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Fluctuating fluorescence of single color centers in lithium fluoride crystals

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Single F_2- and F_3^+- color centers in the LiF crystal were studied by confocal fluorescence microscopy. The time dependences of their fluorescence intensity were analyzed and statistically processed. Our studies show that, the F_3^+- color center, being photoexcited, is able enter the triplet state, while in ground (singlet) state it changes orientation with a frequency of 1.5−2 Hz at room temperature, due to reorientational diffusion, unlike the F_2-center, which is reoriented only being in the triplet state. This subtype of rotational diffusion of the center does not lead to its translational diffusion.

Keywords: fluorescence, spectroscopy, single color center, confocal microscopy.

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Introduction

Lithium fluoride crystals have unique physical characteristics. They have a simple cubic lattice, a maximum lattice energy, an extremely wide band of forbidden energies, and they are practically not hygroscopic. Therefore, in comparison with other alkali-halide crystals (AHC) the lithium fluoride has the widest practical application. In particular, it is used as optical material for the VUV region of the spectrum. LiF crystals are widely used in thermoluminescent dosimetry of various types of ionizing radiation, including the detection of mixed fluxes of gamma and neutron radiation [1]. Under the influence of various sources of ionizing radiation in lithium fluoride crystals the aggregate F-, F_2-, F_2^+-, F_3-, F_3^+-, F_4-, F_4^+-color centers (CC) are formed, as well as centers associated with impurity defects, which are always contained in crystals. They are working quantum systems for creating tunable lasers [2], passive laser shutters [3], as well as bulk storage optical media [4].

For the most part, CCs are complex quantum systems, the symmetry of which differs from the symmetry of the lattice sites. The processes of optical radiation interaction with such systems are studied for a long time and, as a rule, for ensembles of these defects [5–7]. However, it is not always possible to obtain the properties of ensemble components from the ensemble characteristics. The presence of a strong electron-phonon interaction in AHC causes a uniform widening of the spectral lines, which transform into wide overlapping bands. The two types of centers can have the same absorption and luminescence bands. This situation is typical, for example, for lithium fluoride crystals, in which the F_2- and F_3-color centers have one complementary M-absorption band with a maximum of 441 nm, and F_3^--and stabilized F_2^+-centers form overlapping luminescence bands in the region of 800−900 nm [7]. In this case, the main criterion of the difference between defects is the value of the kinetic parameter — the luminescence decay time. However, the luminescence decay times can also be poorly distinguishable. When studying the behavior of ensembles of these centers under these conditions the problems arise related to the determination of the contributions of individual types of centers. This significantly complicates the spectral distinction between color centers and requires the search for new principles of radiation defect spectroscopy that supplement traditional luminescence spectral-kinetic methods.

In this relation, the development of methods for the spectroscopy of single radiation defects can provide new opportunities in comparison with traditional methods for studying ensembles of these defects. This approach makes it possible to implement the principle of learning „from simple to complex“. Consequently, the problem arises of developing methods for studying single radiation defects in dielectric crystals. Due to the small size of the objects under study, the methods used should provide high sensitivity and significant spatial and temporal resolution. In this case the main experimental research method is the method of confocal scanning luminescence microscopy, which implements the principle of time-correlated space-selective counting of single photons, when for each registered photon its arrival time is determined from the moment of a single defect excitation, which makes it possible to measure the kinetics of the enhancement and decay of luminescence, to determine the lifetimes of the excited states of color centers, and to judge the probabilities of quantum transitions in them. This method of high-resolution luminescence spectroscopy is being intensively developed and is widely used in various fields of science [8–11]. The analysis of the world scientific literature shows that earlier such studies on quantum systems created by radiation in AHC were not carried out. In the works published by the authors [12–14], the luminescence of single F_2-centers in LiF crystal was experimentally observed for the first time by confocal fluorescence microscopy, and the results of analysis and statistical processing of time trajectories of fluorescence intensity are presented. By means of computer simulation of the fluorescence intensity trajectories of single F_2-color centers in LiF crystal the frequency of intercombination (singlet-triplet) transitions for these centers was estimated in order of magnitude, and estimates of the lifetime of F_2-center in the first triplet state were obtained [14]. This paper is a continuation of these studies. Below, the flickering nature of the fluorescence of single F_2- and F_3^+-centers in LiF crystals was studied by laser scanning confocal luminescence microscopy. Under the studies carried out a number of interesting results were obtained on the physical properties of these types of color centers.

Experiment description

A gradient-colored γ-irradiated LiF crystal was used as the test sample, which made it possible to study regions with different concentrations of centers. The insert to Fig. 1 shows the concentration gradient, which was created in the bulk of the crystal in order to be able to find the region with the defects concentration necessary to detect single color centers. The types of color centers were determined from the photoluminescence spectra measured on the ensemble of defects. Figure 1 shows the luminescence spectra upon excitation by continuous LED radiation with a wavelength of 455 nm, measured in various regions of the gradient-colored crystal using OceanOptics 6500 spectrometer. In particular, the curves *2–4* shown in Fig. 1 indicate the presence in the emission spectra of bands related to F_2- and F_3^+-color centers.

Luminescence from single F_2- and F_3^+-centers in LiF was observed using a MicroTime 200 laser luminescent confocal scanning microscope (PicoQuant, GmbH). Luminescence was excited by a laser with wavelength of 470 nm, operating in pulsed mode with a pulse repetition rate of 5 and 10 MHz, with pulse width of about 70 ps. The exciting radiation had a linear polarization.

In the experiments the laser beam was directed along the normal to the crystal surface — the plane (100) (cube face); by rotating the crystal around the beam axis, the polarization vector of the exciting radiation was directed along one of the crystallographic axes either along [100] (orientation 0°, along the edge of the cube) or along [110] (orientation 45°, along the diagonal of the cube). The luminescence of the sample was also measured in the direction of plane normal (100).

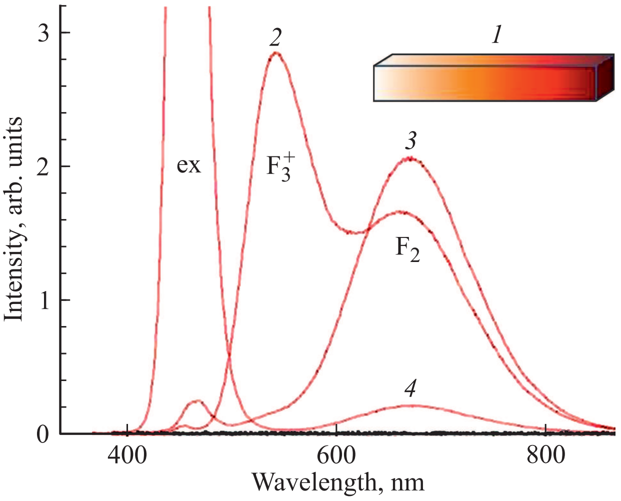

Figure 1. LiF sample under study with a gradient spatial distribution of color centers (*1*) and photoluminescence spectra in the right part (*2*), in the central part (*3*) and in the left part (*4*) of the crystal.

Experimental results

Figure 2 shows fluorescent scanned images of region $6 \times 6\,\mu$m of LiF sample upon excitation by a picosecond laser with an excitation wavelength of 470 nm. MicroTime 200 laser fluorescent confocal scanning microscope software generates luminescence images of defects with decay time selection. The lifetimes of the centers photoluminescence of two types, that we observe, are different. Luminous spots on the image are single F_2-centers (left) with characteristic decay time ~ 17 ns and F_3^+-color centers (right) with characteristic decay time of about 8 ns [7]. The flickering nature of the images is characteristic when observing the fluorescence of single quantum systems. After recording the luminescence image, the device was aimed at one of the luminous spots, and the luminescence intensity as function of time (quantum trajectory) was recorded.

Figure 3 shows the characteristic quantum trajectories of single F_2-center upon polarization of the exciting light along the edge of the cube (left) and along the lateral diagonal of the cube (right). Time intervals when luminescence occurs are usually called *on*-intervals, when it is absent *off*-intervals. The abrupt and complete disappearance of fluorescence („step“ on the quantum trajectory) serves as proof that we are observing just a single color center. As we can see, in addition to the alternation of *on*- and *off*-intervals characteristic for systems with triplet level, jumps in the luminescence intensity I are observed, and for experiments with sample orientation 0° the intensity ratio $I_{\max}/I_{\min}$ had values 1 : 1 or 1 : 2, and with the sample orientation 45° — 1 : 1 or 1 : 8.

In the paper [14] the authors showed that this phenomenon is due to the reorientation of F_2-center in the „dark“ triplet state. Theoretically, the ratio of luminescence

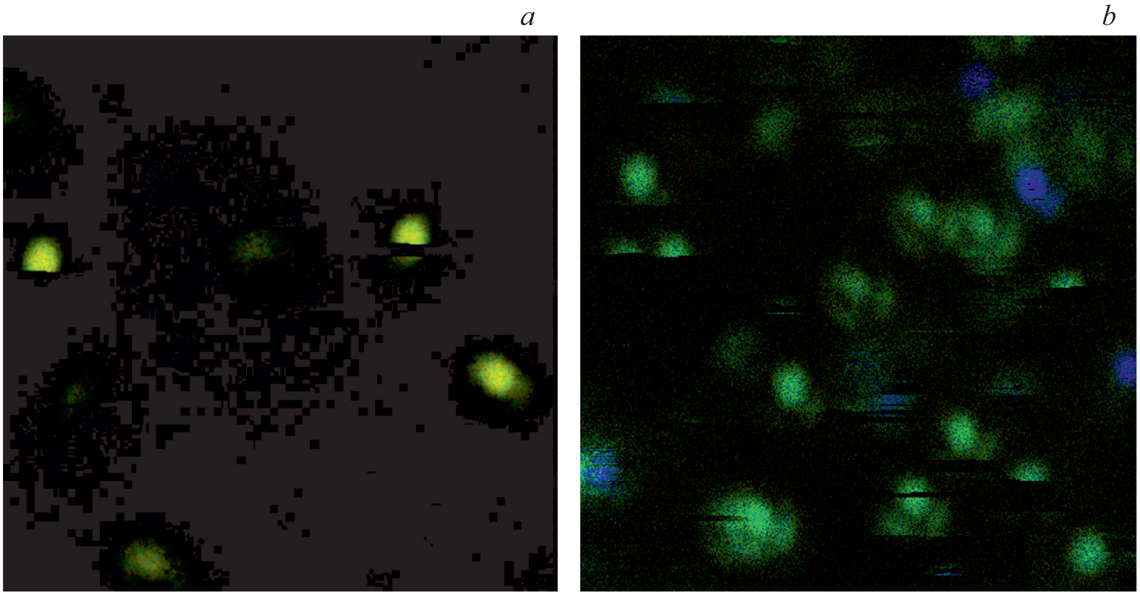

Figure 2. Confocal luminescent images of single F_2- and F_3^+-color centers (*a* and *b*) in the LiF crystal (scanning area $6 \times 6\,\mu$m, excitation 470 nm).

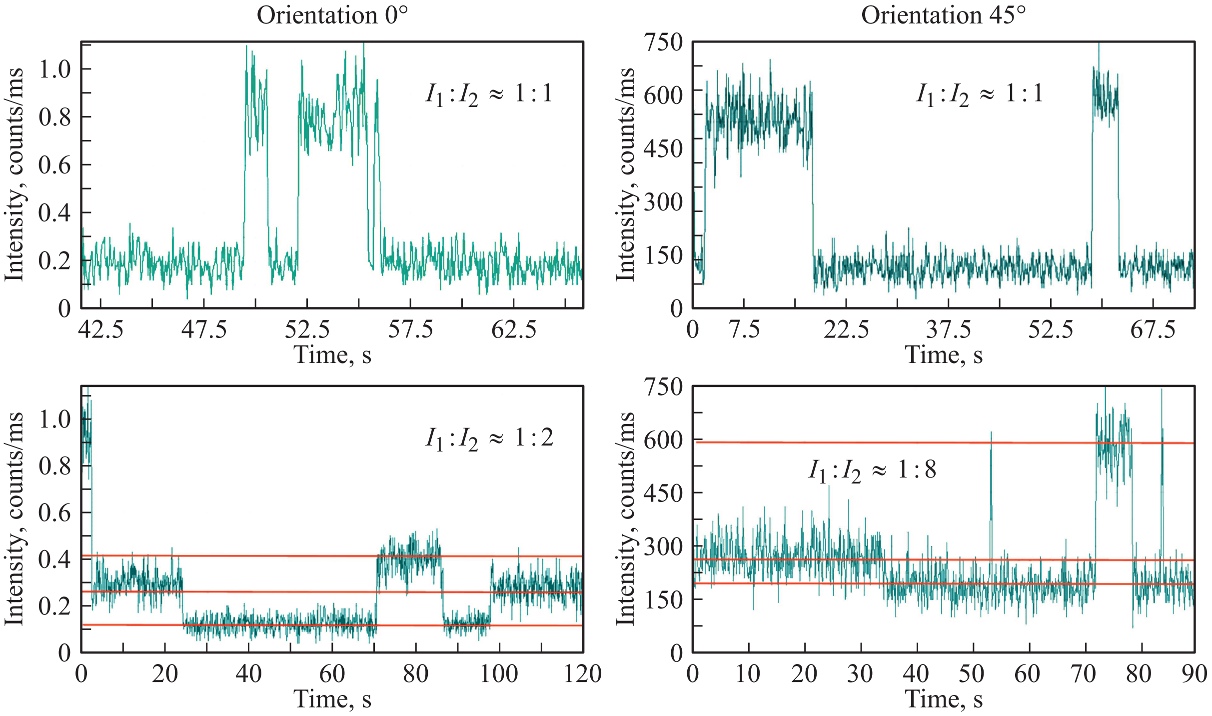

Figure 3.

intensities and the lifetimes of the center in different orientations were calculated for two experimental configurations. The obtained ratios are in good agreement with experiment.

Figure 4 shows a small series of experimentally recorded luminescence intensity trajectories of single F_3^+-centers for sample orientations 0° (Fig. 3, *a, b, c*) and 45° (Fig. 3, *d, e, f*).

As can be seen from Fig. 4, when the sample orientation is 0°, the magnitude of signal fluctuations is comparable to the background value, and when the sample orientation is 45°, the magnitude of signal fluctuations significantly exceeds the background value, and is approximately $\frac{I_{\max}}{I_{\min}} = 3$.

Discussion of results

As can be seen from the experimental data presented in Figs. 3 and 4, the dependence of the luminescence intensity

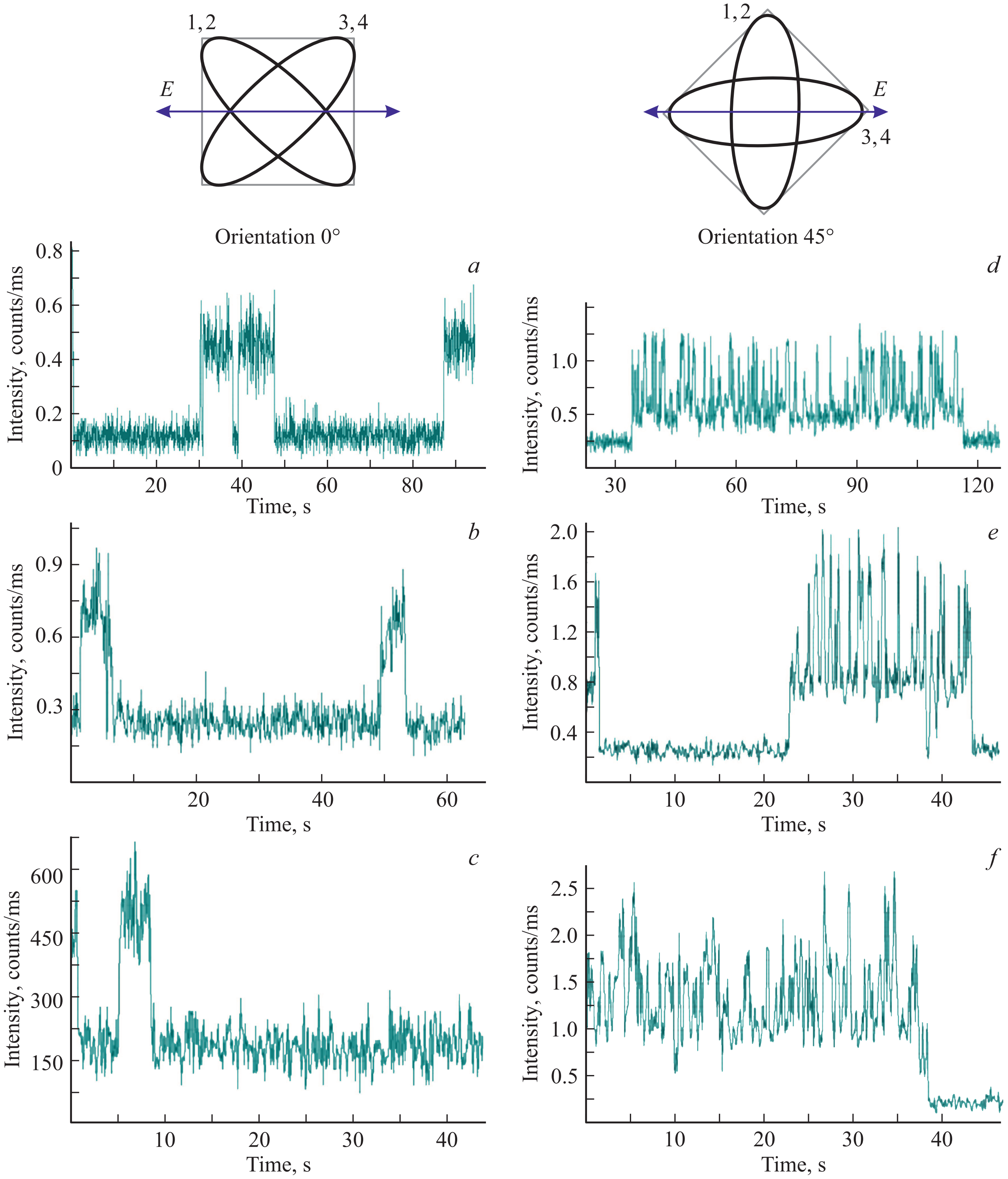

Figure 4. Possible projections of „rotators“ on plane (100) and the vector of the electric field strength of the exciting light are shown above. Luminescence intensity trajectories of single F_3^+-centers for sample orientations 0° (*a, b, c*) and 45° (*d, e, f*).

on the time of single F_3^+-center fundamentally differs from the dependence of single F_2-center, but its character also indicates the center reorientation at room temperature.

It was found that during the experiment the signal (luminescence intensity) from the center disappears and reappears after some time with the same intensity. The observed phenomenon was interpreted as center transition from excited to a long-lived triplet state, followed by relaxation to the ground state. During the experiments, an interesting fact was noticed (with 100% repeatability).

1. If the exciting light was incident along the normal to the plane (100) (cube face), and its linear polarization vector was directed along [100] axis (i.e., along one of the edges of the cube), then the magnitude of the fluctuation of measured luminescence intensity I, in the direction of the same normal to (100), was small and comparable to the background fluctuation. Further, the above conditions will be designated as the experimental configuration 0°.

2. If the vector of linear polarization of the exciting light was directed along [110] axis (i.e., along one of the lateral diagonals of the cube), then the magnitude of the fluctuation of the measured luminescence intensity, in the direction of the same normal to (100), increased sharply and amounted to (experimental configuration 45°).

In order to explain the observed phenomenon, let us recall what F_3^+-center is in alkali halide crystals. As it is known, F_3^+-center is three neighboring anion vacancies (lying in plane the normal to which is directed along one of the four axes C_3) in the lattice of the LiF crystal, capturing a pair of electrons [15] (Fig. 5).

A fairly good model of F_3^+-center is the molecular hydrogen ion H_3^+ in dielectric environment. According to theoretical calculations [16], the molecular ion H_3^+ in the basis of hydrogen-like $1s$-functions has spin singlet states: the ground state, according to the projection of the orbital angular moment is nondegenerate, $^1A_1(1)$; two excited orbital doublets $^1E_1(1)$, $^1E_1(2)$ and one state $^1A_1(2)$, as well as two spin triplet terms ^3E and $^3A_2$ [17].

Well-observed spectral bands of absorption ($\lambda_{\text{abs}}^{\max} = 452\,\text{nm}$) and luminescence ($\lambda_{\text{abs}}^{\max} = 540\,\text{nm}$) of the F_3^+-center are connected with the transition $^1A_1(1) \Leftrightarrow {}^1E_1(1)$ [17]. Such transition between non-degenerate state and state doubly degenerate by orbital moment, according to [18], is described by „rotator"whose normal is oriented along one of the four possible axes C_3.

The reorientation of the center means the jump of anion closest to F_3^+-center (shown in Fig. 5) to the place of one of the three vacancies. As can be seen from Fig. 5, the reorientation of F_3^+-center does not lead to its translational movement (which explains their stability at room temperature). This reorientation diffusion of F_3^+-center causes different fluctuations of the luminescence intensity for experimental configurations 0° and 45°.

As already mentioned, absorption and its conjugate luminescence of F_3^+-center is described by the „rotators"model. That is, the absorption and luminescence of the center are described by a pair of single mutually perpendicular linear oscillators $\mathbf{d}_1^{(i)}$ and $\mathbf{d}_2^{(i)}$ lying in the plane perpendicular to one of the four axes $C_3^{(i)}$ [9]. Then, it is easy to see that for the experimental configuration 0° (Fig. 4, left) all 4 possible orientations of the center with respect to the vector $\mathbf{E}$ are equivalent and, consequently, the luminescence intensity fluctuations will be at the level of background ones.

With the experimental configuration 45° (Fig. 4, right), the orientations of the center 1,2 are not equivalent to the orientations 3,4 (with respect to the vector $\mathbf{E}$). Based on the „rotator" model, we can calculate the ratio of the luminescence intensities of single F_3^+-center for its four possible orientations in the crystal (Fig. 5), for the experiment configuration 45°:

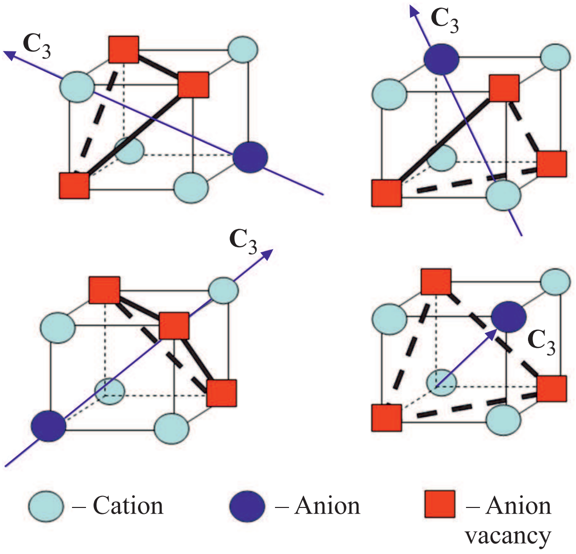

Figure 5. Structure of F_3^+-center and its possible orientations in the crystal lattice.

$$P_{1,2}^{\text{absorb}} = C_1 \cos^2\alpha = C_1\left(\frac{1}{3}\right), \quad P_{1,2,3,4}^{\text{emit}} = C_2\left(1+\frac{1}{3}\right),$$

$$I_{1,2} = C_1C_2\left(\frac{4}{9}\right); \tag{1}$$

$$P_{3,4}^{\text{absorb}} = C_1(1), \quad I_{3,4} = C_1C_2\left(\frac{4}{3}\right); \tag{2}$$

$$\frac{I_{1,2}^{\min}}{I_{3,4}^{\max}} = \frac{1}{3}, \quad \frac{\langle\sqrt{(\Delta I)^2}\rangle}{\langle I\rangle} = 1, \tag{3}$$

where P_i^{absorb}, P_i^{emit} are the probabilities of absorption and emission of photon in given direction per unit time of „rotator" with i-orientation of the normal corresponding to $C_{1,2}$-constant.

The obtained luminescence intensity ratios for configurations 45° are in qualitative agreement with experiment (Fig. 4).

In order to finally verify the correctness of our hypothesis, we calculated and measured the polarized components of the luminescence intensity of single F_3-center, $I_{1,2,3,4}^{\parallel}$ and $I_{1,2,3,4}^{\perp}$, with polarization parallel and perpendicular to the polarization of the exciting light, respectively. For the configuration 0°, due to its high symmetry, we obtain a trivial result: $I_{1,2,3,4}^{\parallel} = I_{1,2,3,4}^{\perp} = \frac{1}{2}I$. For experiment configuration „45°":

$$P_{1,2}^{\text{absorp.}} = C_1\left(\frac{1}{3}\right), \quad P_{1,2}^{\text{rad.}\parallel} = C_2\left(\frac{1}{3}\right), \quad P_{1,2}^{\text{rad.}\perp} = C_2(1),$$

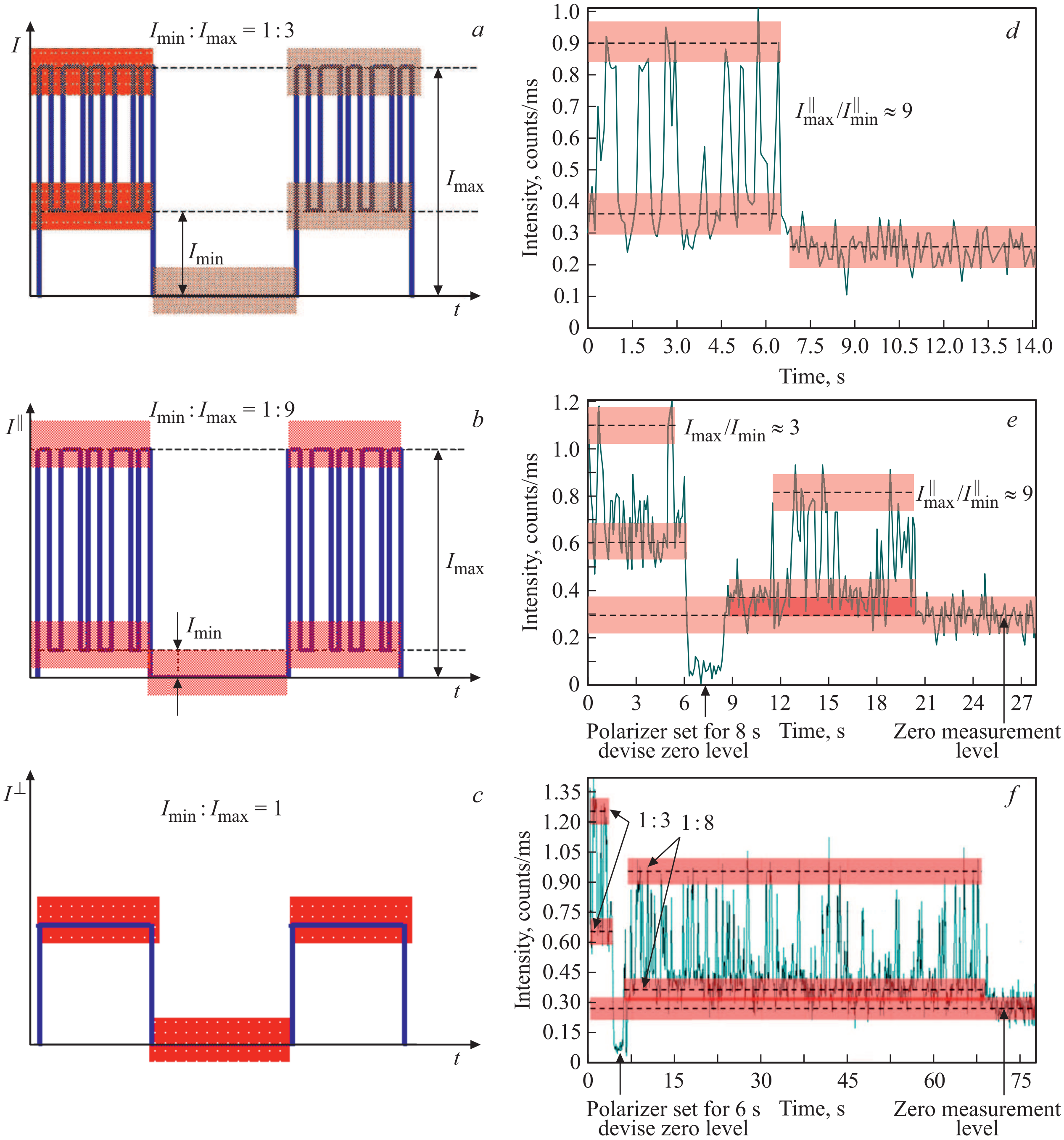

Figure 6. Calculated (a, b, c) and measured (d, e, f) quantum trajectories of the parallel component of the luminescence intensity of single F_3^+-centers for sample orientations 45°.

$$I^{\parallel}_{1,2} = C_1C_2\left(\frac{1}{9}\right), \quad I^{\perp}_{1,2} = C_1C_2\left(\frac{1}{3}\right); \tag{4}$$

$$P^{\text{absorp.}}_{3,4} = C_1(1), \quad P^{\text{rad.}\parallel}_{3,4} = C_2(1), \quad P^{\text{rad.}\perp}_{3,4} = C_2\left(\frac{1}{3}\right),$$

$$I^{\parallel}_{3,4} = C_1C_2(1), \quad I^{\perp}_{3,4} = C_1C_2\left(\frac{1}{3}\right); \tag{5}$$

$$\frac{I^{\parallel}_{1,2}}{I^{\parallel}_{3,4}} = \frac{1}{9}, \quad \frac{I^{\perp}_{1,2}}{I^{\perp}_{3,4}} = 1. \tag{6}$$

Figure 6 (left) shows the results of simulation of quantum trajectories of the center based on the calculation (4)−(6). As we can see, it follows from the calculation that in the case of measuring the trajectory of the luminescence component $I^{\parallel}$, the fluctuations should increase up to $\frac{I^{\parallel}_{1,2}}{I^{\parallel}_{3,4}} = \frac{1}{9}$ (Fig. 6, b), which is confirmed in the experiment (Fig. 6, d, e, f). Thus, it should be considered proven that at room temperature the reorientation diffusion of F_3^+-center takes place in the ground (singlet) state.

Conclusion

Note that the detection of the phenomenon described above became possible due to the use of confocal fluorescence microscopy, which makes it possible to measure the intensity of luminescence from single quantum systems (molecules, luminescence centers, etc.). This would be impossible by traditional methods, when the luminescence intensity (and its polarized components) from a large number of quantum systems is measured. Since the lifetime of the excited state of the center of about 8 ns is much shorter than the average reorientation time of the center (about 1 s), the reorientation effect will have no noticeable effect on the depolarization of the luminescence. Note also that the paper does not consider one more channel for the F_3^+-center movement to the „dark" state: $F_3^+ \Leftrightarrow N_c$ [19].

In conclusion, we present the main findings of the paper.

1. Reorientation of single F_3^+-centers was observed experimentally; the theoretically obtained intensity ratios for different center orientations correspond to experiment.

2. Unlike the F_2-center, which only reorients in the triplet („dark") state, F_3^+-center reorients in the ground state, and such reorientational diffusion does not lead to translational diffusion of the center.

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Conflict of interest

The authors declare that they have no conflict of interest.

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