

Microspectroscopy of single color centers in alkaline halide crystals

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Single color centers in the LiF crystal were studied by confocal fluorescence microscopy with analysis and statistical processing of the time dependences of their fluorescence intensity. The possibility of identifying quantum systems whose selection by luminescence excitation (absorption) spectra, luminescence spectra, and luminescence decay time is difficult due to their overlap or due to the coincidence of the corresponding characteristics of different centers is shown. An additional identification feature in this case is the flicker frequency and other characteristics of the time dependences of the luminescence intensity. The efficiency of the method is demonstrated by the example of two color centers of different nature (F_2 and F_3 , stabilized by an impurity–vacancy dipole) in a lithium fluoride crystal.

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

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Introduction

One of the problems of radiation physics of solids is the difficulty in identifying numerous types of intrinsic and intrinsic-impurity defects created by radiation in crystalline and amorphous media or in nanoparticles based on them. The opportunities of commonly used methods of absorption or luminescence spectroscopy, in contrast to atomic gases or rare-earth impurities with optical transitions in inner electron shells, for condensed media are usually significantly limited by the large electron-phonon and electronic-vibrational homogeneous broadening of spectral lines, which turn into broad bands. Therefore, the combined optical absorption and luminescence spectra of radiation defects (color centers) in irradiated crystals can occupy a wide spectral region from the vacuum ultraviolet to the near-IR area, inclusive [1–3]. This applies, for example, to the most wide-band crystals, such as lithium fluoride, irradiated with gamma radiation or intense femtosecond laser radiation. Under the influence of various sources of ionizing radiation in lithium fluoride crystals the aggregate F_2 , F_2^+ , F_2^- , F_3 , 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 [1–3]. Meanwhile, two types of centers can have identical or strongly overlapping absorption and luminescence bands. For example, in lithium fluoride crystals F_2 and F_3^+ , the color centers form one combined M-absorption band with a maximum near 444 nm (which slightly shifts depending on the concentration ratio of these centers), and F_3^- and stabilized F_2^+ centers have overlapping luminescence bands in the area of 800–900 nm [1].

Thus, the task of spectroscopic differentiation of quantum systems created by radiation in such media, systematization of their spectral bands, construction of energy level

diagrams and quantum transitions is quite complex. It has not been completely solved for any crystal, despite many years of research and numerous publications. Therefore, the development of new principles of spectroscopic discrimination of radiation defects, supplementing the traditional spectral-kinetic methods, the use of new spectroscopic characteristics, is relevant. This is especially emphasized by the practical significance of radiation defects, including color centers, as model quantum systems in various fundamental studies. In addition, color centers in various crystals are widely used as working centers of gamma radiation detectors, charged particle track detectors [4], optical media for visual and digital information [5], laser media and passive laser shutters [6,7], thin-film luminescent screens for X-ray microimage visualization [8] and etc. In recent years, interest in the spectroscopy of single luminescent centers, which are the ideal basis of the elemental base of quantum informatics and nanosensorics, has been growing like an avalanche [9–11]. Therefore, the study of single radiation defects by microspectroscopic methods [12,13], developed in this paper, will undoubtedly expand the opportunities of their further practical use.

Experiment description

The experimental research method in this paper is the method of time-resolved confocal scanning luminescence microscopy, which implements the principle of time-correlated spatially selective counting of single photons. In case when the concentration of centers in the volume under study is significantly lower than L^{-3} , where L — is the diffraction optical limit at the wavelength of the maximum of

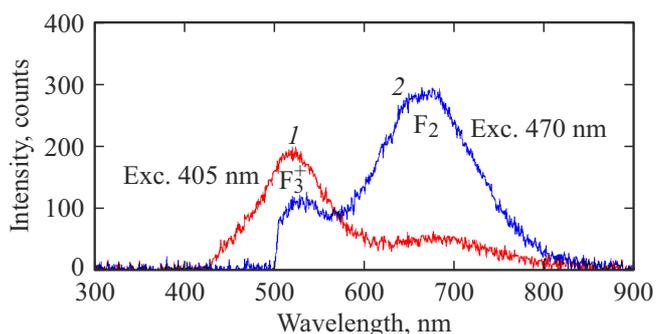


Figure 1. Photoluminescence spectra excited by picosecond laser radiation with a wavelength of 405 (curve 1) and 470 nm (2).

the luminescence spectral band, the conditions for spatially selective excitation of single defects are realized.

Lithium fluoride crystals of two types grown under different conditions were used as objects of study. Some of the samples were grown in air according to the Kyropoulos method. Crystals grown by this method contain oxygen in various complexes with impurities or with intrinsic defects due to the oxidizing atmosphere. The presence of oxygen in crystals, as well as its complexes with other impurities, significantly affects the formation of color centers under the action of ionizing radiation. Another part of the crystalline samples was grown by the Stockbarger method in a graphite crucible. Here, reducing conditions were implemented to prevent contamination of the crystals with oxygen. The studied samples of LiF crystals were subjected to short-term X-ray irradiation for several seconds. The purpose of this processing was to create an ultra-low concentration of color centers, so that in the future, as indicated above, on a confocal microscope it would be possible to select and study a region of the order of $1\ \mu\text{m}^3$, in which one color center is located.

The presence of color centers in the studied samples exposed to X-ray radiation was determined from the measured photoluminescence spectra. Fig. 1 shows the luminescence spectra upon excitation by picosecond laser pulses with wavelengths of 405 and 470 nm measured with an Ocean Optics 65000 spectrometer. The radiation spectra shown in Fig. 1 contain bands associated with the color centers F_2 and F_3^+ .

Observation of luminescence of individual centers in the samples under study was carried out by means of a laser confocal scanning microscope MicroTime 200 (PicoQuant, GmbH). Luminescence was excited by a laser with radiation wavelength of 532 nm, operating in pulsed mode with a pulse repetition rate of 5 or 10 MHz, with pulse width of approximately 70 ps. Exciting radiation with linear polarization was focused using an Olympus UPLSAPO60XW lens (superachromat with full compensation of spherical and chromatic aberrations, x60 magnification, numerical aperture 1.2). The electric vector was oriented in the

edge direction of the crystal lattice of the studied samples. The average power of the exciting radiation directed into the lens of the microscope was measured by a special photodetector included in the scope of the microscope and presented in relative units. To convert these units into microwatts, it is required to multiply the readings of the photodetector in relative units by a coefficient of proportionality of 0.071. To prevent the exciting laser radiation from entering the luminescence registration channel, interference filters with an L-shaped spectral transmission characteristic (corresponding to the wavelength of the exciting radiation) were used. The photoluminescence signal after passing through the lens, confocal diaphragm and light filter, which cuts off the scattered exciting radiation, is recorded by an avalanche detector. The photon density was selected in such a way as to minimize the cases when more than one photon hits the detector during the blind time [14]. In our experiments, we used the method of time-correlated photon counting, and the pulse repetition rate (5–10 MHz) of the exciting radiation was selected in such a way that there were approximately 4 operations of the avalanche photodiode per 100 pulses („blind time“ 30 ns). Thus, the influence „of blind time“ was minimized.

Studies of the luminescence of individual centers begin with a search for them inside the crystal. The construction of scanned pictures containing images of individual luminescence centers occurs when the lens is moved on a piezo-scanning table. Meanwhile, the laser beam focused by the microscope lens carries out line-by-line scanning of the area with the maximum size $80 \times 80\ \mu\text{m}^2$ or less at a certain depth inside the crystal irradiated with X-rays. Then, the exciting picosecond laser radiation is focused on the location of one of the detected color centers, and the recording of the time trajectory of the luminescence intensity begins. The information obtained as a result of time-correlated photon counting is stored in the computer memory and is used to plot the dependences of the luminescence intensity of individual centers on time in the range of seconds-minutes, i.e. intensity trajectories, as well as to display the rise and fall curves of the luminescence intensity in the picosecond range, i.e. luminescence kinetics.

Experimental results

Fluorescent scanned images of the $6 \times 6\ \mu\text{m}^2$ area of one of the studied LiF samples upon excitation by a picosecond laser with an excitation wavelength of 532 nm are shown in Fig. 2 (left). Luminous spots in the photograph are images of single color centers. Some images show that luminescence scintillations sometimes occur at the process of line-by-line scanning of individual centers. The flickering nature of the images is characteristic when observing the fluorescence of single quantum systems [15–17]. After recording the luminescent image, the exciting radiation was directed to the location of one of the luminous spots, and

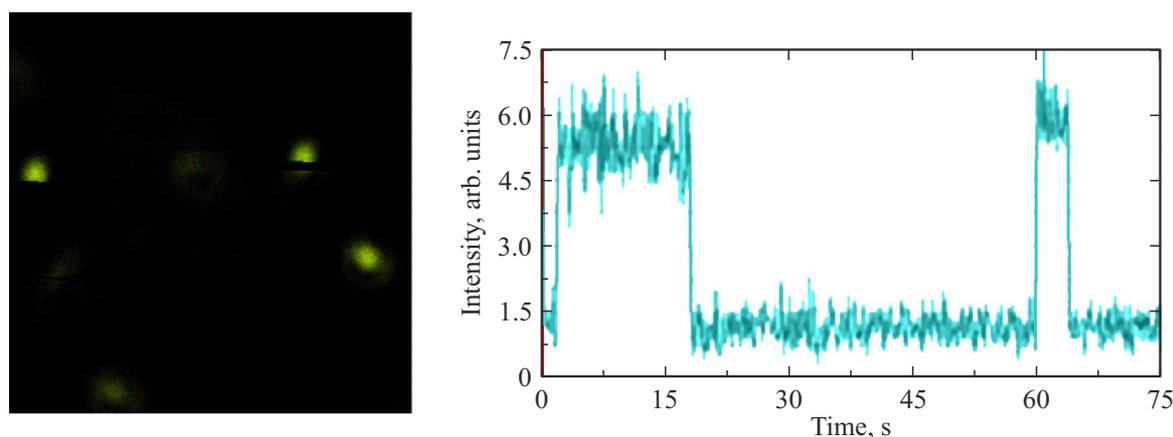


Figure 2. Confocal luminescent images (left) and a fragment of the intensity trajectory (right) characteristic of single F_2 color centers in a LiF crystal (online in color).

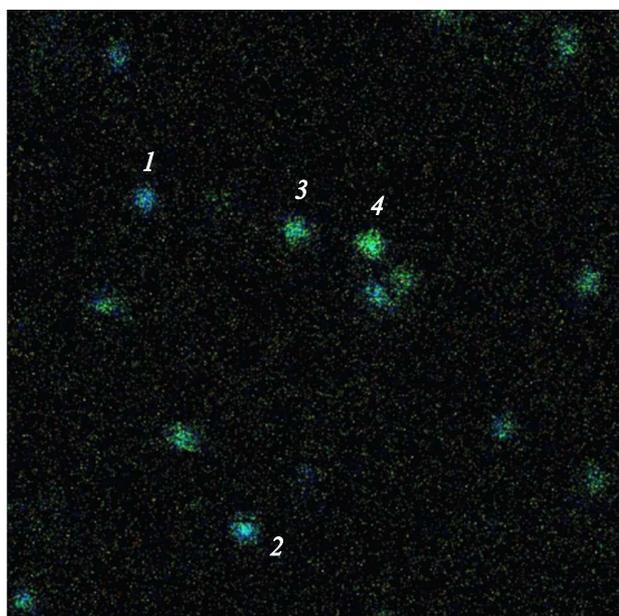


Figure 3. Luminescent images of individual color centers in the test sample. Scan area size $6 \times 6 \mu\text{m}^2$ (online in color).

then the dependence of the luminescence intensity on time was recorded.

Fig. 2 (on the right) shows a fragment of the intensity trajectory characteristic of a single F_2 center. 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 intensity trajectory) serves as proof that we are observing just a single color center.

MicroTime 200 laser fluorescent confocal scanning microscope software generates luminescence images of defects with decay time selection. Fig. 3 shows luminescent images of individual color centers recorded as a result of scanning

on a confocal fluorescent microscope in a LiF crystal grown in air by the Kyropoulos method. The images shown in Fig. 3 differ slightly in color (this can be seen in the online version of the article, where color illustrations are presented). In particular, the images of the centers 1 and 2 are blue, while the images of the centers 3 and 4 — are green. This means that the values of the photoluminescence decay time constants for the centers of the two observed types are different.

The intensity trajectories and kinetic decay curves of photoluminescence for two types of observed centers are shown in Fig. 4. Here 1 and 4 — are the complete survey trajectories, 2 and 5 — enlarged fragments of these trajectories highlighted in black. Let us compare two types of graphs for each type of center. An analysis of the luminescence decay kinetics showed that the photoluminescence decay time of the 3 and 4 centers in Fig. 3 is 17.5 ns, which is consistent with the lifetime F_2 — of the [18] color centers. The lifetime of the 1 and 2 centers is in Fig. 13.4 ns. This difference in the luminescence decay times confirms that these are different types of centers. It should be noted that the difference between these two values is not so great, and it is not always possible to confidently distinguish between these two types of centers, taking into account that both types of centers were excited by radiation with the same wavelength, and the luminescence was recorded in the same spectral range 690 ± 30 nm, selected using a band-pass interference filter.

Fig. 5 shows the measured intensity trajectories (1, 3) and the corresponding kinetic curves (2, 4) of two different single color centers of the same type. These centers have the same luminescence decay time, by which they can be identified as F_2 -centers [18]. Comparing the characteristics of the intensity trajectories, the difference in the parameters of these dependences can be found. In particular, for 3, 4 *on*-intervals are longer than for 1, 2, and the flicker frequency is lower.

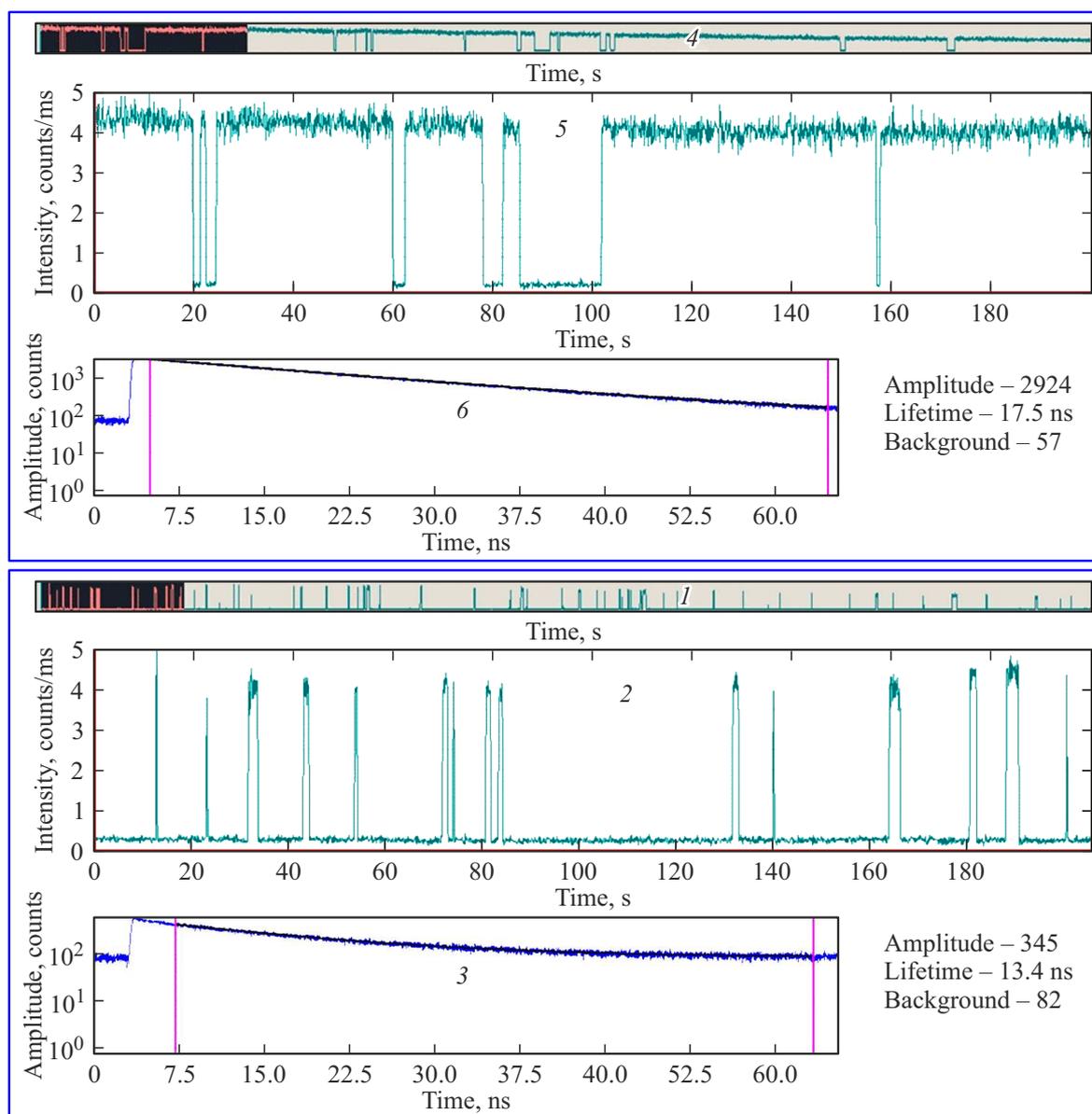


Figure 4. Photoluminescence intensity trajectories (curves 1, 2 and 4, 5) and luminescence decay kinetics (curves 3 and 6) for two types of centers shown in Fig. 3. The repetition rate of exciting pulses is 10 MHz. The inscriptions on the right show the results of software processing of the kinetic curves: the amplitudes and values of the decay constants of the temporal luminescence components, as well as the background value, are shown.

Results and discussion

The experimental data presented above indicate that, at close spectral characteristics and decay times, the parameters of the photoluminescence intensity trajectories of color centers can differ significantly. In this connection, it becomes required to introduce new spectroscopic characteristics for differentiating different centers according to the nature of their intensity trajectories. The following can be considered as spectroscopic characteristics: T_{on} — average lifetime of a radiating state (*off*-interval), T_{off} — average

lifetime of a non-radiating state (*off*-interval), or ratios of these quantities.

F_2 - color center in the first approximation interacts with the exciting laser radiation as a three-level quantum system (Fig. 6). It is assumed that the color center can be in the ground singlet state S_0 , the first excited singlet state S_1 the first triplet state T_1 . This interaction is described by the following system of equations for the density matrix [19]:

$$\begin{cases} \dot{\rho}_0 = -k\rho_0 + \gamma_f\rho_1 + \gamma_{TS}\rho_2; \\ \dot{\rho}_1 = k\rho_0 - (\gamma_f + \Gamma_{TS})\rho_1; \\ \dot{\rho}_2 = \Gamma_{TS}\rho_1 - \gamma_{TS}\rho_2. \end{cases} \quad (1)$$

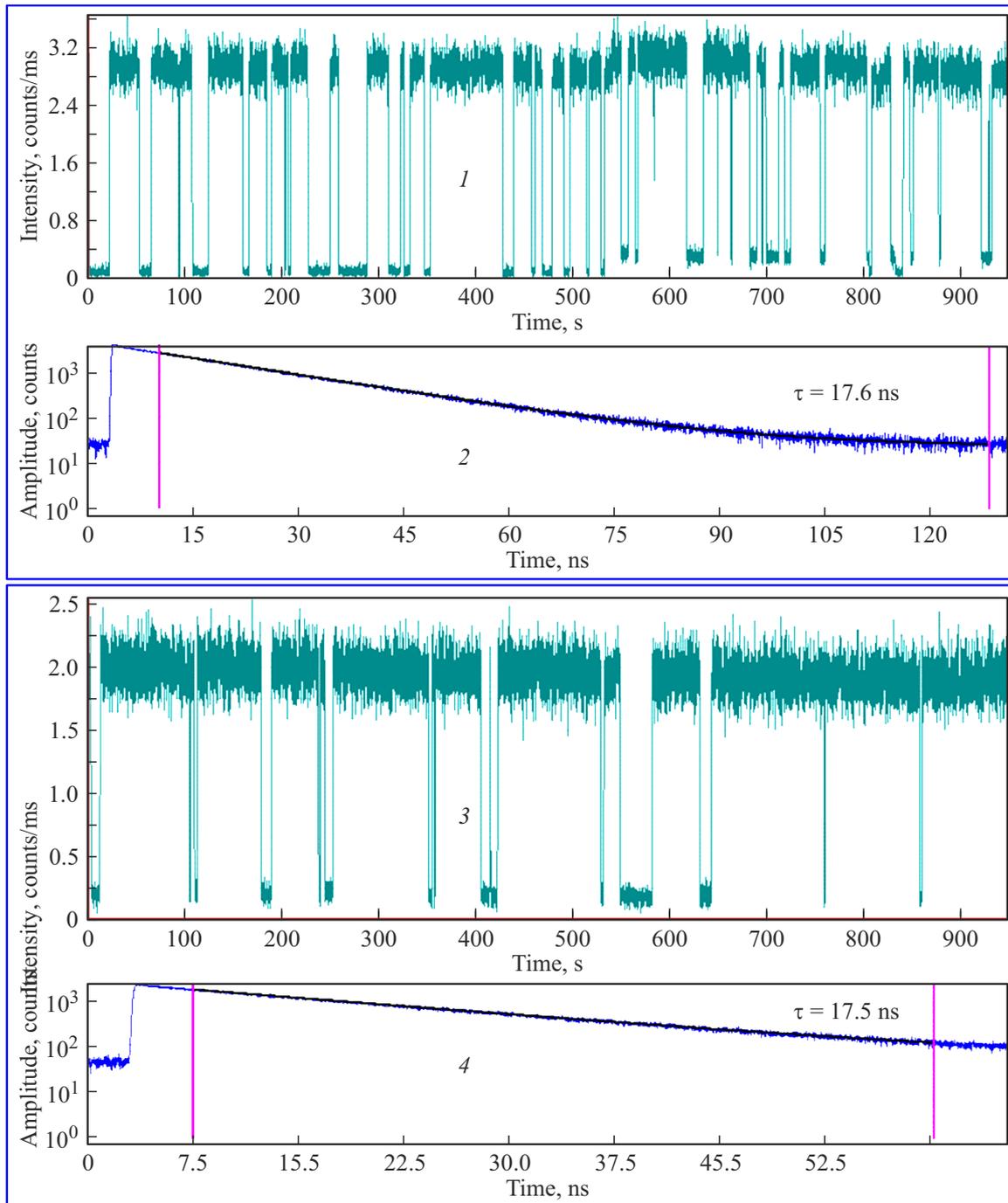


Figure 5. Measured intensity trajectories (1, 3) and corresponding kinetic curves (2, 4) for two single centers with identical luminescence decay times. The repetition rate of exciting pulses is 10 MHz.

Here ρ_0 , ρ_1 and ρ_2 — are the diagonal elements of the density matrix, they have the meaning of the probabilities of the color center being in the states S_0 , S_1 and T_1 respectively. The meaning of the rest of the parameters shown in Figure 6: σ — absorption cross section of the color center, I — intensity of the exciting laser field, τ_f — fluorescence decay time, Γ_{TS} — probability of singlet-triplet transitions, τ_{TS} — average lifetime of the triplet state.

The probability density of *on*-intervals, found from the system of equations (1) under pulsed excitation under the assumption $\tau_p \ll \tau_f \ll 1/\nu$ (pulse duration $\tau_p = 70$ ps, pulse repetition rate $\nu = 10$ MHz), is given by the following expression [19]:

$$w_{on}(t) = \frac{1}{T_{on}} \exp\left(-\frac{t}{T_{on}}\right). \tag{2}$$

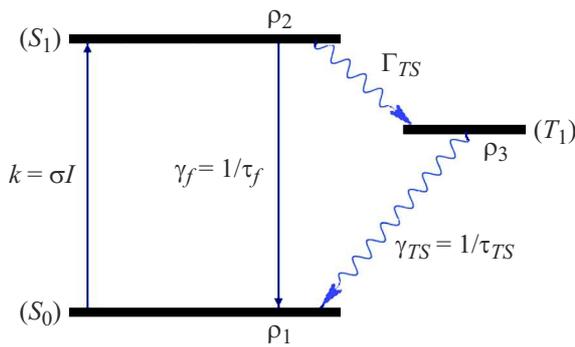


Figure 6. Energy model of a color center with a triplet level.

Table 1. Characteristics of the two types of color centers

Color center	τ_f , ns	T_{on} , s	T_{off} , s	T_{on}/T_{off}
F ₂	17.5	21	5.2	4.04
F ₃ Mg ⁺⁺ V _c ⁻	13.4	1.4	11.8	0.12

Here t — duration of on-intervals, and T_{on} — their average duration. Taking into account the relations $k \ll \gamma_f$, $\gamma_{TS} \ll \gamma_f$, $\Gamma_{TS} \ll \gamma_f$, it is determined by the following expression [17]:

$$T_{on} = \frac{1}{vk\tau_f\Gamma_{TS}\tau_p}. \quad (3)$$

The probability density of *off* of the intervals is given by the expression [19]:

$$w_{off}(t) = \frac{1}{T_{off}} \exp\left(-\frac{t}{T_{off}}\right), \quad (4)$$

where t — duration of the *off*-interval, and their average duration coincides with the lifetime of the triplet state $T_{off} = \tau_{TS}$. By studying the intensity quantum trajectories of single F₂ centers in a lithium fluoride crystal, we were able to measure their physical parameters that determine the nature of luminescence, namely: the average frequency of intercombination (triplet-singlet) transitions for these centers is in the order of magnitude 10^4 s^{-1} [17]. Let us note that to determine the exact value of the Γ_{TS} parameter, it is necessary to analyze the statistics of on-intervals, the average duration of which depends on the $k = \sigma I$ parameter.

The results of statistical processing of the time dependences of the fluorescence intensity shown in Fig. 4 are given in Table 1. The trajectory I in this figure flickers much more frequently, its *on*-intervals are shorter than those of the same trajectory 4 of the second center at the same excitation intensities. It should be noted that this is not related to the higher excitation rate at the first center, because both centers have close absorption cross sections. This fact is confirmed by the value closeness of the radiative lifetime of these two centers. Since absorption and luminescence are associated with the same quantum transition, the same value

Table 2. Characteristics of trajectories for two values of excitation intensity

Intensity of laser excitation, I , arb. units	Medium duration radiating state, T_{on} , s	Medium duration non-radiating state, T_{off} , s
12	2.06	4.65
107	0.13	1.64

of the square of the modulus of the matrix element of the dipole moment of the transition determines the magnitude of the absorption and luminescence cross sections, as well as the probability of absorption (excitation of the center). Significant differences in the temporal characteristics of the intensity trajectories directly confirm that we are dealing with two centers of different types. The scintillation of the I trajectory occurs more often because the probability of singlet-triplet transitions Γ_{TS} is higher at this center.

Thus, the types of centers can be distinguished by the parameters of the trajectories. The measurement results presented in Table 1 show that the trajectory spectroscopic characteristics of T_{on}/T_{off} differ by a factor of 34 for the two centers studied. Such a difference cannot be explained by different potential orientations of F₂ color centers (assuming that both trajectories refer to F₂-centers). In the geometry of our experiment, the excitation probabilities of two such centers of different orientations can differ only by a factor of $\sqrt{2}$. At the same time, the probabilities of detecting luminescence photons are identical. The first type of defect is F₂ - color center. Based on the literature data, the second type seems to be a stabilized impurity-vacancy F₃Mg⁺⁺V_c⁻ color center [20].

In general case, at low intensities $T_{off}(I)$ is a constant value, while $T_{on}(I)$ is not a constant. To establish how the parameters T_{on} and T_{off} change with a change in the excitation intensity, we conducted an experiment during which, when recording the quantum trajectory of the same color center, the excitation intensity was increased by almost ten times. The trajectory recorded at two different laser radiation intensities is shown in Fig. 7. The arrow shows the moment of switching the intensity of the exciting radiation. This was achieved by increasing the average output power of the exciting laser from 12 to 107 arb. units at a constant pulse repetition rate of 10 MHz and the same focusing. Graph (4) characterizes the deviation degree of the decay curve from the exponential.

The values of the parameters of quantum trajectories depending on the intensity of the exciting radiation are presented in Table 2.

The decrease in T_{on} with increasing intensity corresponds to the three-level model of the center shown in Fig. 6. At the same time, the reduction of T_{off} does not fit into the framework of this model. A possible mechanism for the decrease in T_{off} at high intensities of exciting laser radiation

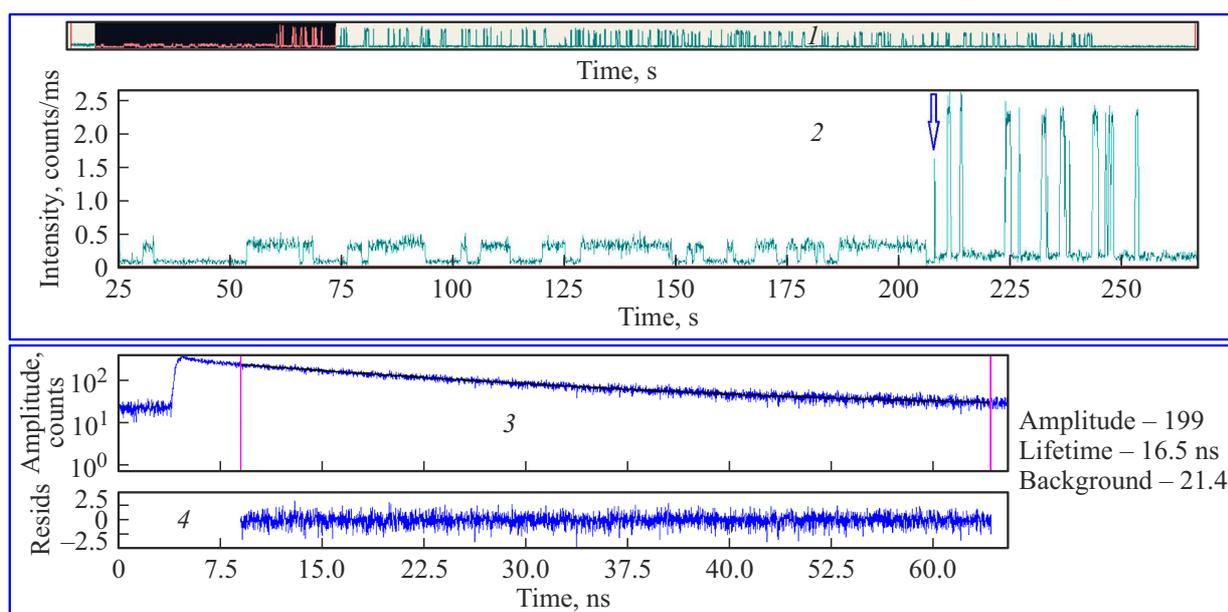


Figure 7. Overview trajectory of the photoluminescence intensity of the color center, recorded at two different excitation intensities (1); an enlarged fragment of this trajectory highlighted in black on the curve 1 (2); the kinetics of rise and fall of luminescence response pulses (3); remainder (4). The arrow on the curve (2) indicates the moment of change in the excitation intensity. On the right are numerical values of the luminescence amplitude and decay time, as well as the background value.

is intersystem transfer of excitation from upper triplet states not shown in Fig. 6, which are apparently populated as a result of transitions from the triplet state under the action of exciting radiation.

Conclusion

Thus, methods for the spectroscopy of quantum systems based on measuring the parameters of their photoluminescence intensity trajectories have been proposed and experimentally substantiated. Spectroscopic parameters are introduced that allow one to numerically characterize various types of quantum systems. A method for distinguishing single centers based on the analysis of the time spent in the radiating and non-radiating states of a quantum system and the frequency of transitions to the non-radiating state at a fixed value of the intensity of the exciting radiation is substantiated. This method can be useful in cases where the identification of centers using conventional luminescence spectroscopy is difficult due to the overlap of the spectra. Meanwhile, it should be taken into account that the characteristics of the trajectories depend on the intensity of the exciting radiation. Differences in the parameters of the trajectories can be caused by differences in the orientation of centers of the same type and the corresponding differences in the efficiency of excitation of centers. An increase in the efficiency of excitation at a singlet junction leads to an increase in the frequency of the singlet-triplet conversion and, accordingly, to a reduction in the *on* intervals (i.e., the time intervals during which

the center luminesces). In addition, heterogeneous local intracrystalline fields can affect the trajectory parameters. A separate study is required to answer the question why centers of the same type have different temporal characteristics of luminescence intensity trajectories.

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Conflict of interest

The authors declare that they have no conflict financial interests or personal relationships that could affect the work presented in this article.

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