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Neutral Magnesium Atoms on Anion Sites in LiF

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X-irradiation of LiF:Mg crystals produces magnesium color centers with an absorption band at 5.5 eV at room temperature (further called 5.5 eV centers). In a previous paper we concluded that the 5.5 eV centers are magnesium atoms on anion sites associated with cation vacancies /1/. Another point of view is that the 5.5 eV centers are Z_3 centers /2 to 4/. Photoluminescence of 5.5 eV centers was found by Mort and Zimmermann /5/. In the present paper we study some polarisation properties of the 5.5 eV center luminescence.

LiF crystals with 0. 7 wt% Mg and 1.5x1.5 cm^2 area and 0.2 to 0.3 cm thickness were used. The 5.5 eV centers were produced by X-irradiation of LiF:Mg at 80 K and bleaching at 330 K by light from a mercury lamp. After this treatment only an absorption band at 5.5 eV was seen in the optical absorption spectra. Luminescence was excited by monochromatised light from a deuterium lamp (grating monochromator MDR-2). Luminescence light was dected with a FEU-'79 photomultiplier in the photon counting regime through suitable filters or MDR-2 monochromator.

Under excitation the 5.5 eV centers emitted light with a maximum at 2.0 eV and halfwidth 0.66 eV (at 80 and 300 K) (Fig. 1). We found a polarisation of this emission and the polarisation sign was reversed with excitation energy from minus (at $E_{exc} < 5.5$ eV) to plus (at $E_{exc} > 5.5$ eV) (Fig. l).From the azimuthal dependence of the polarisation one can conclude that the emission centers are oriented along the trigonal (C_3) axis (Fig. 2). The positive polarisation of luminescence was disappearing at about 450 K, but the negative polarisation did not bleach (Fig. 2).

The reversal of polarisation sign with excitation energy and the high temperature stability of polarisation show that the luminescence centers are associated with a point defect near the activator /6/. The azimuthal dependence of

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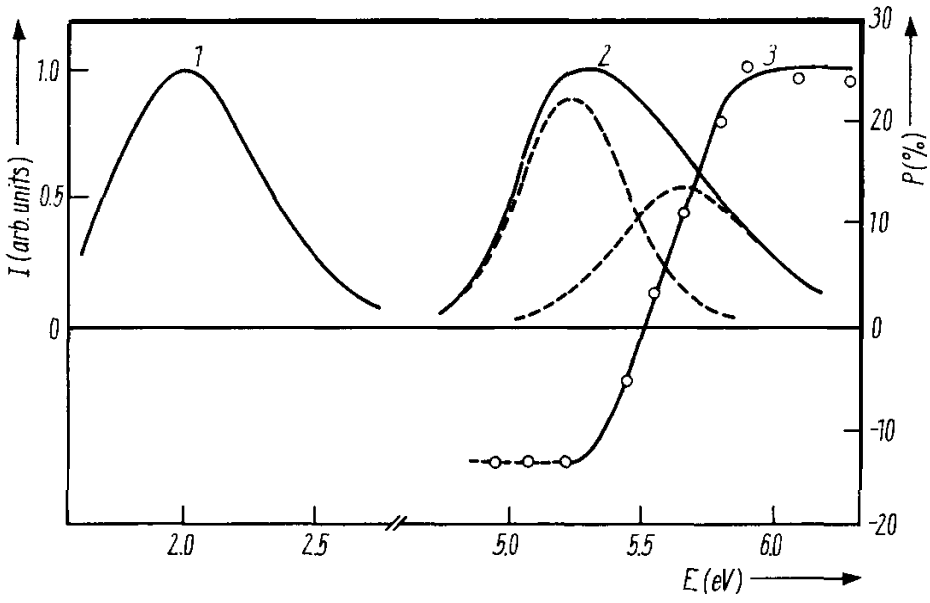

Fig. 1. Corrected emission at 80 K and 295 K (1), excitation (2), and polarisation ($\alpha = 45^{\circ}$) at 295 K (3) spectra of 5.5 eV centers in LiF:Mg. Dashed curves show the resolved bands

polarisation shows that the point defect is in the [111] direction from the activator. This result contradicts the Z_3-model of 5.5 eV centers. The $Z_3 (= Z_2^+)$ center is formed by one impurity ion along with one anion vacancy as nearest-neighbour in [100] direction. One electron is bound to this. In some cases an anion-cation vacancy pair is tied to this system. Without the vacancy pair the center has a simple axial [100] symmetry /7/.

How do the experimental results correspond to our model? Absorption at 5.5 eV and emission at 2.0 eV arise from electronic transitions in magnesium atoms on anion sites. A cation vacancy is bound to the magnesium atom, creating an electrically neutral center. The azimuthal dependence of polarisation shows that the magnesium atom has a cation vacancy in the next-nearest neighbour position (in the [111] direction). The absorption at 5.5 eV arises from $^1S_o - {}^1P$ electronic transitions in magnesium atoms which are blue-shifted from the $^4S_o - {}^1P_1$ transitions in free Mg. The blue-shift is due to the position of the magnesium atom on the anion site /1/. The transition $^1S_o - {}^3P_1$ has a very low oscillator strength ($f(^1S_o - {}^3P_1)/f(^1S_o - {}^1P) = 3 \times 10^{-6}$ /8/) and cannot be seen in the absorption or excitation spectrum. Luminescence arises from

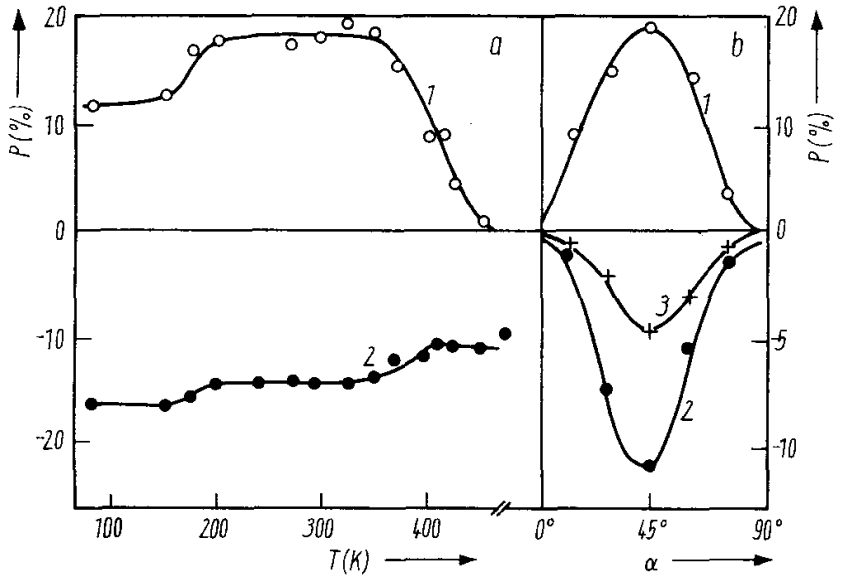

Fig. 2. Luminescence polarisation of 5.5 eV centers in LiF:Mg under excitation by light of energy (1) 5.8 eV, (2) 5.2 eV, and (3) 5.4 eV; a) thermal ($\alpha = 45^{o}$) and b) azimuthal dependence at 295 K

$^{3}P_{1} - {}^{1}S_{0}$ transitions. The $^{1}P_{1}$ level is split into two components in crystal field with trigonal symmetry and the sign of luminescence polarisation has to reverse within the $^{1}S_{0} - {}^{1}P_{1}$ excitation band /6/. The excitation band is resolved into two bands, which have an opposite sign of luminescence polarisation (Fig. 1).

In summary, we conclude that the 5.5 eV centers in LiF are magnesium atoms on anion sites associated with cation vacancies in the next-nearest neighbour positions.

References

/1/ A.I. NEPOMNYACHIKH and E. A. RADYABOV, Optika i Spektroskopiya 48, 273 (1980).

/2/ J. MORT, Phys. Letters 21, 124 (1966).

/3/ R. NINK and H.-J. KOS, phys. stat. sol. (a) 35, 121 (1976).

/4/ S. K. MEHTA, J.F. MERKLIN, and H.J. 'DONNERT, phys. stat. sol. (a) 44, 679 (1977).

/5/ J. MORT and D.W. ZIMMERMAN, Phys. Letters 21, 273 (1966).

/6/ S.G. ZAZUBOVICH, Trudy Inst. Fis. Astron. Akad. Nauk Estonian SSR 36, 109 (1968).

/7/ H.J. PAUS and K.M. STROHM, J. Phys. C 13, 57 (1980).
/8/G. BOLDT, Z. Phys. 150, 205 (1958).

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