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First-principles study of electronic structure of Ce³⁺ centres in alkaline-earth fluorides including spin-orbit and scalar relativistic effects

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Abstract. In this paper we present the results of *ab initio* calculations of Ce³⁺ impurity centres in CaF₂ crystal. The cubic and tetragonal (interstitial fluorine compensated) configurations of centres were considered. The embedded cluster approach with polarizable crystalline lattice and CASSCF/CASPT2 methods were used to study the structural configurations and electronic properties of defects under consideration. Scalar relativistic corrections were taken into account at Douglas-Kroll-Hess level and spin-orbit effects were calculated with the RASSI approach. Calculated optical absorption spectra for cubic and tetragonal centres demonstrate good agreement with the experiment. Small symmetry breaking displacements of neighbouring ions were observed for cubic Ce³⁺ centre ground state.

1. Introduction

Cerium-doped compounds have received considerable interest due to their wide applications in scintillators and solid state lasers. Well established experimental and theoretical data for cerium impurity in alkaline-earth fluoride crystals are to be found in Refs. [1, 2]. In these crystals Ce³⁺ ion is supposed to form centres with cubic symmetry (for example, such centres are considered in Ref. [3]) as well as tetragonal and trigonal centres with charge compensating fluorine interstitial [2]. However, EPR spectroscopy does not confirm the existence of cubic centres [4, 5] although they can be readily observed by the means of optical and infrared spectroscopy, which are less sensitive to the defect symmetry than EPR technique.

The purpose of the present theoretical study is to build adequate model of spatial and electronic structure of Ce³⁺ centres in CaF₂ crystals including scalar relativistic effects and spin-orbit interaction which strongly affects energy levels of rare earth impurities.

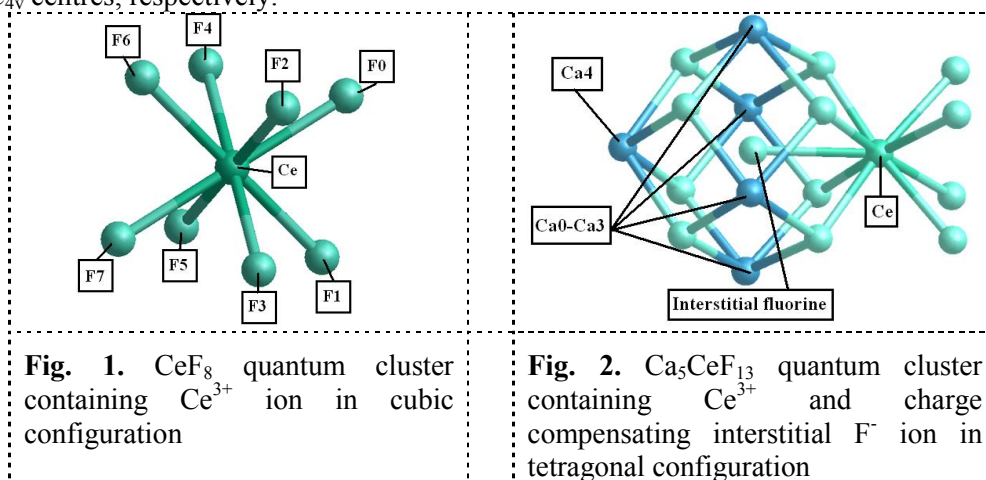
2. Calculation details

Embedded cluster approach used in this work allows one 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. Geometry optimization is allowed for both regions 1 and 2. For quantum chemical calculations we



used the Molcas package [6]. ANO-RCC all electron basis set [7, 8] was used for Ce, F and Ca ions inside QM cluster. In the classical region *ab initio* model potentials (AIMPs) [9] were placed on Ca and F ions in order to avoid possible distortion of QM cluster electronic density caused by the presence of bare Coulomb potentials. Geometry optimization was performed at the complete active space self consistent field (CASSCF) level. State averaged CASSCF calculations with active space containing 4f, 5d and 6s orbitals of Ce ion were performed for treating ground and excited electronic states of the defects. Correlation was taken into account with complete active space second order perturbation theory (CASPT2) method. To calculate spin-orbit coupling we used restricted active space state interaction (RASSI) approach.

We have studied two possible configurations of Ce^{3+} centres: the cubic and the tetragonal one with nearest interstitial fluorine ion. Quantum clusters $(\text{CeF}_8)^{5-}$ (Fig. 1) and $\text{Ca}_5\text{CeF}_{13}$ (Fig. 2) were used for O_h and C_{4v} centres, respectively.



3. Result and discussion

After the geometry optimization of the ground state of the cubic Ce^{3+} centre the symmetry lowering from cubic to trigonal was observed. The symmetry unique displacements are shown in Table 1. The third order symmetry axis is the cube diagonal connecting fluorine ions F0 and F7 as they are denoted in Fig. 1. However, one might see that the displacements breaking O_h symmetry are very small – about 0.006 Å. Such a small value of displacements does not allow us to conclude that the symmetry of so called “cubic” Ce^{3+} centre does indeed break due to Jahn-Teller effect. On the other hand, there is no EPR evidence of the existence of Ce^{3+} centres with cubic symmetry [4,5]. The possible reasons of such behaviour remain unclear and might include dynamic Jahn-Teller effect as well as the presence of other impurities in the vicinity of Ce^{3+} centre.

For the tetragonal Ce^{3+} centre with nearest charge compensating interstitial fluorine ion the results of geometry optimization are shown in Table 2. The notation of atoms in Table 2 is the same as on Fig. 2. In both Tables 1 and 2 X, Y, Z are Cartesian coordinates of the atoms before the geometry optimization and ΔX , ΔY , ΔZ are the resulting displacements. Only symmetry unique atoms are listed. Tables 3 through 6 contain the data on energy levels and optical transitions for the cubic and tetragonal Ce^{3+} centres calculated with multistate CASPT2 method. The 4f-5d optical transitions and absorption spectrum of the cubic centre are shown in Table 4 and on Fig. 2a. The same information for tetragonal centre is represented in Table 6s and Fig. 2b. The calculated optical absorption spectra for both centres demonstrate good agreement with experimental [2,10] and theoretical [1,11,12] works.

According to Ref. [10] the high energy part absorption spectrum of cubic Ce^{3+} centre contains three distinct lines at about 53000 cm^{-1} split by 1700 and 1900 cm^{-1} . It is important to note that in purely cubic O_h coordination the first two of them must be degenerate. In our calculations due to small symmetry breaking displacements three different lines were obtained, but the separation between the

first and the second one is only about 350 cm^{-1} . This possibly indicates that asymmetric distortion of the cubic Ce^{3+} centre should be larger than we obtained.

Concerning the tetragonal Ce^{3+} centre one can see that the representative peak experimentally observed at about 40000 cm^{-1} which is due to the interaction between Ce^{3+} and interstitial fluorine ion is present in the calculated spectrum with both energy and oscillator strength being in good agreement with experiment.

Table 1. Structural parameters of the cubic Ce^{3+} centre.

Atom	X, Å	Y, Å	Z, Å	ΔX , Å	ΔY , Å	ΔZ , Å
Ce	0.00	0.00	0.00	0	0	0
F0	1.38	1.38	1.38	0	0	0
F1	1.38	1.38	-1.38	0.004	0.004	0
F6	-1.38	-1.38	1.38	-0.004	-0.004	0
F7	-1.38	-1.38	-1.38	0	0	0

Table 2. Structural parameters of the tetragonal Ce^{3+} centre

Atom	X, Å	Y, Å	Z, Å	ΔX , Å	ΔY , Å	ΔZ , Å
Ce	1.38	0	0	-0.12	0	0.03
Ca0-Ca3	-1.38	0	2.76	-0.01	0	0.10
Ca4	-4.14	0	0	0.10	0	0
F _i	-1.38	0	0	0.05	0	0

Table 3. 4f energy levels of the cubic Ce^{3+} centre

State	Energy without spin-orbit, cm^{-1}	Energy with spin-orbit, cm^{-1}
1	0.0	0.0
2	18.8	5.0
3	24.7	507.3
4	90.0	2250.5
5	91.0	2272.2
6	94.0	2290.0
7	2406.6	4064.8

Table 4. 5d energy levels and optical transitions of the cubic Ce^{3+} centre

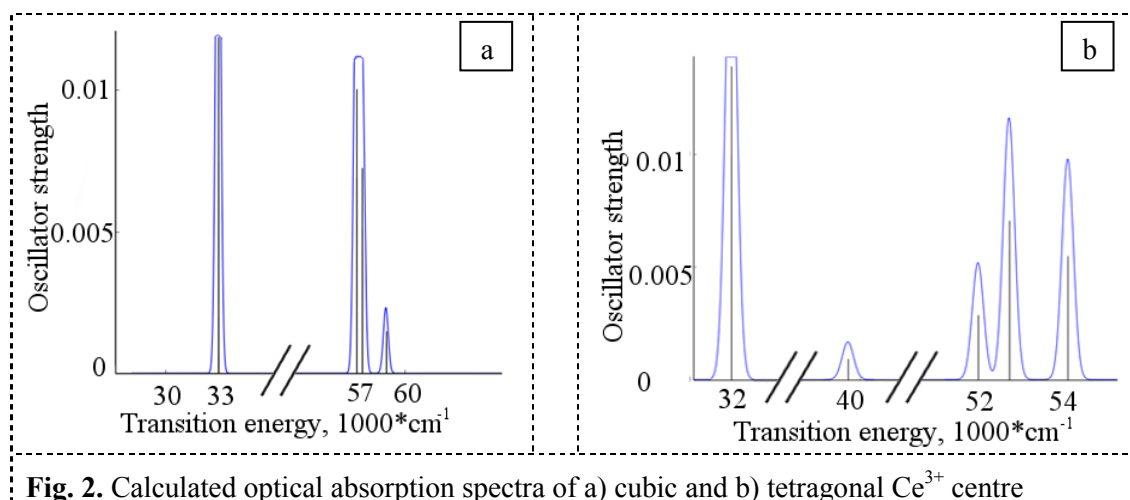
State	Energy without spin-orbit, cm^{-1}	Energy with spin-orbit, cm^{-1}	Energy, cm^{-1} , (calc.) [11]	Energy, cm^{-1} , (expt.) [10]	Oscillator strength
8	31888	33058.9	33633	32300	1.35E-02
9	31892	33072.7		32300	6.8E-03
10	56442	57190.2	48071	51600	9.12E-03
11	56444	57539.5		53300	4.65E-03
12	56708	58909.2		55200	1.35E-03

Table 5. 4f energy levels of the tetragonal Ce^{3+} centre

State	Energy without spin-orbit, cm^{-1}	Energy with spin-orbit, cm^{-1}	Energy, cm^{-1} (calc.) [12]	Energy, cm^{-1} (expt.) [2]
1	0	0	0	0
2	97.3	275.2	281	110
3	98.4	512.5	559	579
4	180.9	2314.7	2276	2192
5	188.9	2316.7	2380	2307
6	636.3	2679.6	2635	2440
7	1892.0	3630.6	3325	3562

Table 6. 5d energy levels and optical transitions of the tetragonal Ce^{3+} centre

State	Energy without spin-orbit, cm^{-1}	Energy with spin-orbit, cm^{-1}	Energy, cm^{-1} (calc.) [11]	Energy, cm^{-1} (calc.) [12]	Energy, cm^{-1} (expt.) [2]	Oscillator strength
8	32692.8	33852.9	32907	30714	32350	1.26E-02
9	38591.3	39708.4	41457	40285		8.28E-04
10	51975.3	52771.9	46377	48992	49490	2.59E-03
11	51975.9	53539.9		49961	51160	5.20E-03
12	53467.3	54997.4	47506	52946	53370	4.80E-03

**Fig. 2.** Calculated optical absorption spectra of a) cubic and b) tetragonal Ce^{3+} centre

4. Conclusion

We performed *ab initio* embedded cluster calculations of Ce^{3+} impurity centres in CaF_2 crystal including scalar relativistic effects and spin-orbit coupling. Cubic and tetragonal centre were investigated. Calculated structural parameters, energy levels and absorption spectrum are in good agreement with experimental and theoretical data. This shows the applicability of the chosen approach for studying rare earth impurities in fluoride crystals.

The “cubic” Ce^{3+} centre turns out not to be perfectly cubic. We obtained small but not negligible asymmetric displacement of surrounding fluorine ions in the ground state of the centre. The deviation of this defect from perfect O_h symmetry can be seen from EPR data and from the splitting of high energy lines in optical absorption spectrum. At present moment it is not clear whether the symmetry breaking of Ce^{3+} centre should be attributed to static or dynamic Jahn-Teller effect or to the presence of other charge compensating impurities in the vicinity of the defect.

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