First-principles relativistic calculation for $4f$–$5d$ transition energy of Ce^{3+} in various fluoride hosts

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Abstract

In this paper, we investigated the $4f$–$5d$ transition energy of Ce^{3+} in various fluoride hosts based on the first-principles discrete-variational Dirac–Slater (DV-DS) calculations using Slater's transition-state theory. Especially, we focused on the lowest energy peak (1st peak) of $4f$–$5d$ transition for Ce^{3+} impurities. As the host crystals, we adopted the 15 fluorides, for which the experimental data of the lowest energy peak (1st peak) in $4f$–$5d$ transitions were available from literature except for $NaMgF_3$ and $BaMgF_4$. A high correlation between the experimental 1st peak energies and the theoretical ones was obtained which suggests a possibility to predict the $4f$–$5d$ transition energy of Ce^{3+} in various fluoride hosts using the first-principles calculation.
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1. Introduction

Recently, $4f$–$5d$ transitions of trivalent cerium ion (Ce^{3+}) in various fluorides have drawn attentions due to their application for luminescent materials in UV and VUV region such as tunable solid-state lasers or phosphors. Although laser oscillation was reported in some Ce^{3+}-doped fluorides such as Ce^{3+}:LiLuF$_4$ or Ce^{3+}:LiCaAlF$_6$, solid-state laser materials which directly lase in UV and VUV region have not been put into practical use [1,2] to date. And then, because of strong expectations for luminescent materials in high energy region, $4f$–$5d$ transition of Ce^{3+} in various fluoride hosts were analyzed intensively both experimentally and theoretically [3–10]. Because $5d$ orbital of trivalent cerium is strongly affected by crystal field, the way of crystal field splitting (cfs) and its magnitude are strongly influenced by many factors such as coordination number, symmetry of Ce^{3+} site and bond lengths between Ce^{3+} ion and the nearest F^- ions. Therefore, understanding how the separation between $4f$ levels and $5d$ levels or the way of $5d$ level splitting and its magnitude are influenced by the local structure via crystal field, is essential for designing the optical materials using the $4f$–$5d$ transition of Ce^{3+} in various hosts. In this paper, $4f$–$5d$ transition energy of Ce^{3+} in various fluoride host crystals were calculated by first-principles relativistic calculations, in which the four-component Dirac equation is directly solved. The $4f$–$5d$ transition energies were estimated within the density functional theory scheme using the so-called Slater's transition state method [11]. The host crystal dependency on $4f$–$5d$ transitions of Ce^{3+} as well as the effects of the lattice relaxation on them were investigated in detail.

2. Computational procedure

$4f$–$5d$ transitions of rare-earth ions are generally attributed to transitions between the multiplet states. However, in case of trivalent cerium, since Ce^{3+} has $[Xe]4f^1$ electronic configuration, there are not multiplet states and $4f$–$5d$ transitions can be attributed to transitions between the molecular orbitals (MOs). In other words, the $4f$–$5d$ transitions can be analyzed within the one-electron

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approximation. Therefore, in this work, MO energy and wave functions were calculated by fully relativistic discrete-variational Dirac–Slater (DV-DS) method [12,13] in which the four-component Dirac equation is directly solved. Then, so as to estimate the $4f$–$5d$ transition energy of Ce^{3+} in various fluorides, we performed MO calculations in the Slater's transition state, in which a half-electron is removed from the lowest $4f$ level and added to the lowest $5d$ level.

The fully relativistic Hamiltonian used in the calculations is expressed as

$$h = c\tilde{\alpha}\,\mathbf{p} + \tilde{\beta}c^2 + V(\mathbf{r})$$
$$= -\mathrm{i}c\left(\tilde{\alpha}_x\frac{\partial}{\partial x} + \tilde{\alpha}_y\frac{\partial}{\partial y} + \tilde{\alpha}_z\frac{\partial}{\partial z}\right) + \tilde{\beta}c^2 + V(\mathbf{r}), \quad (1)$$

where c is the velocity of light, $\mathbf{p} = -\mathrm{i}\nabla$ is the momentum operator and $\tilde{\alpha}$, $\tilde{\beta}$ are the Dirac matrices. Potential $V(\mathbf{r})$ is expressed as

$$V(\mathbf{r}) = -\sum_v \frac{Z_v}{|\mathbf{r} - \mathbf{R}_v|} + \int \frac{\rho(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|}\,\mathrm{d}\mathbf{r'}$$
$$- 3\alpha\left\{\frac{3}{8\pi}\rho(\mathbf{r})\right\}^{1/3} + \sum \frac{Z_\mu^{\mathrm{eff}}}{|\mathbf{r} - \mathbf{R}_\mu|}, \quad (2)$$

where Z_v and $\mathbf{R}_v$ are the charge and position of the vth nucleus , Z_μ and $\mathbf{R}_\mu$ the effective charge and position of the μth ion outside the model cluster ρ the electron density and $\mathbf{r}$ the position of an electron. The four terms represent the nucleus–electron attractive interaction, the electron–electron repulsive interaction, the exchange correlation interaction and the effective Madelung potential, respectively.

In addition, the effects of the lattice relaxation due to the substitution of cation by trivalent cerium ion were estimated using the ionic radius. The Ce^{3+}–F^- bond length with consideration of the effects of the lattice relaxation $d_{\mathrm{relaxed}}(M^{n+} - F^-)$ was estimated as

$$d_{\mathrm{data}}(M^{n+} - F^-)\frac{r(Ce^{3+}) + r(F^-)}{r(M^{n+}) + r(F^-)} = d_{\mathrm{relax}}(Ce^{3+} - F^-), \quad (3)$$

where $d_{\mathrm{data}}(M^{n+} - F^-)$ is an experimental bond length between n cation M^{n+} and F^- in pure crystal, $r(X)$ represents the Shannon's ionic radii of X ion corresponding to the coordination number and the valence state in each host crystal [14]. In case of CeF_3, there is no relaxation since Ce^{3+} is not an impurity. In this work, we calculated using relatively small clusters composed of the central Ce^{3+} ion and the nearest-neighbor F^- ions. Several thousand point charges were located at the external atomic positions so as to reproduce the effective Madelung potential. Hereby, since the bulk crystal environment is reproduced, it could be approximately regarded as neutral stoichiometric condition.

For the adopted 15 fluoride host crystals, crystal structure data such as: (1) space group; (2) substituted site of Ce^{3+}; (3) symmetry of substituted site; (4) coordination number of substituted site; and (5) relaxation rate, are listed in Table 1.

3. Results and discussions

Fig. 1 shows the calculated energy level schemes of the MOs mainly composed of Ce-$4f$ or Ce-$5d$ orbitals. (Hereafter we call the energy levels corresponding to these MOs as Ce-$4f$ levels or Ce-$5d$ levels for simplicity.) obtained for clusters without consideration of lattice relaxations by correction of chemical bond length. The numerical data related to these energy levels, which will be explained later, are also listed in Table 2. Since initial state of $4f$–$5d$ transitions is the lowest Ce-$4f$ level, its energy was set at $0\,\mathrm{eV}$.

Table 1
Crystal structure data of 15 fluoride hosts: (1) space group, (2) substitution site of Ce^{3+}, (3) point symmetry of substitution site, (4) coordination number of Ce^{3+} site, (5) relaxation rate

Compound	(1)	(2)	(3)	(4)	(5)
(a) NaF [15]	$Fm\bar{3}m$	Na^+	O_h	6	0.996
(b) CaF_2 [16]	$Fm\bar{3}m$	Ca^{2+}	O_h	8	0.946
(c) SrF_2 [17]	$Fm\bar{3}m$	Sr^{2+}	O_h	8	0.954
(d) BaF_2 [18]	$Fm\bar{3}m$	Ba^{2+}	O_h	8	0.899
(e) KY_3F_{10} [19]	$Fm\bar{3}m$	Y^{3+}	C_{4v}	8	1.053
(f) $LiBaF_3$ [20]	$Pm\bar{3}m$	Ba^{2+}	O_h	12	0.908
(g) $LiYF_4$ [21]	$I4_1/a$	Y^{3+}	S_4	8	1.053
(h) $LiCaAlF_6$ [22]	$P\bar{3}1c$	Ca^{2+}	S_6	6	1.004
(i) $LiSrAlF_6$ [23]	$P\bar{3}1c$	Sr^{2+}	S_6	6	0.931
(j) CeF_3 [24]	$P\bar{3}c1$		C_2	11	0.000
(k) YF_3 [25]	$Pnma$	Y^{3+}	C_s	9	1.051
(l) LaF_3 [26]	$P\bar{3}c1$	La^{3+}	C_2	11	0.992
(m) $KMgF_3$ [27]	$Pm\bar{3}m$	K^+	O_h	12	0.899
(n) $BaMgF_4$ [28]	$Cmc21$	Ba^{2+}	C_s	8	0.899
(o) $NaMgF_3$ [29]	$Pnma$	Na^+	C_s	12	0.981

At first, we focus on the magnitude of cfs in 5d levels of Ce^{3+}. Here we define energy width E_{cfs} as the energy gap between the highest Ce-5d level and the lowest one. $KMgF_3$ has the smallest E_{cfs} value, while NaF has the largest E_{cfs} value among the calculated 15 host crystals. According to E_{cfs} in Fig. 1 and the crystal data, Ce^{3+} ions with higher coordination number and longer Ce–F bond lengths tend to have the smaller E_{cfs}. The reasons for this tendency can be explained as follows. The higher coordination number provide an environment closer to spherical, while the increase of the bond lengths reduces the magnitude of the crystal field, both of which result in the decrease of E_{cfs}.
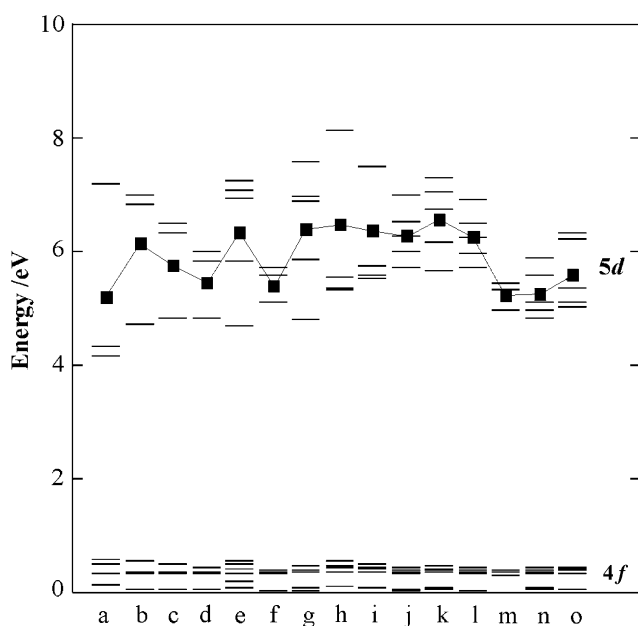

Fig. 1. Energy level scheme corresponding to the MOs mainly composed of Ce-4f and Ce-5d orbitals in each fluoride host crystal without lattice relaxation by correction of chemical bond length. The lowest Ce-4f energy levels are set at 0 eV. The labels a–o represent the host crystals in Table 2.

Next, we focus on the center of gravity for the Ce-5d levels (E_c), which is calculated as the average value of Ce-5d energy values with consideration of the weight of degeneracy. $KMgF_3$ has the smallest E_c value (5.21 eV), while YF_3 has the largest E_c value (6.59 eV) among the calculated 15 host crystals. No clear correlation can be seen between the value of E_c and the crystal structure data in Table 1. In this way, the lowest Ce-5d energy level, i.e., the position of the 1st peak in UV and VUV absorption spectra of Ce^{3+} in fluorides, strongly depends on both E_{cfs} and E_c. The difference in energy between the theoretical 1st peak energy and the experimental 1st peak energy [3] (ΔE_{1st}) is also listed in Table 2. In all cases, the theoretical 1st peak energies are overestimated except for Ce^{3+}: $KMgF_3$. However, the value of ΔE_{1st} does not strongly depend on the host crystals and is within a certain range between 0.55 eV (KY_3F_{10}) and 0.98 eV (NaF) except for $KMgF_3$, $LiBaF_3$, $NaMgF_3$ and $BaMgF_4$. In other words, the trend of 1st peak positions depending on the host crystal is somewhat reproduced. But comparing the ΔE_{1st} values of $KMgF_3$ and $LiBaF_3$ with those of the other host crystals, the former is much smaller than the latter. These values are −0.34 eV for $KMgF_3$ and 0.12 eV for $LiBaF_3$, respectively. This discrepancy presumably comes from the neglect of the effect of correction of bond length due to the substitution of various cations by Ce^{3+}.

On the basis of the above results, we expected that 4f–5d transition energies are significantly affected by lattice relaxation. The effects of lattice relaxation were estimated from the ratio of the ionic radius of substituted cation site and the ionic radius of Ce^{3+} as shown in Table 1 (5). In case of CeF_3, however, since Ce^{3+} is not an impurity, there is no lattice relaxation. The estimated relaxation rates by correction of chemical bond length are between −0.101 and +0.053 depending on the host crystal. Considering these effects, we performed the calculations using clusters with

Table 2
Some values related to the 4f and 5d energy levels for Ce^{3+} in each fluoride host crystals without lattice relaxation by correction of chemical bond length

Compounds	E_{cfs} (eV)	Exp. 1st peak (eV)	Calc. 1st peak (eV)	ΔE_{1st} (eV)	Ce-5d Ave. E_c (eV)
(a) NaF	3.02	3.18	4.16	0.98	5.41
(b) CaF_2	2.30	4.04	4.71	0.67	6.01
(c) SrF_2	1.68	4.17	4.83	0.66	5.77
(d) BaF_2	1.19	4.25	4.83	0.58	5.47
(e) KY_3F_{10}	2.58	4.13	4.69	0.55	6.37
(f) $LiBaF_3$	0.60	5.00	5.12	0.12	5.43
(g) $LiYF_4$	2.76	4.25	4.82	0.57	6.42
(h) $LiCaAlF_6$	2.79	4.49	5.35	0.86	6.51
(i) $LiSrAlF_6$	1.99	4.61	5.53	0.92	6.38
(j) CeF_3	1.27	4.98	5.73	0.75	6.30
(k) YF_3	1.65	4.84	5.66	0.82	6.59
(l) LaF_3	1.20	4.98	5.72	0.76	6.27
(m) $KMgF_3$	0.48	5.30	4.96	−0.34	5.21
(n) $BaMgF_4$	1.08	—	4.82	—	6.34
(o) $NaMgF_3$	1.32	—	5.02	—	5.61

For the meaning of each value, see text.

adjusted bond lengths according to Eq. (3) although the positions of effective point charges were unchanged. Energy level diagrams for Ce-4f and Ce-5d in each fluoride host crystals are shown in Fig. 2, while the related numerical data are also shown in Table 3. Comparing Figs. 2 and 1, ΔE_{1st} dramatically changed in KMgF$_3$ and LiBaF$_3$. ΔE_{1st} of Ce^{3+}:KMgF$_3$ changed from -0.34 to 0.45 eV while that of Ce^{3+}:LiBaF$_3$ changed from 0.12 to 0.69 eV. Although the change of E_{cfs} for Ce^{3+}:KMgF$_3$ is relatively small (from 0.48 to 0.78 eV), E_c significantly changed from 5.21 to 6.16 eV. As a

result, the position of the 1st peak drastically shifted from 4.96 to 5.75 eV, and resultantly the value of ΔE_{1st} changed from -0.34 to $+0.45$ eV which is a value close to ΔE_{1st} values of the other host crystals. A similar tendency can be seen for Ce^{3+}:LiBaF$_3$. E_{cfs} slightly changed from 0.60 to 0.86 eV, while E_c changed significantly from 5.43 to 6.15 eV. As a result, ΔE_{1st} also changed significantly from 0.12 to 0.69 eV which is also close to ΔE_{1st} of the other host crystals. On the other hand, in the case of SrF$_2$, BaF$_2$, KY$_3$F$_{10}$, LiYF$_4$ and BaMgF$_4$, both the cfs (E_{cfs}) and the center of gravity of Ce-5d levels (E_c) change depending on the host crystals. However, the change of the lowest Ce-5d energy levels is relatively small in most cases. Therefore, the lattice relaxation has little influence on the 1st peak position of these materials.

The dispersion of center of gravity for Ce-5d levels (E_c) with respect to the lowest Ce-4f levels is significantly reduced, if the correction of chemical bond length is taken into account.

Fig. 3 shows the correlation between the experimental 1st peak energy and the theoretical 1st peak energy. The coefficients of correlation obtained for unrelaxed and relaxed clusters are 0.78 and 0.98, respectively, which indicates that the correlation between the experimental and theoretical 1st peak energies is significantly improved by consideration of lattice relaxation effects. This result further supports a possibility to predict the 1st peak energy of Ce^{3+} in various fluoride host crystals for which there are no experimental data based on first-principles calculations. Since theoretical 1st peak energy of Ce^{3+}:NaMgF$_3$ is 5.13 eV, we expect that the 1st peak of experimental absorption spectrum to be about 4.43 eV as shown in Fig. 3. In a similar way, in case of Ce^{3+}: BaMgF$_4$, we expect that the 1st peak of experimental absorption spectrum to be about 4.34 eV as also shown in Fig. 3.
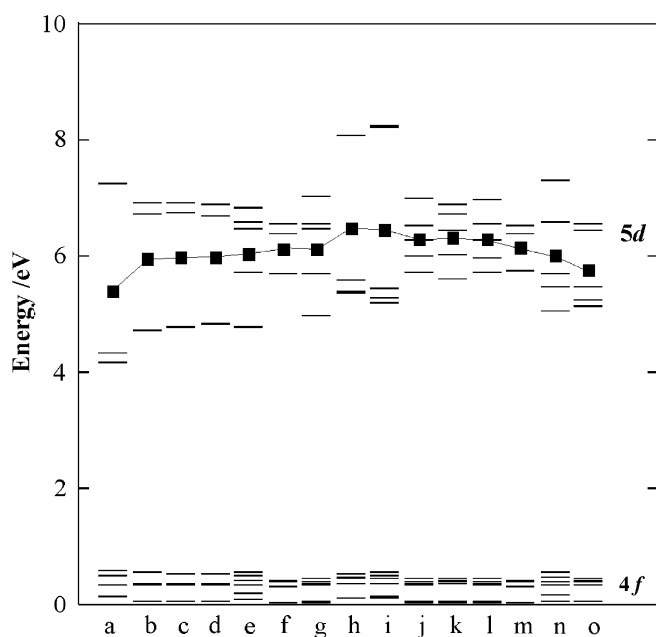

Fig. 2. Energy level scheme corresponding to the MOs mainly composed of Ce-4f and Ce-5d orbitals in each fluoride host crystal with lattice relaxation by correction of chemical bond length. The lowest Ce-4f energy levels are set at 0 eV. The labels a–o represent the host crystals in Table 3.

Table 3
Some values related to the 4f and 5d energy levels for Ce^{3+} in each fluoride host crystals with lattice relaxation by correction of chemical bond length

| Compounds	E_{cfs} (eV)	Exp. 1st peak (eV)	Calc. 1st peak (eV)	ΔE_{1st} (eV)	Ce-5d Ave. E_c (eV)
(a) NaF	3.09	3.18	4.16	0.98	5.43
(b) CaF$_2$	2.19	4.04	4.73	0.69	5.96
(c) SrF$_2$	2.15	4.17	4.78	0.61	6.00
(d) BaF$_2$	2.07	4.25	4.83	0.58	5.99
(e) KY$_3$F$_{10}$	2.04	4.13	4.78	0.65	6.07
(f) LiBaF$_3$	0.86	5.00	5.69	0.69	6.15
(g) LiYF$_4$	2.07	4.25	4.95	0.70	6.13
(h) LiCaAlF$_6$	2.72	4.49	5.26	0.77	6.51
(i) LiSrAlF$_6$	3.05	4.61	5.19	0.58	6.47
(j) CeF$_3$	1.27	4.98	5.73	0.75	6.30
(k) YF$_3$	1.27	4.84	5.62	0.78	6.34
(l) LaF$_3$	1.25	4.98	5.73	0.75	6.31
(m) KMgF$_3$	0.78	5.30	5.75	0.45	6.16
(n) BaMgF$_4$	2.25	—	5.05	—	6.02
(o) NaMgF$_3$	1.44	—	5.13	—	5.38

For the meaning of each value, see text.
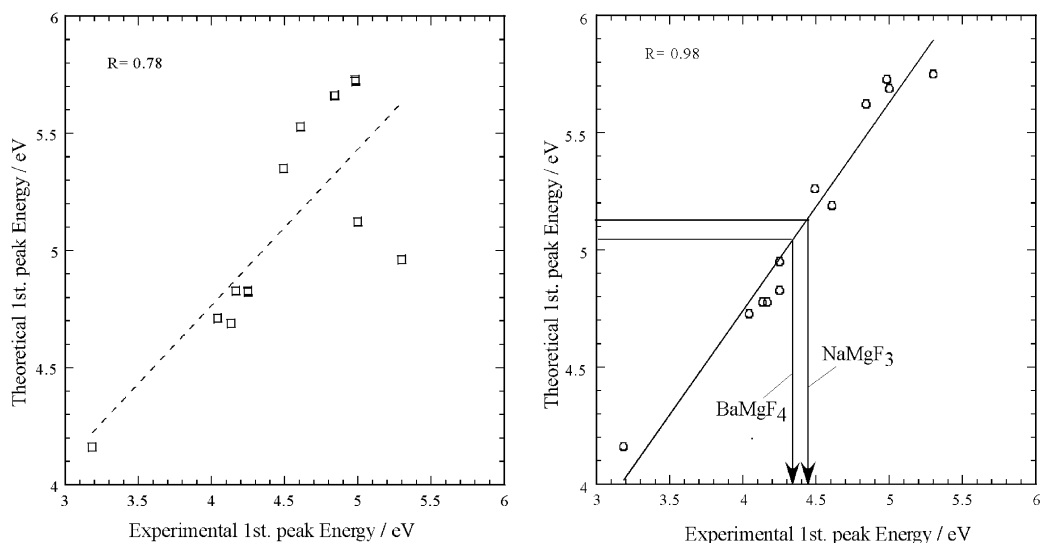
Fig. 3. Correlation diagram between the experimental 1st peak energy and the theoretical 1st peak energy. The left figure (A) shows the results without the lattice relaxation by correction of chemical bond length and right one (B) shows the results with the lattice relaxation by correction of chemical bond length. The corresponding coefficients of correlation R are 0.78 and 0.98, respectively.

4. Conclusion

In this work, we investigated the first-principles calculation for the $4f$–$5d$ transition energy of Ce^{3+} in various fluoride hosts by discrete-variational Dirac–Slater (DV-DS) calculation using Slater's transition-state theory. These calculations were carried out using relatively small clusters in which only Ce^{3+} and the nearest neighbor F^- ions. In spite of the simplicity of the adopted model, we reproduced the tendency of the magnitude of cfs and the way of splitting in each crystal. There is high correlation between the experimental 1st peak of $4f$–$5d$ transition energy and theoretical one. When the effects of the lattice relaxation by correction of chemical bond length were considered, the correlation between the experimental values and the theoretical values was drastically improved. The results provide an effective method to predict the 1st peak of $4f$–$5d$ transition energy for Ce^{3+} in various fluoride host crystals based on the first-principles calculation.

Acknowledgments

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