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# Theoretical study of $Ce^{2+}$ cubic centres in alkaline earth fluoride crystals

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## HIGHLIGHTS

- Ab inito study of $Ce^{2+}$ impurity centres in alkaline earth fluoride crystals.
- Calculated $Ce^{2+}$ ground state in $CaF_2$ and $SrF_2$ is predominantly $4f^15d^1$ singlet.
- Calculated absorption spectra are in good agreement width experimental data.

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## ABSTRACT

In this paper we present theoretical study of $Ce^{2+}$ impurity centres in alkaline earth fluoride crystals ($CaF_2$, $SrF_2$). Only cubic configurations of centres were considered. Electronic levels and related properties were studied using CASSCF/CASPT2 approach within embedded-cluster formalism including scalar relativistic corrections and spin-orbital interaction. Calculated absorption spectra for $Ce^{2+}$ in $CaF_2$ and $SrF_2$ are in good agreement with experimental data. For both crystals the ground state of $Ce^{2+}$ ion has predominantly $4f^15d^1$ singlet character.



## 1. Introduction

Alkaline earth fluorides ($CaF_2$, $SrF_2$, $BaF_2$) activated with trivalent rare earth ions are widely used as the material of scintillators. However, the same impurities can appear in alkaline earth fluoride crystals in divalent form upon additive colouration or irradiation and participate in energy transfer processes (Shendrik et al., 2016; McClure and Kiss, 1963; Merz and Pershan, 1967). The presence of divalent rare-earth ions might lead to the delay of scintillation process and decrease of the crystal light output.

It is well established that the divalent cerium free-ion ground state has $^3H_4$ $4f^2$ configuration and the lowest $4f^15d^1$ levels lie between 3277 and 18,444 $cm^{-1}$ (Sugar, 1965). However, in the crystal the interaction between crystal-field and many-electron wave-function can lower the energy of $4f^15d^1$ states compared to that of $4f^2$ states. Several authors have previously deduced that the ground state of cubic $Ce^{2+}$ centres in $CaF_2$ is $4f^15d^1$ using ab initio methods (Visser et al., 1993) and crystal field theory calculation compared with experimental data (Alig et al., 1969). At the moment, theoretical works about electronic and geometrical structure as well as $4f^15d^1 \rightarrow 4f^2$ transitions of $Ce^{2+}$ centres in $SrF_2$ crystals are not available. Experimental absorption spectrum of $Ce^{2+}$ in $SrF_2$ has been obtained recently by our colleagues. Detailed information of this experimental can be founded in Ref. (Shendrik et al., 2016).

In order to achieve better understanding of the energy transfer process in alkaline earth fluorides further investigation of such centres in necessary. The purpose of this work is to investigate the structure, electronic configuration and electronic transitions for $Ce^{2+}$ in $CaF_2$ and provide new theoretical results for $Ce^{2+}$ in $SrF_2$.

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## 2. Calculation details

Electronic structure calculations of cubic $Ce^{2+}$ centres in $CaF_2$ and $SrF_2$ were performed with Molcas quantum chemistry package (Aquilante et al., 2010). Combined quantum mechanics/molecular mechanics (QMMM) embedded cluster approach which we used in this work allows us to divide the crystal with the defect into several regions described at different levels of theory:

1. Quantum-mechanical (QM) cluster which is calculated ab initio
2. Classical region where the interaction between ions is described with pair potentials
3. Region of fixed point charges reproducing proper crystalline field inside 1 + 2 region.

Using geometry optimization procedure we can obtain lattice polarization under defect presence. Lattice relaxation in this scheme is allowed for both classical and QM regions. Classic molecular mechanics interaction were described by Buckingham pair potentials. Parameters for Buckingham potential were obtained from Stoneham and Taylor (1981) and optimized for our model systems. This scheme has already shown good results in the works of various authors (Myasnikova et al., 2010; Mysovsky et al., 2011, 2004; Sushko et al., 2005).

Electronic structure calculations were performed at the state – average completed active space level of theory (SA-CASSCF).

ANO-RCC all electron basis sets were used for Ce (Roos et al., 2008), Ca (Roos et al., 2004) and Sr (Roos et al., 2004) ions. Ab initio model potentials (AIMPs) were placed on Ca, F (Pascual and Seijo, 1995) and Sr (Pascual et al., 2007) ions in the classical region in order to avoid possible distortion of QM cluster electronic density caused by the presence of bare Coulomb potentials created by point charges. Correlation of rare earth electronic states was taken into account using complete active space second order perturbation theory (CASPT2) (Andersson et al., 1990).

We decided to use such combination of electronic structure calculation methods because heavy elements (rare earth) exhibit strong static and dynamic correlation effects as a consequence of having a number of near degenerate electronic configurations. This combination shows good results in calculation of rare earth electronic structure (Ning et al., 2012).

SA-CASSCF spin-free calculations with 12 active orbitals (4f, 5d) and 2 active electrons performed with equal weight for all states provided the following state list (the absence of spin values in the term means this term appears for both singlet and triplet states):

1) $4f^15d^1$ with 5d electron belonging to $E_g$ irreducible representation: $T_{1u} + T_{2u}$, $T_{1u} + T_{2u}$, $E_u$
2) $4f^15d^1$ with 5d electron belonging to $T_{2g}$ irreducible representation: $T_{2u}$, $A_{2u} + E_u + T_{1u} + T_{2u}$, $A_{1u} + E_{u+}$ $T_{1u} + T_{2u}$
3) $4f^2$ electrons in the same irreducible representation: ${}^3T_{1u} + {}^3T_{2u} + {}^3T_{3u}$, $2 \times {}^1T_{1u} + 2 \times {}^1T_{2u} + {}^1A_{1u}$.
4) $4f^2$ electrons in the different irreducible representation: $A_{2g} + E_g + T_{1g} + T_{2g}$, $T_{1g}$, $T_{2g}$
5) $5d^2$ electrons in the same irreducible representation: ${}^3T_{2g}$, ${}^3E_g$, $2 \times {}^1T_{2g}$, $2 \times {}^1E_g$
6) $5d^2$ electrons in different irreducible representation: $T_{1g} + T_{2g}$

Absorption spectrum was obtained for a set of correlated states including spin–orbit interaction with the restrictive active space state interaction method (RASSI). In our model system spin–orbit coupling does not affect structural parameters of the defect and is ignored during structure relaxation process.

We have studied cubic configuration of the $Ce^{2+}$ centres in $CaF_2$ and $SrF_2$ represented by the smallest possible $(CeF_8)^{5-}$ quantum cluster (see Fig. 1). Geometry optimization was performed in $O_h$ symmetry.

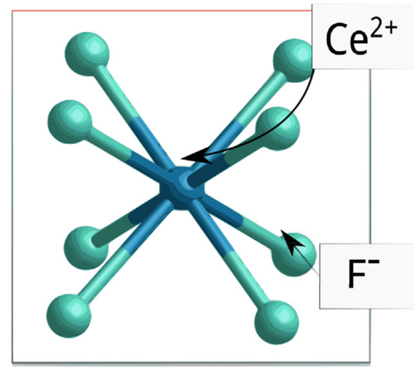


**Fig. 1.** $(CeF_8)^{5-}$ quantum cluster, $Ce^{2+}$ at the centre and nearest neighbour $F^-$.

We have already used the same QMMM/CASPT2/RASSI combination of electronic structure methods in our previous work for $Ce^{3+}$ $O_h$ and $C_{4v}$ centre in $CaF_2$ and obtained a good agreement with experimental data (Popov et al., 2015).

## 3. Result and discussion

### 3.1. Electronic and geometric properties

The distance between impurity $Ce^{2+}$ ion and its nearest neighbours slightly increased during the geometry optimization of the defect ground state (See Table 1). As it was mentioned earlier the interaction of 5d $E_g$ electron and the crystal field can lead to difference between free-ion and ion-in-the-crystal ground state electronic configuration. We obtained that the ground state of $Ce^{2+}$ in both crystal is predominantly singlet $4f^15d^1$. Spin–orbit interaction leads to the ground state with the larger amount of singlet (80%) and small admixture of triplets states (20%). It is consistent with previous results for $Ce^{2+}$ in $CaF_2$ where the ground state is mixture of ${}^1G_4 + {}^3F_3 + {}^3H_4$.

The lowest 14 spin-free states are 4f5d for both spin multiplicities. The character of lowest $4f^15d^1$ spin–orbit states in $CaF_2$ agree qualitatively with the results of crystal field calculation (Alig et al., 1969). Energies of these levels are shown in the first column of Table 2. The same energies with systematic error subtracted (around 600 $cm^{-1}$) are shown in column 4 as "Corrected".

It should be noted that absorption spectrum can be obtained only if all considered states are included in the same state-averaged CASSCF calculation. The specifics of state-averaged CASSCF method is, simply speaking, that the more states are included in the calculation the worse is the accuracy of each particular state. The reason of energies overestimation in all-state averaging calculation is the intruder state inclusion, i.e. small admixture of some higher energy state.

This is why the energies obtained in such calculation turned out to be overestimated with respect to experiment by approximately 600 $cm^{-1}$ for $4f^15d^1$ and by 4000 $cm^{-1}$ for $4f^2$. In order to explain the nature of this systematic error we applied different state averaging schemes. Column 2 of Table 2 shows the energies of

**Table 1**
Nearest neighbour $Ce^{2+}$ – $F^-$ distance before and after geometry optimization.

| System | Before, Å | After, Å |
|---|---|---|
| $Ce^{2+}$ in $CaF_2$ | 2.60 | 2.69 |
| $Ce^{2+}$ in $SrF_2$ | 2.77 | 2.81 |

**Table 2**
Energy levels (in $cm^{-1}$) of $Ce^{2+}$ in $CaF_2$, Δ SEC-systematic error correction.

| State averaging | | Δ SEC | Corrected | Expt. (Alig et al., 1969) |
|---|---|---|---|---|
| All | Separate | | | |
| $4f^15d^1$: | | | | |
| $0(T_2)$ | $0(T_2)$ | | $0(T_2)$ | $0(T_2)$ |
| 850(E) | 140(E) | 600 | 250(E) | 192(E) |
| $980(T_2)$ | $340(T_2)$ | | $380(T_2)$ | $427(T_2)$ |
| $1610(A_2)$ | $984(A_2)$ | | $1010(A_2)$ | $1074(A_2)$ |
| $1720(T_1)$ | $1232(T_1)$ | | $1120(T_1)$ | $1089(T_1)$ |
| 2250(E) | 1730(E) | | 1650(E) | 1488(E) |
| $2283(T_1)$ | $1756(T_1)$ | | $1683(T_1)$ | $1686(T_1)$ |
| $2700(A_2)$ | $2214(A_2)$ | | $2100(A_2)$ | $1831(A_2)$ |
| $4f^2$: | | | | |
| $11{,}000(T_2)$ | $7086(T_2)$ | 4000 | $7000(T_2)$ | $7011(T_2)$ |
| 11,400(E) | 7560(E) | | 7400(E) | 7479(E) |
| $11{,}450(T_1)$ | $7633(T_1)$ | | $7450(T_1)$ | $7520(T_1)$ |
| $11{,}715(A_1)$ | $7802(A_1)$ | | $7715(A_1)$ | |
| $12{,}825(T_1)$ | $8756(T_1)$ | | $8825(T_1)$ | $8818(T_1)$ |
| 12,950(T) | $8822(T_1)$ | | $8950(T_1)$ | $8954(T_1)$ |
| 13,130(E) | 9104(E) | | 9130(E) | 9174(E) |
| $13{,}410(T_1)$ | $9222(T_1)$ | | $9410(T_1)$ | $9320(T_1)$ |

$4f^15d^1$ states with state averaging only over those states, as well as the energies of $4f^2$ states with averaging again only over this group of states. All these energies demonstrate excellent agreement with the experiment.

It can be observed from comparison of column 1 (all-state averaging) and column 2 (separate averaging over $4f^15d^1$ and $4f^2$ groups of states) that the order of states and their relative positions are the same. The energies obtained with all-state averaging can be corrected by subtraction of Δ SEC (systematic error correction) which is also shown in Table 2.

Concerning $4f^2$ one can see that lowest levels are described as $^3H_4$ with $T_2 + E + T_2 + A_1$ and $^3H_5$ with $T_1 + E + T_2 + T_1$. Splitting between this terms is around 2000 $cm^{-1}$. Next set of calculated levels($^3H_6$) appear before 10,000 $cm^{-1}$. Energy of such lowest levels were introduced in Table 2 for $CaF_2$ including systematic error subtraction (around 4000 $cm^{-1}$). Characteristic splitting of $4f^15d^1$ $E_g - T_{2g}$ is around 11,000 $cm^{-1}$. It was observed that lowest $5d^2$ state appears above 35,000 $cm^{-1}$ for $Ce^{2+}$ in $CaF_2$.

Similar calculations were performed for $Ce^{2+}$ in $SrF_2$. The resulting structure of energy levels is the same as in the case of $CaF_2$. Calculated energy levels are presented in Table 3 for $4f^15d^1$ and $4f^2$. The only difference is that for $SrF_2$ the obtained energies are lower than for $CaF_2$ due to larger nearest neighbour distance. The $4f^2$ states in $SrF_2$ lie by 1000 $cm^{-1}$ lower than in $CaF_2$. Characteristic splitting of $4f^15d^1$ $E_g - T_{2g}$ is around 10,000 $cm^{-1}$. The lowest $5d^2$ state for $Ce^{2+}$ in $SrF_2$ appears above 32,000 $cm^{-1}$.

### 3.2. Absorption spectrum

Calculated absorption and experimental data from Shendrik et al. (2016) spectra are shown in Fig. 2 for $Ce^{2+}$ in $CaF_2$ and in Fig. 3 for $SrF_2$. Calculated oscillator strengths have been renormalized to compare better with experimental data. Highest calculated oscillator strength for $CaF_2$ is $10^{-3}$ and $SrF_2$ is $5 \times 10^{-4}$.

**Table 3**
$4f^15d^1$ and $4f^2$ energy levels (in $cm^{-1}$) of $Ce^{2+}$ in $SrF_2$.

| $4f^15d^1$ calc. | $4f^2$ calc. |
|---|---|
| $0(T_2)$ | $6070(T_2)$ |
| 300(E) | 6150(E) |
| $420(T_2)$ | $6600(T_1)$ |
| $1060(A_2)$ | $6940(A_2)$ |
| $1150(T_1)$ | $8100(T_1)$ |
| $1650(E_2)$ | 8200(E) |
| $1735(T_1)$ | $8540(T_2)$ |
| $1800(A_2)$ | $8640(T_1)$ |

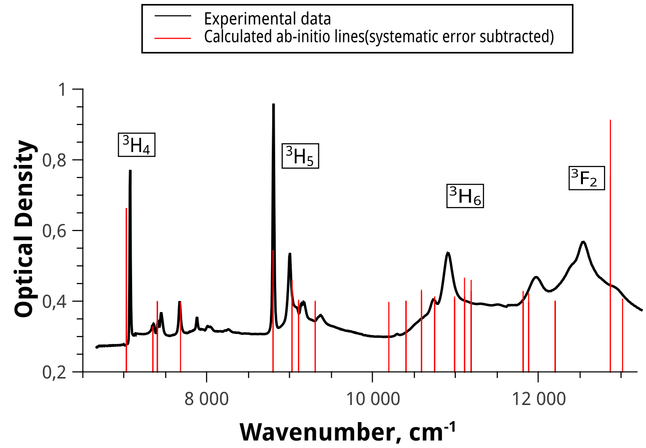


**Fig. 2.** $Ce^{2+}$ cubic centre in $CaF_2$ optical absorption spectrum ($4f^15d^1 \rightarrow 4f^2$).

As it was introduced in Refs. (Shendrik et al., 2016) and (Sizova and Radzhabov, 2012) for divalent cerium in $CaF_2$ one can observe two sets of absorption lines after x-ray irradiation in region of interest. There are: 6452, 9679, 10,490 $cm^{-1}$ narrow bands and 16,940, 22,580 $cm^{-1}$ wide bands. Narrow bands correspond $4f^15d^1 \rightarrow 4f^2$ transitions and the wide band is associated with photochromic $PC^+$ – centre (Sizova and Radzhabov, 2012). For $Ce^{2+}$ in $SrF_2$ at 80 K we have a few sharp lines around 8100 $cm^{-1}$ and wide bands at 11,290 and 18,550 $cm^{-1}$.

Comparing theoretically calculated and experimental spectra it can be concluded that narrow bands in both crystals are due to $4f^15d^1 \rightarrow 4f^2$ transitions.

## 4. Conclusion

In this paper we had shown that divalent cerium centres can appear in $CaF_2$ and $SrF_2$ after additive colouration or x-ray irradiation. Using quantum chemistry calculation within embedded cluster formalism we have established that the ground state of cubic rare-earth defect is $4f^15d^1$ and has predominantly singlet character in with some triplet admixture.

The correct quantum-chemical description of these defects

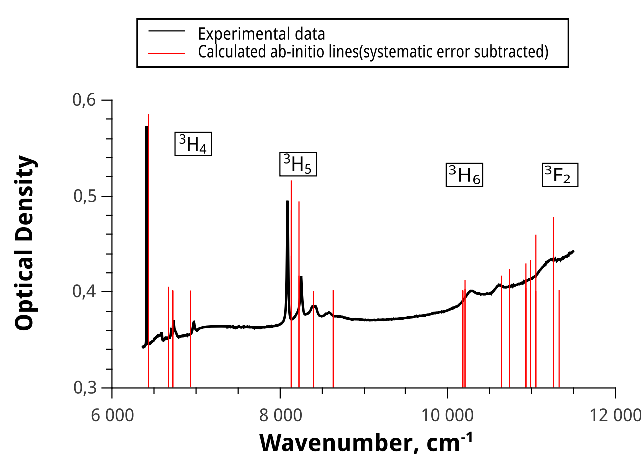


**Fig. 3.** $Ce^{2+}$ cubic centre in $SrF_2$ optical absorption spectrum ($4f^15d^1 \rightarrow 4f^2$).

requires accounting for the dynamic correlation, scalar relativistic, spin-orbital and lattice polarization effects. Using this treatment we confirmed previous results of crystal-field and ab initio calculations (Visser et al., 1993) of cubic $Ce^{2+}$ $O_h$ centre in $CaF_2$ and obtained new results for $Ce^{2+}$ $O_h$ in $SrF_2$. Experimentally obtained narrow absorption lines for cubic $Ce^{2+}$ in $CaF_2$ and $SrF_2$ are in good agreement with calculated $4f^15d^1 \rightarrow 4f^2$ transition spectrum.

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All calculations were performed on a Fock supercomputer at Irkutsk National Research Technical University.

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