The luminescence spectroscopy and theoretical study of 4f-5d transitions of Ce^{3+} ions in SrAlF_5 crystals

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Abstract. The present research is focused on the 4f-5d transitions in Ce^{3+} centers doped into tetragonal $\beta\text{-SrAlF}_5$ single crystals belonging to $I4_1/a$ space group. The presence of 4 non-equivalent Sr^{2+} sites in this compound leads to appearance of 3 spectroscopically non-equivalent Ce^{3+} luminescence centers, which can be well distinguished using time-resolved laser spectroscopy technique. All 4f-5d transitions have slightly varying excitation and emission energies with the characteristic probabilities resulting in several decay times determined experimentally. One of these centers experiences strong perturbation due to a defect nearby, probably the O^{2-} impurity ion substituting F^- ion and acting as charge compensator as well. Identification of these photoluminescence centers is performed using crystal field calculations. The crystal field parameters are calculated for two identified centers using the structural data for SrAlF_5 ; diagonalization of the crystal field Hamiltonian results in getting the splitting of the Ce^{3+} 5d states. This method allowed assigning of “regular” unperturbed Ce^{3+} centers with selected Sr^{2+} sites.

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1. Introduction

Recently $SrAlF_5$ (SAF) crystals have been identified to be among the most promising candidates for the realization of all-solid-state lasers and other non-linear optical applications, whose working range extends to the ultraviolet and vacuum ultraviolet (VUV) part of spectrum. Understanding the exact structure, symmetry of crystallographic sites and etc. of this promising host is of crucial importance for developing of applications. However, still there is no common opinion about detailed structure of tetragonal β - $SrAlF_5$ crystals. In several papers devoted to structural studies [1, 2, 3] it has been shown that the suggested space group for this compound is $I4_1/a$. This space group contains an inversion center and therefore ferroelectric properties in this compound are essentially forbidden. However, in some successful studies of ferroelectric properties of this host [4, 5], in agreement with an early work [6] it was suggested that this compound belongs to the $I4$ space group without an inversion center. For the detailed description of these controversial points of view we refer to the publication [3]. In that work the samples of the the same origin, that those investigated in the present work, were identified as belonging to the $I4_1/a$ group. Therefore, further in this paper under the general name $SrAlF_5$ (SAF) we assume tetragonal crystal β - $SrAlF_5$ belonging to $I4_1/a$ space group.

It has been shown previously that $SrAlF_5$ is highly transparent down to the cutoff wavelength near 150 nm. Recently the actual energy gap of SAF was estimated to be 12.3 eV [7]. As already discussed earlier, the crystal structure is very complex, having 64 formula units per one unit cell, and each ion in this compound occupies several non-equivalent crystallographic positions. For Sr^{2+} ions, which are known to be substituted with lanthanide ions in doped compounds [7], the number of non-equivalent positions is 4. The nearest environment of these ions has low symmetry with 8 to 9 fluoride ions in the first coordination sphere. Such structural properties make this compound interesting for studying 4f-5d transitions of lanthanides in this host. However, not so many studies have been devoted to spectroscopy of rare earth ions in $SrAlF_5$ host lattice. Namely, photon cascade emission in the $Pr^{3+}:SrAlF_5$ system [8, 9], luminescence of Sm^{2+} [10] and Gd^{3+} [11, 12] ions have been investigated. Some properties of Ce^{3+} [13] were reported, confirming that analogously to $Ce:LiCaAlF_6$ [14] the $Ce:SrAlF_5$ has future as material for femtosecond pulsed lasers tunable in UV. Our own previous investigations concerned the role of lattice defects, behavior of electronic excitations and energy transfer processes in pure and doped $SrAlF_5$ crystals [7, 15]. The presence of several PL centers emitting near 4 eV due to 5d-4f transitions of Ce^{3+} ions substituting for non-equivalent Sr^{2+} sites was revealed, but the spectroscopic properties of those various non-equivalent Ce^{3+} centers were not analyzed in detail yet. However, as the lasing process is closely related to the properties of dopant centers, the main goal of the present paper is to study the luminescence of Ce^{3+} ions under direct intra-center excitation, identify non-equivalent Ce^{3+} centers and the splitting of 5d states by crystal field calculations, and discuss the future applications prospects of SAF:Ce crystals as a laser material in sight of results

of the present work.

The structure of the paper is as follows: in the next sections we describe the experimental part (laser and synchrotron radiation measurements), then we proceed with a description of the crystal field calculations and comparison of their results with experimental data, and finally we conclude a paper with a short summary.

2. Experiment details

2.1. Laser spectroscopy

The photoluminescence (PL) spectra (shown only on figure 1) and decay kinetics under laser excitation was measured using a Shamrock SR-303i spectrometer, where the Andor DH-501 ICCD camera cooled by Peltier thermoelectric device to $-15^{\circ}C$ is used as a detector. This ICCD camera has been used successfully in the time resolved study in [16]. The time resolved PL spectra were measured in the time window with the length of 200 ns and delayed by 20 ns relative to the exciting laser pulse. This allowed registering only Ce^{3+} emission, without significant contribution either from other slow emissions or of fast laser excitation pulse. For PL decay kinetics measurements in nanosecond range the second output of the spectrograph was equipped with Hamamatsu H3177-51 PMT working in current mode. The signal from PMT was digitized by Tektronix TDS 380 oscilloscope. The curves obtained for different laser shots were further summated by a computer program.

As the UV excitation source an optical parametric oscillator (OPO) *NT 342/1/UVE (EKSPLA, Lithuania)* was used, pumped by YAG:Nd laser. It generates short (5 ns) monochromatic ($FWHM < 5 \text{ cm}^{-1}$) pulses of radiation with variable energy of photons covering energy range 0.6 - 6.0 eV. The pulses repetition rate was 10 Hz. The laser radiation intensity illuminating the sample was regulated by a set of color filters and polarization filter with variable transmittance. Typically the average energy of one laser pulse was in the range of 1 - 3.5 $\mu J/mm^2$, depending on the used filters and wavelength. For measurements at low temperatures (down to 5 K) the sample was mounted into an immersion Utreks-type liquid helium cryostat.

2.2. Synchrotron radiation spectroscopy

PL excitation spectra in the range of 4-7 eV and PL decay kinetics at $E_{exc} > 6 \text{ eV}$ were recorded using synchrotron radiation excitation (SR) at the SUPERLUMI station (Beam-line I of HASYLAB at DESY) [17]. The 0.3 m ARC Spectra Pro-308i spectrometer equipped with a R6358P (Hamamatsu) photomultiplier was used as the registration system. The convolution method was used to analyze fast components of the PL decay kinetics. The time resolution of the whole detection system was 1 ns (FWHM).

Figure 1. The photoluminescence spectra of Ce:SAF at 10 K recorded in time resolved mode under laser excitation. Thin green lines show decomposition of emission spectra into Gaussian bands.

Figure 2. The photoluminescence excitation spectra of various Ce^{3+} emissions in the range of 4-7 eV at $T = 8.5$ K: $E_{exc} = 3.8$ eV (1), $E_{exc} = 4.0$ eV (2), $E_{exc} = 4.2$ eV (3) $E_{exc} = 4.5$ eV (4). The arrows show the excitation wavelengths (in nm units) for which the PL emission spectra were recorded using laser excitation.

2.3. Samples

All examined single crystals have been grown from the melt in the Institute of Geology and Mineralogy SB RAS (Novosibirsk, Russia) using the Bridgman technique. AlF_3 (99.99 %) and SrF_2 (99.99 %) were used as starting reagents. CeF_3 was added as a dopant with concentration of 0.5 mol% ($1.5 \cdot 10^{20}$ at/cm³). Due to high volatility of AlF_3 it was added with a 2% excess to the initial mixture of chemicals. A surplus pressure under the N_2 filling of ampoules suppressed sublimation. All operations were performed in dry atmosphere to avoid contamination by oxygen and related impurities. Growth process was carried out in a specially treated glass-graphite container, which was placed inside a silica ampoule. The latter was inserted into a two-region furnace: a melt temperature was hold at 890 C, a temperature gradient near the crystallization zone was 10 to 20 degrees/cm. CF_4 (99.99 %) was added into reactor as an F-agent. Deviation from the stoichiometry was studied by XRF (using energy-dispersion spectrometer) as well as using the differential dissolving technique combined with inductively coupled plasma methods. The analysis confirmed that the composition of crystals grown was practically stoichiometric.

3. Experimental results and discussion

Figure 1 depicts several PL spectra of SAF:Ce recorded in the fast time window at different laser excitation energies, selected according to the maxima in the PL excitation spectra, shown by arrows on figure 2. Decomposition of the luminescence spectra into single Gaussians showed that the number of emission bands is up to 4, peaked at 3.85, 4.05, 4.27 and 4.50 eV. The position of the peaks and their width (here and below FWHM is supposed) do not change significantly while varying excitation energy. For the 3.85 eV peak the FWHM equals to 0.4 eV and for other bands these values are in the range of 0.15 - 0.19 eV.

The PL decay curves were also recorded for each emission peak at all examined excitation energies (see examples on figure 3). Not only the decay times are different but the slower rise time at certain curves is noticeable as well. However, the analog bandwidth of used detection system (400 MHz) is too low to perform rise time analysis.

Figure 3. The photoluminescence decay curves of various Ce^{3+} emission bands at $T=10$ K $E_{exc}=4.95$ eV: Decay of PL center (a) at $E_{em}=3.79$ (1), center (b) at $E_{em}=4.02$ (2), and (c) at $E_{em}=4.27$ (3) and 4.47 (4) eV; the shape of laser pulse at $E_{exc}=4.86$ eV (5).

The numerical values of decay constants were obtained by fitting with the convolution of multiexponential functions and the excitation pulse curve. The longest component of each recorded curve having decay time in the range 20-40 ns was assigned to cerium emission (table 1 - upper part). Some curves had shorter components in the decomposition as well (1-12 ns), which can appear due to small instability of laser pulse shape. The lower part of this table has been reproduced from our earlier study [15], where the decay kinetics was investigated under VUV excitation corresponding to the indirect excitation of Ce^{3+} . Some of the decay curves (having close decay times) practically match while plotted, and therefore can be reliably assigned to the same PL center (see figure 3, curves 3 and 4 for example). The conclusions on the amount of PL centers and their decay constants were based on this assumption (denoted with the letters in table 1). As it is practically impossible to distinguish components with close decay times in one curve, overlapping of bands results in an average value between two mixing components (indicated by ‘+’ sign in table 1).

As it was already discussed, the UV emission bands in the PL spectra of $Ce:SrAlF_5$ are assigned to 5d-4f transitions of Ce^{3+} ions substituting Sr^{2+} ions in several non-equivalent sites of the host crystal lattice. So, the revealed peaks in the 4.2-5.8 eV energy range in the PL excitation spectra (see figure 2) correspond to the interconfigurational transitions from the ground 4f level to the $4f^05d^1$ configuration. The results of the laser spectroscopy allow distinguishing of 3 non-equivalent luminescence centers with different emission energies and probabilities of radiative transitions. By choosing proper excitation energy, we were able to prove that each of 3 Ce^{3+} centers possesses doublet structure, due to splitting of 4f ground state to $^2F_{5/2}$ and $^2F_{7/2}$ energy levels of Ce^{3+} ion with typical value of ~ 2000 cm^{-1} in various hosts [18]. Summarizing the luminescence data with decay kinetics analysis shown in table 1 we identified the following Ce^{3+} centers designated by letters from a to c:

- a) The center emitting at 3.79 eV and 4.02 eV, decay time $\tau = 36$ ns;
- b) The center emitting at 4.02 and 4.27 eV, $\tau = 28$ ns;
- c) The center emitting at 4.27 and 4.47 eV, $\tau = 25$ ns;

The higher lying 5d states can overlap with the conduction band states, and therefore the shortening of the decay time may occur at higher excitation energies (see middle part of table 1), which can be explained by autoionization of Ce^{3+} 5d excited states. Further studies are required to locate the 4f and 5d levels position relative to the top of the valence band according to [19].

As figure 1 demonstrates clearly, the emission bands of different PL centers are strongly overlapping. Thus only for the center (c) emitting at $E_{em}=4.47$ eV a “pure”

Table 1. The PL decay constants of SAF:Ce (ns) at different excitation and emission energies (T = 10 K). Small letters in the brackets show assignments to various Ce^{3+} centers – see details in text.

Excitation energy, eV (wavelength,nm)	Emission energy, eV (wavelength, nm)			
	3.79 (327)	4.02 (308)	4.27 (290)	4.47 (277)
Direct intra-centre excitation (using laser source)				
4.62 (268)	35.3 (a)	34.7 (a)	No emission	No emission
4.86 (255)	32.0 (a+b)	28.6 (b)	27.8 (b)	25.7 (c)
4.95 (250)	38.4 (a)	31.5 (a+b)	27.3 (b+c)	24.1 (c)
5.14 (241)	40.7	29.2 (b)	28.8 (b)	26.0 (c)
5.41 (229)	40.3	31.2 (a+b)	28.8 (b)	26.8 (c)
5.84 (212)	36.3 (a)	30.0 (b)	26.0 (b+c)	25.9 (c)
Direct intra-centre excitation(using synchrotron radiation source)				
6.49 (191)	38	26	21	21
6.70 (185)	33	30	22	21
Indirect excitation (using synchrotron radiation source reported in [15])				
8.2	30	27	24	24
9.7	30	27	24	24
10.4	29	26	23	23
11.3	28	24	21	19
12.7	18	21	17	13

Figure 4. The PL excitation spectrum of 4.5 eV emission at T = 8.5 K representing the (c) center. The decomposition of excitation bands into Gaussians is shown. The bars represent the calculated splitting of 5d states of Ce^{3+} ions substituted into different non-equivalent positions (refer to part 4 for details)

Figure 5. The PL excitation spectra of 4.2 eV emission at T = 8.5 K. The decomposition of excitation bands into Gaussians is shown: green Gaussians have the same positions as in the decomposition shown on figure 4, whereas the “new” bands are shown in blue.

Figure 6. The difference spectrum between excitation spectra of 3.8 eV and 4.0 eV emissions (see text for details) and its decomposition into Gaussians. This curve represents excitation spectrum of the (b) center. The bars represent the calculated splitting of 5d states of Ce^{3+} ions substituted into different non-equivalent positions (refer to Part 4 for details)

excitation spectrum was recorded (see figure 2). The spectrum recorded at $E_{em}=4.2$ eV is a superposition of (b) and (c) centers, while at $E_{em}=4.0$ eV – (b) and (a) centers, respectively. The spectrum at $E_{em}=3.8$ eV can be in principle a “pure” spectrum of (a) center, but the emission energy of (c) is high enough for enabling radiative energy transfer between centers $(c) \Rightarrow (a)$. This position is supported by slight increase (up to 40 ns) of decay constant of (a) center under direct excitation into higher lying 5d states (table 1). Therefore, much care should be applied while analyzing excitation spectra. We applied decomposition procedure in the same manner as of PL emission spectra for some excitation spectra, with results shown on figures 4-6. It is obvious, that the excitation spectrum of the 4.5 eV emission (see figure 4) shows all characteristic features of Ce^{3+} ions in wide gap hosts, well described in literature [18]. It consists of 5 broad bands peaked at 5.01, 5.41, 5.88, 6.10 and 6.53 eV due to interconfigurational $4f^1 - 4f^05d^1$ transitions. The degeneracy of 5d states is removed completely by low symmetry crystal field. The widths of the bands (except the 6.53 eV, which is broader) are approximately equal with the value of 0.2 eV. This data allows to calculate such parameters of this Ce^{3+} site as a centroid shift and crystal field shift, as described in [20]. The results are presented in table 2. The decomposition of the excitation spectrum of 4.27 eV band is not so straightforward (see figure 5). Among previously mentioned excitation bands, some new ones are obviously present. The Gaussian peak at 4.65 eV (not shown in decomposition) originates from the overlap with the (c) center emission, while 4.84, 5.16 and relatively weaker 6.32 eV peaks belong to the center (b), because their widths are smaller (approx. 0.10 eV). The two “old” (from figure 4) bands at 5.41 and 5.88 eV are broadened, indicating the probable overlap with the excitation bands of (b) and (c) centers in these positions. An attempt to obtain a “pure” excitation spectrum of (b) center was performed. The intensities of excitation spectra recorded at $E_{em}=4.0$ eV and $E_{em}=3.8$ eV were normalized at the 4.6 eV peak (corresponding to center (a) emission), thereafter the latter spectrum was subtracted from the first one and the result is shown on figure 6. It comprises of five peaks, which coincide with ones attributed to center (b) in the excitation spectra of 4.27 eV band. Therefore, we can consider it as a “pure” excitation spectrum of this center. Using the positions of the peaks, the centroid and crystal field shift were calculated for this center as well, shown in table 2. At the excitation spectrum of center (a) all the higher-energy peaks are significantly broadened, smoothed and hardly distinguishable. Such behavior is partly assigned to the probable radiative energy transfer process from (c) center as was described above. It can be also due to the assumption that higher 5d energy states lie already in the conduction band, and partly due to the reasons, which will be discussed in the next paragraph. However, interpreting the peaks at 4.62, 5.04, 5.84, 6.34 and 6.7 eV as the excitation bands of center (a), it is possible to obtain its parameters listed in table 2 for this center as well. However, we admit these values are less reliable than those for other centers.

The properties of PL center (a) are significantly different than that of the others. It has wider PL emission band and longer decay time. This type of Ce^{3+} luminescence

Table 2. The Ce^{3+} site parameters calculated according to the methodology described in [20]. The accuracy of the values (both due to finite experimental resolution and Gaussian fitting error) is estimated as 100 cm^{-1} . Values in brackets are taken from the spectrum maxima and therefore are less reliable (see text for details).

Parameter	units	PL center notation		
		(a)	(b)	(c)
Highest f-d excitation band	eV	(6.68)	6.35	6.53
(vibronic band center)	cm^{-1}	53880	51220	52670
Second band	eV	(6.36)	5.86	6.17
	cm^{-1}	51300	47260	49800
Third band	eV	(5.92)	5.46	5.89
	cm^{-1}	47750	44070	47470
Fourth band	eV	(4.90)	5.17	5.41
	cm^{-1}	39520	41670	43670
Lowest excitation band	eV	4.63	4.84	5.01
	cm^{-1}	37340	39060	40420
Highest d-f emission	eV	4.05	4.28	4.49
(vibronic band center)	cm^{-1}	32670	34520	36210
Stokes shift	cm^{-1}	4680	4600	4280
Redshift	cm^{-1}	12000	10280	8920
Crystal field shift	cm^{-1}	8610	5590	6390
Crystal field splitting	cm^{-1}	16530	12150	12260
Centroid	cm^{-1}	45960	44650	46800
Centroid shift	cm^{-1}	5270	6580	4430

center is usually referred in literature as “perturbed”, and consist of cerium ion with a defect nearby. The origin of this perturbing defect in Ce:SAF, however, is not clarified yet. For Ce:LaF₃ [21], a fluorine vacancy is reported to be the most probable “perturber”. However, in our case this is not favorable, because Ce^{3+} substitutes for Sr^{2+} and the compensation of excess positive charge is required, whether anion vacancy would introduce an additional positive charge. Expecting the perturbing defect to be a charge compensator at the same time, it can be either cation vacancies V_c^{2+} (or even V_c^{3+}), anion interstitial or an oxygen impurity. Both latter cases were analyzed for Ce:CaF₂ [22], where it has been shown, that anion interstitials do not cause significant perturbation to Ce^{3+} ions being situated in its second coordination sphere. In a high symmetry crystal (as CaF₂) the position of interstitial can change the symmetry of a PL centers and thus lead to creation of different types of a latter ones, but in our low-symmetry

surrounding this effect should not be noticeable. In the work [3], which describes the growth of a samples used in the present investigation, it is noted that certain crystal growth conditions lead to creation of aluminum oxyfluoride (AlOF) crystal phase in addition to the main $SrAlF_5$ phase. This proves that despite the special measures performed to prevent oxygen contamination, a noticeable amount of this impurity can be incorporated into crystal. That makes possible the charge compensation of Ce^{3+} by O^{2-} -ion substituting F^- position, which is more likely to be located in the first coordination sphere. It was shown that this kind of perturbation influences properties of PL center exactly in a way found in the present study: the PL bands are shifted to the red, one of them is broadened, and the first PL excitation band is shifted to lower energies as well [22].

Comparing the values of parameters in table 2 for different centers, one can see that for (a) and (c) centers these values are in agreement with the trends described in [20]. The low symmetry of Ce^{3+} sites and the presence of a small-sized Al^{3+} cation lead to relatively small centroid shift (4430 cm^{-1}) of “regular” (c) center as well as small crystal field splitting (12260 cm^{-1}). Thus, the relative strength of crystal field is low. Introduction of crystal field perturbation by a defect increases both of these parameters for (a) center to 5270 and 16530 cm^{-1} , respectively. However, (b) center has abnormally high for fluorides centroid shift (5590 cm^{-1}), whereas crystal field splitting remain rather low (12150 cm^{-1}), which together are responsible for a quite usual redshift. The reasons for such high centroid shift require further investigations. The deviations from general trends based on semi-empirical approach as described in (see [20] and references therein) can be possible.

The results obtained are important from practical point of view. For the design of all-solid-state femtosecond Ce^{3+} -based tunable pulsed lasers the YAG:Nd laser was proposed as a pumping source [13]. Its fourth harmonic has the wavelength of 266 nm , which is very close to the absorption maximum of (c) center (268 nm). As the PL band of this “perturbed” center is the widest, the use of such pumping can lead to a better tunability than for the other centers, as well as for $Ce:LiCaAlF_6$ host [14]. Thus, further research on the nature of (c) center is important, and understanding the type of its “perturbing” defect may lead to creating crystals, in which this type of PL centers dominates.

4. Crystal field calculations of the Ce^{3+} 5d levels splitting in $SrAlF_5$

Energy levels of an impurity ion in a crystal can be determined as the eigenvalues of the following crystal field Hamiltonian:

$$H = \sum_{p=0}^{2l} \sum_{k=-p}^p B_p^k O_p^k \quad (1)$$

where O_p^k are the suitably chosen linear combinations of the irreducible tensor operators acting upon the angular parts of the impurity ion’s wave functions. The B_p^k entries are

the crystal field parameters (CFPs), which can be calculated directly from the crystal structure data. The index of summation p takes all even values from 0 to $2l$, with l being the orbital quantum number of electrons in the unfilled shell of an impurity ion.

In the exchange charge model (ECM) of crystal field, the CFPs B_p^k are represented as a sum of two different contributions [23]:

$$B_p^k = B_{p,q}^k + B_{p,S}^k \quad (2)$$

where

$$B_{p,q}^k = -K_p^k e^2 \langle r^p \rangle \sum_i q_i \frac{V_p^k(\theta_i, \phi_i)}{R_i^{p+1}} \beta_p(R) \quad (3)$$

$$B_{p,S}^k = -K_p^k e^2 \frac{2(2p+1)}{5} \sum_i (G_s S(s)_i^2 + G_\sigma S(\sigma)_i^2 + \gamma_p G_\pi S(\pi)_i^2) \frac{V_p^k(\theta_i, \phi_i)}{R_i^{p+1}} \quad (4)$$

The first term $B_{p,q}^k$ is the point charge contribution to the CFPs, which describes the electrostatic interaction between the central ion and the crystal lattice ions enumerated by the index i with charges q_i and spherical coordinates, R_i, θ_i, ϕ_i (in the reference system centered at the impurity ion itself). The averaged values $\langle r^p \rangle$ of the radial coordinate of electrons from an unfilled shell of the impurity ion can be easily calculated numerically, using the radial parts of the corresponding ion's wave functions. The values of the numerical factors K_p^k, γ_p , the expressions for the polynomials V_p^k and the definitions of the operators O_p^k can all be found in Ref. [23]. The β_p coefficients are related to the extended distribution of the 5d states of a rare earth ion [24, 25]. The second term $B_{p,S}^k$ given by equation (4) is proportional to the overlap between the wave functions of the central ion and ligands (different s-, p-, and d-states are considered here), thus distinguishing between different quantum mechanical states of interacting ions and including into consideration all covalent effects. The $S(s), S(\sigma), S(\pi)$ entries in equation (4) correspond to the overlap integrals between the d -functions of the central ion and p -, s -functions of ligands: $S(s) = \langle d0|s0 \rangle, S(\sigma) = \langle d0|p0 \rangle, S(\pi) = \langle d1|p1 \rangle$, (here the $\langle lm|$ notation is employed, where l and m are the orbital and magnetic quantum numbers, respectively). The G_s, G_σ, G_π entries are the dimensionless adjustable parameters of the model, whose values are determined from the positions of the first three absorption bands in the experimental spectrum by a direct matching the calculated energy levels to those deduced from the experimental spectra.

The ECM has been successfully applied to the calculations of the 5d states of rare earth ion in crystals and modeling of the 4f-5d absorption spectra for Ce^{3+} in $LiYF_4$ [25, 26] and Gd^{3+}, Lu^{3+} in several fluorides [27].

When calculating the CFPs values, special attention should be paid to the convergence of the crystal lattice sums, especially of the second rank, which depend on distance as $1/R^3$. To ensure convergence, a large cluster consisting of 21176 ions was generated using the crystal structure data for $SrAlF_5$ from Ref. [1].

The overlap integrals between the 5d states of Ce^{3+} and 2s, 2p states of F^- were calculated numerically using the Ce^{3+} 5d wave functions from Ref. [28] and the F 2p,

Table 3. Calculated crystal field splitting of the 5d energy levels (all in cm^{-1}) for four possible Ce^{3+} positions (corresponding to four Sr^{2+} sites) in $SrAlF_5$. Calculation is given for experimental excitation spectra of both (c) and (b). The parameters for actually identified positions are shown in bold. The enumeration of Sr^{2+} sites is according to [1].

For (c) experimental data				For (b) experimental data			
Sr-1	Sr-2	Sr-3	Sr-4	Sr-1	Sr-2	Sr-3	Sr-4
40528	40528	40528	40528	39313	39313	39313	39313
42804	42179	42074	42304	41812	41372	41068	41054
47410	48219	44794	46661	46679	45920	44109	45671
49439	50863	47837	50894	48276	48816	47074	49925
52756	52748	52764	52753	51888	51888	51888	51888

2s functions from Ref. [29]. For a convenience of application, they were approximated by the following exponential functions of distance R ($5 > R > 8$ a.u.):

$$S(s) = \langle d0|s0 \rangle = 17.5360 \exp(-1.0333R) \quad (5)$$

$$S(\sigma) = \langle d0|p0 \rangle = 4.6183 \exp(-0.6868R) \quad (6)$$

$$S(\pi) = \langle d1|p1 \rangle = 4.9017 \exp(-0.8511R) \quad (7)$$

The electron density distribution moments are $\langle r^2 \rangle = 1.578 \text{ \AA}^2$, $\langle r^4 \rangle = 3.8628 \text{ \AA}^4$ [28].

The energy level splitting for all possible Ce^{3+} positions, calculated using two experimental PL excitation spectra (for (c) and (b) PL centers), is shown in table 3 and as bars on figures 4 and 6. The enumeration of Sr^{2+} sites is according to [1]. Direct comparison of the calculated splittings of the cerium 5d states with the experimental excitation spectra can help in identifying the Sr positions, which are preferably occupied by Ce^{3+} ions. Figure 4 shows that the calculated levels for cerium ions at the Sr-1 position agree best of all with the 4.5 eV excitation spectrum (corresponding to PL center (c)). Being based on that we assume that the center emitting at 4.5 eV is formed by the cerium ions occupying the Sr-1 position. Another excitation spectrum on figure 6 (which corresponds to the (b) center) matches best of all the calculated energy levels for Ce^{3+} at the Sr-3 position. On these grounds, we attribute the center (b) to the Ce^{3+} ions occupying the Sr-3 site. Table 4 below contains the values of the crystal field parameters for two identified Ce^{3+} positions, along with the exchange charge model fitting parameters. The latter were determined by matching the calculated crystal field splitting of the Ce^{3+} 5d energy levels to the observed peaks in the excitation spectrum. For all positions the total splitting of the 5d states were kept the same, to correspond to the overall width of the excitation spectrum.

Although the suggested method of identifying emitting centers is based on the semi-empirical crystal field model and its outcome can be not absolutely conclusive, we believe

Table 4. Crystal field parameters (Stevens normalization, all in cm^{-1}) for two identified Ce^{3+} positions (corresponding to Sr^{2+} sites) in $SrAlF_5$. Calculation for Sr-1 site is given for experimental excitation spectra of PL center (c), for Sr-3 site - of center (b).

CFP	Sr-1	Sr-3
B_2^{-2}	3190	3441
B_2^{-1}	-6296	8276
B_2^0	1708	3998
B_2^1	1068	3356
B_2^2	8740	4662
B_4^{-4}	962	-1318
B_4^{-3}	1871	1672
B_4^{-2}	-3898	2893
B_4^{-1}	-1156	968
B_4^0	1408	2036
B_4^1	-1149	-876
B_4^2	2235	859
B_4^3	20445	-2398
B_4^4	-6179	-6739
G_s	2.07	1.000
G_σ	2.07	2.550
G_π	2.85	4.450

that with a certain degree of confidence it can shed some light upon the complicated structure of Ce^{3+} emitting centers in $SrAlF_5$ crystal. The reliability of this method is yet unknown and it might be checked out by means of the *ab initio* calculations as well as EPR experiment. This is beyond the scope of the present paper; however, these studies are planned for the future.

5. Conclusions

In the present paper we have reported the results of a complete investigation of Ce^{3+} ions in $SrAlF_5:Ce^{3+}$ crystals, which include the sample preparations and experimental spectroscopic analysis supported by the crystal field calculations of the Ce^{3+} energy levels. Complicated crystal structure of the chosen host results in intricate excitation and emission spectra. In particular, presence of 4 non-equivalent Sr^{2+} sites in $SrAlF_5$ leads to occurrence of 3 spectroscopically non-equivalent Ce^{3+} PL centers which can be well distinguished using the time-resolved laser spectroscopy technique. These centers have different energies and probabilities of the Ce^{3+} 4f-5d transitions. One of the centers

is affected by a strong perturbation caused by a closely located defect, probably O^{2-} impurity substituting F^- ion, which acts as charge compensator as well. This center is the most promising for use in Ce^{3+} -based lasers, because being pumped by fourth harmonic of commercially available Nd:YAG laser (266 nm) offers wider tunability.

For the first time for the title host, the crystal field analysis of the cerium 5d states splitting has been performed; it is essential that no *a priori* symmetry assumptions have been imposed before starting the crystal field calculations, but on the contrary actual crystal structure data were used for calculating the crystal field parameters with subsequent diagonalization of the Ce^{3+} crystal field Hamiltonian. These calculations formed a basis for a method of identification of PL centers, which is based on the crystal field analysis of the Ce^{3+} 5d levels splitting. This method allows assigning “regular” unperturbed Ce^{3+} centers to a certain Sr^{2+} sites, by a direct matching the calculated energy levels for each possible position of impurity ion to the experimental spectra. Application of this method to our data has shown, that PL center (c) is due to Ce^{3+} ion occupying Sr-1 position and PL center (b) is due to Ce^{3+} ion occupying Sr-3 position.

The suggested method of identifying PL centers can be readily applied to other crystals with several possible sites, which can accommodate impurity ions.

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