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Magnesium Colour Centres in NaF

By

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The absorption, emission, excitation spectra, and polarized luminescence of magnesium centres in sodium fluoride are studied. Three types of magnesium centres are observed. The first one, which is produced by X-irradiation at 300 K and absorbs at 3.32 eV, is attributed to the Mg_C^+ centre. The two other centres have the electronic structure of the Mg^0 atom perturbed by lattice defects. Optical excitation of the Mg^0 type centres leads to two emission bands, which are attributed to the $^3P_1 \rightarrow$ $\rightarrow ^1S_0$ and $^1P_1 \rightarrow ^1S_0$ transitions. However, the structure of both of these centres are not still completly established.

Исследованы спектры поглощения, излучения, возбуждения и поляризованная люминесценция магниевых центров в кристаллах фтористого натрия. Обнаружено три типа магниевых центров. Первый, имеющий полосу поглощения 3,32 eV и образующийся после рентгеновского облучения кристаллов при 300 K, отождествлен с Mg_C^+-центром. Два других имеют электронную структуру Mg^0-атома, возмущенного дефектом решетки. При возбуждении Mg^0-центров наблюдается свечение, состоящее из двух полос, которые были приписаны $^3P_1 \rightarrow ^1S_0$ и $^1P_1 \rightarrow ^1S_0$ переходам. Однако структура обоих центров еще полностью не установлена.

1. Introduction

Mg-doped LiF is widely investigated as a thermoluminescent dosimeter material. In the opinion of some authors magnesium colour centres in LiF are Z-centres [1]. However, it was recently established that they are efficient traps for electrons [2, 3]. Also in NaCl and KCl crystals the Mg^{2+} ion was found as a direct electron trap changing its valency [4, 5].

The optical absorption band at about 3.44 eV is created in NaF:Mg after electron irradiation and F-bleaching at room temperature. The band was attributed to Z centres [6]. However, Watterich and Foldvazi [7] obtained an anisotropic EPR spectrum in NaF:Mg after X-irradiation at room temperature and subsequent thermal bleaching. In this case, the observed SHF interaction with six fluorine ions indicated the presence of a Mg^+ ion as a central nucleus on the cation site. Nevertherless an optical absorption band corresponding to this centre was not found, but according to Watterich might be hidden under the F- or F-aggregate bands.

The present paper describes results of an optical study with the aim of elucidating the nature of magnesium centres in NaF.

2. Experimental Procedure

NaF crystals with 0.2 to 0.5 wt% MgF_2 in the melt were used. Absorption measurements were performed with a "Specord UV/VIS". Luminescence was excited by monochromatized light from a deuterium lamp (grating monochromator MDR-4). Luminescence light was detected with an FEU-79 photomultiplier in the photon count-

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ing regime through suitable filters or grating monochromator MDR-2. A pile of six fused silica plates was used to obtain absorption or emission spectra with polarized light. Polarized emission was observed under the angle 45° to the passing beam.

3. Experimental Results

3.1 Absorption spectra

In NaF:Mg crystals, X-irradiated at a temperature below 270 K, we have not found the absorption bands which might be associated with magnesium colour centres. After X-irradiation above 270 K the NaF:Mg crystals exhibit, in addition to the normal F-, F'-, and M-bands, an absorption band with peak energy of 3.32 eV and halfwidth 0.44 eV at 80 K (Fig. 1 a). This band is hidden under the F' absorption band at room temperature. When the temperature is raised, the absorption band at 3.32 eV is destroyed at about 480 K. Subsequent F-bleaching at a temperature at which the anion and cation vacancies are not moved (at about 220 K) leads to a partial or
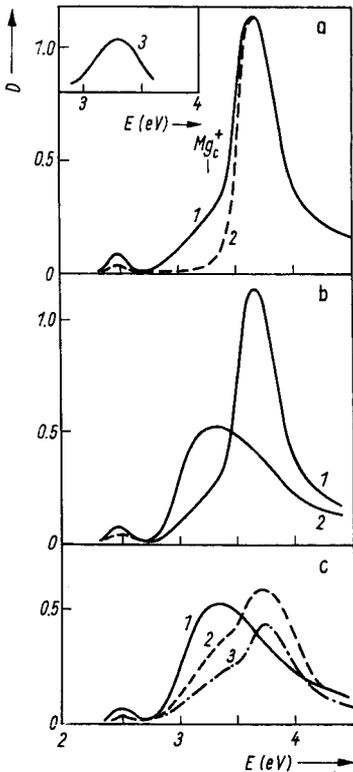

Fig. 1   Fig. 2

Fig. 1. Absorption spectra of NaF:Mg crystals at 80 K. a) After X-irradiation at 300 K, (1) F'-bleaching and (2) thermal bleaching at 480 K. Curve 3 was obtained by subtracting (2) from (1). b) After X-irradiation, (1) F'-bleaching and (2) prolonged F-bleaching at 300 K. c) After X-irradiation, (1) F-bleaching at 300 K, (2) thermal bleaching at 450 K, and (3) optical bleaching with light at 4.0 eV at 80 K
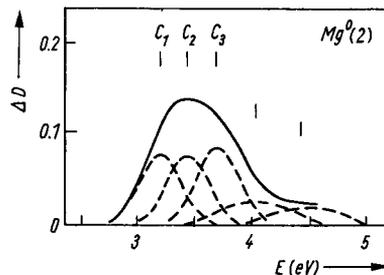
Fig. 2. Absorption band obtained by subtracting curve (3) from (2) in Fig. 1 c. Dashed curves show the resolved bands

to a complete recovery of the band at 3.32 eV. After this treatment the optical bleach-
ing of these centres at 80 K leads to an increase of the F-band absorption. No dichroism
of the 3.32 eV absorption band can be induced in the [100] or [110] directions upon
preferential bleaching at liquid nitrogen temperature. The behaviour of this centre
is in agreement with the behaviour of the Mg^+ centre in NaCl:Mg crystals [8]. There-
fore, the absorption band at 3.32 eV is likely due to the Mg_c^+ centre.

The absorption band at about 3.3 eV is produced by X-irradiation and optical
bleaching of the F-centres at room temperature (Fig. 1 b). The band is not destroyed
by optical bleaching at 80 K. As the temperature is raised above 430 K, this absorption
band is quenched and a new absorption band at 3.7 eV appears (Fig. 1 c).

The latter band can be optically bleached at 80 K with light of 4.0 eV. The difference
spectrum, due to bleaching with light of 4.0 eV, has a complicated composite struc-
ture (Fig. 2).

At this stage it might be concluded that in the spectral region near the F absorption
band at least three absorption bands, which are associated with the magnesium colour
centres, are present.

3.2 Emission and excitation spectra

The room temperature luminescence of NaF:Mg has been investigated after the same
thermal and optical bleaching treatments as for absorption measurements.

In NaF:Mg crystals X-irradiated at 300 K only the M-emission band is observed.
After prolonged F-bleaching at 300 K of the X-irradiated crystals, two additional
emission bands centred at 2.6 and 2.25 eV with halfwidth of 0.2 and 0.22 eV, respect-
ively, appear as shown in Fig. 3. The excitation spectra for both emission bands as
well as the polarization spectrum for the emission band at 2.25 eV are shown in Fig. 4.
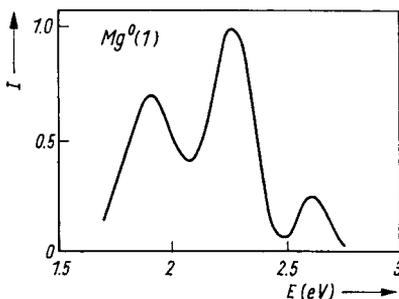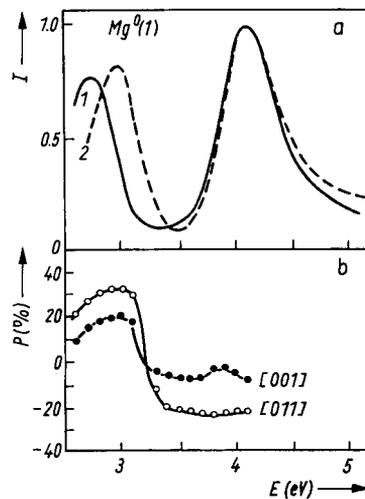

Fig. 3   Fig. 4

Fig. 3. Corrected emission spectrum at 300 K for excitation with light at 3.0 eV of NaF:Mg crys-
tals after X-irradiation and prolonged F-bleaching at 300 K

Fig. 4. a) Excitation and b) polarization spectra of 2.25 eV (curve 1 in a) and part b) and 2.6 eV
(curve 2 in a)) emissions (Fig. 3) at 300 K
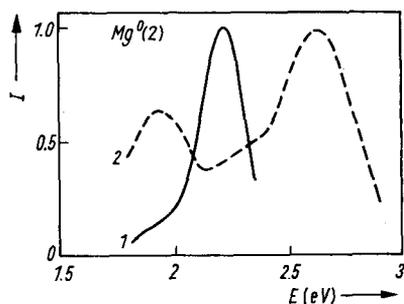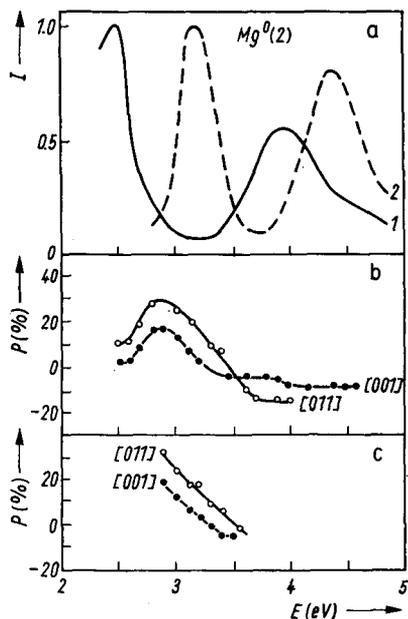
Fig. 5   Fig. 6

Fig. 5. Corrected emission spectra at 300 K for excitation with light at (1) 2.6 and (2) 3.2 eV of NaF:Mg crystals after X-irradiation, F-bleaching at room temperature, and thermal bleaching at 450 K

Fig. 6. a) Excitation and b), c) polarization spectra of 2.22 eV (curve 1 of a) and part b) and 2.65 eV (curve 2 of a) and part c) emissions (Fig. 5) at 300 K

The polarization properties of the 2.6 eV band emission have not been investigated because of its small intensity. The third emission band at about 1.9 eV is known to be due to M-centres.

Subsequent thermal annealing above 430 K leads to a slight shift of the emission bands at 2.25 and 2.6 eV to 2.22 and 2.65 eV, respectively (Fig. 5). As shown in Fig. 6, the change in excitation spectra is larger than that observed in the emission spectra.

It should be noticed that the structure of the emission, polarization, and excitation spectra in both cases is generally the same. The result suggests that the emission bands at 2.25 and 2.22 eV as well as those at 2.6 and 2.65 eV arise from identical transitions in magnesium colour centres and the valency of magnesium is the same in both cases.

4. Discussion

The observed luminescence can be explained if we assume that emission is due to electronic transitions of the Mg^0 atom perturbed by lattice defects. This agrees with the EPR results reported earlier [7]. Two types of Mg^0 centres differing by the location and/or type of neighbouring point defects are labeled as $Mg^0(1)$ and $Mg^0(2)$ in the order of their formation after X-irradiation.

The ground state configuration of the Mg^0 atom being $(3S)^2\,{}^1S_0$, says that a very similar luminescence should be observed as for mercury-like centres in alkali halides. For mercury-like centres there are four low-lying excited states ${}^3P_0$, ${}^3P_1$, ${}^3P_2$, and ${}^1P_1$. The ${}^1S_0 \to {}^1P_1$ transition is an electric dipole-allowed transition and shows a strong absorption band (C-band), while the ${}^1S_0 \to {}^3P_1$ transition, which is partially allowed due to spin–orbit coupling, exhibits a weak absorption band (A-band).

For a free Mg^0 atom the ${}^1S_0 \to {}^3P_1$ transition has a very low oscillator strength $f({}^1S_0 \to {}^3P_1)/f({}^1S_0 \to {}^1P_1) = 2.5 \times 10^{-6}$ and is placed at 2.71 eV [9]. The latter value is close to the peak position of the low-energy excitation bands at 2.75 eV for $Mg^0(1)$ and 2.6 eV for $Mg^0(2)$. From this fact, the above excitation is likely due to the ${}^1S_0 \to {}^3P_1$ transition. The corresponding A-absorption band, which is weak and overlaps with other bands such as the M-band, could not be observed by absorption measurements. Similar results for A- band excitation and absorption of the Ag^- centre were obtained earlier in KCl [10].

Since the A-band excitation induces only the 2.25 eV emission for $Mg^0(1)$ or 2.22 eV emission for $Mg^0(2)$, it is reasonable to attribute this emission to the inverse process of A-band absorption, namely ${}^3P_1 \to {}^1S_0$.

As shown in Fig. 4 and 6, the polarization properties of all emissions are quite similar, that is, the polarization sign is reversed from plus to minus with increasing excitation energy. The result suggests that they are associated with an electronic transition between undegenerated states $A_1 \leftrightarrow A_1$ [11] and therefore the emission bands at 2.6 eV for $Mg^0(1)$ and 2.65 eV for $Mg^0(2)$ are due to the ${}^1P_1 \to {}^1S_0$ transition (C-band emission).

The peak positions of the C-band excitation are placed at about 3.0 eV for $Mg^0(1)$ and 3.2 eV for $Mg^0(2)$. The corresponding C-absorption band of the $Mg^0(1)$ centre is strongly overlapping with other bands, such as F-, M_c^+-centre absorption bands, therefore, the excitation spectrum could not be identified with the absorption spectrum. However, above 430 K the low-energy excitation band at 3.0 eV disappears and the higher energy excitation band at 3.2 eV grows during this annealing. As shown in Fig. 1c, the changes in the absorption spectrum produced by the same thermal treatment are similar to those in the excitation spectrum.

In alkali halides the C-absorption band is usually split into three components. As shown in Fig. 2, the $Mg^0(2)$ centre related difference spectrum might be resolved into three components (C_1, C_2, and C_3), but the excitation spectrum has only one C_1-band at 3.2 eV. The other excitation bands have apparently a weak intensity.

In conclusion, in the present work, we propose a model for a centre which is produced by X-irradiation at 300 K and absorbs at 3.32 eV. This is a substitutional, singly ionized magnesium ion (Mg_c^+). No emission was detected during Mg_c^+ centre related excitation. Two other centres have the electronic structure of the Mg^0 atom perturbed by lattice defects. However, the atomic arrangement of these centres is still unknown. A detailed investigation of the nature of lattice distortions in the vicinity of the Mg^0 atom with the aim of establishing the structure of Mg^0-type centres are necessary and planned.

References

[1] R. NINK and H.-J. KOS, phys. stat. sol. (a) **35**, 121 (1976).
[2] E. A. RADYABOV and A. I. NEPOMNYACHIKH, phys. stat. sol. (a) **68**, 77 (1981).
[3] E. A. RADYABOV and A. I. NEPOMNYACHIKH, phys. stat. sol. (b) **108**, K75 (1981).
[4] A. WATTERICH and R. VOSZKA, Acta phys Hungar. **33**, 323 (1973).
[5] R. VOSZKA and A. WATTERICH, phys. stat. sol. (b) **55**, 787 (1973).
[6] T. YAZAKI, T. IMAI, and Y. KISHI, Appl. Optics **17**, 3391 (1978).

[7] A. WATTERICH and I. FOLDVAZI, Internat. Conf. Defects in Insulating Crystals, Riga (USSR) 1981 (p. 460).

[8] A. V. EGRANOV and A. I. NEPOMNYACHIKH, Optika i Spektroskopiya **53**, 954 (1982).

[9] M. G. KOZLOV, Spectri poglosheniya parov metallov v vacuumnom ultraviolete, Izd. Nauka, Moscow 1981 (p. 98).

[10] K. KOJIMA, S. SHIMANUKI, M. MAKI, and T. KOJIMA, J. Phys. Soc. Japan **28**, 1227 (1970).

[11] N. E. LUSHCHIK and S. G. ZAZUBOVICH, Physics of Impurity Centers in Crystals, Tallin 1972 (p. 483).