

# Aggregate colour centres in impurity LiF crystals

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**Abstract.** LiF crystals with colour centres exhibiting a zero-phonon line (ZPL) at 1080 nm in absorption and luminescence are studied. The decay time of luminescence of colour centres at 10 K is 260–280 ns, the ZPL half-width is  $4.7 \text{ cm}^{-1}$ , and colour centres are characterised by a weak electron–phonon interaction (the Huang–Rhys factor is  $S < 0.11$ ). The polarisation analysis of luminescence showed that the transition dipole moments of colour centres are oriented along the crystal axes [100], [010], and [001]. The model of aggregate  $F_4$  colour centres having a spatial structure with three symmetry axes  $C_2$  may correspond to the colour centres studied in the paper.

**Keywords:** colour centres, zero-phonon lines, luminescence, degree of polarisation.

## 1. Introduction

This paper is devoted to the study of LiF crystals with colour centres, which have the most long-wavelength (1050–1080 nm) zero-phonon lines (ZPLs) in absorption and luminescence among all the known colour centres in LiF. These colour centres feature a weak electron–phonon interaction, which is not observed for other colour centres, and exhibit ZPLs that are relatively narrow at low temperatures. They attract attention because of the new possibilities of applying LiF crystals as active laser media and passive nanosecond saturable absorbers in the near-IR spectral region.

The spectrum and properties of these colour centres are most close to those of  $F_2^-$ -centres [1] having the ZPL at 1040 nm in the absorption spectrum [2], which have been studied for many years. For this reason, we will call these centres the  $F_2^-$ -like centres or  $(F_2^-)^*$ -centres.

Earlier, the attempts were made to assign similar defects to neutral  $O_2$  molecules [2–5], which were produced upon radiolysis of  $OH^-$  ions [3], or to colour centres containing

impurity–vacancy dipoles  $Me^{2+}O_2^-$  [4]. The results of the paper presented here show that the spatial orientations of the  $(F_2^-)^*$ - and  $F_2^-$ -centres do not coincide although the wavelengths of their ZPLs are close.

## 2. Experimental method and spectral characteristics

We studied LiF crystals containing impurity  $OH^-$  ions at different concentrations that were controlled by the IR absorption spectra (at 2.7  $\mu\text{m}$ ), and doped with the ions of metals of different valence (Mg, Ca, Cu, Fe, K, Na) at weight concentrations from  $10^{-3}\%$  to  $10^{-4}\%$ . After irradiating the crystals by gamma rays or fast electrons, the absorption bands of  $OH^-$  ions disappeared, and new absorption bands emerged, which were shifted to the red by  $\sim 1000 \text{ nm}$  and were more than one hundred times stronger than the absorption bands of the  $OH^-$  ions. By varying the irradiation dose and temperature, we prepared crystals in which either  $F_2^-$ - or  $(F_2^-)^*$ -centres dominated.

As shown in [5], the absorption and luminescence spectra of  $(F_2^-)^*$ -centres at 77 K exhibit three narrow lines at 1055, 1060, and 1080 nm and broad phonon bands extending up to 900 and 1300 nm in the absorption and luminescence spectrum, respectively. The coincidence of the wavelengths of the narrow lines in the absorption and luminescence spectra at low temperatures suggests that they are ZPLs. The polarisation dependences of all the three lines proved to be different, which indicates that these lines belong to different optical centres.

Note that the lifetime of all the three colour centres at 77 K was approximately 260 ns. Here, we studied  $(F_2^-)^*$ -centres exhibiting the most intense ZPL at 1080 nm.

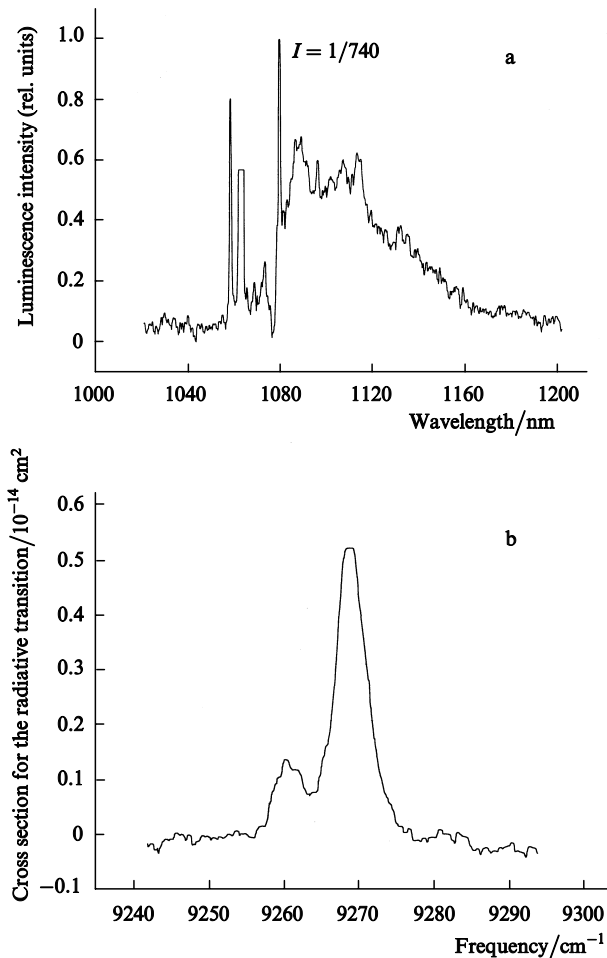
Fig. 1a shows the luminescence spectrum of the LiF crystal at 10 K. Samples were cooled in a continuous-flow optical helium cryostat. Luminescence was excited by a free-running Nd:YAG laser at 1064 nm. The luminescence spectrum was measured with a FEU-83 photomultiplier, which had the long-wavelength sensitivity edge up to 1200 nm. Upon such excitation, the ZPL at 1080 nm (with the half-width of  $\sim 5 \text{ cm}^{-1}$ ) dominates in the spectrum. The Debye–Waller factor  $\alpha$ , which characterises the strength of the electron–phonon interaction and is equal to the ratio of the area under the ZPL to the total area under the ZPL and the phonon sideband, was 0.897, which corresponds to the Huang–Rhys factor  $S = 0.109$ . These values were obtained by neglecting the contribution to the phonon sideband from the sidebands corresponding to colour centres with ZPLs at 1055 and 1060 nm, which gives

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Received 22 April 2002

Kvantovaya Elektronika 32 (8) 659–662 (2002)

Translated by M.N. Sapozhnikov



**Figure 1.** (a) Luminescence spectrum of  $(F_2^-)^*$ -centres in a LiF crystal excited by a laser at 1064 nm at 10 K (laser radiation was attenuated by a neutral filter). The luminescence line at 1080 nm is attenuated by a factor of 740; the line at 1060 nm is not attenuated. (b) The structure of the 1080-nm luminescence line.

the estimates for  $\alpha$  and  $S$  from below and from above, respectively. Note that the 1060-nm ZPL was observed in the spectrum even upon anti-Stokes excitation. The Debye–Waller and Huang–Rhys factors for  $F_2^-$ -centres measured from the absorption spectrum at 10 K were 0.12 and 2.12, respectively (the value of  $\alpha$  was obtained taking into account the correction for the spectral sensitivity of the photomultiplier). Therefore, the electron–phonon interaction strength for  $(F_2^-)^*$ -centres in the LiF crystal is substantially (more than twenty times) smaller than that for  $F_2^-$ -centres.

Note the 1080-nm line in the luminescence spectrum at 10 K is split into two lines: an intense line at  $\nu \sim 9270 \text{ cm}^{-1}$  (1078.9 nm) and a weaker line at  $\nu \sim 9261 \text{ cm}^{-1}$  (1079.9 nm) (Fig. 1b). Both these lines have the inhomogeneous width  $\Gamma_{\text{inh}} \approx 4.7 \text{ cm}^{-1}$ . The presence of the low-intensity ZPL shifted to the red by  $9 \text{ cm}^{-1}$  with respect to the main ZPL is probably explained by the isotope effect for  $\text{Li}^6$  and  $\text{Li}^7$  ions, whose natural abundances are 92.5% and 7.5%, respectively. The isotope effect in LiF crystals with different colour centres was studied in detail earlier [1], both the red and blue shifts of ZPLs from 1 to  $10 \text{ cm}^{-1}$  being reported.

We estimated the cross section for the 1080-nm radiative transition by measuring the decay time  $\tau$  of luminescence excited by a 1064-nm nanosecond laser pulse. The decay

time was 260–280 ns at 10 K and did not change up to 77 K. Therefore, we can assume that the decay time  $\tau = 260 - 280 \text{ ns}$  is radiative. Note that the peak cross section for the radiative transition  $\sigma = 0.52 \times 10^{-14} \text{ cm}^2$  is comparatively large, which makes this crystal promising for various laser applications in nonlinear spectroscopy.

We studied the spatial structure and orientation of the colour centres by the Feofilov method of polarised luminescence [6]. The crystals were cut along the planes (100), (110), and (111). The luminescence was excited and detected in a longitudinal scheme using polarisation Glan prisms and film polarisers. The luminescence emission was focused on an entrance slit of a DFS-12 double spectrometer, which selected the spectral lines. We measured the azimuthal dependences of the degree of polarisation and intensity of luminescence by rotating the polarisation plane of laser radiation with respect to crystal axes. The data were corrected for the polarisation of emission produced by a diffraction grating of the spectrometer. The measurements were performed at 10 K, when the ZPLs are best resolved in the spectra (Fig. 1b).

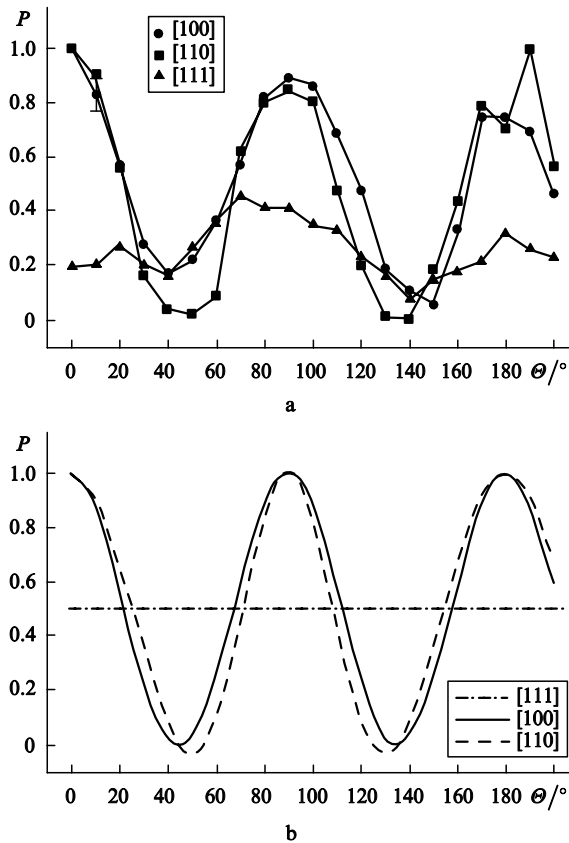
### 3. Polarisation dependences

Fig. 2a shows the azimuthal dependences of the degree  $P$  of polarisation of luminescence for the 1080-nm line (Fig. 1) for three orientations of the crystal. When the polarisation of laser radiation was directed along the [100] or [110] axis, luminescence was virtually completely linearly polarised in the same direction. A substantially different situation was observed for the [111] orientation. Fig. 2b shows the theoretical dependences for dipoles oriented in the direction of three fourth-order  $C_4$  axes of the crystal [6]. The experimental and theoretical curves were in good agreement in the case of the [100] and [110] orientations, whereas the experimental curve noticeably deviated from the theoretical one for the [111] orientation. We explain this by the optical inhomogeneity of a sample with the [111] orientation. It is known [6] that the transition dipole moments of the  $F_2^-$ -centres are directed along the [110] axis, which we specially verified in similar measurements.

The azimuthal dependence of the degree  $P$  of polarisation for the phonon sideband in the luminescence spectrum at 1090 nm ( $\nu \sim 9174 \text{ cm}^{-1}$ ) (Fig. 1a) proved to be similar to that for the 1080-nm ZPL in Fig. 2. For  $\theta = 0$  and  $90^\circ$ , the degree of polarisation  $P = 0.3$ , corresponding to a partial depolarisation of luminescence. In particular, the depolarisation can be explained by the fact that the phonon sideband corresponds not to one but to different optical centres, for example, to colour centres with ZPLs at 1055, 1060, and 1080 nm. The measurements of the azimuthal dependence of the degree of polarisation of the luminescence ZPLs at 1055 and 1060 nm at 77 K showed that these colour centres had no distinct orientation (the lines were excited by laser lines at 1053 and 1059 nm).

### 4. Discussion of results

The results of polarisation measurements presented above show that, although the spectrum of  $(F_2^-)^*$ -centres with the ZPL at 1080 nm is located in the region close to that of  $F_2^-$ -centres with the ZPL at 1040 nm, the spatial structures of these centres are different, and the symmetry group of



**Figure 2.** (a) Experimental dependences of the degree  $P$  of polarisation of luminescence for the 1080-nm line (Fig. 1) for three orientations of the LiF crystal at 10 K and (b) the theoretical dependences of  $P$  for dipoles directed along three fourth-order  $C_4$  axes of the crystal [6]:  $P_{[100]}(\theta) = \cos^2 2\theta$ ,  $P_{[110]}(\theta) = \cos 2\theta(3 \cos^2 \theta - 1)/(1 + \cos^2 \theta)$ , and  $P_{[111]} = 0.5$ .

$(F_2^-)^*$ -centres should contain the rotation axis  $C_n$  oriented along the crystallographic axis  $C_4$ .

Let us discuss the possible structural models of the  $(F_2^-)^*$ -centre. Among the known aggregate  $F$ -centres, the  $C_n$  axes are inherent in  $F$ -centres itself ( $C_4$ ) and in  $F_2$ - ( $C_2$ ) and  $F_4$ -centres ( $C_2$ ) (we omit the charge indices in the notation of these colour centres because their spatial symmetry is independent of the number of trapped electrons). However, the absorption spectrum of  $F$ -centres in a LiF crystal is located in the region of 245 nm, whereas the dipole moment of transition from the ground state to the first excited state in  $F_2$ -centres is directed along the [110] axis.

The  $F_4$ -centre has the spatial symmetry group  $T_d$ , which contains three axes  $C_2$  directed along crystallographic axes [100] ( $x$ ), [010] ( $y$ ), and [001] ( $z$ ). The group  $T_d$  contains the three-dimensional representation  $T_2$ , whose basis functions (which we denote as  $T_x$ ,  $T_y$ , and  $T_z$ ) are transformed as  $x$ ,  $y$ , and  $z$ , respectively. If we assume, as usual, that the ground electronic state is totally symmetric (has the symmetry  $A$ ), then the electric dipole transitions  $(A|x|T_x)$ ,  $(A|y|T_y)$  and  $(A|z|T_z)$  are allowed by the selection rules. Therefore, the  $F_4$ -centre has transition dipole moments directed along the three axis [100] ( $x$ ), [010] ( $y$ ), and [001] ( $z$ ) of the crystal. However, this is not yet sufficient for the polarisation dependences of luminescence for the  $F_4$ -centre to be the same as the theoretical dependences for dipoles directed along the three fourth-order symmetry axes  $C_4$  of the crystal

[6] whose analytic expressions are presented in the caption to Fig. 2.

Because the electronic states of the excited level are degenerate, the Jahn–Teller effect causes mixing of the wave functions of the electronic states, and the adiabatic potential surfaces in the configurational space of nuclear displacements can be no longer treated (in the general case) as the nuclear potential-energy surfaces [7]. Due to the Jahn–Teller effect, the traditional interpretation of optical spectra of colour centres based on the Born–Oppenheimer approximation [1, 8] becomes invalid. Nevertheless, it is for the electronic states of the symmetry  $T_2$  that the situation can exist (the linear  $T-e$  problem [7]) when adiabatic potentials have the physical meaning of the nuclear potential energy, while the nuclear potential-energy surfaces in the configurational space of nuclear displacements represent three paraboloids of revolution with separated minima [7]. In this case, the initial wave functions  $T_x$ ,  $T_y$ , and  $T_z$  of the electronic states are not mixed, while the new wave functions  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$ , obtained taking into account the Jahn–Teller effect, are such that  $\psi_1 \sim T_x$ ,  $\psi_2 \sim T_y$ , and  $\psi_3 \sim T_z$  for the first, second, and third minima, respectively. In this case, the polarisation characteristics of  $F_4$ -centres at low temperatures will be the same as those for colour centres whose transition dipole moments are directed along the [100], [010], and [001] axes of the crystal.

At temperature  $T \gg E_{JT}/k$  (where  $E_{JT}$  is the Jahn–Teller stabilisation energy), fast relaxation can occur (compared to the spontaneous emission lifetime  $\tau = 260$  ns), which will equalise the populations of the  $T_x$ ,  $T_y$ , and  $T_z$  states. When the populations of these states are completely equalised, the  $F_4$ -center will behave as a spherical rotator. In this case, luminescence should be depolarised with increasing temperature. In the one-configurational coordinate model,  $E_{JT} \approx \hbar\omega_0 S$ , where  $\omega_0$  is the effective frequency of the model. By substituting to this expression the effective frequency  $\omega_0 \approx 300 \text{ cm}^{-1}$  for the LiF crystal [9–11] and the Huang–Rhys factor  $S \approx 0.1$  reported above, we obtain the estimate for  $E_{JT} \approx 30 \text{ cm}^{-1} = 43 \text{ K}$ . Therefore, the low-temperature criterion is satisfied in our case (for  $T = 10 \text{ K}$ ).

Because specially prepared LiF crystals contain impurity metal ions, linear  $F-I^+-F$  structures can also exist in them, which are directed along the crystal axes [100], [010], and [001] (here,  $I^+$  is a positively charged impurity replacing the  $Li^+$  ion). It is obvious that the symmetry group of such colour centres should contain the rotation axis  $C_n$  directed along the crystallographic axis  $C_4$ .

It is impossible to propose unambiguously a structural model for the  $(F_2^-)^*$ -centre at this stage of the research, and further experimental and theoretical studies are required.

**Acknowledgements.** This work was supported by the CRDF grant no. RP2-2257 and the Russian Foundation for Basic Research (Grant No. 01-02-16309).

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