

## SOLID-STATE SPECTROSCOPY

# Dual Nature of $R_N$ -centers in LiF Crystals

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**Abstract**—An alternative model of the  $N_c$ -center as a complex defect consisting of the  $F_2^+$ -center perturbed by the  $F_L$  defect (where  $F_L$  is  $Li^0$  in the F-center) is confirmed by the methods of optical spectroscopy and X-ray diffraction analysis of LiF crystals. Upon selective optical excitation, these centers are decomposed into  $F_2$  and  $F_L$  defects. © 2000 MAIK “Nauka/Interperiodica”.

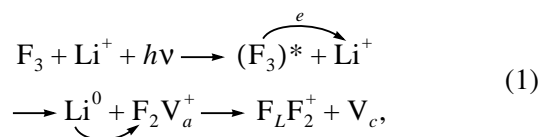
### INTRODUCTION

The  $R_N$  spectral region attracts the attention of researchers because LiF( $F_2$ ,  $F_3^+$ ) crystals are used as laser media [1, 2]. To optimize parameters of the active elements, it is necessary to know the nature of color centers absorbing at the emission wavelength of working centers ( $F_3^+$ ) and in the pumping region ( $F_2$ ). In this paper, we studied the behavior of color centers upon photometric transformations, mechanisms of formation, and destruction of  $R_N$ -centers in order to determine their nature.

In the  $R_N$  spectral region (500–550 nm), the  $N_1$ - and  $N_2$ -centers were earlier identified in  $\gamma$ -irradiated crystals, with the absorption bands at 512 and 542 nm at 78 K and at 520 and 550 nm at 300 K [3, 4], and also the  $N_a^-$  (500 nm),  $N_b^-$  (525 nm), and  $N_c$ -centers (550 nm) [5]. The  $N_a^-$ ,  $N_1$ -, and  $N_2$ -centers can be efficiently produced by annealing  $\gamma$ -irradiated crystals, and the  $N_b^-$  and  $N_c$ -centers, by exposure to light. In [6], the model of  $N_c$ -centers as reoriented  $F_3$ -centers was suggested. It was assumed that upon optical excitation in the  $R_1$  region at room temperature, the  $F_3 \rightarrow F_2 + F$  dissociation takes place, and at a low temperature (78 K) the F-center hops from the lattice site no. 1 to the lattice site no. 7 or 9, with the formation of the reoriented  $F_3$ -center (Fig. 1). However, this mechanism [6] of formation of  $N_c$ -centers is unlikely at low temperature because the reorientation of the defect requires the energy consumption, as its dissociation.

We assumed [7] that upon optical excitation the electron density of the  $F_3$ -center is localized at the nearest lithium cation lying on the axis of symmetry of the center, along the  $\langle 111 \rangle$  direction. The lithium atom is displaced simultaneously to one of the anion vacancies of the  $F_3^+$ -center, and a complex defect is formed, which

is responsible for absorption in the  $N_c$ -band:



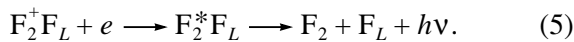
where  $F_L$  is  $Li^0$  in the F-center. It is obvious that the displacement of the lithium atom to the (111) plane located at a distance of  $a\sqrt{3}/6$  from the nearest cation requires the energy consumption, which is, however, considerably lower than that required for the F-center to hop by a distance of  $a\sqrt{2}/2$  ( $a$  is the lattice parameter). This mechanism of transformation of the color center is confirmed by the increase in the ionic conductivity in bleached samples. One of the aims of this paper is to prove the existence of the  $F_LF_2^+$  defect.

### EXPERIMENTAL

We studied  $\gamma$ -irradiated ( $D = 1.5 \times 10^7$  R) LiF samples grown by the Stockbarger technique in vacuum. The crystals were irradiated by xenon lamps of a Kvant-17 laser (1 MW) to produce the  $R_N$ -centers and also by the second and fourth harmonics of an Nd:YAG laser to induce phototransformations of color centers. The isochronous annealing was performed in the temperature range from 373 to 573 K with a step of 50 K and a time lag of 15 min. The absorption spectra were recorded with an MPS-50L spectrophotometer at 78 and 300 K. The luminescence was excited by an Nd:YAG laser. The X-ray diffraction analysis was performed with a DRON 2.0 (Cu  $K_{\alpha 1, \alpha 2}$ ) diffractometer. The spacing of lattice planes  $d_{hkl}$  and broadening  $\beta = S/I_{\max}$  (where  $S$  is the area under the contour of the resolved peak) of all reflexes were measured.

## RESULTS AND DISCUSSION

Figure 2 shows absorption spectra of a crystal with the induced  $R_N$  bands before and after irradiation by the fourth harmonic of an Nd : YAG laser at 78 K. One can see that irradiation results in the decrease in the  $N_c$  absorption band and increase in the  $M$  band. In addition, the red emission appears at 650 nm, which is typical for the  $F_2$ -centers; i.e., the  $F_2$ -centers are formed. Consider the possible mechanisms of formation of the  $M$  band:



Optical bleaching occurs at low temperature (78 K), which suggests that anion vacancies and the F-centers are immobile. For this reason, we can exclude reactions (3) and (4) from consideration. Assume that the  $F_3$ -center undergoes the transition to the predissociation state. In this case, the  $F_2^-$  and F-centers will be excited in collisions and come apart with the decreased kinetic energy. Then, the F absorption band should increase; however, the reverse is observed. Note that no variations occur in the absorption region of the  $F_2^+$ - and  $F'$ -centers ( $\lambda_m = 350$  nm) [8]). Therefore, the concentration of the  $F_2$ -centers cannot increase due to reaction (2). However, the destruction of the F-centers is observed, along with the  $N_c$  band. The photocurrent was not detected [9], which suggests that an electron is tunneling from the excited level of the F-center to the level of a positively charged defect. The tunneling occurs most likely to the excited level of the  $F_2^+$ -center perturbed by the  $F_L$  defect, because the intensity of the 550-nm absorption band decreases and the emission intensity of the  $F_2$ -centers increases upon photobleaching at 78 K. Upon selective optical excitation, these centers decompose into the  $F_2^-$  and  $F_L$ -centers. In [10], the spectral parameters of the  $F_L$ -centers were calculated. It was shown that these centers have the doublet absorption band, with one of the components located from the high-energy side of the F band (213 nm) and the other one, from the low-energy side (274 nm). The overlap with the F band complicates the observation of these centers.

The existence of the  $F_2^+ F_L$  defects does not exclude the light-induced formation of the reoriented  $F_3$ -centers at 300 K. We should take into account these defects in the X-ray diffraction analysis. The crystal lattice parameter increases after  $\gamma$ -irradiation, when the defects are produced both in the anion (F-centers) and cation (V-centers) sublattices. The lattice parameter

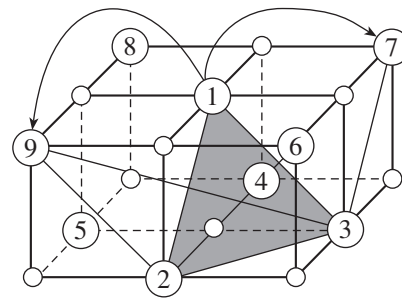


Fig. 1. Model of the  $N_c$ -center in a LiF crystal proposed in [6].

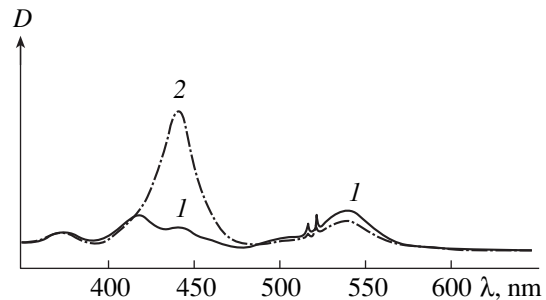


Fig. 2. Absorption spectra of a LiF crystal containing  $R_N$ -centers (1) before and (2) after irradiation by the fourth harmonic of an Nd : YAG laser at 78 K.

does not change after photobleaching of samples by radiation from xenon lamps, when along with the reconstruction of the regular lattice sites ( $F_n + H \longrightarrow F_{n-1}, \dots, F + H \longrightarrow R$ ) the photoinduced defects are formed. However, we detected the increase in the relative broadening  $\beta = S/I_{\max}$  of the reflexes, which suggests the appearance of local stresses in the crystal lattice caused by photoinduced defects. If these defects were the reoriented  $F_3$ -centers, their formation would not affect appreciably the value of  $\beta$ . Therefore, the lithium atom ( $R = 1.56 \text{ \AA}$ ) in the F-center remains as a possible defect producing local stresses in the sample.

It was assumed in [5] that the  $N_c$ - (550 nm) and  $N_b$  (525 nm) centers have high-energy transitions ( $N_c$ )\* corresponding to the 415 and 365-nm absorption bands, respectively. However, the behavior of these bands upon photometric transformations, especially the absence of the cymbate dependence of the 365 and 525-nm bands upon excitation by the second harmonic of an Nd : YAG laser, is inconsistent with this assumption.

## CONCLUSION

Our study of processes of the radiation-thermal and optical transformations of color centers in LiF crystals grown by the Stockbarger technique in vacuum confirmed the alternative model of the  $N_c$ -center as a com-

plex defect consisting of the  $F_2^+$ -center perturbed by the  $F_L$  defect, where  $F_L$  is  $Li^0$  in the F-center. Upon selective optical excitation, these centers are decomposed into  $F_2^-$ - and  $F_L$ -centers. It is shown that the  $N_c$  band has the dual nature. To establish the nature of the 525-nm  $N_b$  band, further studies should be performed.

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