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TIME-RESOLVED VACUUM ULTRAVIOLET SPECTROSCOPY OF Er^{3+} IONS IN THE SrF_2 CRYSTAL

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The photoluminescence and photoexcitation spectra as well as the luminescence decay kinetics of Er^{3+} *ions in the visible ultraviolet and vacuum ultraviolet (VUV) regions have been studied by the method of low-temperature, time-resolved VUV-spectroscopy on excitation by synchrotron radiation. In the VUV spectral region of the luminescence of* SrF_2*:1%* Er^{3+}*, the 146.5-nm band with a time of decay of less than 0.6 nsec was revealed together with the well-known emission band at 164.3 nm (decay constant in the microsecond range). Its possible nature is discussed. The specific features of the formation of photoexcitation spectra of the f–f and f–d transitions in the* Er^{3+} *ion are considered. Competition between the processes of excitation of f–f and d–f luminescence has been revealed. It manifests itself in the inverse relationship of their photoexcitation spectra in a range of energies of incident photons that are close to the position of the* $4f^{n-1}5d$ *configuration levels.*

Keywords: *VUV spectroscopy, rare-earth element, strontium fluoride.*

Introduction. At present, among the promising trends in the research on wide-band crystals activated by rare-earth elements (REE), particular attention has been given to VUV spectroscopy, which enables one to study the structure of energy levels and the mechanisms of relaxation of excited high-energy states of REE ions. The investigations in this field have been inspired by the need to create a new class of optical materials active in the VUV range. Such materials are required to develop mercury-free fluorescent lamps and color plasma displays where a discharge with oscillating electrons (Penning discharge) in xenon or neon is used to excite the phosphors of the screen. Compact solid-state lasers operating in the VUV region are called for in the contemporary technologies of photochemistry, isotope separation, thermonuclear synthesis, lithography, etc. In high-energy physics and medical diagnostics (positron-emission tomography), as well as in other fields where one uses registration equipment with a high time resolution based on photodiodes of TMAE or TEA type that are sensitive only to the VUV radiation, fast VUV scintillators are required [1–3].

Crystals of SrF_2 activated by REE have long been known as promising scintillators [4] that possess luminescent-optical as well as physical properties (low refraction index, high radiation resistance, mechanical strength, low hygroscopicity). In this work, we present the results of measuring the spectral and kinetic characteristics of the visible and VUV luminescence of Er^{3+} ions in the SrF_2:1% Er^{3+} system.

Experimental. The SrF_2:1% Er^{3+} single crystals were grown by K. K. Rivkina and E. G. Morozov at the pilot plant GIREDMET (Verkhnyaya Pyshma, Russia) by the Stockbarger method in a fluorinating atmosphere [5].

The photoexcitation and luminescence spectra as well as the kinetics of luminescence decay were measured on selective excitation by synchrotron radiation at the SUPERLUMI station of the laboratory HASYLAB (DESY, Hamburg, Germany). For excitation in a region of 4–25 eV, a 2-m vacuum monochromator with a resolution of 3.2 Å was used. The luminescence in the visible region was registered with the aid of a 0.3-m ARC Spectra Pro-308i monochromator (USA) and an R6358P photoelectric multiplier (Hamamatsu, Japan). In the VUV region, the luminescence was registered with the aid of a 0.5-m vacuum monochromator and an R6836 sun-blind photoelectric multiplier (in spectral measurements) as well as with the aid of a 0.4-m vacuum monochromator (Seya–Namioka scheme) and a microchan-

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nel detector (MCP 1645 U-09, Hamamatsu) (in measurements of the luminescence decay kinetics). The photoexcitation and luminescence spectra were measured both without time resolution (time-integrated) and in time windows of widths Δt_1 = 1.8 nsec (fast component) and Δt_2 = 19.3 nsec (slow component), which are delayed relative to the onset of a synchrotron pulse by δt_1 = 0.6 nsec and δt_2 = 12 nsec, respectively. The photoexcitation spectra are normalized to an equal number of photons incident on a sample, using sodium salicylate. The VUV luminescence spectra are given without correction for the spectral sensitivity of the optical section. The measurements were conducted at T = 8 K in a cryostat that provides an oilless vacuum not worse than $1 \cdot 10^{-7}$ Pa.

Results and Discussion. Interconfiguration radiative transitions in Er^{3+} ions can occur from the lowest levels of the $4f^{10}5d$ configuration to the levels of the ground state $4f^{11}$. The *d-f* transitions from the high-spin state HS ($2S + 1 = 6$) are parity-forbidden and result in the emergence of bands of luminescence with a large decay time. The spin-allowed *d-f* transitions, characterized by a fast kinetics of luminescence decay, occur from the low-spin state LS ($2S + 1 = 4$) having a higher-energy position [6–9]. In most cases (for example, in the $LiYF_4$, BaY_2F_8, and YF_3 crystals), the spin-allowed and spin-forbidden radiative *d–f* transitions are manifested simultaneously [8–10]. The presence of radiationless cross-relaxation between the excited LS and HS states of Er^{3+} ions can lead to the absence of the fast luminescence related to the transitions $4f^{10}5d(\mathrm{LS}) \rightarrow 4f^{11}$. Such a nature of VUV luminescence was observed in the matrices of KYF_4 and SrF_2 [10, 11].

In the time-resolved spectra of VUV luminescence of the SrF_2:1%Er^{3+} crystal in the 135–175-nm region at λ_{exc} = 133.7 nm, apart from the known band at 164.3 nm (FWHM = 1470 cm^{-1}) associated with the transition $4f^{10}5d(\mathrm{HS}) \rightarrow {}^4I_{15/2}$ and manifesting itself in the "slow" time window (Fig. 1, curve 1), we succeeded, for the first time for the system $SrF_2:Er^{3+}$, in observing the band at 146.5 nm (FWHM = 1380 cm^{-1}) in the "fast" time window (curve 2). The decay-time constant of this emission, which is determined by the method of calculating a convolution integral, does not exceed 0.6 nsec (Fig. 2). These data confirm the results obtained by us earlier on excitation by ondulator radiation in the region of ultrasoft x-rays with a photon energy of 140 eV in the BW3 channel (HASYLAB, DESY) [12, 13].

The luminescence photoexcitation spectrum at 164.3 nm associated with the spin-forbidden transition $4f^{10}5d(\mathrm{HS}) \rightarrow {}^4I_{15/2}$ is characterized by the most intense bands in the vicinity of 154, 144, and 134 nm (Fig. 1, curve 3). The low-intensity band at 159 nm corresponds to the spin-forbidden transition ${}^4I_{15/2} \rightarrow 4f^{10}5d(\mathrm{HS})$ and to the onset of luminescence excitation at 164.3 nm. We also note the presence of weak-intensity bands in the spectrum at 129 and 139 nm. In the region 119–127 nm corresponding to the longwave edge of the fundamental absorption of the SrF_2 crystal (E_g = 11.2 eV [14]), luminescence at 164.3 nm is excited to be of less intensity than on direct optical excitation of an impurity center. On further decrease in the wavelength of incident photons down to 60 nm, the luminescence is not excited during the transition $4f^{10}5d(\mathrm{HS}) \rightarrow {}^4I_{15/2}$ (this region is not shown in the figure).

The weak band at 159 nm in the luminescence photoexcitation spectrum during the transition $4f^{10}5d(\mathrm{HS}) \rightarrow {}^4I_{15/2}$ corresponds to the spin-forbidden *f–d* transition and, in accordance with Hund's rule, to the lowest-energy state of the $4f^{10}5d$ configuration of the Er^{3+} ion in SrF_2, and the intense band at 154 nm corresponds to the onset of the spin-allowed *f–d* transitions. The Stokes shift for the excited low-spin state of the $4f^{10}5d$ configuration of the Er^{3+} ion in SrF_2 is estimated by us to be about 1750 cm^{-1}. By assuming the equality of the Stokes shifts for the excited and quartet and sextet states, one may expect the emergence of a band of *d–f* luminescence with fast kinetics of decay in the region 155–158 nm — the band which is due to the spin-allowed *d–f* transition from the excited lowest state LS. However, this band has not been revealed in our experiments, just as it has not been revealed in the spectrum of $SrF_2:Er^{3+}$ in [10]. This is related to the presence of the strong radiationless cross-relaxation between the LS and HS levels of Er^{3+} in SrF_2, the energy difference between which is about 2100 cm^{-1}, which is considerably less than, for example, in the $LiYF_4$ crystal, where both radiative *d–f* transitions are observed and the difference indicated amounts to 3335 cm^{-1} [15].

The energy difference between the maxima of the bands of the "slow" luminescence at 164.3 nm ($4f^{10}5d(\mathrm{HS}) \rightarrow {}^4I_{15/2}$) and "fast" luminescence at 146.5 nm is about 7340 cm^{-1}. It is obvious that the band of the "fast" luminescence at 146.5 nm cannot be assigned to the transition from the excited lowest levels of the $4f^{10}5d$ configuration. The photoexcited spectrum of this luminescence measured in the "fast" time window is represented by a broad band with a maximum at 133.5 nm (Fig. 1, curve 4). The longwave edge of this band coincides with that of the band at 134 nm in the photoexcited luminescence spectrum associated with the spin-forbidden transition $4f^{10}5d(\mathrm{HS}) \rightarrow {}^4I_{15/2}$.

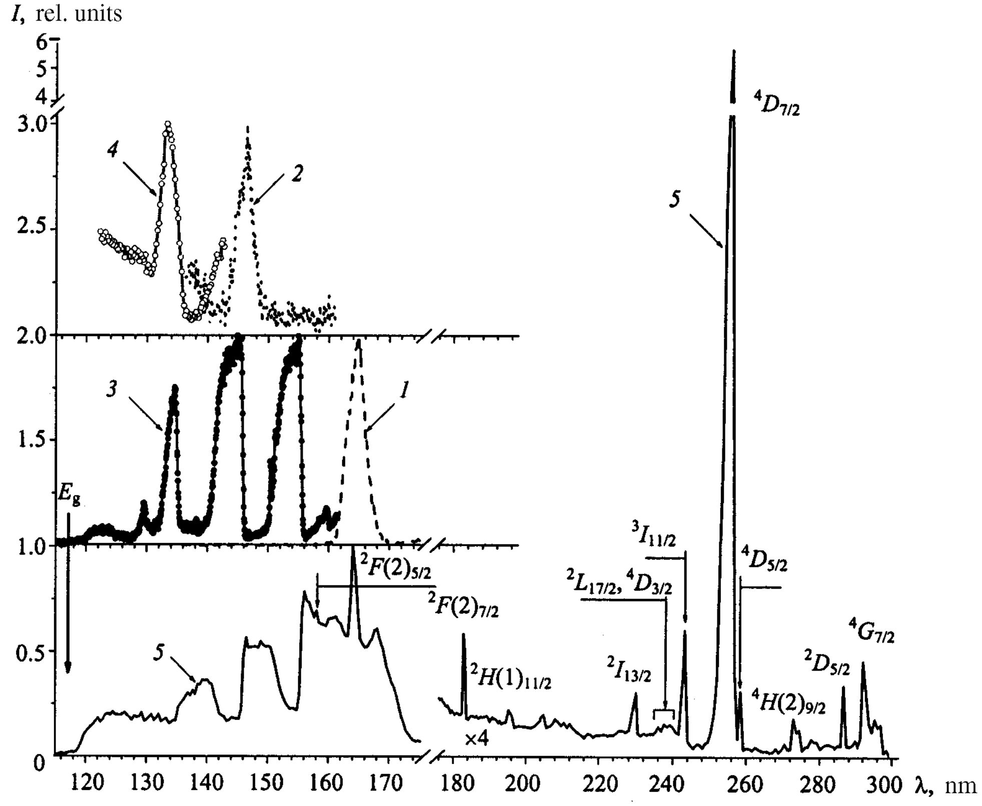

Fig. 1. Luminescence spectra of SrF_2:1%Er^{3+} in "slow" (1) and "fast" (2) time windows on excitation by 133.7-nm photons; spectra of photoexcited luminescence at 164.3 nm in the "slow" time window (3), at 146.5 nm in the "fast" time window (4), and at 551 nm without time resolution (5); T = 8 K.

Based on the foregoing, it may be suggested that the observed fast emission at 146.5 nm in SrF_2:Er^{3+} is most likely due to a higher-lying radiative level of the $4f^{10}5d$ configuration with a low spin. It is also possible that the reason for such fast kinetics of luminescence decay has to do with additional channels of relaxation of the excited state with participation, for example, of the high-energy states of the $4f^{11}$ configuration; however, this mechanism usually takes place at high concentrations of impurity. Moreover, we cannot exclude the participation of the processes associated with charge transfer in the formation of this luminescence.

The known luminescence band at 550 nm of the Er^{3+} ion, which is caused by the intraconfiguration transition $^4S_{3/2} \rightarrow {}^4I_{15/2}$, is excited in the region of the crystal transparency and longwave edge of fundamental absorption (Fig. 1, curve 5). The photoexcitation spectrum of this luminescence is represented by a number of narrow lines of the f–f transitions that are identified by us according to the calculated and experimental data on the energy levels of the $4f^{11}$ configuration of the Er^{3+} ion in $LiYF_4$ [16, 17]. In the UV region of the spectrum, transitions to the following multiplet levels are observed: $^4G_{7/2}$(292), $^2D_{5/2}$(287), $^2H(2)_{9/2}$(273), $^4D_{5/2}$(259), $^4D_{7/2}$(256), $^2I_{11/2}$(243), inseparable $^2L_{17/2}$ and $^4D_{3/2}$(235–241), and $^2I_{13/2}$(230 nm). In the VUV region the lines of transitions to the multiplets $^2H(1)_{11/2}$(195) and $^2F(2)_{7/2}$(183 nm) are well defined. The band associated with the transition to the level $^2F(2)_{5/2}$ and mentioned in [17] is slightly exhibited in our case at 158 nm against the background of the broad nonelementary band 155–173 nm. The latter has a complex structure, wherein an intense narrow line stands out at 164.3 nm. On decrease in the wavelength of incident photons, broad 145–153- and 134–142-cm bands are seen in the photoexcited spectrum.

In the region adjacent to the fundamental absorption edge as well as at high energies of incident photons, the spectrum of the photoexcited f–f luminescence at 551 nm is similar to that of the d–f luminescence at 164.3 nm associated with the transition $4f^{10}5d$(HS) $\rightarrow {}^4I_{15/2}$. The low intensity of excitation of the f–f and d–f luminescence in the

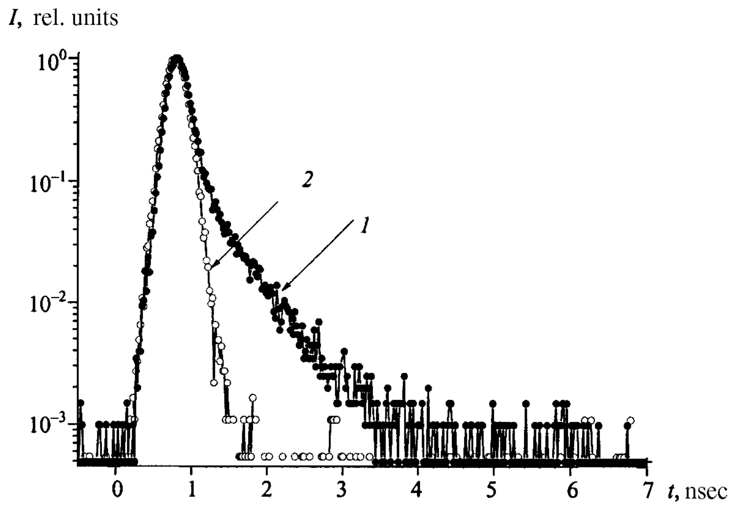

Fig. 2. Kinetics of the 146.5-nm luminescence decay (1) of SrF_2:1%Er^{3+}; excited by a synchrotron pulse (instrument function) (2); $T = 8$ K.

region of the longwave fundamental absorption edge and the absence of this excitation at energies exceeding the band gap E_g of the crystal up to the region of photon multiplication mean a low efficiency of energy transfer by the electron–hole mechanism as well as a small degree of the participation of excitons in the processes of energy transfer to the levels of the $4f^{10}5d$ configuration of the Er^{3+} ion in SrF_2.

The reason for the more effective excitation of the *f–f* luminescence in the region of the longwave fundamental absorption edge, as compared to the *d–f* luminescence, can be associated with the presence of the process of autoionization, the initial act of which is the formation of the Ln^{4+} ion. The further capture of a free electron is described by the model of an exciton localized at the impurity center Ln^{4+}+e^-. The predominant way of relaxation of the autoionization state is the energy transfer to the levels of the $4f^n$ configuration through the dipole–dipole interaction [18].

We call attention to the fact that in the region 126–161 nm the spectra of the photoexcited *d–f* luminescence during the transition $4f^{10}5d(HS) \rightarrow {}^4I_{15/2}$ and *f–f* luminescence during the transition ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ are inversely related. Moreover, note should be made of the presence of the intense broad nonelementary band 155–173 nm in the spectrum of the photoexcited *f–f* luminescence. The narrow line at 164.3 nm in the structure of this band corresponds to the position of the maximum of luminescence in the course of $4f^{10}5d(HS) \rightarrow {}^4I_{15/2}$ (Fig. 1, curve 5). The characteristic features listed reflect the existence of a pronounced competition between the processes of intracenter energy relaxation in the Er^{3+} ions in SrF_2 when excited to radiative levels of the $4f^{10}5d$ and $4f^{11}$ configurations. Such behavior of the spectra of the photoexcited *f–f* and *d–f* luminescence is, however, not typical of the Er^{3+} ion in other matrices (see, for example, [19]). Obviously, in the system SrF_2:1%Er^{3+} the process of relaxation of the excited states of the $4f^{10}5d$ configuration is accompanied by a strong dipole–dipole interaction between the excited levels of the $4f^{10}5d$ configuration and the electron continuum of the $4f$ shell of the Er^{3+} ion.

Conclusions. In the low-temperature spectra of VUV luminescence of SrF_2:1%Er^{3+}, apart from the known band at 164.3 that is due to the transition $4f^{10}5d(HS) \rightarrow {}^4I_{15/2}$, a new band at 146.5 nm ($\tau < 0.6$ nsec) has been revealed, which is most likely associated with the transition from one of the high excited states of the $4f^{10}5d$ configuration. Competition between the processes of excitation of the *f–f* and *d–f* luminescence of the Er^{3+} ions in SrF_2 has been established. This competition is exhibited by the inverse relationship of their photoexcited spectra in a region of the energies of incident photons which are close to the position of the levels of the $4f^{10}5d$ configuration. This phenomenon is unique and has been observed earlier for Er^{3+} in other matrices.

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