PD Research Report for the 2016 year

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Research Theme Creation of Practical Energy Diagram for Transition Metal and Rare Earth Ions Using Non-Empirical First Principles Calculations
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Research Results （about 2,500 characters in Japanese, about 65 lines times 90 characters in English）

Transition metal (TM) and rare earth (RE) ions doped compounds have attracted great interest due to a wide variety of applications such as phosphors used in white light emitting diode (LED). The current white LED was constructed by combination of a blue InGaN LED chip and yellow $Y_3Al_5O_{12}$: Ce^{3+} phosphor. However, with the current two-color white LED it is impossible to obtain white LEDs with high color rendering index. The combination of yellow $Y_3Al_5O_{12}$: Ce^{3+} emission and blue LED radiation produces a pseudo white light due to a deficiency of red emission. The easiest way to improve the quality of the current white LED can be done by either adding the red phosphor component or broadening the yellow phosphor emission. Recently, Mn^{4+} activated in K_2SiF_6 crystal has received increasing attention as potential red phosphor. However, they are unstable against high temperature and high humidity. Hence, Mn^{4+} doped in more stable host materials such as oxides are desired. On the other hand, search of new luminescence materials in the higher energy region which generally correspond to the high-lying $4f^n$ and $4f^{n-1}5d^1$ configuration of lanthanide ions (Ln) is also important. Since, the trial and error experiments are rather ineffective, the theoretical prediction of the optical spectra is indispensable for theoretical design of novel optical materials. In this work, we constructed practical energy diagrams of TM and RE ions in crystals non-empirically using first-principles calculations. Several effects such as lattice relaxation and the energy corrections are taken into account. The multiplet energy levels of ruby (α-Al_2O_3: Cr^{3+}) were estimated using one-electron discrete variational Xα (DV-Xα) method.[1] On the other hand, the $4f^n$-$4f^{n-1}5d^1$ transition energies of $LiYF_4$: Ln^{3+} and CaF_2: Ln^{3+} were estimated using the relativistic versions of discrete variational multi-electron (DVME) method.[2]

1. α-Al_2O_3: Cr^{3+}

We used two different types of model clusters consisting of 7 atoms and 63 atoms with C_3 symmetry. The effect of lattice relaxation was taken into account by performing the geometry optimization using CAmbridge Serial Total Energy Package (CASTEP) code[3] with pressure from 0-110 GPa. One Cr^{3+} ion was located at the center of the model clusters. The $^4A_2 \rightarrow {}^4T_2$ transition energy or the so called U-band energy ($\varepsilon(^4T_2)$) was calculated from the energy difference between $^4A_2$ and $^4T_2$ (ΔE_U). On the other hand, the $^2E \rightarrow {}^4A_2$ transition energy or the so called R-line energy was calculated using two different methods. First is based on Ohnishi and Sugano's work,[4] the R-line energy is described as $\varepsilon_1(\,^2\mathrm{E}) = 4/5 \times \Delta E_R$. Here, ΔE_R is the spin-flip transition energy based on one-electron calculations from $t_{2g}\uparrow$ spin to $t_{2g}\downarrow$ spin. However, if we see carefully, Ohnishi-Sugano interpreted ΔE_R to the transition from quartet $^4A_2$ state to doublets ^2E, $^2T_1$, and $^2T_2$ states, which is similar with the transition from S_Z=1/2 to

S_Z=-1/2. Nevertheless, the spin-flip transition is actually occur from S_Z=3/2 to S_Z=1/2. The initial state is S_Z=3/2 consists of only $^4A_2$ states, while the final state is S_Z=1/2 consists of $^2T_2$, $^2T_1$, ^2E, and $^4A_2$ states. Since they belong to different spin states, the transition from $^4A_2$ of S_Z=3/2 to $^4A_2$ of S_Z=1/2 should also be taken into account. Therefore, the R-line energy should be estimated by $\varepsilon_2(\,^2\mathrm{E}) = 9/10 \times \Delta E_R$. Next, in order to obtain the energies of ΔE_R and ΔE_U, Slater's transition state (TS) method[5] was utilized. In this case, the spin polarization calculation is performed. Since the 3d configuration is defined as $(t_{2g}\uparrow)$, $(e_g\uparrow)$, $(t_{2g}\downarrow)$ and $(e_g\downarrow)$ levels, the energy of ΔE_R can be obtained by a transition from $(t_{2g}\uparrow)$ to $(t_{2g}\downarrow)$ while the energy of ΔE_U can be obtained by a transition from $(e_g\uparrow)$ to $(t_{2g}\uparrow)$.

Fig.1 shows the practical energy diagram of ruby calculated based on one-electron calculations using 7-atom (left) and 63-atom (right) model clusters constructed from optimized ruby structures. The energies of R-line ($\varepsilon(^2\mathrm{E})$) and U-band ($\varepsilon(^4\mathrm{T}_2)$) are indicated by circle (●) and square (■) symbols, respectively. The experimental data[6,7] are also shown together. The results show that $\varepsilon_1(^2\mathrm{E})$ calculated based on 7-atom model clusters agree the experiment very well. However, when we used the larger clusters, the R-line energy calculated using the Ohnishi-Sugano's method was no longer agreed the experiment. Despite of the underestimation of U-band energy, we suggest the theoretical R-line energy obtained by 63-atom model clusters is reasonable. According to ligand field theory, the U-band energy is actually higher than $10Dq$, the discrepancy of $\varepsilon(^4\mathrm{T}_2)$ is therefore inferred. This study has been presented at ECS conference on Oct 2-7, 2016 in Honolulu, Hawaii, USA (oral presentation) and at 2nd SENS conference on Oct 15, 2016 in University of PGRI Semarang, Indonesia (keynote speaker).

2. $LiYF_4$: Ln^{3+} and CaF_2: Ln^{3+}

Nine-atom model clusters (LnF_8^{6-}) were constructed based on the crystal structures of $LiYF_4$ and CaF_2. One Ln^{3+} ion i.e., Ce^{3+}, Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, or Yb^{3+} was substituted into Y^{3+} and Ca^{2+} sites of the clusters. The effect of lattice relaxation was considered by a simple correction of bond lengths using the Shannon's crystal radii [8]. As the energy correction, we adopted a combination of CI calculation and TS method [5]. The energy difference corresponding to the interconfiguration *f-d* transition obtained from many-electron CI calculations was equated to those obtained from one-electron TS calculations.

Fig.2 shows the practical energy diagram of $LiYF_4$: Ln^{3+} and CaF_2: Ln^{3+} calculated based on many-electron calculations. The theoretical $4f^n$-$4f^{n-1}5d^1$ transition energies obtained based on the unrelaxed and the relaxed cluster models were presented by square (■) and circle (○), respectively. The solid lines connected the theoretical energies calculated with simple CI, without any energy correction. On the other hand, the dashed lines connected the theoretical energies calculated with energy correction TS. The experimental energies[9-13] are indicated by triangle (▲). The results obtained by simple CI calculations show that the theoretical $4f^n$-$4f^{n-1}5d^1$ transition energies of light lanthanides are overestimated, while underestimated for heavy lanthanides. When the correction based on one-electron TS method was considered, the overestimation of $4f^n$-$4f^{n-1}5d^1$ transition energies in the light lanthanide and the underestimation of $4f^n$-$4f^{n-1}5d^1$ transition energies in the heavy lanthanide have been successfully reduced. This study has been presented at DV-Xα conference on Aug 8-9, 2016 in Tokyo Univ. of Technology (poster presentation) and to be published in the 29th DV-Xα Bulletin.

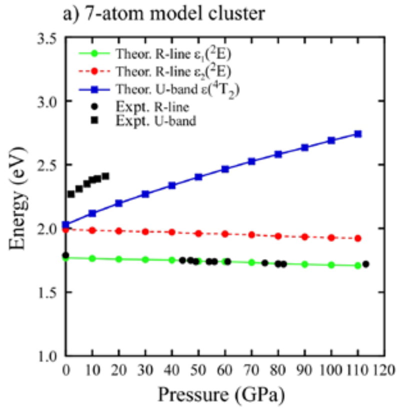

Fig. 1. Practical energy diagram of ruby under pressure calculated based on one-electron calculations using (a) 7-atom and (b) 63-atom model clusters.

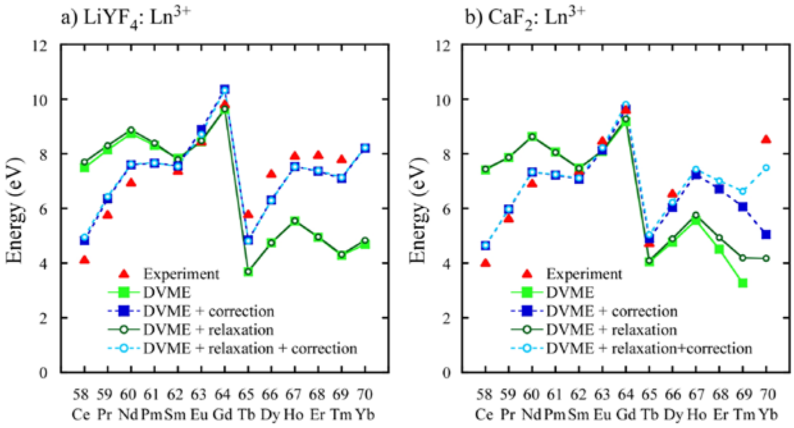

Fig. 2. Practical energy diagram of (a) $LiYF_4$: Ln^{3+} and (b) CaF_2: Ln^{3+} calculated based on many-electron calculations.

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ACHIEVEMENT

1. **(Poster Presentation)** First-Principles Calculation of $4f^n$ - $4f^{n-1}5d$ Transition Energy of Trivalent Lanthanides Ions in CaF_2
   Mega Novita and Kazuyoshi Ogasawara
   The 29th DVXα Workshop, 8-9 Aug, 2016, Tokyo Univ. of Technology, Japan.
2. **(Oral Presentation)** First-Principles Calculation on the Emission Energy Level of Ruby Based on DV-Xα Molecular Orbital Method and Ligand Field Theory,
   Mega Novita, Akane Ito, and Kazuyoshi Ogasawara,
   230th ECS Meeting, 2-7 October, 2016, Honolulu, Hawaii, USA.
3. **(Keynote Speaker)** Investigation on the excitation and emission energies of ruby based on one-electron and many-electron quantum mechanical calculations.
   Mega Novita
   2nd SENS Conference, 15 October 2016, Univ. of PGRI Semarang, Indonesia. .
4. **(Non-referred paper)** First-Principles Calculation of $4f^n$ - $4f^{n-1}5d$ Transition Energy of Trivalent Lanthanides Ions in CaF_2
   Mega Novita and Kazuyoshi Ogasawara
   Bulletin of the Society for Descrete Variational Xα 29 (2016) *In Press.*