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Luminescence Centers in LiF:Li<sub>2</sub>O

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The titanium-oxygen impurity makes effective luminescence centers in lithium fluoride /1/. There are two groups of excitation bands connected with titanium and oxygen ions in titanium-oxygen centers and in lithium and sodium fluorides doped with TiO<sub>2</sub>, respectively /2/. The O<sup>2-</sup> ions are connected with anion vacancies in alkali halides /3/. But the nature of luminescent electron transitions in oxygen related centers in lithium fluoride is still unknown. The present note deals with the nature of oxygen luminescence centers in lithium fluoride.

Lithium fluoride crystals doped with 0.08 wt% Li<sub>2</sub>O in the melt were studied. The crystals were heated at 450 °C for 15 min and cooled in air. The optical equipment was described elsewhere /2/. The luminescence decay design consists of a time-to-amplitude converter (TAC) (on the base of Ch 3-34A), a pulse amplitude analyser (AI-256), and two delay lines. One line is used for dead time correction of TAC and the other for stop-pulse supply.

There are two bands in the excitation spectrum of LiF:Li<sub>2</sub>O with peaks at 6.4 and 7.6 eV (Fig. 1b). The emission spectrum of LiF:Li<sub>2</sub>O consists of one band which peaks at 2.88 and 2.96 eV at excitation by 6.3 and 7.6 eV light, respectively (see Fig. 1a). The emission band maxima have a very small blue shift ( $\approx 0.04$  eV) due to temperature decrease from 295 to 85 K. This speaks in favour of a strong localisation of emission center electrons.

The luminescence centers in LiF:Li<sub>2</sub>O have two components of decay time - a "fast" (in the nanosecond range) and a "slow" (in the microsecond range) component (Fig. 2). Both components of the decay time depend on the crystal temperature, their values rise with temperature decrease. The same temperature dependence of "fast" and "slow" decay time components was found in other alkali halides with TI<sup>+</sup> ions /4, 5/. The results are explained by a metastable level

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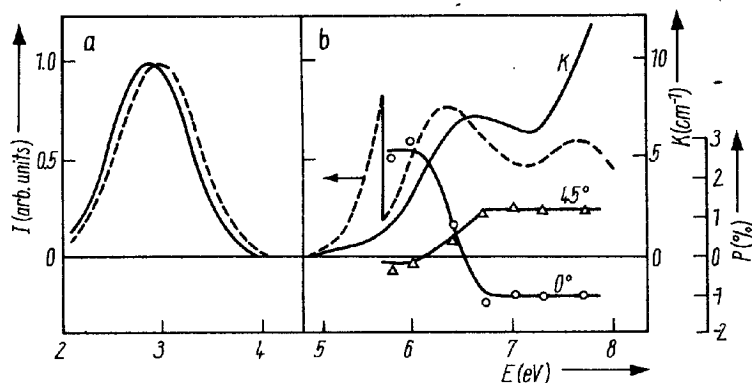


Fig. 1. a) Emission spectrum of LiF:Li<sub>2</sub>O for excitation with 6.3 eV (solid line) and 7.6 eV light (dashed line, measured at 85 K); b) excitation spectrum (dashed line) and absorption spectrum (solid line) of LiF:Li<sub>2</sub>O. Points refer to polarization of emission at 295 K

under the emitting level. The "slow" decay time component is due to thermal transitions of electrons from metastable levels to emitting levels. The temperature dependence of the "fast" decay time shows that there is some activation energy for the electron transition from the emitting level to the metastable one.

There are two models for electron transitions of  $O^{2-}$  centers in crystals /6, 7/. All  $O^{2-}$  absorption bands have been interpreted as electron transfer from  $O^{2-}$  ions to the surrounding  $K^+$  ions, considering different excited states of potassium atoms in KCl /6/. For the first charge transfer  $O^{2-}$  band one can write /8/

$$E_{\text{cht}} = E_{\text{exc}} + A(O^-) - A(\text{hal}) ,$$

where  $E_{\text{exc}}$  exciton band energy,  $A(O^-)$ ,  $A(\text{hal})$  electron affinity of  $O^-$  ions and halide atoms, respectively. The electron affinity of the  $O^-$  ion is 5.3 eV and of the F atom 3.5 eV /9/. Consequently, the charge transfer band of  $O^{2-}$  ions in lithium fluoride has to lie near the exciton band (about 13 eV). The excitation bands at 6.4 and 7.6 eV in LiF:Li<sub>2</sub>O are most probably not related to the charge transfer  $O^{2-}$  ion bands:

According to the other model the absorption and emission of  $O^{2-}$  ions in CdF<sub>2</sub> are related to electron transitions inside the  $O^{2-}$  ions /7/. The  $O^{2-}$  ion has a complete p-shell as the noble gas atoms. The lowest unexcited energy

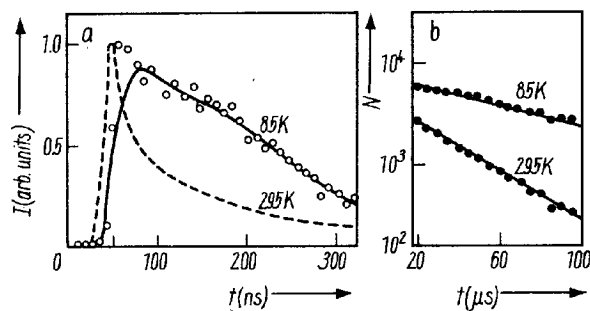


Fig. 2. The a) "fast" and b) "slow" component of decay time of LiF:Li<sub>2</sub>O emission. Emission was excited at 6.25 eV. The solid curve in a) is the convoluted curve from the instrumental response curve. Decay time was  $\tau_1 = 35$  ns,  $\tau_2 = 86$   $\mu$ s. The convoluted and experimental data fit except for the initial part where there are "very fast" components of decay time. The "fast" component of the decay time at 295 K is lower than 5 ns. The values of the "slow" decay time are 35 ns and 85  $\mu$ s at 85 K and 295 K, respectively

level is  $2p^6 ({}^1S_0)$ , the first excited levels are  $2p^5 3s ({}^3P_j, {}^1P_1)$ . The excitation was assigned to the  ${}^1S_0 - {}^1P_1$  transitions and emission to the  ${}^3P_1 - {}^1S_0$  ones /7/. There is a metastable level  ${}^3P_0$  (or  ${}^3P_2$ ) under the emitting  ${}^3P_1$  level of the  $O^{2-}$  ion and it is consistent with our results. The "fast" decay time of LiF:Li<sub>2</sub>O luminescence is 35 ns at 85 K. The oscillator strength of the transition is  $f = 0.075$  and relates to the intercombination  ${}^3P_1 - {}^1S_0$  transition. The reversal of the polarization sign shows that the luminescence centers are associated with a point defect /10/. Probably, the anion vacancy is a charge compensator of the  $O^{2-}$  ion in LiF:Li<sub>2</sub>O. The emitting level in LiF:Li<sub>2</sub>O ( ${}^3P_1$  level) is split into two emitting levels (see Fig. 1, two emission bands) due to an associated anion vacancy.

In summary, the emission of the LiF:Li<sub>2</sub>O crystal can be assigned to the  ${}^3P_1 - {}^1S_0$  electron transitions of the  $O^{2-}$  ions.

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