Cubic and tetragonal Ce^{3+} ions in strontium fluoride

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Abstract
Optical absorption spectra in the vacuum ultraviolet region and high resolution
emission and absorption spectra in the ultraviolet region for cubic and tetragonal
Ce^{3+} centres in SrF_2 crystals were measured. Cubic centres are characterized
by a $33\,250$ cm^{-1} zero-phonon line and a sharp phonon line spaced from the
zero-phonon line by 410 cm^{-1}. The decay times of cubic and tetragonal centre
luminescences are 32 ns. Comparison of cubic and tetragonal spectra allows us
to establish the influence of charge compensating interstitial fluorine ions on f
and d levels of Ce^{3+} ions.

Non-empirical Hartree–Fock calculations for Ce states in molecular
clusters of alkaline-earth fluorides were performed. To make the calculated
transitions coincide with the experimental ones one needs to take into account
a shift of Ce^{3+} and interstitial F^- towards each other by 10% of the initial
distance.

1. Introduction

Trivalent rare-earth ions introduced into alkaline-earth crystals were investigated by different
methods: using optical spectroscopy, ESR, ionic thermocurrent etc. The excess positive
charge is compensated by interstitial fluorine ions, which can occupy the nearest, next nearest
or remote interstitial positions. These different positions for charge compensating fluorine
result in tetragonal, trigonal and cubic centres.

Ce^{3+} ion has the $4f^1$ electronic configuration and has a $^2F_{5/2}$ ground term. The $^2F_{7/2}$ term
lies 2300 cm^{-1} above. In a cubic crystal field both levels are split. The structure of the 4f states
of tetragonal centres in CaF_2 and SrF_2 was carefully investigated by high resolution optical
spectroscopy [1, 2]. The zero-phonon line at $33\,173$ cm^{-1} was attributed to tetragonal centres
in SrF_2 crystals [2]. The line for cubic cerium centres in SrF_2 of O_h symmetry has not been

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observed so far. However, in the light of the results for the $CaF_2:Ce^{3+}$, Na^+ samples, it was concluded that $33\,267$ cm^{-1} in $SrF_2:Ce^{3+}$, Na^+ is the energy of the cubic O_h site [2].

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

In this paper we investigate the absorption and emission spectra of SrF_2 crystals containing only tetragonal and crystals containing predominantly cubic cerium centres. Therefore the influence of interstitial fluorine ions on all 5d cerium states has been experimentally studied.

2. Experimental details

Crystals were grown in vacuum with the addition of a few per cent of PbF_2 as an oxygen scavenger[4]. No oxygen luminescence was observed in the crystals investigated under excitation by ultraviolet deuterium light.

The high resolution absorption and emission spectra were measured with the double-grating 1 m spectrometer SDL1. The effective resolution was 1 cm^{-1} for the absorption spectra and 2.6 cm^{-1} for the emission spectra. Usually x-axes in high resolution spectroscopy are represented in nm or cm^{-1} and x-axes in usual optical spectroscopy are represented in eV or cm^{-1}.

The Ce emissions were excited by a 200 W xenon discharge lamp over a grating monochromator, MDR2. Absorption spectra in the vacuum ultraviolet at 6–11 eV were obtained using the grating monochromator VMR2.

The lifetime measurements were performed using a time resolved spectrofluorimeter (Horiba Ltd, NAES 1100), on the basis of a time correlated photon counting technique, described elsewhere [3]. Two grating monochromators were used for selection of excitation and emission wavelengths.

Non-empirical calculations were performed using Gamess (US) [4] and PCgamess [5] codes. For calculations we took the molecular cluster containing a central Ce^{3+} ion surrounded up to five shells of lattice ions. The SBKJC basis with an ECP (effective core potential) was chosen for the calculations. The energy and oscillator strengths of 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 SrF_2–Ce crystals. The first type, observed for most crystals (figure 1), were similar to those investigated previously [6, 1]. These spectra show the $33\,150$ cm^{-1} zero-phonon line which belongs to tetragonal cerium centres [1]. There is a 20 cm^{-1} discrepancy with the data of paper [1]. The charge compensating fluorine ion of the tetragonal centre is in the nearest interstitial position in the [100] direction from the cerium. However, for several crystals we observed a significantly different spectrum (see figure 1). This spectrum shows a sharp line at $33\,250$ cm^{-1}. This position is close to the proposed position $33\,267$ cm^{-1} of cubic Ce centres [2]. The tetragonal centre line was very weak in this spectrum and can be seen only at liquid helium temperature. For the moment, we refer to these crystals as ones containing cubic or tetragonal centres.

The absorption spectra of two samples taken from the same boule of SrF_2–0.01 wt% CeF_3 (from the 'cubic' and from the 'tetragonal' part of the boule) are shown in figure 1.

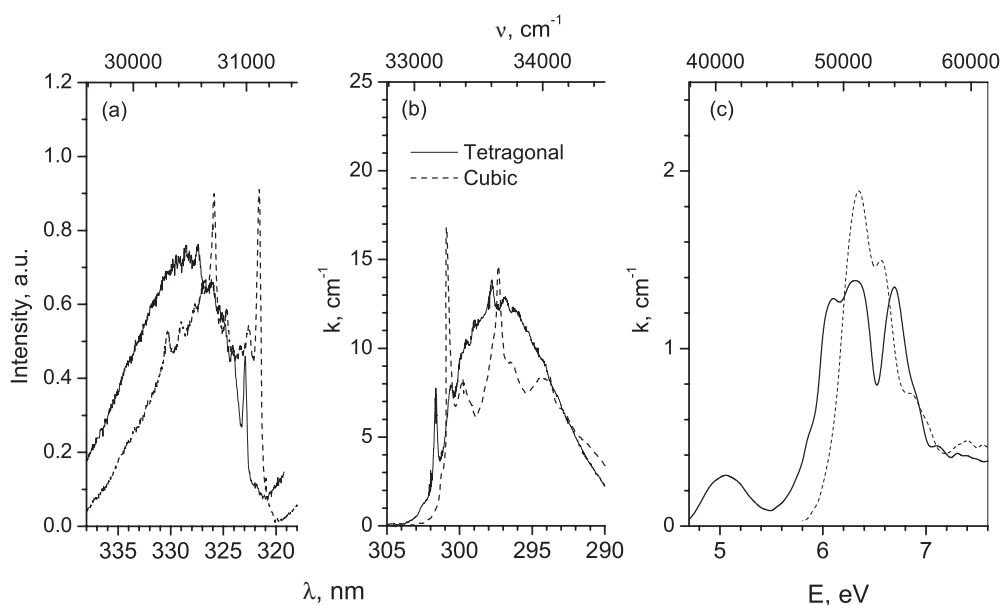[4] Crystals were grown in our laboratory by P Figura.

Figure 1. Long wavelength emission spectra (a) and absorption spectra ((b), (c)) of cerium centres of two types in SrF$_2$–0.01% CeF$_3$. Spectra measured at 80 K ((a), (b)) and at 295 K (c). Absorption spectra in the vacuum ultraviolet region were measured for samples taken from 'cubic' and 'tetragonal' parts of the same crystal boule.

The concentrations of cerium are the same in the two parts of the boule, as follows from the 4.2 eV absorption bands. With these samples we have the possibility of investigating in detail the influence of interstitial fluorine on optical transitions of Ce 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 of the cerium centres. However, it is difficult to imagine tetragonal centres having the ability to aggregate while the cubic centres have no such ability.

The group of bands in the 6–7 eV region, which belong to 4f t$_{2g}$ transitions, is more distinct for tetragonal centres.

On the basis of these experimental results we conclude that some of our SrF$_2$:Ce crystals contain predominantly cubic Ce^{3+} ions with remote charge compensation. Using the x-ray coloration ability of cubic centres we found that in some boules the central part contains predominantly cubic centres while the outer part of the boule contains predominantly tetragonal centres. However, in other boules the order is reversed. The cubic centres were observed in boules with 0.01 wt% of CeF$_3$ and less. The annealing of the sample with cubic centres up to 600 °C does not transform them to tetragonal centres. Therefore the charge compensated interstitial fluorides are strongly trapped somewhere. The high temperature annealing of a CaF$_2$:Ce^{3+} sample with tetragonal Ce centres at 1100 °C followed by quenching in water is known to produce cubic Ce^{3+} ions [2]. We tried annealing the sample with tetragonal Ce centres in an evacuated quartz tube for 1 h and then quenching the tube into water. However, no zero-phonon line or ultraviolet absorption bands of cubic Ce^{3+} appeared in the spectra.

3.2. High resolution spectra

It is known that only the spectra of 4f 5d(e$_g$) transitions of Ce ions show sharp lines [1].
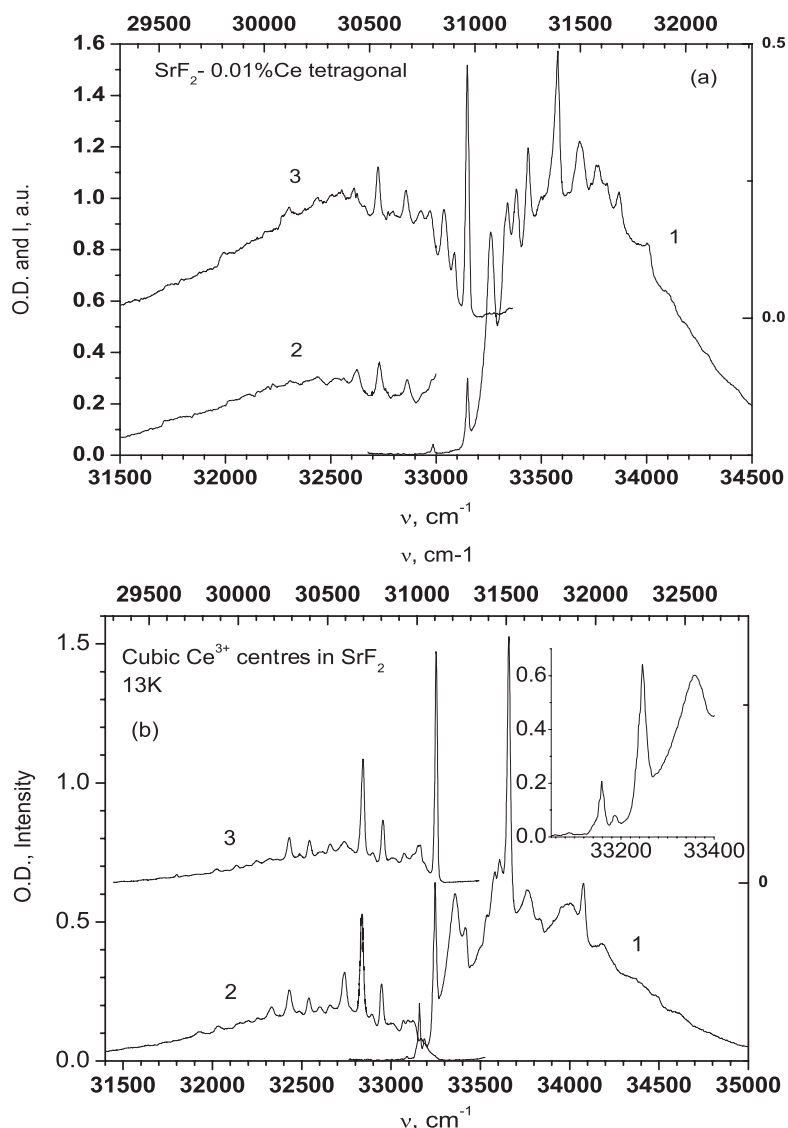
Figure 2. Highly resolved absorption (curves 1) and emission (curves 2, 3) spectra of cubic and tetragonal Ce centres in SrF_2–0.01% CeF_3 at 13 K. Emission spectra of the 5d $^2F_{7/2}$ band (curves 3, top x-axis) are shifted on the x-axis to coincide with the zero-phonon absorption line.

Highly resolved luminescence and absorption spectra of cubic and tetragonal Ce^{3+} centres were measured at 13 K (figure 2). Emission transitions started from the lowest d level of the Ce ion. Comparison of the emission spectra as regards the two emission bands allows us to establish the structure of the $^2F_{7/2}$ and $^2F_{5/2}$ ground states [1]. Unfortunately the temperature of our measurements was not low enough to allow us to investigate the full range of splitting of the cerium ^2F ground states. We observe also hot bands in the absorption spectra of both tetragonal and cubic Ce centres (see figure 2). The levels which caused the appearance of the hot band at 78 K are situated 40 cm^{-1} above the ground state for cubic Ce centres and 100 cm^{-1} for tetragonal Ce centres.

The additional zero-phonon line was observed for the samples containing cubic centres at 33 159 cm^{-1}. This position is slightly higher than the position of the tetragonal line at 33 150 cm^{-1}. Additionally, weaker low energy side bands are observed for cubic and tetragonal centres (see figure 2).

3.3. Decay of Ce emission

The decay curves for the luminescence bands of cubic and tetragonal centres observed with excitation into the first 4f 5d(e$_g$) band at 4.15 eV at room temperature were the same. The lifetime was 32 ns. Similar decay was observed using 5.04 eV excitation (only for tetragonal centres) and using 6.0 eV excitation into the 4f 5d(t$_{2g}$) band. The measured lifetime is close to previously reported data [7]. The results show that, despite 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 atomic d$_{x^2-y^2}$ is predominant. Therefore due to the large spatial separation of 2p orbitals of interstitial fluorine and the d$_{x^2-y^2}$ orbital of the Ce ion the wavefunctions of the lowest excited states of cubic and tetragonal centres are the same and the probabilities of transition to the ground state 4f are equal.

3.4. Calculations

The comparison of the absorption spectra of cubic and tetragonal centres indicates that in tetragonal centres the e$_g$ band and the t$_{2g}$ band are split by 1 and 0.3 eV, respectively. Calculations for cubic centres give the e$_g$–t$_{2g}$ splitting of d cerium atomic orbitals. The e$_g$ orbitals consist of d$_{z^2}$ and d$_{x^2-y^2}$ orbitals while the t$_{2g}$ orbitals involve the d$_{xy}$, d$_{yz}$, d$_{xz}$ orbitals. The addition of interstitial fluorine leads to a small splitting of e$_g$ states while the t$_{2g}$ states remain unsplit. From ENDOR studies it follows that the Ce^{3+} ion is shifted by nearly 5% towards interstitial fluorine [8]. This shift of the cerium ion from its site leads to the splitting of the t$_{2g}$ state into two levels. The lowest level contains d$_{xz}$, d$_{yz}$ orbitals and the higher level consists of d$_{xy}$ orbitals. The splitting of the e$_g$ state is also enhanced. This splitting is commonly due to overlapping of the d$_{z^2}$ orbital of the Ce ion and the 2p$_z$ orbital of the interstitial F$^-$ ion. Nevertheless, the splitting of the e$_g$ state remains too small. The splitting of the e$_g$ state becomes comparable with the experimental one when we shift the Ce and interstitial fluorine, reducing the distance between them by 10% of the original distance (figure 3). Calculations on CaF$_2$:Ce show that shifting Ce by 3% of the original Ce–F$_i^-$ distance gives a reasonable 1 eV splitting of the t$_{2g}$ states. Additionally, the shift of interstitial fluorine is not needed because the Ce–F$_i^-$ distance is short enough. According to this, the ENDOR measurements do not show any shift of interstitial fluorine from the cube centre position in CaF$_2$:Ce [8].

4. Discussion

In a recent paper [9] the optical spectra of cubic Ce^{3+} centres in CaF$_2$ doped with Ce^{3+} and Na$^+$ ions were investigated in UV and vacuum UV regions. CaF$_2$ doped with equal molar concentrations of Ce^{3+} and Na$^+$ ions contains predominantly cubic Ce ions due to the large distances between Ce^{3+} and Na$^+$ ions [2]. The observed spectra of CaF$_2$:Ce, Na qualitatively correspond to our spectra for cubic Ce centres in SrF$_2$. First, the excitation spectrum in the 6–7 eV region (f t$_{2g}$) consists of three bands with almost equal distances between them. Second, the absorption and emission spectra near 4 eV (f e$_g$) show a strong sharp phonon line separated by 430 cm^{-1} from the zero-phonon line [9]. In the case of SrF$_2$ we observe this line
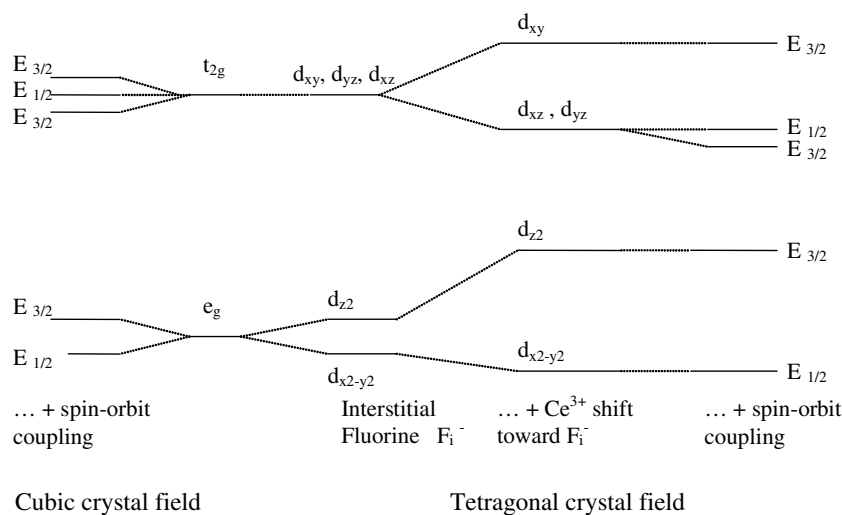
Figure 3. Energy levels of the 5d orbital of Ce^{3+} as split by the cubic and tetragonal crystal field plus spin–orbit coupling. The fluorine ion in the nearest interstitial position only slightly splits the e_g states and does not split the t_{2g} states at all. Against this, even a small shift of the Ce^{3+} ion towards the interstitial fluorine splits the e_g states considerably and also splits, to a lesser extent, the t_{2g} states.

at 410 cm^{-1} (see figure 1). The energy separation between the zero-phonon line and phonon line was explained in terms of phonon frequencies corresponding to local modes involving the Ce^{3+} ion and its nearest neighbours, such as the local breathing mode oscillations of the eight fluoride ions surrounding the RE ion [9]. 410 cm^{-1} is rather close to 395 cm^{-1}, a longitudinal phonon frequency in SrF$_2$ [10]; however, the value 430 cm^{-1} is less than the phonon frequency 482 cm^{-1} in CaF$_2$ [10]. Third, the excitation spectrum of CaF$_2$:Ce, Na not does not contain the 5.0 eV band. Similarly, there is no absorption (and excitation) band at 5 eV in SrF$_2$ with cubic Ce centres, while the band is observed in the crystal containing the tetragonal Ce centres (see figure 1). So we may conclude that the weak band at 5 eV appears due to the influence of interstitial fluorine on the e_g cerium states. At higher Ce concentration the 5 eV band becomes more evident. At high dopant concentrations above 0.05%, cluster sites containing two or more RE ions will start to dominate. Possibly the cluster formation process will lead to increasing of the 5 eV band.

Recently the local distortion around the Ce^{3+} ion was re-estimated [11] from previously published ENDOR experimental data for Ce doped CaF$_2$, SrF$_2$ and BaF$_2$. It was concluded that the distance Ce^{3+}–F_i^- in SrF$_2$ decreased by 9.9% from the initial value. The authors claim that not only does Ce^{3+} shift by 6.5% towards interstitial fluoride, but also interstitial fluorine shifts by 3.4% towards the Ce^{3+} ion. Our calculations are in agreement with the results of this paper [11]. We conclude that the local distortion around the Ce ion leads to a large splitting of the e_g levels, by 1 eV. This splitting is nearly the same in the row CaF$_2$–SrF$_2$–BaF$_2$ because the Ce^{3+}–F_i^- distances, which are the main reason for the splitting, are nearly the same in all the crystals [11], while the lattice constant is gradually changed. The splitting of the t_{2g} states is due to their interaction with four F^- ions when Ce shifts towards interstitial fluorides.

Non-empirical 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 of 0.025 for the 4.2 eV band. The oscillator strength of the 4f–5d$_{z^2}$ transition is much less, which is not

surprising because the $5d_{z^2}$ state is substantially more distant than the $5d_{x^2-y^2}$ state, so the overlapping between 4f and $5d_{z^2}$ is much less than the overlapping of 4f with the $5d_{x^2-y^2}$ state. The experimental oscillator strength of the 5.0 eV band is at least ten times less than the strength for the 4.17 eV band (see figure 1).

One can find a similarity between the spectrum of the cubic centres in SrF_2 (figure 1) and the spectrum of the centres in BaF_2 [6]. The spectra in the 4f $5(t_{2g})$ region for both crystals show a triple band with equal distances between neighbouring peaks. It is known that the C_{3v} centres are predominant in BaF_2. This follows from ionic thermocurrent measurements [12] and from theoretical calculations [13, 14]. The splitting of 4f t_{2g} transitions 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, similarly to the observed splitting for cubic centres in SrF_2.

5. Conclusion

The presence of predominantly cubic Ce^{3+} centres in some parts of a SrF_2 boule was proved and the influence of charge compensated interstitial F^- on f and d cerium atomic levels was investigated. The presence of interstitial fluorine led 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 take into account the shift of Ce^{3+} and interstitial F^- towards each other by 10% of the initial distance.

Acknowledgment

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