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SPECTROSCOPY OF CONDENSED MATTER

Electron–Phonon Interaction of Color Centers with a Zero-Phonon Line 436.55 nm in Crystals LiF–O, OH

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Abstract—The absorption spectra have been measured at temperatures of 7.2–300 K of a γ-irradiated and UV-exposed LiF crystal with an admixture of oxygen and hydroxyl. The coupling force (*S*) with the phonons of the lattice of the electronic–vibrational transition with the zero-phonon line 436.55 nm is determined from the ratio of the intensities of the zero-phonon line and the vibronic absorption band. Based on the value of *S*, the nature of the color center responsible for the absorption band of 390 nm and radiation of 490 nm is proposed.

Keywords: lithium fluoride, oxygen, hydroxyl, color centers, absorption, luminescence, zero-phonon line
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INTRODUCTION

Laser recording of digital and visual information in three-dimensional and multilayer optical systems is one of the important sections of photonics [1]. The authors of [2] developed a new method for laser recording of three-dimensional color luminescent images in the volume of an optical carrier based on lithium fluoride crystals with F_{2^-} (λ_m = 670 nm, red glow) and F_3^+ (λ_m = 545 nm, green glow) color centers (CCs). To record a full-color image in accordance with the additive RGB model, which describes how to encode color using the three primary colors, a blue glow is required. The formation of color centers for these purposes, luminescent in LiF in the blue range, was announced in [3]. At the same time, the structure and model of the detected centers have not been reliably established and require further study.

In this work, we set the task to establish the nature of the center with the absorption maximum λ = 390 nm and radiation 490 nm, using such a characteristic as the coupling strength of electrons with phonons of the lattice (*S*).

To date, two models of centers with an absorption band of 390 nm and an emission band of 490 nm have been proposed: the F_3-model in zero-oxygen crystals [4, 5] and the F_3^+-model $(F_3^+)^*$ in LiF–O, OH crystals [6, 7]. The first mention of these centers is found in the work of Okuda [4]. The authors found an absorption band of 380 nm with a width of $\Delta\nu$ = 27 nm and a radiation band of 490 nm with $\Delta\nu$ = 84 nm in oxygen-free crystals. Studying the luminescence polarization of these defects, the structure of CC was proposed as F_3 with the center of symmetry C_{2v}. In a later work, Voitovich et al. [5], share the same point of view on the nature and structure of the centers under study. They also note that UV treatment increases the concentration of these defects. This experimental fact must be taken into account when considering the mechanism of formation of the studied defects.

Since low-temperature irradiation is used in the technology of preparing centers at 390 nm, which also leads to an increase in the efficiency of formation of F_2^+-like centers, a number of authors have proposed a model of F_3^+-like centers. Ivanov in [6] notes an analogy of the properties of F_3^+ and centers with an absorption band of 390 nm, which consists in the presence of metastable states in both centers. The simultaneous appearance of ZPhL F_3^+-centers and centers at 390 nm upon annealing of LiF–OH crystals, as well as the coincidence of the kinetics of center accumulation upon irradiation, allowed the author to attribute the band with λ_m = 390 nm to $(F_3^+)^*$-centers, which are an F_3^+-center perturbed by radiolysis products OH$^-$. Basiev et al. [7] also proposed a model of $(F_3^+)^*$-defects for these centers based on the coincidence of the lifetimes of radiative transitions. The electron lifetime in the excited state of the centers under study is 7.2 ns, which is very close to those for F_3^+-centers (τ = 11 ns).

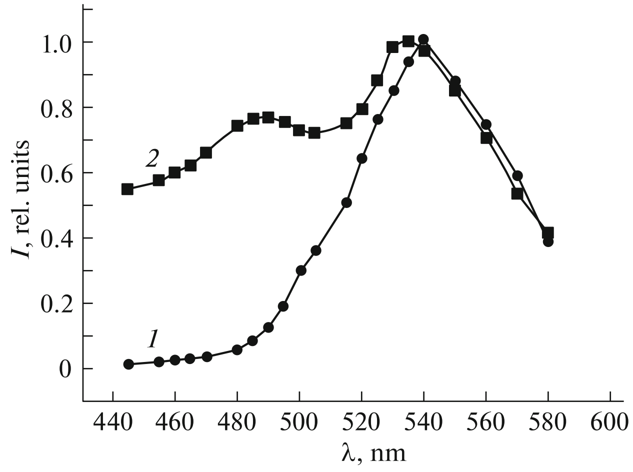

Fig. 1. Normalized emission spectra of γ-irradiated (*1*) dose of 7.7×10^3 C/kg (300 K) + 1×10^4 C/kg (273 K) and optically discolored (*2*) sample LiF–O, OH.

As can be seen from the analysis of literature data, the authors did not come to a consensus on the nature of the blue glow. We propose a slightly different view of the nature of the center with $\lambda_{ex} = 390$ nm and radiation 490 nm based on such a characteristic as the coupling strength of electrons with phonons of the lattice.

MATERIALS AND METHODS

In this work, we studied single crystals of lithium fluoride grown from industrial raw materials by the Kyropoulos method in air and enriched with an admixture of oxygen. To enrich with oxygen, the samples during the growth process were either activated by lithium nitrite (this salt is thermally unstable and, when heated to the melting point, LiF decomposes to form Li_2O), or the melt was kept in air for a long time. The crystals were irradiated with γ-radiation at a temperature of about 273 K in order to create a high concentration of F_3^+-centers. Optical discolored was carried out by integrated light of INP 3-7/120 xenon lamps in a KVANT-17 laser illuminator with a pulse of energy of about 50 J. The absorption spectra were measured on a Perkin-Elmer-Lambda 950 spectrophotometer (0.1 nm gap) in a closed-loop helium cryostat in the range temperature 7.2–300 K. To estimate the coupling force (S) of the electronic transition with the phonons of the lattice, the temperature dependences were measured

$$I_0/I = \exp[-S(1 + 2\pi^2 T^2/3T_D^2)],$$

where T is the measurement temperature, T_D is the Debye temperature ($T_D = 730$ K), I_0 is the intensity of the zero-phonon line, I is the intensity in the vibronic absorption band [8]. Based on the data obtained, a graph was constructed in the coordinates $\ln(I_0/I)$ and $(1 + 2\pi^2T^2/3T_D^2)$. The slope of the straight line constructed in the coordinates given above will be equal to the value of the electron–phonon coupling force S.

RESULTS AND DISCUSSION

In Fig. 1 the normalized emission spectra of γ-irradiated (curve *1*) and subjected to optical discolored with UV radiation (curve *2*) samples of LiF–O, OH upon excitation by an LED with $\lambda_m = 397$ nm are presented. As noted above, treatment with UV radiation creates the maximum concentration of the studied color centers.

In the absorption spectrum (Fig. 2a), the bands with $\lambda = 390$ nm (the centers under study), 450 nm (F_3^+), and the band in the region of ≈510 nm are observed, the nature of which was established and discussed in [9]. Recent defects play a significant role in the formation of the studied CCs and will be discussed below. The band of 390 nm has a zero-phonon line 436.55 nm and, probably, its phonon repetitions, which appear in the spectrum as weak peaks at 391.06, 395.83, 407.16, and 421.05 nm. The absorption (390 nm) and emission (490 nm) bands are located symmetrically with respect to the ZPhL position of 436.55 nm. For this line (Fig. 2b) the temperature dependence was plotted, which is shown in Fig. 2e, using the measurement data (Figs. 2c and 2d).

The presence of ZPhL in the centers under study makes it possible to estimate the magnitude of the electron – phonon coupling and determine the type of center by its magnitude. In the temperature dependence $\ln(I_0/I)$ (Fig. 2e), two straight lines can be distinguished in the low-temperature region with parameter $S_1 = 4.3$ and in the high-temperature region (55–77 K) with $S_2 = 27$. The obtained values of the coupling force indicate that in the high-temperature region, defects with strong coupling ($S_2 = 27$) with phonons of the lattice appear, and in the low-temperature region with weak coupling ($S_1 = 4.3$). Comparing the obtained values with the coupling force of the electronic transition with the phonons of the lattice for different CCs in LiF crystals, given in the Table 1 [8, 10, 11], we can attribute the weak coupling centers ($S_1 = 4.3$) to F_3-centers. Judging by the tabular data, the factor S for F_3-centers is 3.9, while the value we obtained is $S_1 = 4.3$. The observed difference is within the measurement error (10%). However, the concentration of F_3-centers in oxygen crystals is insignificant and charged F_3^+-centers predominate. Taking into account the presence of a metastable state in the studied CC, we come to the conclusion that other defects are responsible for the blue glow. Metastable states are observed at two-electron centers as a result of population of triplet levels with a total spin quantum number $s = 1$ [6]. In addition, F_3-centers should also be

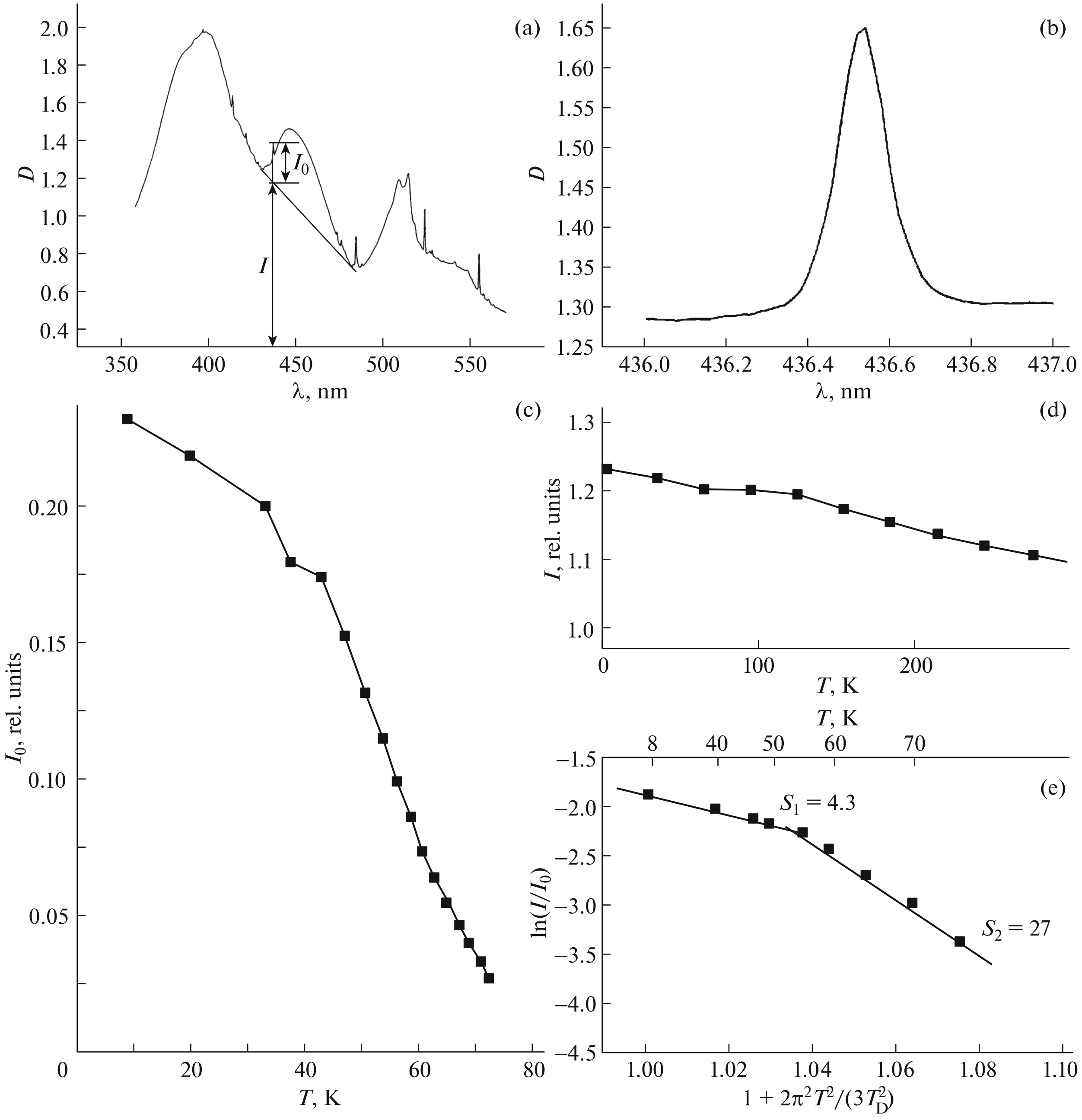

Fig. 2. Absorption spectrum of an irradiated dose of 3×10^3 C/kg (300 K) + 1×10^4 C/kg (273 K) and an optically discolored sample of LiF–O, OH, measured at $T = 7.3$ K, gap 0.5 nm (a). Enlarged ZPhL fragment is 436.55 nm. $T = 7.3$ K. Gap 0.1 nm (b). The temperature dependence of the change in the intensity (I_0) of the ZPhL is 436.55 nm (c); changes in the intensity (I) in the integrated absorption band of 390 nm (d); and the dependence $\ln(I_0/I) = f(1 + 2\pi^2T^2/2T_D^2)$ for the ZPhF of 436.55 nm (e).

observed in the initial γ-irradiated crystal, however, the blue luminescence is effectively induced as a result of optical discoloration of xenon lamps by integrated light (Fig. 1, curve *2*). What happens when optical exposure to UV radiation occurs? The crystal is discolored as a result of the interaction of defects with the interstitial halogen by the reaction

$$F_n + \mathrm{H}(\mathrm{i}_\mathrm{a}^0) \to F_{n-1}.$$

Along with this reaction, the following transformations take place [9]:

$$(F_3^+)^* + \mathrm{Li}^+ \to FV_a^+V_a^+ + \mathrm{Li}^0 \to F_LV_a^+ + V_a^+V_c^-.$$

As a result of this action, the electron density of the F_3^+-center, which is in the excited state, shifts to the nearest lithium cation with the formation of a lithium atom, which is located in the [111] plane. Such a defect

Table 1. The coupling strength of the electronic transition with the phonons of the lattice for various color centers in LiF crystals

Center type	Crystal	I_0/I (4 K)	S
$N_1(F_4)$	LiF	~0.37	1 [8]
$R_2(F_3)$	LiF	0.02	3.9 [8]
F_2^+	LiF	–	21 [10]
F_3^+	LiF	–	9.76 [11]
$M(F_2)$	LiF	3×10^{-4}	8 [8]
F	LiF	$\sim 10^{-17}$	40 [8]

Li^0 in the plane of the F-center is denoted by the symbol $F_L = Li^0 + F$. Conversion of F_3^+-centers to $F_LV_a^+$-centers with an absorption band in the region of 510 nm is observed [9]. Having a positive charge, they capture an electron and transform into two-electron point defects with an absorption band of 390 nm (F_LF) [9].

This model is also supported by the results of electron–phonon interaction with the factor $S_2 = 27$, with strong coupling to the phonons of the lattice. Taking into account that F-centers have $S = 40$, the presence of a lithium atom in the plane of the F-center decreases the electron–phonon interaction of the electronic transition of the complex two-electron center (F_LF).

The presence of a metastable state, the effective formation of the studied defects in optically discolored crystals, the detection of a strong electron–phonon coupling ($S_2 = 27$) allows us to state that F_LF-defects are responsible for the blue glow.

CONCLUSIONS

The value of the coupling force of the electronic transition corresponding to the absorption band of 390 nm with the phonons of the lattice in LiF crystals ($S = 4.3$ and 27) is established. It is shown that, using the parameter S, one can make an assumption about the nature of the unknown color center responsible for the observed electronic transition. In magnitude of S two-electron F_LF-centers with strongly coupling are preferred.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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