

Spectroscopy of  $f^{13}$ - lanthanides in fluoride crystals© E.A. Radzhabov<sup>1</sup>, R.Yu. Shendrik<sup>1</sup>, V. Pankratov<sup>2</sup><sup>1</sup> Vinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences Irkutsk, 664033 Irkutsk, Russia<sup>2</sup> The Institute of Solid State Physics, University of Latvia, LV1063 Riga, Latvia  
e-mail: eradzh@igc.irk.ru

Received October 17, 2022

Revised February 15, 2023

Accepted February 19, 2023

The absorption and luminescence spectra of  $4f-4f$ - transitions of  $\text{Yb}^{3+}$  ions in crystals of  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$  fluorides have been studied. The crystal splitting of the  ${}^2F_{7/2}$ ,  ${}^2F_{5/2}$  levels in  $\text{Tm}^{2+}$ ,  $\text{Yb}^{3+}$  by the cubic field decreases linearly with increasing lattice constant. Both lines intersect at the energy of  ${}^2F_{7/2}-{}^2F_{5/2}$  transitions in unperturbed  $\text{Tm}^{2+}$ ,  $\text{Yb}^{3+}$  ions. The positions of the  $f^{13}$ - levels of  $\text{Tm}^{2+}$  or  $\text{Yb}^{3+}$  in fluoride crystals are well described by ab-initio relativistic calculations

**Keywords:** absorption spectra, emission spectra,  $f^{13}$ - levels, alkaline-earth fluorides.

DOI: 10.61011/EOS.2023.04.56352.54-22

## Introduction

The structure of the atomic levels of lanthanides (and actinides) with the configuration  $f^{13}$  (and  $f^1$ ) is the simplest among the lanthanides. Owing to the spin-orbit interaction, 14 degenerate states are split into two groups: ground  ${}^2F_{7/2}$  and excited  ${}^2F_{5/2}$ . In the octahedral environment of Oh lanthanide ions  $4f^{13}$ -, the  ${}^2F_{7/2}$  state splits into three ( $D_6$ ,  $D_7$ ,  $D_8$  — according to Bethe notation [1,2]), and the excited state  ${}^2F_{5/2}$  splits into two ( $D_7$ ,  $D_8$ ). The dependence of the crystal splitting on the lattice constant is studied in detail in this paper by experimental and computational methods.

Halide crystals doped with  $\text{Tm}^{2+}$  are actively studied in connection with their potential use as solar radiation concentrators [3].  $\text{Tm}^{2+}$  radiation in the infrared area can be converted into electrical energy [4].

The aim of our studies was to study the structure of the  $f^{13}$  levels of cubic  $\text{Tm}^{2+}$  and  $\text{Yb}^{3+}$  centers in fluoride crystals ( $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$ ).

## Experimental methodology

$\text{MeF}_2$  (Me — Ca, Sr, Ba) crystals were grown by the Bridgman method in a six-barreled graphite crucible in vacuum [5]. A few percent of  $\text{CdF}_2$  was added to the raw material to remove oxygen impurities. Crystals of alkaline earth fluorides activated by Tm or Yb were grown (the introduced concentration was 0.01–10 mol.%). In a number of crystals, a certain fraction of  $\text{Yb}^{3+}$  ions (approximately 10%) during growth was transformed into a divalent form.

Absorption spectra in the 190–3000 nm area were measured on an Perkin-Elmer Lambda-950 spectrophotometer. The luminescence spectra in the area of 200–890 nm

were measured using an MDR2 monochromator and a Hamamatsu H6780- photomodule. The luminescence spectra in the long-wavelength region were measured by a cooled PMT83 photomultiplier, a photodetector with a cooled Ge- photodiode FPU- FDG LOMO-PHOTONIKA (up to 1600 nm) and a cooled photoresistor PbS-FSV19AA (up to 2500 nm).

The emission spectra of  $f-f$   $\text{Tm}^{2+}$  and  $\text{Yb}^{3+}$  at low temperatures consist of two narrow lines and a vibronic wing towards the long wavelength. The  $\text{MeF}_2$ –Yb luminescence was excited by laser radiation at a wavelength of 940 nm, as well as by vacuum ultraviolet in the 6–9 eV area at the FINESTLUMI [6] photoluminescent station of the MAXIV synchrotron facility (Lund, Sweden).

## Scheme of calculation

The  $f$ - schemes of the levels of  $\text{Tm}^{2+}$  and  $\text{Yb}^{3+}$  in fluoride crystals were calculated using the ORCA 5.0.3 [7] software package. Relativistic effects were taken into account by the ZORA [8] method. The basis functions ZORA-def2-TZVP for ligands and SARC2-ZORA-QZVP for the  $f^{13}$  ion were used for the calculation.  $\text{TmF}_8$  (or  $\text{TmF}_8\text{Me}_{12}$ ) cluster was surrounded by point charges (approximately 1000 charges) to simulate a crystal field.

In accordance with the recommendations [8], the calculation of  $f$ -levels was carried out in three steps. At the first step, the initial orbitals of the cluster were calculated. At the second step, the initial orbitals were used and seven  $f$ -orbitals of the impurity ion were selected and moved, if required, to calculate the spin-orbital corrections using the CASSCF method. All seven  $f$ -orbitals were included in the active space for the correct calculation of their energies. The obtained orbitals were used at the third step for CASSCF

-NEVPT-calculation of  $4f$ -levels and transitions between them [8].

Since the value of the crystalline splitting of the  $f^{13}$  ion levels largely depends on the first sphere of ligands, the geometry of the central cluster (Tm or Yb) $F_8$  surrounded by a sphere of alkaline earth ions and point charges was optimized. The geometry was optimized using the Gaussian03 package with SDD (Tm, Yb, F) and LANL2MB (Ca, Sr, Ba) [9] basis sets.

## Results

The optical properties of  $MeF_2-Tm^{2+}$  were studied in detail in a previous paper [10], in which a decrease in the energies of absorption lines of  $Tm^{2+}$  with increasing lattice constant was found.

**Absorption of  $Yb^{3+}$ .**  $Yb^{3+}$  replaces  $Me^{2+}$ , so it needs an additional negative charge to compensate. This charge is supplied, as a rule, by interstitial fluorine, which additionally splits the levels and change spectra of absorption and luminescence. In  $CaF_2-Yb^{3+}$  crystals, lines of cubic centers were identified in the paper [11] (Fig. 1). In  $SrF_2$  and  $BaF_2$  crystals, the lines of cubic centers clearly stand out against the background of lines of other centers (Fig. 1).

The dependences of the lines of cubic centers  $Yb^{3+}$  positions on the lattice constant converge linearly to the energy of atomic transitions (Fig. 2). Meanwhile, they intersect at the value of the interionic distance (Fig. 2), which is larger than for  $Tm^{2+}$  [10].

**Luminescence  $Yb^{3+}$ .** For  $Yb^{3+}$  in  $CaF_2$  crystal, a large number of luminescence lines were observed in the luminescence spectrum (Fig. 3). The luminescence lines of cubic centers in  $CaF_2-Yb$  are marked with arrows [11]. The luminescence lines of cubic centers dominate in  $SrF_2$  and  $BaF_2$  crystals (Fig. 3). The luminescence  $Yb^{3+}$  lines converge with increasing lattice constant.

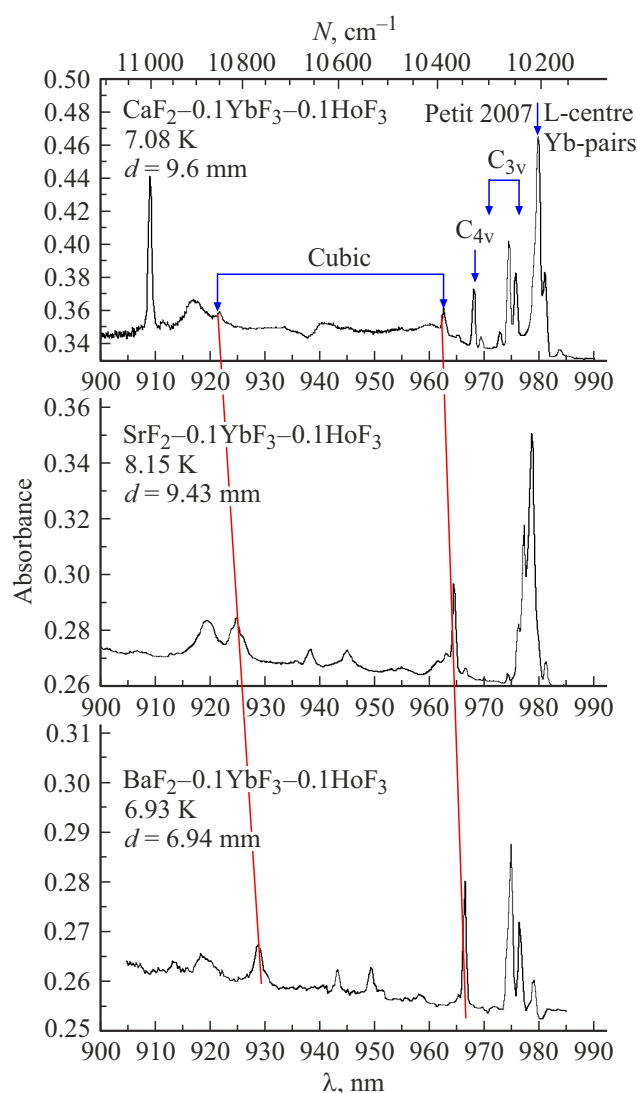
The  $f-f$  lines of the  $Yb^{3+}$  ions are also excited in the vacuum ultraviolet area. By selecting the excitation wavelength in vacuum ultraviolet, it is possible to obtain practically single luminescence lines of  $Yb^{3+}$  cubic centers in all alkaline fluorides (Fig. 4). The wavelengths of the lines of cubic centers are the same as in the case of excitation of the  $f-f$ - area at 940nm (Fig. 3, 4).

The linear dependence of the positions of the luminescence lines on the lattice constant is very unusual, since the potential of a point charge varies as  $1/r$ .

## Calculations

The calculated transition energies between the  $f$ - levels of free ions fairly agree with the experimental ones. The calculated energies of the  ${}^2F_{7/2}-{}^2F_{5/2}$  transitions in free  $Tm^{2+}$  and  $Yb^{3+}$  ions are approximately 2–3% less than the experimental ones.

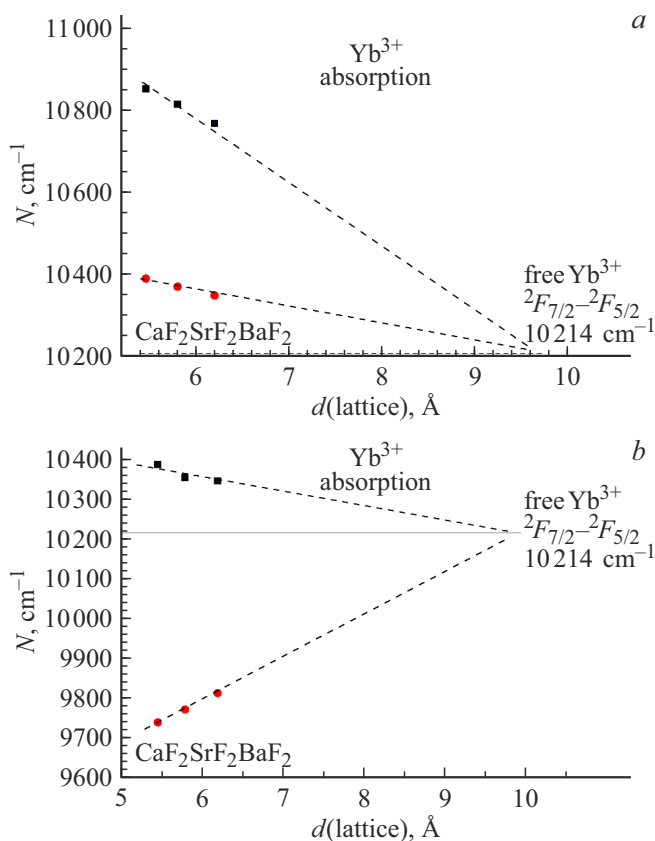
When  $Tm^{2+}$  and  $Yb^{3+}$  ions are placed in a crystalline environment, the initially degenerate levels  ${}^2F_{7/2}$  and  ${}^2F_{5/2}$



**Figure 1.** Absorption spectra of crystals  $MeF_2-0.1 \text{ mol.}\% YbF_3-0.1\% HoF_3$ .  $Ho^{3+}$  ions have no absorption in this area,  $d$  — crystal thickness.

split in energy. However, the dependence of the level energy on the lattice constant calculated for an ideal lattice turns out to be nonlinear, as follows from the dependence of the charge potential on the distance to it. The calculated energy of transitions between levels also turns out to be nonlinear, which is inconsistent with the experimental linear dependences (Fig. 2). The calculated spin splitting - of the orbital levels by the crystal field decreases exponentially with increasing distance between the ions. When the lattice constant reaches approximately  $7.5 \text{ \AA}$  for  $Tm^{2+}E$  and  $10 \text{ \AA}$  for  $Yb^{3+}$ , the splitting decreases almost to zero.

It was found that the distance to the ions of the nearest environment has a significant effect on the positions of the spins-orbital levels split by the crystal field. Since the central impurity ion remains the same in different lattices, the nearest environment should shift more toward the central ion ( $Tm^{2+}$  or  $Yb^{3+}$ ) relative to the undistorted lattice with



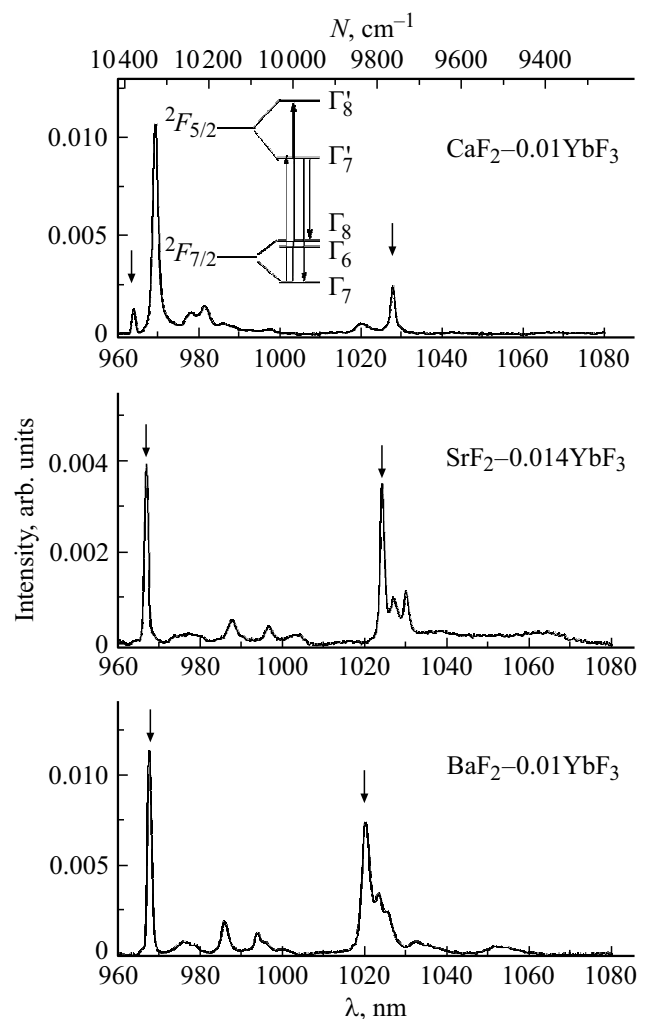
**Figure 2.** Dependence of the energy positions of the absorption (a) and luminescence (b)  $\text{Yb}^{3+}$  lines on the crystal lattice constant.

increasing lattice constant. For this reason, relaxation of the positions of the fluorine atoms closest to  $\text{Tm}^{2+}$  or  $\text{Yb}^{3+}$  in fluoride crystals  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  was calculated (Fig. 5).

The positions of the nearest fluorine atoms were calculated using the Gaussian 03 program in the  $\text{Yb}^{2+}$  (or  $\text{Tm}^{2+}$ )  $\text{F}_8\text{Me}_{12}$  cluster. The positions of the central ion and the nearest fluorines varied, while the positions of the outer  $\text{Me}^{2+}$  were fixed.

For  $\text{Yb}^{3+}$  ions, the equilibrium distances to fluorine atoms are smaller than the lattice distances (Fig. 5) in all crystals. This fairly agrees with the smaller ionic radius of  $\text{Yb}^{3+}$  (0.98 Å) compared with the radii of the  $\text{Ca}^{2+}$  (1.26 Å),  $\text{Sr}^{2+}$  (1.4 Å),  $\text{Ba}^{2+}$  (1.56 Å) [12] alkaline earth ions. The calculated distances from the central impurity  $\text{Tm}^{2+}$  ion to the nearest fluorine are longer than the lattice distance in  $\text{CaF}_2$  and shorter in  $\text{BaF}_2$  (Fig. 5). This also agrees with the radius of the  $\text{Tm}^{2+}$  (1.3 Å [13]) ion. It is also important that the slope of the dependence of the calculated distances  $\text{Tm}-\text{F}$  or  $\text{Yb}-\text{F}$  on the distances in an ideal lattice is much less than one.

The use of the calculated distances to fluorine (Fig. 5) significantly improves the agreement between the theoretical and experimental results and leads to a linear dependence of the energies of the absorption and emission lines of the  $\text{Tm}^{2+}$  and  $\text{Yb}^{3+}$  ions on the lattice constant (Fig. 6).

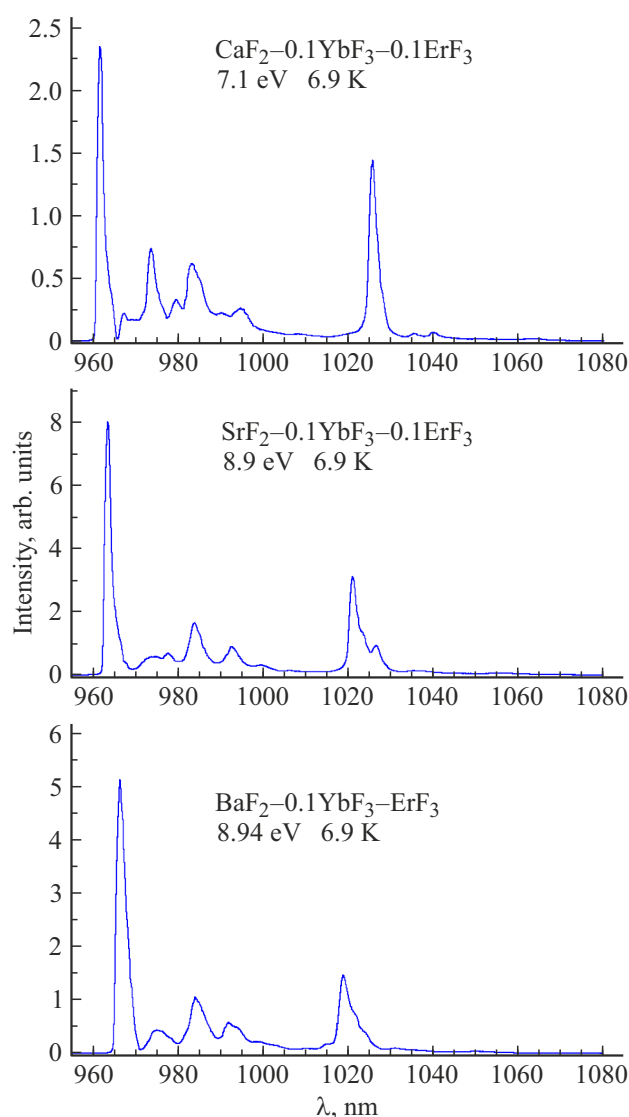


**Figure 3.** Luminescence spectra of crystals of alkaline earth fluorides  $\text{MeF}_2-0.01\% \text{YbF}_3$  at 85 K at 940 nm excitation. The insert shows the diagram of the energy levels of  $f^{13}$  ( $\text{Tm}^{2+}$  or  $\text{Yb}^{3+}$ ) ions, and the arrows show the transitions during absorption and luminescence.

## Discussion

The order of the lower levels of  $\text{Tm}^{2+}$  is defined as  $E_{3/2}$ ,  $E_{1/2}$ ,  $G$  [14] (according to Bethe —  $D_7$ ,  $D_6$ ,  $D_8$ ) or as  $D_7$ ,  $D_8$ ,  $D_6$  [15,16]. The same sequence for the levels of  $\text{Yb}^{3+}$  in alkaline earth fluorides is followed in the papers [17,18]. It is assumed that transitions to  $D_6$  in  $\text{CaF}_2-\text{Tm}^{2+}$  are forbidden and do not appear in the optical spectra [14–16]. At the same time, some weak long-wavelength bands in the luminescence spectra in  $\text{MeF}_2-\text{Yb}^{3+}$  are attributed to transitions to  $D_6$  [17,18]. They can also belong to vibronic transitions [19]. According to our calculations, the levels  $D_8$ ,  $D_6$  are separated by 30–40  $\text{cm}^{-1}$ , which is a small part of the energies of optical transitions 9000–10000  $\text{cm}^{-1}$ .

With an increase in the interionic distance in alkaline earth metal fluoride crystals, the energy of the  $D_7-D'_7$  and  $D_7-D'_8$  transitions of the  $\text{Tm}^{2+}$  or  $\text{Yb}^{3+}$  ions decreases linearly, which is associated with a decrease in the crystal

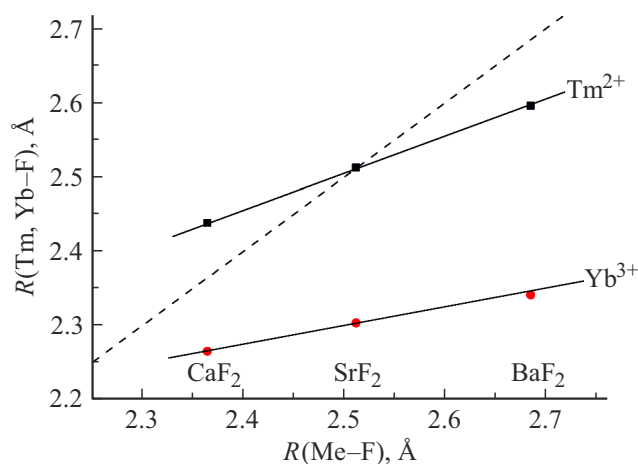


**Figure 4.** Luminescence spectra of  $\text{MeF}_2-0.1 \text{ mol.}\% \text{ Yb-Er}$  crystals at 6.9 K upon vacuum ultraviolet excitation.  $\text{Er}^{3+}$  ions have no luminescence bands in this area.

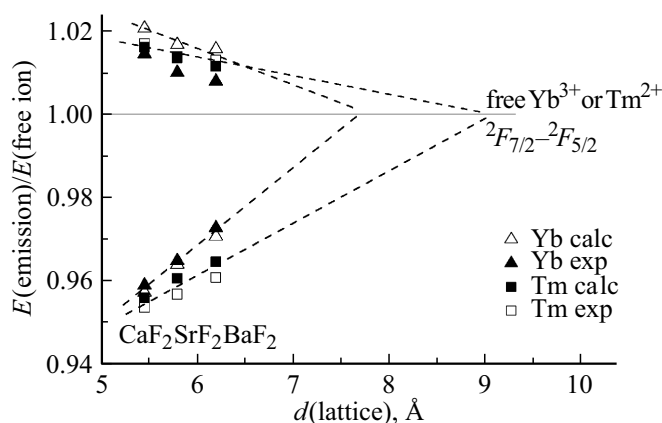
splitting of the spin-orbital- of the  ${}^2F_{7/2}$  and  ${}^2F_{5/2}$  levels. The straight lines of both dependences converge at an energy of about  $8780 \text{ cm}^{-1}$  for  $\text{Tm}^{2+}$  [10] or  $10200 \text{ cm}^{-1}$  for  $\text{Yb}^{3+}$  (Fig. 2), which is close to the distance between the  ${}^2F_{7/2}$  and  ${}^2F_{5/2}$  levels in free ions (Fig. 2, a). There is another behavior for emission lines (Fig. 2, b). With an increase in the lattice constant, the energy of the long-wavelength line  $D'_7-D_8$  increases, and the energy of the short-wave line  $D'_7-D_7$  decreases. This behavior of the transition energies also agrees with a decrease in the crystalline splitting of states when emission transitions occur from the lower excited state to two split levels of the ground state. The observed changes in the positions of the luminescence lines are due to different slopes of the dependence of the levels  ${}^2F_{5/2}$  ( $D_8, D_7$ ) on the lattice constant. The lines of both dependences (Fig. 2, b, Fig. 6) also intersect at an energy close to the energy

of the  ${}^2F_{7/2}-{}^2F_{5/2}$  transition in free ions ( $8774.02 \text{ cm}^{-1}$  or  $10214 \text{ cm}^{-1}$  for  $\text{Tm}^{2+}$  and  $\text{Yb}^{3+}$  respectively [19,20]).

Taking into account the lattice distortion near the impurity ion, we obtained a fairly good agreement between the calculated experimental dependences (Fig. 6). The slopes of the linear dependence of line positions on the lattice constant are different for  $\text{Yb}^{3+}$  and  $\text{Tm}^{2+}$  ions (Fig. 6). A different slope of the dependences of the calculated distances from the  $\text{Yb}^{3+}$  and  $\text{Tm}^{2+}$  ions to neighboring fluorine atoms was also obtained by optimizing the geometry of the nearest environment (Fig. 5). The difference in the slopes of the dependences in Fig. 6 is due to the different radii of the impurity ions. The radius  $\text{Tm}^{2+}$  is equal to  $1.3 \text{ \AA}$ , and the radius  $\text{Yb}^{3+}$  is —  $0.98 \text{ \AA}$ ; therefore, near  $\text{Yb}^{3+}$ , the lattice contracts more strongly and changes to a lesser extent with the change in the lattice constant (Fig. 5).



**Figure 5.** Calculated equilibrium distances from the central ion ( $\text{Tm}^{2+}$  or  $\text{Yb}^{3+}$ ) to the nearest fluorine atoms depending on the distances in the undistorted lattice. The dependence for an ideal lattice is indicated by a dashed line.



**Figure 6.** Dependence of the experimental and calculated luminescence lines of  $\text{Tm}^{2+}$  and  $\text{Yb}^{3+}$  on the lattice constant. The line energies are normalized to the energies of the  ${}^2F_{7/2}-{}^2F_{5/2}$  transitions in free ions.

## Conclusion

The optical spectra of  $4f-4f$ -transitions of  $\text{Yb}^{3+}$  ions in fluoride crystals  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  were studied. In fluoride crystals for  $\text{Yb}^{3+}$  ions, just as earlier for  $\text{Tm}^{2+}$  [10] ions, a linear decrease in the splitting of the spin-orbital - of the  $^2F_{7/2}$ ,  $^2F_{5/2}$  levels with increasing lattice constant was found. In contrast to the  $\text{Tm}^{2+}$  ions, the dependence of the splitting on the lattice constant for  $\text{Yb}^{3+}$  has a smaller slope, which is obviously related to the smaller size of the ytterbium ions.

The positions of the  $\text{Tm}^{2+}$  or  $\text{Yb}^{3+}$  bands in fluoride crystals are well described by ab initio CASSCF+NEVPT calculations taking into account the relaxation of the nearest sphere of fluorine atoms around the impurity ion.

## Acknowledgments

In the work, we used the equipment of the - isotope shared use center for geochemical studies of the IGC SB RAS. The authors thank V.A. Kozlovsky for growing the crystals.

The paper was carried out as part of the project 0284-2021-0004 „Materials and technologies for the creation of radiation detectors, phosphors and optical glasses of the Russian Academy of Sciences“. The Institute of Solid State Physics, University of Latvia as the Center of Excellence, has received funding from the European Union's Horizon 2020 Framework Programme H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement no. 739508, project CAMART2. The authors are grateful to K. Chernenko for help in carrying out the experiments at MAX IV.

## Funding

The study was carried out as part of the implementation of the state assignment under the RAS Project 0284-2021-0004 The study of optical spectra in vacuum ultraviolet was carried out at the MAX IV Laboratory on Beamline FinEstBeams in accordance with the contract (Offer) 20200308.

## Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by E.Potapova