

# Cubic and tetragonal $\text{Ce}^{3+}$ ions in strontium fluoride

E. Radzhabov<sup>a,\*</sup>, T. Kurobori<sup>b</sup>

<sup>a</sup>*Radiation Physics Department, Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Favorskii Street 1a, P.O. Box 4019, 664033 Irkutsk, Russia*

<sup>b</sup>*Department of Materials Science and Engineering, Division of Physical Sciences, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan*

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## Abstract

Optical absorption spectra in the vacuum ultraviolet, and high resolution emission and absorption spectra in the ultraviolet region of cubic and tetragonal  $\text{Ce}^{3+}$  centres in  $\text{SrF}_2$  crystals were measured. Cubic centres are characterised by the zero phonon line at  $33250 \text{ cm}^{-1}$  and a sharp phonon line is spaced from the zero phonon line by  $410 \text{ cm}^{-1}$ . The decay times of the luminescence from the cubic or tetragonal centres are equal to 32 ns. A comparison of the cubic and tetragonal spectra allows us to determine the influence of the charge compensating interstitial fluorine ion on the f and d levels of the  $\text{Ce}^{3+}$  ions.

Unrestricted Hartree–Fock calculations of Ce states in molecular clusters of alkaline-earth fluorides were performed. To make the calculated transitions coincide with the experimental one it is necessary to take into account the shift of the  $\text{Ce}^{3+}$  and interstitial  $\text{F}^-$  ions toward each other by 10% of initial distance.

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## 1. Introduction

Trivalent rare-earth ions introduced into alkaline-earth crystals have been investigated by different methods—including optical spectroscopy, electron spin resonance (ESR), ionic thermocurrents, etc. The excess positive charge is compensated by an interstitial fluorine ion, which can occupy the nearest, next-nearest or remote interstitial positions. These different positions of charge compensating fluorine result in tetragonal, trigonal and cubic centres.

The  $\text{Ce}^{3+}$  ion has a  $4f^1$  electronic configuration with a  $^2F_{5/2}$  ground term. The  $^2F_{7/2}$  term lies above  $2300 \text{ cm}^{-1}$ . In a cubic crystal field both levels are split. The structure of the 4f states of the tetragonal centres in  $\text{CaF}_2$  and  $\text{SrF}_2$  was carefully investigated by high resolution optical spectroscopy (Manthey, 1973; Pack et al., 1989). The zero phonon line at  $33173 \text{ cm}^{-1}$  was attributed to tetragonal centres in  $\text{SrF}_2$  crystals (Pack et al., 1989). A line of cubic cerium centres

in  $\text{SrF}_2$  of  $O_h$  symmetry was not observed so far. However, it has been proposed that the line of cubic Ce centres in  $\text{SrF}_2$  should be observed at  $33267 \text{ cm}^{-1}$  (Pack et al., 1989).

The 5d levels are split in a cubic  $O_h$  crystal field to  $e_g$  and  $t_{2g}$  levels. The transitions from the 4f ground state to the  $e_g$  and  $t_{2g}$  states in the alkaline-earth fluorides are found near 4 and 6 eV, respectively. The details of the influence of the interstitial charge compensating fluorine on the Ce 5d– $t_{2g}$  states are still unknown.

In this paper we investigate the emission and absorption spectra of  $\text{SrF}_2$  crystals containing only tetragonal cerium centers, and crystals containing predominately cubic cerium centres. Therefore, the influence of interstitial fluorine ions on all 5d cerium states was experimentally studied.

## 2. Experimental

The crystals were grown in a vacuum with the addition of a few percent of  $\text{PbF}_2$  as an oxygen scavenger. No oxygen luminescence was observed in the investigated crystals under excitation by ultraviolet deuterium light.

\* Corresponding author. Tel.: +7-395-251-1462; fax: +7-395-242-5070.

E-mail address: [eradz@igc.irk.ru](mailto:eradz@igc.irk.ru) (E. Radzhabov).

The high-resolution absorption and emission spectra were measured with a double-gratings 1 m spectrometer, type SDL1. The spectra in the vacuum ultraviolet at 6–11 eV were obtained using a grating monochromator, type VMR2.

The lifetime measurements were performed using time-resolved spectrofluorimeter (Horiba Ltd. NAES 1100), based on the time-correlated photon-counting technique described elsewhere (Kurobori et al., 1988). Two grating monochromators were used for selection of the excitation and emission wavelengths.

Calculations were performed using Gamess (US) (Schmidt et al., 1993) and PCgamess (Granovsky, 2003) codes. For the calculations the molecular cluster containing the central  $\text{Ce}^{3+}$  ion surrounded by 2 or 3 shells of lattice ions—SBKJC basis with ECP (effective core potential) was chosen for the calculations. The energy and oscillator strengths of the Ce 4f–5d transitions were calculated using the CI (configuration interaction) method.

### 3. Results

#### 3.1. Optical spectra

Two different optical absorption and luminescence spectra were observed in our  $\text{SrF}_2:\text{Ce}$  crystals. The first type, observed in most crystals (Fig. 1), was similar to that investigated previously (Loh, 1967; Manthey, 1973). This spectrum shows the  $33150\text{ cm}^{-1}$  zero phonon line which belongs to tetragonal cerium centres (Manthey, 1973). There is a  $20\text{ cm}^{-1}$  discrepancy with the data of Manthey (1973). The charge compensating fluorine ion of the tetragonal centre is in a nearest interstitial position in the [1 0 0] direction from

cerium. However in several crystals we observed a significantly different spectrum (see Fig. 1). This spectrum shows a sharp line at  $33250\text{ cm}^{-1}$ . This position is close to the proposed position  $33267\text{ cm}^{-1}$  of cubic Ce centres (Pack et al., 1989). The tetragonal centres line was very weak in this spectrum and can be seen only at liquid helium temperature. At this moment we name these crystals as those crystals containing cubic or tetragonal centres.

Based on this experimental result we conclude that some of our  $\text{SrF}_2:\text{Ce}$  crystals contain predominantly cubic  $\text{Ce}^{3+}$  ions with remote charge compensation. The cubic centres were observed in boules with 0.01 wt% of  $\text{CeF}_3$  or less. One may assume that some crystals were rapidly cooled after the growth process so that a considerable concentration of the cerium ions remains remotely compensated, as at high temperature.

#### 3.2. Broadband absorption spectra

The absorption spectra of two samples taken from the same boule  $\text{SrF}_2; 0.01\text{ wt}\% \text{ CeF}_3$ , from the “cubic” and “tetragonal” parts of the boule, are shown in Fig. 1c. The concentration of cerium is the same in both parts of boule as it follows from observation of the 4.15 eV absorption bands (see Fig. 2). With these samples we obtain the possibility of investigating the influence of interstitial fluorine on the rather simple optical transition of the cubic centres.

The 5.05 eV absorption band is observed only for tetragonal centres. Therefore, we conclude that the band at 5.05 eV belongs to tetragonal cerium centres. Earlier this band was assigned to some aggregate cerium centres. However, it is difficult to imagine that tetragonal centres have the ability to aggregate while the cubic centres have no such ability.

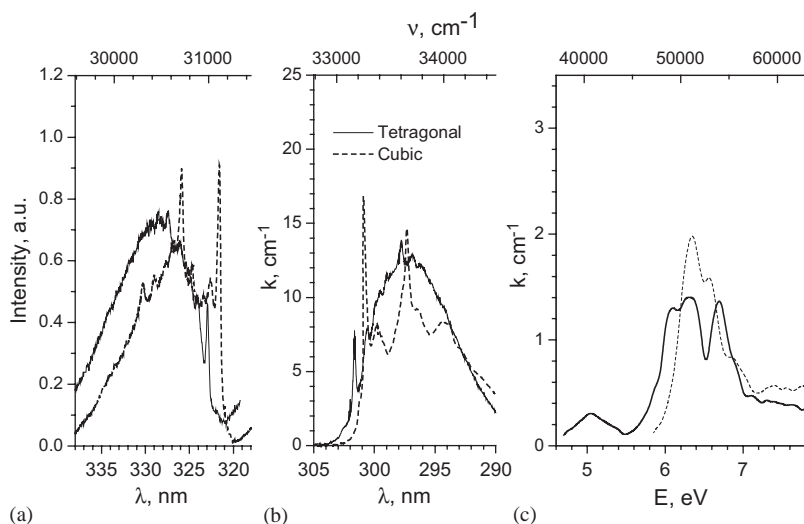


Fig. 1. Long wavelength emission spectra (a) and absorption spectra (b, c) of two types of cerium centres in  $\text{SrF}_2:0.01\%\text{CeF}_3$ . Spectra measured at 80 K (a, b) and at 295 K (c).

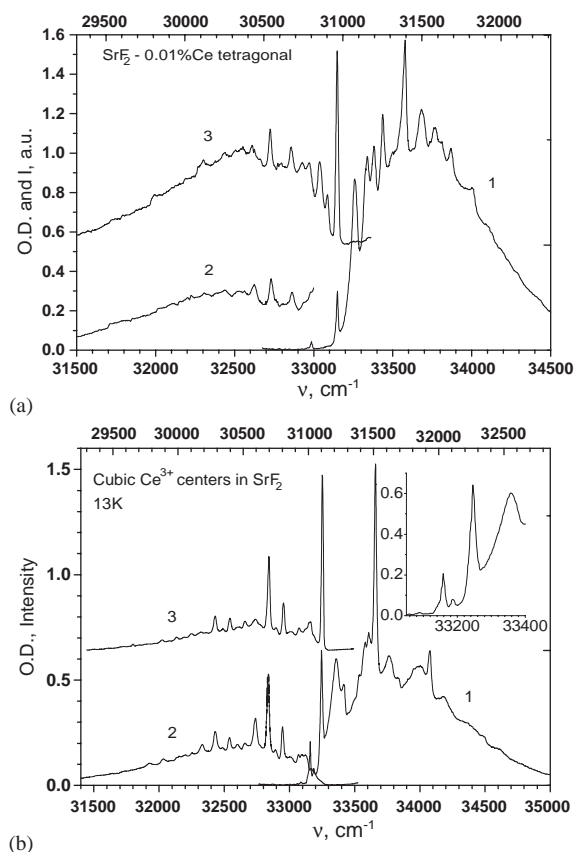


Fig. 2. High resolved absorption (curves 1) and emission (curves 2,3) spectra of cubic and tetragonal Ce centres in SrF<sub>2</sub>:0.01% CeF<sub>3</sub> at 13 K. Emission spectra of 5d–<sup>2</sup>F<sub>7/2</sub> band showed by curves 3 (see upper x-axis) shifted on x-axis to coincide with zero phonon absorption line.

The group of bands in the 6–7 eV region, which belong to 4f–t<sub>2g</sub> transitions, and is more distinct for tetragonal centres.

### 3.3. High resolution spectra

It is known that only the spectra of the 4f–5d(e<sub>g</sub>) transitions of Ce ion show the sharp lines (Manthey, 1973).

The high-resolution luminescence and absorption spectra of cubic and tetragonal Ce<sup>3+</sup> centres were measured at 13 K (Fig. 2). Emission transitions started from the lowest d level of the Ce ion. The comparison of emission spectra of both emission bands allows us to establish the structure of the <sup>2</sup>F<sub>7/2</sub> and <sup>2</sup>F<sub>5/2</sub> ground states (Manthey, 1973). Unfortunately the temperature of our measurements was not low enough to measure the full picture of the splitting of cerium the F ground states. We observe also a hot band in the absorption spectrum of both the tetragonal and the cubic Ce centres (see Fig. 2). The levels which caused the appearance of the hot band at 78 K are situated 40 cm<sup>-1</sup> above

the ground state for the cubic Ce centres and 100 cm<sup>-1</sup> for the tetragonal Ce centres.

An additional zero phonon line was observed in the samples containing cubic centres at 33159 cm<sup>-1</sup>. This position is slightly larger than the position of the tetragonal line at 33150 cm<sup>-1</sup>. Additionally weaker, low energy side bands are observed in the cubic and tetragonal centres (see Fig. 2).

### 3.4. Decay of Ce emission

The same decay curve for both luminescence bands of the cubic and tetragonal centres was observed with excitation into the first 4f–5d(e<sub>g</sub>) band at 4.15 eV at room temperature. The lifetime was 32 ns. Similar decay was observed using the 5.04 eV excitation (only for tetragonal centres) and using the 6.0 eV excitation into the 4f–5d(t<sub>2g</sub>) band. The measured lifetime is close to the previously reported data (Visser et al., 1993). The results show that apart from the strong influence on the absorption and emission spectra the interstitial fluorine ion has no influence on the emission lifetime. According to our calculation (see later) the lowest excited orbital of the Ce centre is the orbital in which the atomic d<sub>x<sup>2</sup>-y<sup>2</sup></sub> is predominant. Due to the large spatial separation of the 2p orbitals of interstitial fluorine and the d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital of the Ce ion the wavefunction of the lowest excited state of the cubic and tetragonal centres are the same and the transition probabilities to the ground state 4f are equal.

### 3.5. Calculations

The comparison of the absorption spectra of cubic and tetragonal centres illustrates that in tetragonal centres the 4f–e<sub>g</sub> and 4f–t<sub>2g</sub> bands are split by 1 and 0.3 eV, respectively. We evaluate the splitting by the crystal field and by the interstitial fluorine by using an unempirical Hartree–Fock method. Calculations of cubic centre give the e<sub>g</sub>–t<sub>2g</sub> splitting of the cerium d atomic orbitals. The e<sub>g</sub> orbitals consist of d<sub>z<sup>2</sup></sub> and d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbitals while t<sub>2g</sub> orbitals involve the d<sub>xy</sub>, d<sub>yz</sub>, d<sub>xz</sub> orbitals. The addition of interstitial fluorine leads to small splitting of the e<sub>g</sub> states while the t<sub>2g</sub> states remain unsplit (Fig. 3). From ENDOR studies it follows that the Ce<sup>3+</sup> ion in CaF<sub>2</sub> is shifted by nearly 5% toward the interstitial fluorine (Baker et al., 1968). This shift of the cerium ion from its site leads to the splitting of the t<sub>2g</sub> state on two levels. The lowest level contains the d<sub>xz</sub> d<sub>yz</sub> orbitals and the higher level consists of the d<sub>xy</sub> orbital. The splitting of the e<sub>g</sub> state is also increased. This splitting is commonly due to overlapping of the d<sub>z<sup>2</sup></sub> orbital of the Ce ion and the 2p<sub>z</sub> orbital of the interstitial F<sup>-</sup> ion. Nevertheless the splitting of the e<sub>g</sub> state remains too small. The splitting of e<sub>g</sub> state becomes comparable with that observed in the experiment when we shift the interstitial fluorine ion toward the Ce<sup>3+</sup> by 10% of the original distance between them. Spin–orbit coupling splits the d<sub>xz</sub>, d<sub>yz</sub> orbitals to amount  $\frac{3}{2}\xi_{5d} - 1500$  cm<sup>-1</sup> (see Fig. 3). Calculations on CaF<sub>2</sub>: Ce show that the shift of Ce by 3% of the original Ce–F<sup>-i</sup>-distance gives reasonable

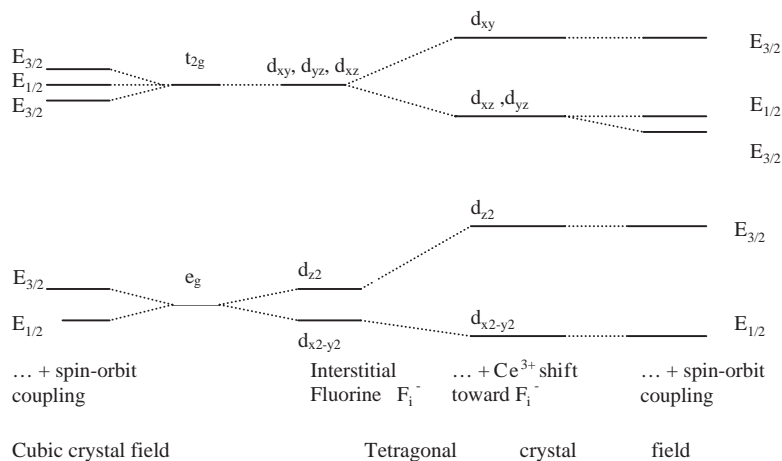


Fig. 3. Energy levels of the 5d orbital of  $\text{Ce}^{3+}$  as split by the cubic and tetragonal crystal field plus spin–orbit coupling. Fluorine ion in the nearest interstitial position only slightly splits the  $t_{2g}$  states and completely does not split the  $e_g$  cerium states. Against to this even small shift of  $\text{Ce}^{3+}$  ion toward the interstitial fluorine considerably splits the  $e_g$  states and also splits in less extent the  $t_{2g}$  states.

splitting of  $t_{2g}$  states. Additionally, the shift of interstitial fluorine is not needed because the  $\text{Ce}-\text{F}^{-i}$ -distance is short enough. According to this the ENDOR measurements do not show any shift of the interstitial fluorine from the cube centre position in  $\text{CaF}_2:\text{Ce}$  (Baker et al., 1968).

#### 4. Discussion

In a recent paper (van Pieterse et al., 2002) the optical spectra of the cubic  $\text{Ce}^{3+}$  centres in  $\text{CaF}_2$  doped with  $\text{Ce}^{3+}$  and  $\text{Na}^+$  ions were investigated in the UV and vacuum UV region. The  $\text{CaF}_2$  crystal doped with equal molar concentrations of  $\text{Ce}^{3+}$  and  $\text{Na}^+$  ions contains predominantly cubic Ce ions due to the large distances between the  $\text{Ce}^{3+}$  and  $\text{Na}^+$  ions (Pack et al., 1989). The observed spectra of  $\text{CaF}_2:\text{Ce}$ ,  $\text{Na}$  qualitatively correspond to our spectra of cubic Ce centres in  $\text{SrF}_2$ . Firstly the excitation spectrum in the 6–7 eV ( $f-t_{2g}$ ) region consists of three bands with almost equal distances among them. Secondly the absorption and emission spectra near 4 eV ( $f-e_g$ ) show a strong sharp phonon line separated by  $430\text{ cm}^{-1}$  from the zero phonon line (van Pieterse et al., 2002). In the case of  $\text{SrF}_2$  we observe this line at  $410\text{ cm}^{-1}$  (see Fig. 1). The energy separation between the zero-phonon line and the phonon line was explained in terms of the phonon frequencies corresponding to local modes involving the  $\text{Ce}^{3+}$  ion and its nearest neighbours, such as the local breathing mode oscillations of the eight fluoride ions surrounding the RE ion (van Pieterse et al., 2002). The  $410\text{ cm}^{-1}$  is rather close to  $395\text{ cm}^{-1}$ , a longitudinal phonon frequency in  $\text{SrF}_2$  (Lowndes, 1971). However the value of  $430\text{ cm}^{-1}$  is less than the phonon frequency of  $482\text{ cm}^{-1}$  in  $\text{CaF}_2$ . Thirdly, the excitation spectrum of  $\text{CaF}_2:\text{Ce}$ ,  $\text{Na}$  does not contain the 5.0 eV band. Sim-

ilarly there is no absorption (and excitation) band at 5 eV in  $\text{SrF}_2$  with cubic Ce centres, while the band is observed in crystal containing the tetragonal Ce centres (see Fig. 1). So we may conclude that the weak band at 5 eV appears due to the interstitial fluorine influence on the  $e_g$  cerium states. At higher Ce concentrations the 5 eV band becomes more evident. At high dopant concentrations above 0.05% cluster sites containing two or more rare earth ions will start to dominate. Possibly, the cluster formation process will lead to an increase of the 5 eV band.

Recently the local distortion around the  $\text{Ce}^{3+}$  ion was re-estimated (Gavasheli et al., 2002) from previously published ENDOR experimental data for tetragonal  $\text{Ce}^{3+}$  ions in  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$ . It was concluded that the distance  $\text{Ce}^{3+}-\text{F}_i^-$  is nearly the same in all three lattices and in  $\text{SrF}_2$  the distance decreased by 9.9% from its initial value. The authors claim that not only does the  $\text{Ce}^{3+}$  shift by 6.5% with respect to the interstitial fluoride, but also the interstitial fluorine shifts by 3.4% toward the  $\text{Ce}^{3+}$  ion. Our calculations are in agreement with the results of this paper (Gavasheli et al., 2002). We conclude that the local distortion around the Ce ion leads to a relatively large splitting of the  $e_g$  levels by 1 eV. This splitting is nearly the same in row  $\text{CaF}_2-\text{SrF}_2-\text{BaF}_2$  because the  $\text{Ce}^{3+}-\text{F}_i^-$  distances, which is the main reason for the splitting, is nearly the same in all lattices, while the lattice constant is gradually increased. The splitting of the  $t_{2g}$  states is due their interaction with the four  $\text{F}^-$  ions when the Ce shifts toward the interstitial fluorides.

Unempirical calculation shows that the oscillator strength of the  $4f-5d_{x^2-y^2}$  transition is equal to 0.034, which is comparable with the experimental oscillator strength for the 4.2 eV band, which is equal to 0.025. The oscillator strength of the  $4f-5d_{z^2}$  transition is much less, which is not surprising because the  $5d_{z^2}$  state is more distant than  $5d_{x^2-y^2}$  state,

so the overlap between the  $4f$  and  $5d_{z^2-y^2}$  states is much less than the overlap of  $4f$  with the  $5d_{x^2-y^2}$  state. The experimental oscillator strength of the 5.0 eV band is at least 10 times less than the strength of the 4.2 eV band (see Fig. 1).

One could find similarity with the spectrum of cubic centres in  $\text{SrF}_2$  (see Fig. 1) and the spectrum of centres in  $\text{BaF}_2$  (Loh, 1967). The spectra in the  $4f-5(t_{2g})$  region of both crystals show the triple band with equal distances among neighbouring peaks. It is known that the  $C_{3v}$  centres predominate in  $\text{BaF}_2$ . This follows from ionic thermocurrent measurements (Laredo et al., 1979) and from theoretical calculations (Corish et al., 1982; Sobolev et al., 2002). The splitting of the  $t_{2g}$  states by interstitial  $C_{3v}$  fluorine is minimal due to the long distance between them. Therefore, the splitting of these transitions is due only to spin-orbital coupling, similar to the observed splitting of cubic centres in  $\text{SrF}_2$ .

## 5. Conclusion

The presence of predominant cubic  $\text{Ce}^{3+}$  centres in some parts of the  $\text{SrF}_2$  boule was proved and the influence of charge compensated interstitial  $\text{F}^-$  ions on the  $f$  and  $d$  cerium atomic levels was investigated. The presence of interstitial fluorine leads to splitting of the  $e_g$  states by 1 eV and the  $t_{2g}$  states by 0.3 eV.

To make the calculated transitions coincide with the experimental ones we need to take into account the shift of the  $\text{Ce}^{3+}$  and interstitial  $\text{F}^-$  ions toward each other by 10% of the initial distance.

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