Comparative Study on R-line and U-band Energies of Ruby Estimated from One-Electron and Many-Electron First-Principles Approaches

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Abstract. We carried out a comparative study on R-line and U-band energies of α-Al₂O₃: Cr³⁺ material, or the so-called ruby, estimated from one-electron and many-electron first-principles calculations. The estimations were performed without relating to any observed parameter. Although there are numerous reports on the ab-initio calculations of absorption spectra and multiplet energies of ruby based on many-electron approach, the investigation based on one-electron approach is basically impossible except for some particular states such as ⁴T₂ and ²E. Here we compared the transition energies from the ⁴A₂ state (ground state) to ⁴T₂ state (U-band) and to ²E (R-line) of ruby estimated by one-electron and many-electron first-principles approaches. The one-electron calculations were carried out utilizing using discrete variational Xα (DV-Xα) method combined with ligand field theory, while the many-electron calculations were carried out utilizing using the discrete variational multi-electron (DVME) method. The results show that generally both of the one-electron and the many-electron first-principles calculations can be utilized to estimate the multiplet energies such as U-band and R-line energies. Nevertheless, the refined formula to estimate the R-line energy based on one-electron approach is necessary to enhance the concurrence with the observed data.

1. Introduction

Alumina (α-Al₂O₃) doped with trivalent chromium (Cr³⁺), known as ruby, is not only beautiful, but industrially and technically important material for laser or phosphor technology. In the mechanism of luminescence process, the optical properties of ruby are strongly related to the electronic structures. The absorption spectrum of ruby has been known to consist of two broad excitation peaks; U at 2.25 eV and Y at 3.07 eV, while the emission spectrum consists of a strong emission peak R-line at 1.79 eV [1]. Nevertheless, in the strong crystal field, there are some other emission lines such as R' and B-lines. In the strong crystal field, these peaks originate from the transitions from ⁴A₂ ground state to ²E, ²T₁, ⁴T₂, ⁵T₂ and ⁴T₁a, states for R, R', U, B and Y peaks, respectively [2].

Owing to the development of ligand field theory, the first-principles calculations have been useful to obtain a comprehensive understanding on the behavior of R-line energy. Although there are many reports on the ab-initio calculations of absorption spectra and multiplet energies of ruby based on many-electron approach, the investigation based on one-electron approach is basically impossible except for...
some particular states such as $^4T_2$ and $^2E$. In 1982, Ohnishi et al. [3] performed the first-principles one-electron calculations utilizing the discrete variational-Xα (DV-Xα) method [4] to calculate the R-line energy of a CrO$_6^{18}$ cluster at various bond lengths under $O_h$ symmetry. They compared the results with the experimental data of ruby. In their estimation, the barycenter of $t_{2g}^3$ configuration plays an important role in the estimation of R-line energy. Despite of the coincidental agreement, the barycenter was introduced as the average of only 3 multiplet states i.e. $^2E$, $^2T_1$, and $^2T_2$ states. Therefore, in this work we carried out similar calculations with significant improvements in various aspects. Two different sizes of model clusters consisting of 7 atoms and 63 atoms were generated from the actual structure of ruby. An improved formula to estimate the R-line energy which is based on 4 multiplet states including the $^4A_2$ ground state was suggested. We thus compared the results with those estimated from many-electron calculations utilizing discrete variational multi-electron (DVME) method [5].

2. Computational Procedure

2.1. Model clusters
In this work we used two different types of model clusters i.e., non-optimized and optimized model clusters consisting of 7 atoms (CrO$_6^{18}$) and 63 atoms (CrAl$_{14}$O$_{48}^{51}$) with $C_3$ symmetry for each type, as shown in Figure 1. The non-optimized clusters were generated from the $\alpha$-Al$_2$O$_3$ crystal [6]. Differently, the optimized model clusters which includes the lattice relaxation effect were generated by performing the geometry optimization using CAMbridge Serial Total Energy Package (CASTEP) code [7].

2.2. One-electron approach
The molecular orbitals (MO) were calculated using DV-Xα method [4]. Next, in order to estimate the multiplet energies based on the ligand field theory, the $^4A_2 \rightarrow ^4T_2$ transition energy or the so called U-band energy ($\varepsilon_1(4^t_2)$) can be calculated from the transition energy from $t_{2g}$ to $e_g$ ($\Delta E_{t}$). On the other hand, the $^2E \rightarrow ^4A_2$ transition energy or the so called R-line energy is described as $\varepsilon_1(4^E_2) = 4/5 \times \Delta E_R$, as reported by Ohnishi et al. [3]. Here, $\Delta E_R$ 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 $\Delta E_R$ to the transition from quartet $^4A_2$ state to doublets $^2E$, $^2T_1$, and $^2T_2$ states, which corresponds to the transition from $S_T=1/2$ to $S_T=1/2$ in the one-electron state. Nevertheless, the spin-flip transition is actually occurred from $S_T=3/2$ to $S_T=1/2$ in the many-electron state. The initial state $S_T=3/2$ consists of only $^4A_2$ states, while the final state $S_T=1/2$ consists of $^2T_2$, $^2T_1$, $^2E$, and $^4A_2$ states within the $t_{2g}^3$ configuration. Since they belong to different spin states, the transition from $^4A_2$ of $S_T=3/2$ to $^4A_2$ of $S_T=1/2$ should also be taken into account. Therefore, the R-line energy should be estimated by $\varepsilon_2(4^E_2) = 9/10 \times \Delta E_R$. Next, in order to obtain the energies of $\Delta E_R$ and $\Delta E_U$, Slater’s transition state method [8] was utilized. In this case, the spin polarization calculation was performed. Since the 3d configuration is defined by $(t_{2g}^\uparrow)$, $(e_g^\uparrow)$, $(t_{2g}^\downarrow)$ and $(e_g^\downarrow)$ levels, the energy of $\Delta E_R$ can be obtained by a transition from $(t_{2g}^\uparrow)$ to $(t_{2g}^\downarrow)$ while the energy of $\Delta E_U$ can be obtained by a transition from $(t_{2g}^\uparrow)$ to $(e_g^\uparrow)$.
2.3. Many electron approach

In order to estimate the multiplet energies of ruby using many-electron approach, here we used the DVME method. The first step of DVME method is molecular orbital calculations utilizing the DV-Xα method which has been explained previously. After that the many-electron calculations using the configuration interaction (CI) approach were performed. Since there are overestimations on the multiplet energies estimated from CI approach [9], several corrections i.e., configuration-dependent correction (CDC) and correlation correction (CC) were used. These corrections were delivered based on the consistency between the spin-restricted many-electron calculations and the spin-unrestricted one-electron calculations. We have successfully studied the transition energies using the DVME method in the past several years [10-15] and has been proved to be powerful. The detailed procedure of the DVME method were originally described in Ref 5.

3. Results and discussion

In the geometry optimization process, the Cr-O bond lengths were estimated to be 1.96 and 2.01 Å. These results are in accordance with the results of Extended X-Ray Absorption Fine Structure (EXAFS) experiment performed by Kizler et al. [16]. The observed Cr-O bond lengths are 1.97 and 2.00 Å. These results have been used in our previous papers [10-11].

| Cluster size | Computational condition | R-line ($\Delta E_R$) | U-band ($\Delta E_U$) |
|--------------|-------------------------|----------------------|---------------------|
|              |                         | $\varepsilon_1$ ($2E$) | $\varepsilon_2$ ($2E$) | $\Delta E_1$ ($\Delta E_1$) |
| Experiment (Fairbank et al. [1]) | 1.79 | 2.25 |
| 7-atom       | Non-optimized           | 1.7469               | 1.9652              | 2.2284 |
|              | Optimized               | 1.7694               | 1.9906              | 2.0309 |
| 63-atom      | Non-optimized           | 1.5611               | 1.7562              | 2.2664 |
|              | Optimized               | 1.5694               | 1.7656              | 1.6400 |

| Cluster size | Computational condition | Without CDC-CC | With CDC-CC |
|--------------|-------------------------|----------------|-------------|
|              | R-line (eV) | U-band (eV) | R-line (eV) | U-band (eV) |
| Experiment (Fairbank et al. [1]) | 1.79 | 2.25 | 1.79 | 2.25 |
| 7-atom       | Non-optimized | 2.3779 | 2.5376 | 2.0234 | 2.3548 |
|              | Optimized      | 2.3580 | 2.3907 | 2.0680 | 2.1442 |
| 63-atom      | Non-optimized | 2.0603 | 2.6045 | 1.7745 | 2.3807 |
|              | Optimized      | 2.0700 | 2.3764 | 1.8559 | 2.1498 |

The theoretical R-line and U-band energies calculated using one-electron and many electron approaches are shown in Table 1 and 2 respectively. The results shown in Table 1 were calculated under different computational conditions with cluster size and the considerations of lattice relaxation-effect as their variables. On the other hand, the results shown in Table 2 were calculated under different computational conditions with cluster size, the considerations of lattice relaxation-effect and the considerations of CDC-CC corrections as their variables. The experimental data reported by Fairbank et al. [1] were also shown together in each table.
Our results obtained from one-electron approach (Table 1) show that compared to the experimental data, the R-line energy calculations based on 7-atom model clusters \( \varepsilon_1(2E) \) have better agreement than \( \varepsilon_2(2E) \). However, this tendency is reversed when we used 63-atom model clusters. On the other hand, the results of U-band energies show that simple calculations based on non-optimized model clusters have better agreement than those based on optimized model clusters. In the case of many-electron calculations shown in Table 2, the calculated R-line and U-band energies obtained from the combination of larger cluster size and CDC-CC correction give good agreement with the experimental data. Therefore, these indicate that the theoretical R-line energies obtained from one-electron approach using the refined formula \( \varepsilon_2(2E) \) agree with the experimental data very well.

4. Conclusion
We have successfully reproduced the energy levels of ruby, i.e., R-line and U-band energies using both one-electron and many-electron first-principles approaches. Based on many-electron approach, the multiplet energies calculated based on either 63-atom non-optimized or optimized model clusters are in accordance with the experimental data. On the other hand, despite of the slight underestimation, the calculated R-line energies utilizing the improved formula \( \varepsilon_2(2E) \) based on either 63-atoms non-optimized or optimized model cluster give relatively good agreement with the experimental data. However, since the U-band energy (\( \varepsilon(4T_2) \)) calculated based on one-electron approach was a simple estimation equals to \( 10D_q \), there are significant underestimation.

5. References
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