First Principle Calculation of $4f^{n} \rightarrow 4f^{(n-1)}5d$ Absorption Spectra of Ce^{3+} and Pr^{3+} Ions in Alkaline Earth Fluorides

Alexandra Myasnikova, Andrey Mysovsky, and Evgeny Radzhabov

***Abstract*—In this paper we present the results of an *ab initio* calculations of df-absorption spectra for alkaline earth fluoride matrix doped with Pr^{3+} and Ce^{3+} ions. The density-functional theory (DFT) calculations have been performed in embedded-cluster approach. All our results were obtained with taking into account the lattice relaxation in the presence of trivalent impurity ion. The calculation have been made both for cubic and tetragonal centers. For the tetragonal centers we estimate the crystal field splitting of e_g level.**

***Index Terms*—Absorption, alkali-earth fluoride, Ce^{3+}-doping, embedded cluster approach, Pr^{3+}-doping.**

I. INTRODUCTION

TODAY many excellent scintillators doped with rare earth ions such as Pr^{3+} or Ce^{3+} have been developed [1], [2]. The fast luminescence of Pr^{3+} and Ce^{3+} activators is due to dipole allowed transition from $4f^{n-1}5^{d}$ configuration to $4f^{n}$ ground state (df-emission). Ce^{3+} ion still remains the most popular activator for halide and oxide scintillators introducing both high efficiency of registration and fast decay time [3]. For alkaline earth fluorides (CaF_2, SrF_2 and BaF_2) doped with Pr^{3+} or Ce^{3+} ions df-emission in the region of 4–6 eV and 4 eV are observed respectively [4].

The $4f^{n} \rightarrow 4f^{(n-1)}5d$ absorption spectra of lanthanides have been studied for a long time in different lattice environment [5]–[7]. It was shown that the 5d level of rare earth ions is very sensitive to local surrounding, and so the crystal field splitting of 5d level in accordance with the defect symmetry was observed. The experimental data are summarized in Table I. In the Ce^{3+} or Pr^{3+} doped alkali earth fluorides the impurity ions replaced the cation lattice positions and therefore the interstitial fluorine ions are formed for compensating the excess charge. According to theoretical results [8] the rare-earth sites compensated by interstitial fluorine (F_i^-) in nearest-neighbor (NN) positions are favored by small lattice constants and sites compensated by a F_i^- in the next-nearest-neighbor (NNN) positions are favored by larger lattice constants. Therefore, tetragonal C_{4v} symmetry sites are predicted for CaF_2 lattice, trigonal C_{3v} sites for BaF_2 lattice, and both types are predicted for SrF_2. In addition to these types of charge-compensating the cubic symmetry (O_h) of rare earth ions may be observed when the distance between impurity and interstitial fluorine is several times greater than the lattice constant. Moreover for BaF_2 crystal the C_{3v} defect symmetry may be assumed with single ion (O_h) in accordance with the large $R^{3+} - F_i^-$ distance and slight influence on the $5d-$ level splitting. In accordance with the different symmetry sites the energy of 5d level of rare earth ions split by the cubic or tetragonal crystal fields and so one may expect a number of bands in absorption spectra connected with the defect symmetry.

TABLE I
PEAK POSITIONS OF $4f^{n} \rightarrow 4f^{(n-1)}5d$ ABSORPTION BANDS IN ALKALINE-EARTH FLUORIDE CRYSTALS DOPED WITH Ce^{3+} OR Pr^{3+} IONS.

Crystal	Transition energies (eV), ref. [5, 6]		Denoted in the paper
	Ce^{3+}	Pr^{3+}	
CaF_2	4.02	5.62	A
	5.08	6.82	C
	6.14	7.69	
	6.34	8.06	B
	6.68	8.38	
SrF_2	4.17	5.80	A
	5.08	6.96	C
	6.05	7.66	
	6.24	7.87	B
	6.62	8.33	
BaF_2	4.24	5.86	A
	6.20	7.81	
	6.41	7.91	B
	6.63	8.24	

In this work we present the results of an *ab initio* calculations of lattice relaxation and the energies of the $4f^{n} \rightarrow 4f^{(n-1)}5d$ absorption bands of Ce^{3+} and Pr^{3+} ions embedded in alkaline earth fluoride matrix. We used clusters with O_h and C_{4v} symmetries for both obtaining the crystal-field splitting and comparing the calculated results with experimental ones.

II. CALCULATION DETAILS

The calculations have been performed in embedded cluster approach implemented in the GUESS computer code [9]. The

---

Manuscript received November 15, 2011; revised January 19, 2012; accepted February 06, 2012. This work was supported in part by the Russian Foundation for Basic Research (grant 11-02-00717-a).

The authors are with the A. P. Vinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Science, 664033 Irkutsk, Russia (e-mail: sasham@igc.irk.ru).

Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/TNS.2012.2187931

0018-9499/$31.00 © 2012 IEEE

TABLE II
CALCULATED PARAMETERS OF Ce^{3+} ION IN DIFFERENT MATRIX

Crystal	Symmetry	R*, Å	Energy of 4f→5d transitions, eV	f_{osc}
CaF_2	O_h	-	4.17	0.0063
			5.96	0.0083
	C_{4v}	2.25 (91%)	4.08	0.0152
			5.14	0.0068
			5.75	0.0086
			5.89	0.0194
SrF_2	O_h	-	4.21	0.0243
			5.77	0.0165
	C_{4v}	2.28 (96%)	4.23	0.0130
			4.99	0.0038
			5.81	0.0192
			5.93	0.0106
BaF_2	O_h	-	4.29	0.0148
			6.13	0.0157

* R – the distance between interstitial fluorine and cerium ions: F_i^- - Ce^{3+}. The distance was obtained both in angstroms and in percent from the F-F distance in unrelaxed cluster.

embedded cluster method was described in [10] in detail, and so we do some remarks about our calculations. In the approach the system of interest is divided into several groups:

(i) quantum—mechanical cluster (QM), which includes the defect and its nearest neighbors and is treated with B3LYP (40% of Hartree–Fock and 60% of DFT exchange) density functional method. This modified functional gives the accurate electron state localization and was successfully used for DFT calculations of different defects in alkali earth fluorides [11]–[13].

(ii) classical region consists of several hundreds of ions are treated classically in the shell model. We used pair potential parameters in buckingham form from [13]. Both QM and classical region are allowed to move to provide the accurate lattice distortion around the defect.

(iii) the classical region, in its turn, is surrounded by point charges necessary to provide correct Madelung potential inside the classical and QM regions. These atoms are fixed during the geometry optimization run.

We obtained the time dependent DFT (TD DFT) method for calculation of transition energies and oscillators strength with the Gaussian 03 [14] computer code. We used 6–31G basis set of George Petersson and coworkers [15] on fluorine and calcium ions and SDD basis on strontium, barium, cesium and praseodymium ions. We replaced all cations in the radius of 6 Å around QM cluster with the interface ions, which had LANL1 ECP (Hay-Wadt large core pseudopotential) and no basis functions.

The following QM clusters were selected and used to model the point defects in the present work: $Me_{12}F_{32}$-R^{3+} for modeling a cubic symmetry O_h, and Me_5F_{17}-R^{3+} for representation of selectively charge-compensated C_{4v} site $(Me - Ca^{2+},\ Sr^{2+},\ Ba^{2+})$.

III. RESULTS AND DISCUSSION

A. Ce^{3+} *Ion*

The absorption spectra of Ce^{3+} doped alkaline earth fluorides have been experimentally investigated in detail in [5]. It was shown that the absorption spectra consist of three main parts, labeled as A, B and C (see Table I), with the band C observed only for CaF_2 and SrF_2 crystals. It was also shown that the intensity of the band C grows steadily with increasing the Ce^{3+} concentration. This band was associated with the "cluster-ion" absorption, when the Ce^{3+} ion and nearest interstitial fluorine ion tend to cluster with another identical pair. For the BaF_2:Ce^{3+} crystal only bands in regions A and B were observed.

First of all we have calculated the lattice distortion induced by the presence of Ce^{3+} ion in crystalline matrix. The calculations have been performed both for the single (with O_h symmetry) and for Ce^{3+} ion locally compensated by the interstitial fluorine (C_{4v} symmetry). The displacements of nearest 8 fluorine ions induced by the single Ce^{3+} ion were 0.015, 0.12 and 0.32 Å toward the impurity ion for CaF_2, SrF_2 and BaF_2 crystals respectively. In the case of the presence of interstitial fluorine the displacements of nearest fluorine ions were lager. The directions of shifts are shown in Fig. 1. One can see that the interstitial fluorine and Ce^{3+} ions get closer. The calculated distances between these ions in different matrices are summarized in Table II. The displacements of the F_i^- ion cause the large displacements of four fluorines, which are situated between Ce^{3+} and F_i^- ions. The maximum displacements of fluorine ions were 0.21 and 0.17 Å for CaF_2 and SrF_2 respectively. These results are in agreement with the results in [16].

For the barium fluoride crystal the interstitial and cerium ions shifted in opposite directions. Therefore, we conclude that this

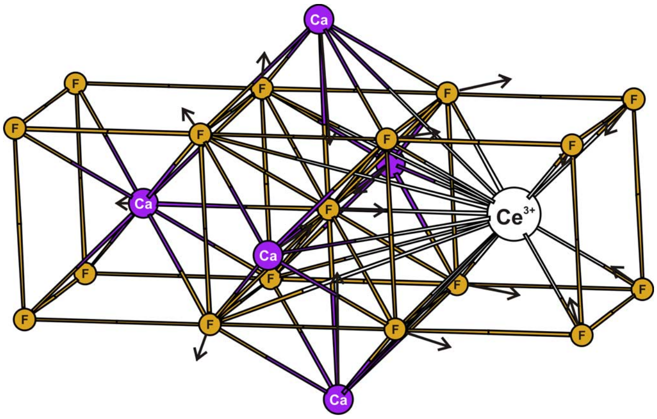

Fig. 1. Cluster Ca_6F_{17} representing the C_{4v} interstitial fluorine position. Arrows indicate the displacements of ions during the lattice relaxation induced by $Ce^{3+} - F_i^-$ defect.

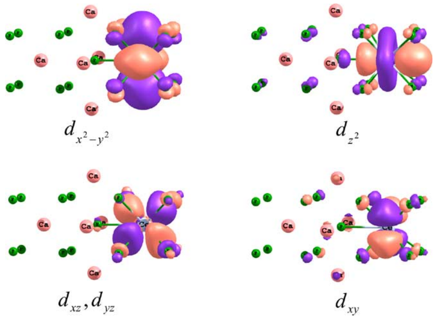

Fig. 2. One-electron 5d states of Ce^{3+} or Pr^{3+} participating in the optical absorption transition.

symmetry group is unstable in BaF_2. This result agrees well with theoretical work [8] as was mentioned above.

Using the geometry of the ground state we performed the calculation of $4f^n \rightarrow 4f^{(n-1)}5d$ absorption spectra. The results of TD DFT calculations are listed in Table II. For the single ion calculation only two bands were observed. These bands are connected with the O_h crystal-field splitting of 5d state to e_g and t_{2g} levels. Our results agree well with experimental data of investigation of cubic Ce^{3+} centers in CaF_2 [17] and SrF_2 [18] crystals. Authors of [17] showed the excitation spectra of CaF_2 doped with Ce^{3+} and Na^+, where only cubic centers were formed. Two bands at 4.04 and 6.51 eV were observed in this spectrum. For the cubic centers in SrF_2:Ce^{3+} also two bands at 4.14 and 6.7 eV were observed [17]. So we can conclude that the bands A and B for BaF_2:Ce^{3+} crystal correspond to cubic centers too. In all cases of single Ce^{3+} ions the 6–7 eV band consists of three bands which are due to spin-orbit splitting of t_{2g} level.

In the case of the interstitial fluorine ion presence in NN position the 5d level splits into four levels: $5d_{x2-y2}$, $5d_{z2}$, $5d_{(yz\ and\ xz)}$ and $5d_{xy}$. Two former states correspond to crystal field splitting of e_g level, the latter two corresponds t_{2g} level. Fig. 2 shows molecular orbitals (MO) of 5d state participating in TD DFT calculations. The MO located largely on the cerium ion, with the shape of each orbital corresponds to an orbital type as identified in the figure.

TABLE III
CALCULATED PARAMETERS OF Pr^{3+} ION IN DIFFERENT MATRIX

Crystal	Symmetry	R*, Å	Energy of 4f→5d transitions, eV	f_{osc}
CaF_2	O_h	-	5.83	0.0545
			9.01	0.1105
	C_{4v}	2.57 (93%)	5.77	0.0238
			7.03	0.0610
			8.69	0.0314
			9.05	0.0733
SrF_2	O_h	-	5.94	0.0592
			8.96	0.1084
	C_{4v}	2.92 (98%)	5.83	0.0044
			6.59	0.0381
			8.29	0.0072
			8.61	0.0106
BaF_2	O_h	-	6.04	0.0496
			8.61	0.0956

* R – the distance between interstitial fluorine and cerium ions: F_i^- - Ce^{3+}. The distance was obtained both in angstroms and in percent from the F-F distance in nonrelax cluster.

According to our calculations (Table II) the e_g level is more sensitive to the distance between Ce^{3+} and F_i^- ions. We observed three main bands in absorption spectra as was obtained in experiments for CaF_2:Ce^{3+} and SrF_2:Ce^{3+} crystals. The calculated energies agree well with experimental data, but the high-energy bands were underestimated by TDDFT calculation. We have been making our calculations without taking into account relativistic effects. We assume that these effects can cause the error in DFT results of transition energies as was presented in [19].

In spite of the assumption of authors [5] that bands C are due to "cluster-ion" absorption we can attribute the band near 5 eV to the $4f \rightarrow 5d_{z2}$ transitions of Ce^{3+} ions. This conclusion agrees with experimental data [18], where the 5 eV band was observed only for tetragonal Ce^{3+} center. The complicated structure of the band B is also due to both crystal field and spin-orbit splitting of the t_{2g} level.

B. Pr^{3+} *Ion*

The experimental investigation of the Pr^{3+} ion absorption in CaF_2, SrF_2 and BaF_2 crystals is presented in [6], [20]. The UV absorption spectra of Pr^{3+} ion in alkali earth fluorides are similar to those of Ce^{3+}: as listed in Table I the $4f^n \rightarrow 4f^{(n-1)}5d$ spectra consist of three bands A, B and C.

The results of calculation are presented in Table III. According to our calculation of lattice relaxation of cubic and tetragonal Pr^{3+} centers, the size and directions of nearest fluorine displacements are the same as in the case of Ce^{3+} ion. But the distances between Pr^{3+} and interstitial fluorine are somewhat larger, so the crystal-field splitting of e_g level is smaller than in the Ce^{3+} doped fluorides. All obtained TD DFT results for Pr^{3+} are comparable with those for Ce^{3+} ion: (i) for single Pr^{3+} ion we observed only two bands, which correspond to cubic crystal field splitting of 5d band as experimentally obtained for BaF_2:Pr^{3+}; (ii) for Pr^{3+} ion with

NN charge compensator we observed four bands which agree with tetragonal splitting of 5d state; (iii) the band C correspond to $4\mathrm{f} \rightarrow 5\mathrm{d}_{z2}$ transitions of tetragonal Pr^{3+} center. The latter result agrees well with the theoretical work presented in paper [21], [22].

IV. CONCLUSION

We have performed *ab initio* calculations of lattice distortion and $4\mathrm{f}^{\mathrm{n}} \rightarrow 4\mathrm{f}^{(\mathrm{n}-1)}5\mathrm{d}$ absorption of Ce^{3+} and Pr^{3+} doped alkaline earth fluorides. The calculations have been made for both cubic and tetragonal centers. For the tetragonal centers we estimate the crystal field splitting of the e_g level. We conclude that the C bands of experimental spectra connect not only with the defects aggregation but also with $4\mathrm{f} \rightarrow 5\mathrm{d}_{z2}$ transitions of rare earth ions.

ACKNOWLEDGMENT

The authors gratefully appreciate the use of Blackford and MVS-1000 computational clusters located in the Institute of System Dynamics and Control Theory SB RAS.

REFERENCES

[1] P. A. Rodnyi, “Progress in fast scintillators,” *Radiat. Meas.*, vol. 33, pp. 605–614, 2001.

[2] P. Dorenbos, “Fundamental limitations in the performance of Ce, Pr and Eu activated scintillators,” *IEEE Trans. Nucl. Sci.*, vol. 57, no. 3, pp. 1162–1167, Jun. 2010.

[3] K. W. Kramer, P. Dorenbos, H. U. Gudel, and C. W. E. vanEijk, “Development and characterization of highly efficient new cerium doped rare earth halide scintillator materials,” *J. Mater. Chem.*, vol. 16, pp. 2773–2780, 2006.

[4] E. Radzhabov and V. Nagirnyi, “Excitation of Pr^{3+} ions in alkaline-earth fluorides,” in *Proc. IOP Conf. Ser.: Mater. Sci. Eng.*, 2010, vol. 15, pp. 012029–012029.

[5] E. Loh, “Ultraviolet absorption spectra of Ce^{3+} in alkaline-earth fluorides,” *Phys. Rev.*, vol. 154, no. 2, pp. 270–276, 1967.

[6] E. Loh, “Ultraviolet absorption spectra of Pr^{3+} ion in alkaline-earth fluorides,” *Phys. Rev.*, vol. 158, no. 2, pp. 273–279, 1967.

[7] P. Dorenbos, “The $4\mathrm{f}^{\mathrm{n}} \rightarrow 4\mathrm{f}^{\mathrm{n}}$-$15\mathrm{d}$ transitions of the trivalent lanthanides in halogenides and chalcogenides,” *J. Lumin.*, vol. 91, pp. 91–106, 2000.

[8] J. Corish, C. R. A. Catlow, P. W. M. Jacobs, and S. H. Ong, “Defect aggregation in anion-excess fluorites. Dopant monomers and dimers,” *Phys. Rev. B*, vol. 25, pp. 6425–6438, 1982.

[9] P. V. Sushko, A. L. Shluger, and C. R. A. Catlow, “Relative energies of surface and defect states: Ab initio calculations for the MgO(001) surface,” *Surface Science*, vol. 450, pp. 153–153, 2000.

[10] A. S. Mysovsky, P. V. Sushko, E. A. Radzhabov, M. Reichling, and A. L. Shluger, “Structure and properties of oxygen centers in CaF_2 crystals from ab initio embedded cluster calculations,” *Phys. Rev. B*, vol. 84, pp. 064133–064133, 2011.

[11] A. Myasnikova, E. Radzhabov, A. Mysovsky, and V. Shagun, “Impurity luminescence in $\mathrm{BaF2}{:}\mathrm{Y}^{3+}$ and $\mathrm{BaF2}{:}\mathrm{Yb}^{3+}$ crystals,” *IEEE Trans. Nucl. Sci.*, vol. 55, no. 3, pp. 1133–1137, Jun. 2008.

[12] A. Myasnikova, E. Radzhabov, and A. Mysovsky, “Ab initio calculation of BaF_2 cross-luminescence spectrum,” *J. Lumin.*, vol. 129, pp. 1578–1580, 2009.

[13] A. S. Myasnikova, E. A. Radzhabov, and A. S. Mysovsky, “Ab initio calculation of charge-transfer absorption in CaF_2 and SrF_2 crystals with Eu^{3+} and Yb^{3+} impurities,” *IEEE Trans. Nucl. Sci.*, vol. 57, no. 2, pp. 1193–1195, Apr. 2010.

[14] M. J. Frisch *et al., Gaussian 03 (Revision E.1)*. Pittsburgh, PA: Gaussian Inc., 2007.

[15] G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, and J. Mantzaris, “A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements,” *J. Chem. Phys.*, vol. 89, pp. 2193–2218, 1988.

[16] T. A. Gavasheli, D. M. Daraseliya, D. L. Dzhaparidze, R. I. Mirianashvili, O. V. Romelashvili, and T. I. Sanadze, “Method for estimating local lattice distortions near a magnetic ion based on the parameters of the ligand hyperfine interaction: Ce^{3+} in the fluorite homologous series,” *Phys. Solid State*, vol. 44, pp. 1880–1884, 2002.

[17] L. vanPieterson, M. F. Reid, R. T. Wegh, S. Soverna, and A. Meijerink, “$4\mathrm{f}^{\mathrm{n}} \rightarrow 4\mathrm{f}^{\mathrm{n}-1}5\mathrm{d}$ transitions of the light lanthanides: Experiment and theory,” *Phys. Rev. B*, vol. 65, pp. 045113–045113, 2002.

[18] E. Radzhabov and T. Kurobori, “Cubic and tetragonal Ce ions in strontium fluoride,” *J. Phys.: Condens. Matter*, vol. 16, pp. 1871–1877, 2004.

[19] J. Andriessen, E. van der Kolk, and P. Dorenbos, “Lattice relaxation study of the 4f-5d excitation of Ce^{3+}-doped LaCl3, LaBr3, and NaLaF4: Stokes shift by pseudo Jahn-Teller effect,” *Phys. Rev. B*, vol. 76, pp. 075124–075124, 2007.

[20] E. Radzhabov, “Photon cascade emission of Pr^{3+} ion in alkaline-earth fluorides,” *J. Lumin.*, vol. 159, pp. 1581–1585, 2009.

[21] T. Chen, C. K. Duan, S. Xia, and M. Yina, “Calculations for 4f-5d excitation spectra of $\mathrm{C}_{4\mathrm{v}}$ site-selective F charge-compensated $\mathrm{CaF2}{:}\mathrm{Pr}^{3+}$ and $\mathrm{CaF2}{:}\mathrm{Ce}^{3+}$,” *J. Lumin.*, vol. 122–123, pp. 51–54, 2007.

[22] K. Ogasawara, S. Watanabe, H. Toyoshima, and M. G. Brik, “First-principles calculations of $4\mathrm{f}^{\mathrm{n}} \rightarrow 4\mathrm{f}^{\mathrm{n}-1}5\mathrm{d}$ transition spectra,” in *Handbook on the Physics and Chemistry of Rare Earths*. North-Holland: Elsevier, 2007, vol. 37, ch. 231.