

# First-Principles Calculation of $4f^n-4f^{n-1}5d^1$ Transitions of Rare-Earth Ions in $\text{LiYF}_4$ and $\text{LiYbF}_4$

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In the present work, we have performed systematic calculations of  $4f^n - 4f^{n-1}5d^1$  absorption spectra of lanthanide ( $\text{Ln}^{3+}$ ) ions in  $\text{LiYF}_4$  and  $\text{LiYbF}_4$  based on the recently developed relativistic configuration-interaction (CI) calculation method. In this program, the many-electron wave functions are obtained as linear combination of relativistic Slater determinations by diagonalization of the many-electron Dirac Hamiltonian. From the comparison between the theoretical absorption spectrum of  $\text{Ln}^{3+}$  in  $\text{LiYF}_4$  and that in  $\text{LiYbF}_4$ , it was found that the first peak shifts toward lower energy side while the other peak shift toward higher energy side in  $\text{LiYbF}_4$  than in  $\text{LiYF}_4$ . By detailed analyses of the molecular orbital (MO) energy level structure and the multiplet energy level structure, it was shown that this characteristic spectral shift was clearly explained by the dominance of the crystal field effects compared to the Coulomb repulsive interactions or spin-orbit interactions.

Key words: first-principles calculation, multiplets, absorption spectra, solid-state lasers

## 1. INTRODUCTION

Recently  $4f^n - 4f^{n-1}5d^1$  transitions of trivalent lanthanoid ( $\text{Ln}^{3+}$ ) ions in crystals have been attracting increasing attention due to their potential applications as solid state lasers in the ultraviolet (UV) region[1]. Although development of novel solid-state laser materials with required wavelengths is quite important, the dependence of the  $4f^n - 4f^{n-1}5d^1$  transition spectra on host crystals is still unclear due to the strong mixing between  $\text{Ln}5d$  orbitals and the ligand orbitals. In order to clarify the effects of cation substitution in host crystals, we have performed systematic calculations of multiplet energy levels and absorption spectra for  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions in  $\text{LiYF}_4$  and  $\text{LiYbF}_4$ . The latter crystal has the same type of crystal structure as former one but has slightly shorter lattice constants due to the smaller radius of Yb than Y. By analyses of the molecular orbital (MO) energy levels, compositions of the MOs, and multiplet energy levels, the influence of three important factors such as crystal field effects, spin-orbit interactions, and Coulomb repulsion interactions, have been investigated and compared quantitatively.

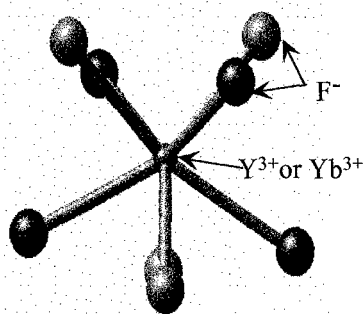


Fig.1 Model Cluster for  $\text{LiYF}_4$  and  $\text{LiYbF}_4$

## 2. COMPUTATIONAL METHOD

A model cluster composed of nine atoms was constructed as the model cluster of  $\text{LiYF}_4$  or  $\text{LiYbF}_4$ . As shown in Fig. 1, the central atom of the cluster is  $\text{Y}^{3+}$  or  $\text{Yb}^{3+}$  which is coordinated by eight fluorine ions. In order to consider effective Madelung potential, several thousand point charges were located at the external atomic sites. For the calculation of impurity  $\text{Ln}^{3+}$  ions in  $\text{LiYF}_4$  or  $\text{LiYbF}_4$ , the central atom in the cluster was substituted by  $\text{Ln}^{3+}$  ions. The MO calculations were performed using the relativistic SCAT computation code, which was originally developed by Rosen *et al.* [2] and improved later by Adachi *et al.* The configuration-interaction (CI) calculations were performed using the relativistic CI computation code developed by Ogasawara *et al.* [3]. In this method, Slater determinants corresponding to all the possible electronic configurations within the considered MOs and electrons are constructed using the calculated four-component relativistic MOs. Then by diagonalization of the many-electron Hamiltonian, the multiplet energies were obtained as eigenvalues and the many-electron wave functions were obtained as linear combination of the Slater determinants. The transition probabilities of electric dipole transitions were calculated using the explicit many-electron wave functions. The theoretical absorption spectra were obtained by broadening the each peak by a Gaussian function with 0.3-eV full-width at half maximum (FWHM).

## 3. RESULTS AND DISCUSSIONS

### 3.1 MO calculations

The MO energy levels obtained by the relativistic MO calculations are shown in Fig.2. The absolute MO energy levels in  $\text{LiYbF}_4$  are higher than those in  $\text{LiYF}_4$  implying the stronger Madelung potential. Since  $\text{LiYF}_4$

and  $\text{LiYbF}_4$ , have the same type of crystal structure, the difference in the Madelung potential can be ascribed to the difference in the Ln-F bond lengths originating from the difference in the cation radius.

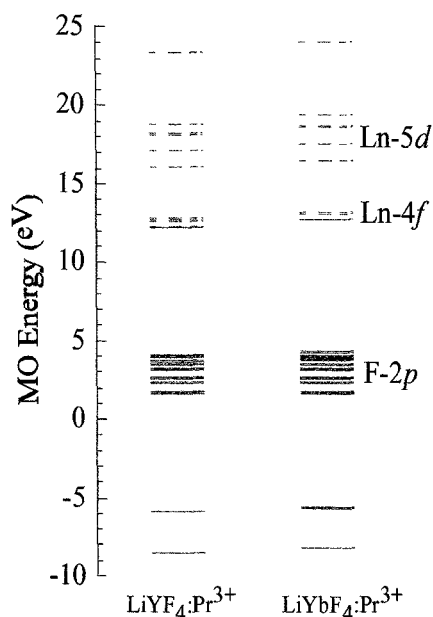


Fig.2 MO Energy of  $\text{LiYF}_4:\text{Pr}^{3+}$  or  $\text{LiYbF}_4:\text{Pr}^{3+}$

The results of population analysis of the MOs mainly composed of Pr- $4f$  or Pr- $5d$  are listed in Table 1. The difference in the compositions of F- $2sp$  orbitals in the MOs mainly composed of Pr- $5d$  orbitals is quite small between  $\text{Pr}^{3+}:\text{LiYF}_4$  and  $\text{Pr}^{3+}:\text{LiYbF}_4$ . These results indicate that the difference in the spatial extension of these MOs is also small and accordingly indicate small difference in the Coulomb repulsion interactions among Ln  $4f$  electrons.

Table 1 Population analysis of the molecular orbitals mainly composed of Pr- $4f$  or Pr- $5d$  in  $\text{LiYF}_4:\text{Pr}^{3+}$  and  $\text{LiYbF}_4:\text{Pr}^{3+}$

LiYF <sub>4</sub>					
Energy (eV)	Irreducible representation	Pr 4f <sub>5/2</sub>	Pr 4f <sub>7/2</sub>	Pr 5d	F 2sp
12.207	E <sub>1/2</sub>	98.4	0.7	0.0	0.8
12.234	E <sub>3/2</sub>	98.6	0.2	0.4	0.8
12.276	E <sub>1/2</sub>	94.7	4.0	0.4	0.9
12.599	E <sub>1/2</sub>	1.3	97.8	0.2	0.7
12.607	E <sub>3/2</sub>	0.0	98.9	0.1	0.8
12.623	E <sub>3/2</sub>	0.2	98.6	0.4	0.8
12.719	E <sub>1/2</sub>	3.1	94.7	0.9	1.3
16.102	E <sub>3/2</sub>	0.0	0.0	97.0	2.9
17.113	E <sub>1/2</sub>	0.2	0.6	93.8	5.1
18.124	E <sub>1/2</sub>	0.2	0.2	93.2	6.4
18.223	E <sub>3/2</sub>	0.1	0.3	93.2	6.3
18.799	E <sub>3/2</sub>	0.2	0.1	92.8	6.9

LiYbF <sub>4</sub>					
Energy (eV)	Irreducible representation	Pr 4f <sub>5/2</sub>	Pr 4f <sub>7/2</sub>	Pr 5d	F 2sp
12.612	E <sub>1/2</sub>	98.2	0.9	0.0	0.8
12.638	E <sub>3/2</sub>	98.6	0.2	0.4	0.8
12.684	E <sub>1/2</sub>	94.3	4.3	0.4	1.0
13.003	E <sub>1/2</sub>	1.3	97.6	0.2	0.8
13.011	E <sub>3/2</sub>	0.0	98.9	0.2	0.8
13.029	E <sub>3/2</sub>	0.2	98.5	0.4	0.9
13.129	E <sub>1/2</sub>	3.4	94.2	1.0	1.4
16.458	E <sub>3/2</sub>	0.0	0.0	96.9	3.1
17.545	E <sub>1/2</sub>	0.3	0.7	93.6	5.2
18.628	E <sub>1/2</sub>	0.2	0.2	93.0	6.4
18.730	E <sub>3/2</sub>	0.1	0.3	93.0	6.4
19.356	E <sub>3/2</sub>	0.2	0.1	92.6	7.0

### 3.2 Multiplet calculations

The multiplet energy levels obtained by relativistic CI calculations are shown in Figs.3,4 and Tables 2-4. The  $\Delta E_{\text{CF}}$  and  $\Delta E_{\text{SO}}$  in the diagram indicate the width of the crystal field splitting and that of the spin-orbit splitting, respectively. These are defined by the following equations where A or B represents a certain spectral term such as  $^3\text{H}_4$ , and  $E_{\text{Max}}$ ,  $E_{\text{Min}}$ , and  $E_{\text{Ave}}$  indicate maximum energy, minimum energy, and average energy for that term, respectively.

$$\Delta E_{\text{CF}}(\text{A}) = E_{\text{Max}}(\text{A}) - E_{\text{Min}}(\text{A})$$

$$\Delta E_{\text{SO}}(\text{A-B}) = E_{\text{Ave}}(\text{A}) - E_{\text{Ave}}(\text{B})$$

The influence of the pure Coulomb repulsion interactions can be also estimated quantitatively by the energy separation between certain LS terms. As shown in Tables 2-4, the difference in the  $^3\text{H}-^1\text{S}$  energy separation between  $\text{Pr}^{3+}:\text{LiYF}_4$  and  $\text{Pr}^{3+}:\text{LiYbF}_4$  is  $9 \text{ cm}^{-1}$  and the difference in  $\Delta E_{\text{SO}}$  is  $2-4 \text{ cm}^{-1}$ , while that of  $\Delta E_{\text{CF}}$  is  $30-80 \text{ cm}^{-1}$ .

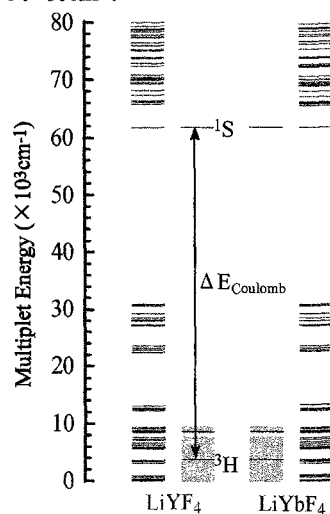
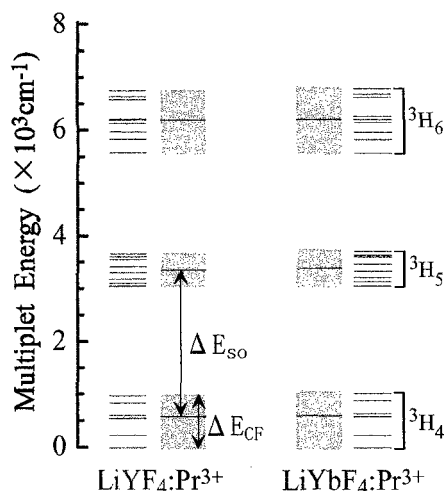


Fig.3 Multiplet Energy of  $\text{LiYF}_4:\text{Pr}^{3+}$  and  $\text{LiYbF}_4:\text{Pr}^{3+}$

Table 2 Values of  $\Delta E_{\text{C}}$  and the difference ( $\text{cm}^{-1}$ )

	LiYF <sub>4</sub>	LiYbF <sub>4</sub>	LiYF <sub>4</sub> -LiYbF <sub>4</sub>
$^1\text{S}-^3\text{H}$	57997	58006	9

Fig. 4 Multiplet Energy of  $\text{LiYF}_4:\text{Pr}^{3+}$  and  $\text{LiYbF}_4:\text{Pr}^{3+}$ Table 3 Values of  $\Delta E_{\text{CF}}$  and the difference ( $\text{cm}^{-1}$ )

	$\text{LiYF}_4$	$\text{LiYbF}_4$	$\text{LiYF}_4\text{-LiYbF}_4$
${}^3\text{H}_4$	977	1029	52
${}^3\text{H}_5$	631	661	30
${}^3\text{H}_6$	1149	1224	75

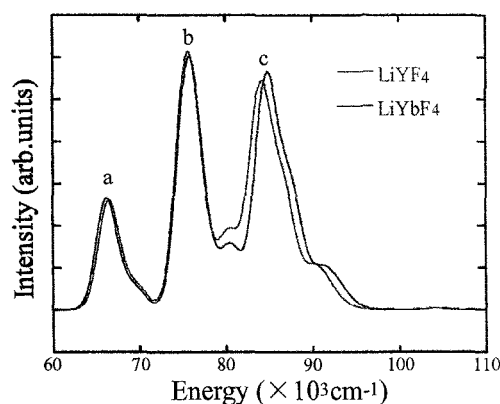
Table 4 Values of  $\Delta E_{\text{SO}}$  and the difference ( $\text{cm}^{-1}$ )

	$\text{LiYF}_4$	$\text{LiYbF}_4$	$\text{LiYF}_4\text{-LiYbF}_4$
${}^3\text{H}_5\text{-}{}^3\text{H}_4$	2795	2793	2
${}^3\text{H}_6\text{-}{}^3\text{H}_5$	2837	2833	4

Therefore these results indicate that the crystal field splittings ( $\Delta E_{\text{CF}}$ ) are the most sensitive to the cation substitution in the host crystal.

### 3.3 $4f^A - 4f^{A-1}5d^1$ theoretical absorption spectrum

The theoretical  $4f^2 - 4f^15d^1$  absorption spectra for  $\text{Pr}^{3+}$  in  $\text{LiYF}_4$  and  $\text{LiYbF}_4$  and their peak energies are shown in Fig. 5 and Table 5, respectively. As shown in the figure, there are 3 broad peaks a, b, and c in each spectrum.

Fig. 5 Theoretical absorption spectra of  $\text{LiYF}_4:\text{Pr}^{3+}$  and  $\text{LiYbF}_4:\text{Pr}^{3+}$ Table 5 Energies of peaks a,b,c ( $\times 10^3\text{cm}^{-1}$ )

	$\text{LiYF}_4$		$\text{LiYbF}_4$
a	66.54	>	66.30
b	75.65	<	75.82
c	84.20	<	84.85

When the host crystal is changed from  $\text{LiYF}_4$  to  $\text{LiYbF}_4$ , peak a shifts toward lower energy side while the other peaks shift toward higher energy side. This variation can be easily understood as a result of stronger crystal field, since the separation of peaks a, b, and c mainly originates from the crystal field splitting.

## 4. SUMMARY

In the present work, we have performed systematic calculations of electronic structures for  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions in  $\text{LiYF}_4$  and  $\text{LiYbF}_4$ . By quantitative analyses of the MO energy levels, compositions of MOs, and multiplet energy levels, we have investigated the relative strengths of the three important factors such as the crystal field effects, spin-orbit interactions, and Coulomb repulsion interactions. The calculated MO energy levels indicate that the difference in the Madelung potential is the most dominant factor which is consistent with the calculated multiplet energy levels indicating that the crystal field effects are the most dominant factor.

In the theoretical  $4f^A - 4f^{A-1}5d^1$  absorption spectra, peak positions exhibit characteristic dependence on the host crystals. This dependence can be clearly interpreted as the change of the crystal-field splitting.

The results of the present work indicate that a cation substitution mainly causes the change of Madelung potential and the change of covalency between the Ln  $5d$  and  $\text{F}2sp$  is quite small. This information makes the prediction of the effects of cation substitutions in the host crystals easier, and therefore quite important for theoretical design of the novel solid-state-laser materials in the UV region.

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