irradiation at 80 K

It has been shown that the annihilation of the  $I_z$  centres coincides with the strongest regeneration of  $Mn^{2+}v_c^-$  dipoles and the maximum rate of this process occurs at a temperature near glow peak at 220 K in NaCl-Mn [5].

Taking into account these facts we came to the conclusion that the absorption band at about 6.2 eV in NaCl-Mg is associated with the  $I_z$  centre and the 195 K (NaCl-Mg) and 220 K (NaCl-Mn) glow peaks are connected with the thermal destruction of the  $I_z$  centres. Since these TL related centres are also produced by VUV-light irradiation, it could then be concluded that the decay of self-trapped excitons near the divalent metal ions, which are connected with cation vacancies leads to the formation of  $\alpha-I_z$  pairs at 80 K. A similar result was obtained by Lushchik et al. [12]. The decay of excitons near  $Rb^+$  creates  $\alpha-I$  pairs in Rb-doped KCl crystals.

However, no luminescence associated with the  $\alpha-I$  recombination has been found [13]. Most of the  $\alpha$ -centre annealing occurs at the temperature at which the anion vacancies become mobile (above 240 K [14]). This process is not correlated with the thermal destruction of the  $I_z$  centres. The results are analogous to those for  $Ca^{2+}$ -doped KCl [15]. It has been concluded that the glow peaks at 220 and 195 K are due to a recombination process in which the  $\alpha$ -centres are not involved.

#### 4. Summary

In our previous paper [4] and this one we have studied the radiative and nonradiative decay of self-trapped excitons in the vicinity of impurity-vacancy dipoles in NaCl. It is known that in specimens quenched from about 300 K, the largest part of the impurities are in the form of associated pairs with positive ion vacancies. In this case, the creation of excitons is possible which are either perturbed by the cation vacancy associated with the divalent metal ion or by the divalent metal ion connected with the cation vacancy. The decay of these self-trapped excitons in each case leads to different reaction products.

The first case (creation of an exciton near the cation vacancy associated with the  $Mg^{2+}$  ion) has been considered in our previous paper [4]. This self-trapped exciton decays radiatively with emission at 2.9 eV at 80 K. Upon increasing the temperature the emission is quenched. Above 150 K exciton decay induces the destruction of  $Mg^{2+}v_c^-$  dipoles and produces  $Mg_c^+$  and  $V_F$  centres,  $Mg^{2+}v_c^- + e^0 \rightarrow Mg^{2+}v_c^-e^0 \rightarrow Mg_c^+ + V_F$ . It was found that the temperature dependence of the yield of radiative transitions from this perturbed self-trapped exciton and the destruction of the  $Mg^{2+}v_c^-$  complex are anticorrelated in NaCl-Mg crystals.

The second case (creation of an exciton near the divalent metal ion associated with the cation vacancy) is considered in this paper. The decay of this exciton leads to the formation of  $\alpha-I_z$  pairs at 80 K and radiative decay is not observed.

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