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Magnesium Color Centers at 3.5 and 5.0 eV in Lithium Fluoride

By

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Centers at 3.5 and 5.0 eV are created by X-irradiation of LiF:Mg or by optical bleaching of $Mg_c^+V_a^+V_c^-$ (at 4.0 eV) centers in LiF:Mg at 80 K. Both centers have [100] and [110] absorption dichroism. The thermal bleaching of centers at 3.5 eV is related with a glow peak at 150 K which obeys second-order kinetics. The energy of the absorption band of $Mg_c^+V_c^-$ -centers in LiF is calculated to be about 3.5 eV. The absorption band shape and the oscillator strength of the centers at 5.0 eV and F-centers are almost equal. The color centers at 3.5 eV seem to be $Mg_c^+V_c^-$ -centers and those at 5.0 eV seem to be F-centers near $Mg_c^{2+}V_c^-$ dipoles.

Центры при 3,5 и 5,0 eV образуются в процессе рентгеновского облучения LiF:Mg или путем оптического обесцвечивания $Mg_c^+V_a^+V_c^-$ (при 4,0 eV)-центров при 80 К. Обе полосы поглощения характеризуются как [100] так и [110] дихроизмом. Термообесцвечивание центров при 3,5 eV сопровождается термостимулированной люминесценцией с максимумом при 150 К, имеющей кинетику второго порядка. Согласно оценкам максимум полосы поглощения $Mg_c^+V_c^-$ -центров в LiF должен находиться около 3,5 eV. Центры при 5,0 eV и F-центры в LiF:Mg имеют близкую форму полосы поглощения и одинаковые силы осциллятора. Предполагается, что центры при 3,5 eV представляют собой $Mg_c^+V_c^-$ -центры, а центры при 5,0 eV представляют собой F-центры около диполей $Mg_c^{2+}V_c^-$.

1. Introduction

Magnesium color centers in alkali halides are good electron traps [1 to 3]. This property of magnesium color centers in lithium fluoride is widely used in thermoluminescence dosimetry [4]. Some authors propose that magnesium color centers in LiF with absorption band at 4.0 eV are Z_2 -centers and centers at 5.5 eV are Z_3 -centers [5 to 7]. In a previous paper we have studied the thermal and optical bleaching of color centers at 4.0 eV from 85 to 440 K and found that the conversion of centers at 4.0 and 5.5 eV does not correspond to the Z_2 - Z_3 center conversion in other alkali halides. We propose that centers at 4.0 eV are $Mg_c^+V_a^+V_c^-$ -centers and those at 5.5 eV are magnesium atoms at anion site associated with cation vacancies [8]. The optical bleaching of the centers at 4.0 eV at liquid nitrogen temperatures leads to a creation of new centers at 3.5 and 5.0 eV [5, 6, 8], the nature of which is still unknown. The studies of centers at 5.0 eV are difficult due to the neighbourhood of the absorption bands of these centers and those of F-centers (at 5.1 eV at 80 K). We have studied LiF crystals with a large magnesium concentration (700 ppm) and there is no F-band in our crystals after X-irradiation at 85 K and warming up to 400 K. The present work deals with the nature of magnesium centers at 3.5 and 5.0 eV in LiF:Mg crystals.

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2. Results and Discussion

When the temperature is rising, the centers at 3.5 eV are bleaching at about 150 K (Fig. 1). Centers at 5.0 eV have three ranges of thermal bleaching at about 150, 230, and 320 K. Thermal bleaching of centers at 3.5 and 5.0 eV leads to an almost perfect recovery of $\text{Mg}_c^+\text{V}_a^+\text{V}_c^-$ -centers. One can conclude the centers at 3.5 and 5.0 eV to be magnesium electron-trapping centers.

A pile of six fused silica plates was used to obtain absorption spectra with polarized light. Exposure of LiF:Mg to [001] polarized light at about 4.0 eV results in the preferential bleaching of $\text{Mg}_c^+\text{V}_a^+\text{V}_c^-$ -centers having a definite orientation and in the creation of centers at 3.5 and 5.0 eV with the same orientation (Fig. 2). Curves on Fig. 2b show the [100] anisotropic absorption spectra which were obtained by subtracting the spectra taken with [010] polarized light from that taken with [001] light. By the

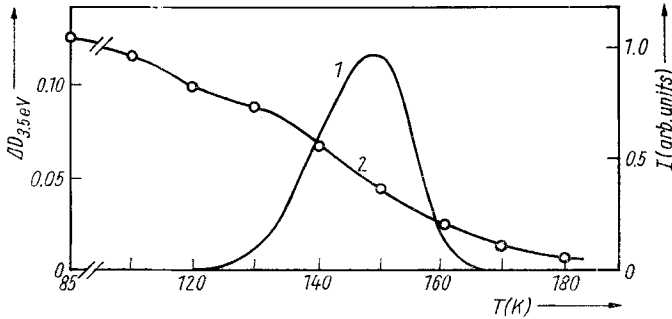


Fig. 1. TSL curve (1) and bleaching curve at 3.5 eV (2) of LiF:Mg crystal after optical bleaching of $\text{Mg}_c^+\text{V}_a^+\text{V}_c^-$ -centers at 85 K

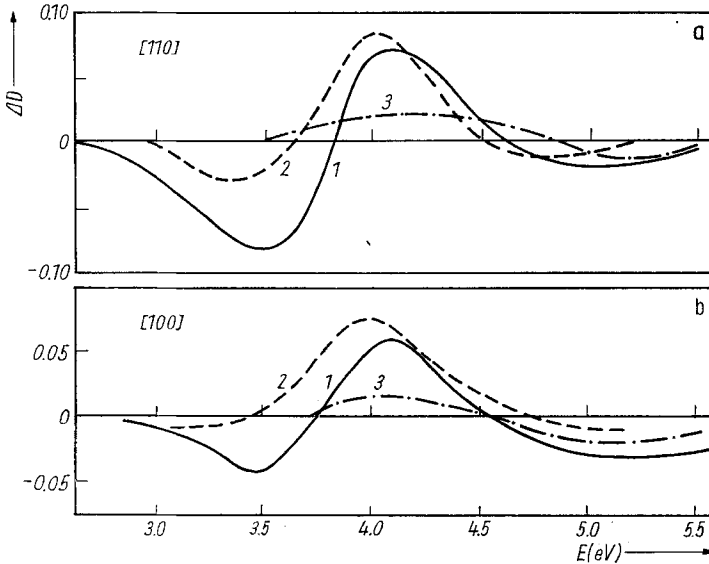


Fig. 2. Anisotropic absorption spectra of LiF:Mg crystal with $\text{Mg}_c^+\text{V}_a^+\text{V}_c^-$ -centers after exposure to polarized light at (1) 4.14 eV, (2) 4.0 eV at 80 K and (3) 4.14 eV at 160 K

same way we obtained the [110] anisotropic spectra (Fig. 2a). These spectra coupled with [100] anisotropy show that all three centers are [110] polarized. We mark that the exposure of LiF:Mg with the centers at 3.5 and 5.0 eV to polarized light at 3.5 or 5.0 eV leads to a very small dichroism in these bands.

2.1 Color centers at 3.5 eV

The bleaching of these centers is related with thermostimulated luminescence (TSL) (Fig. 1) and with the recovery of $Mg_c^+V_a^+V_c^-$. One can find the order of TSL kinetics from the relations:

$$\ln(I/\int IdT) = \text{const} - E/kT \quad \text{for first order,}$$

$$\ln(I/(\int IdT)^2) = \text{const} - E/kT \quad \text{for second order.}$$

The TSL at about 150 K obeys a second-order kinetics (Fig. 3).

Color centers at 3.5 eV are created by X-irradiation of LiF:Mg crystals at 85 K too, but the absorption of these centers lies under the large absorption of V_k -centers (at 3.57 eV [9]). The V_k -centers in LiF are bleaching when the crystal is warming up to 145 K. After that the glow curve peak at 150 K is separated from the V_k -peak and the TSL at about 150 K obeys a second-order kinetics, too (Fig. 3). The two absorption bands in X-irradiated LiF:Mg bleached in the range 145 to 170 K (Fig. 4). One band is the absorption band of the centers at 3.5 eV and the other one lies within the range of V_k absorption and is probably a V_F band (in literature there are no data about the shape of the V_F band in LiF). Consequently, heating releases electrons from centers at 3.5 eV and they may be retrapped or recombine with hole (V_F , X_3^-) centers.

Two centers with Mg^+ ions are created in NaCl crystals after X-irradiation and F-bleaching at room temperature: Mg_c^+ - and $Mg_c^+V_a^+V_c^-$ -centers [1]. The calculation concludes that the absorption band energy of these centers in alkali halides has to be shifted to longer wavelength than the absorption energy of the free Mg^+ ions [10]. The shift is inversely proportional to the lattice constant [11], i.e.

$$E = \text{const}/d,$$

where E energy shift, d lattice constant. The energy of the $3s^1-3p^1$ transition of the free Mg^+ ion is 4.43 eV [12]. We calculated the absorption band energy of Mg_c^+ and

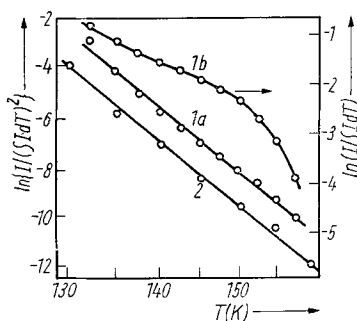


Fig. 3

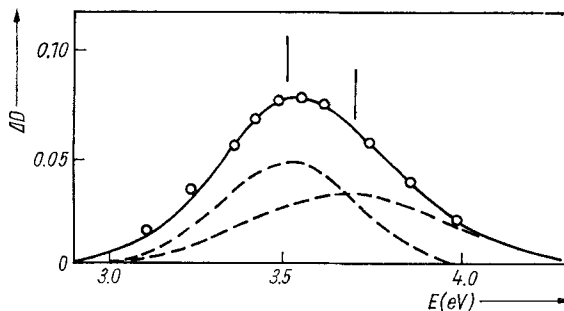


Fig. 4

Fig. 3. Determination of the order of TSL kinetics in the peak at 150 K, after bleaching of $Mg_c^+V_a^+V_c^-$ -centers (1a and 1b) at 85 K and (2) after X-irradiation of LiF:Mg at 85 K

Fig. 4. Absorption band of the centers which are bleaching in the range 145 to 170 K in X-rayed LiF:Mg crystals. Dashed curves show the resolved bands

$Mg_c^+V_a^+V_c^-$ in LiF and KCl crystals on the base of the absorption band energy of these centers in NaCl crystal (Table 1). One can see that the calculated and experimental

Table 1
Energies of absorption bands of centers with Mg^+ ions in alkali halides

| centers | NaCl | | | KCl | | LiF | |
|--------------------|----------------------|-----------------|----------------------|----------------------|------|-------|------|
| | absorption band (eV) | ΔE (eV) | const (10^6 eV m) | absorption band (eV) | | | |
| | | | | calc. | exp. | calc. | exp. |
| Mg_c^+ | 3.76 | 0.68 | 1.93 | 3.83 | 3.8 | 3.49 | |
| | [1] | | | | [11] | | |
| $Mg_c^+V_a^+V_c^-$ | 4.14 | 0.30 | 0.85 | 4.17 | | 4.01 | 4.0 |
| | [1] | | | | | | [8] |

data for the known centers are in good agreement. The calculated absorption band peak of Mg_c^+ -centers in LiF lies at 3.5 eV. The Sn_c^+ electron transitions in KCl are shifted by cation vacancies in nearest neighbour position by about 0.1 eV [13]. Consequently $Mg_c^+V_c^-$ -centers in LiF must have the absorption band near 3.5 eV. This center has [110] orientation. We can conclude that centers at 3.5 eV seem to be Mg_c^+ ions, connected with cation vacancies in nearest neighbour positions.

2.2 Color centers at 5.0 eV

When the $Mg_c^+V_a^+V_c^-$ -centers are bleaching at 85 K, electrons do not enter the conduction band, because there is no photoconductivity of X-rayed LiF:Mg crystals with 4.0 eV light at room temperatures [14]. Consequently, electrons of excited levels of $Mg_c^+V_a^+V_c^-$ -centers are trapped by levels of other centers due to a tunneling process. Electrons may be trapped by anion vacancies from $Mg_c^+V_a^+V_c^-$ -centers and this creates F-centers near the $Mg_c^{2+}V_c^-$ dipoles. There are also some other results which support this conclusion:

1. When excited by polarized light $Mg_c^+V_a^+V_c^-$ -centers are converted into centers at 5.0 eV with the same orientations (see Fig. 2).

2. The absorption band at 5.0 eV is near the F-band. Experiments have shown the band at 5.0 eV to be asymmetric (Fig. 5). The high energy side of this band is about 20% wider than the low energy side. A similar asymmetry is found for the F-band [3, 6].

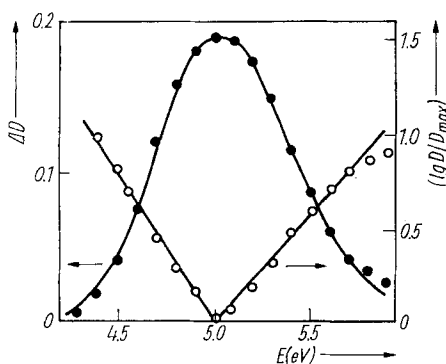


Fig. 5. Experimental shape (points) and theoretical shape (line) of the absorption bands at 5.0 eV

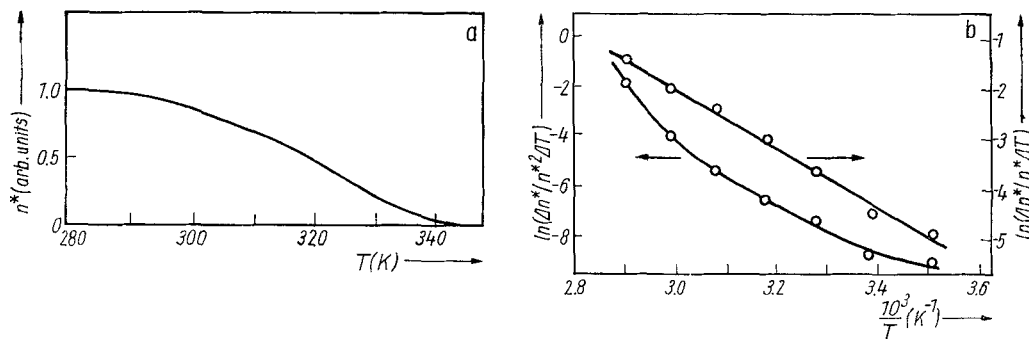


Fig. 6. a) Thermal bleaching of the centers at 5.0 eV at about 320 K and b) determination of the order of bleaching kinetics

3. We determined the relative oscillator strength $f(4.0 \text{ eV})/f(5.0 \text{ eV}) = 1.1 \pm 0.1$ in LiF:Mg crystals (where f is the oscillator strength of the corresponding bands). The relative oscillator strength $f(3.8 \text{ eV})/f(F) = 1.19$ in KCl:Mg crystals (where the band at 3.8 eV is the absorption band of Mg_c^+ -centers) [11]. Because $f(F)$ in LiF is almost equal to $f(F)$ in KCl [15] the oscillator strengths of the centers at 5.0 eV and F-centers differ only slightly. It is well known that the oscillator strength of F-centers does only weakly depend on the surroundings (for example Z_1 -centers [15]).

4. When the temperature rises the centers at 5.0 eV are bleaching and converting into $\text{Mg}_c^+ \text{V}_a^+ \text{V}_c^-$ -centers. The bleaching at about 320 K obeys a first-order of kinetic (Fig. 6). Electrons are probably tunneling from the F-center levels to the levels of neighbouring Mg^{2+} ions.

Consequently centers at 5.0 eV seem to be F-centers near $\text{Mg}_c^+ \text{V}_c^-$ dipoles.

References

- [1] A. WATTERICH and R. VOSZKA, Acta phys. (Acad. Sci.) Hungar. **33**, 323 (1973).
- [2] R. VOSZKA and A. WATTERICH, phys. stat. sol. (b) **55**, 787 (1973).
- [3] M. R. MAUHYGH, R. W. CHRISTY, and N. M. JOHNSON, J. appl. Phys. **41**, 2968 (1970).
- [4] T. G. STOEBE and S. WATANABE, phys. stat. sol. (a) **29**, 11 (1975).
- [5] R. NINK and H.-J. KOS, phys. stat. sol. (a) **35**, 121 (1976).
- [6] S. K. MEHTA, J. F. MERKLIN, and H. J. DONNERT, phys. stat. sol. (a) **44**, 679 (1977).
- [7] J. MORT, Phys. Letters (Netherlands) **21**, 124 (1966).
- [8] A. I. NEPOMNYACHIKH and E. A. RADYABOV, Optika i Spektroskopiya **48**, 273 (1980).
- [9] C. J. DELBECQ, W. HAYES, and P. H. YUSTER, Phys. Rev. **121**, 1043 (1961).
- [10] K. RAKSÁNYI and A. WATTERICH, Symp. Thermodynamics, Spectral and Structural Features of Interaction between Molecules, Excited Molecules or Ions, Wepion (Belgium) 1974 (p. 232).
- [11] A. WATTERICH and K. RAKSÁNYI, phys. stat. sol. (b) **80**, 105 (1977).
- [12] A. R. STRIGANOV and A. S. SVENTITSKII, Tablitsi spektralnikh linii, Atomizdat Nauka 1966 (p. 250).
- [13] C. J. DELBECQ, R. HARTFORD, D. SHOEMAKER, and P. YUSTER, Phys. Rev. B **13**, 3631 (1976).
- [14] W. E. NELSON, J. F. MERKLIN, and R. S. LEE, Nuclear Instrum. Methods **133**, 387 (1976).
- [15] D. Y. SMITH and D. L. DEXTER, Progr. Optics **10**, 167 (1974).

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