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A First-Principles Investigation of the Crystal-Field and Racah Parameters of Transition Metal Ions: Cr³⁺ in Alumina

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The crystal-field and Racah parameters of ruby were evaluated based on the first-principles calculations using the relationship between the ligand-field theory and the molecular orbital theory derived by Sambe and Felton. It is found that the combination of the discrete variational (DV)-X α calculations and the discrete variational multi-electron (DVME) calculations is effective for prediction of reasonable values for the crystal-field and Racah parameters for Cr³⁺ in alumina. These results indicate that the corrections to the DVME calculations based on the DV-X α method provide a theoretical basis for the configuration-dependent correction and the correlation correction which were introduced in the previous calculation based on an intuition that the average transition energy should be reproduced better by one-electron calculations than many-electron calculations. This method could be used to predict the d-d transitions for Mn⁴⁺ to find a suitable host for a red phosphor for LED applications.

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The development of blue LEDs^{1,2} has made it possible to construct white light sources by combining them with appropriate phosphors.³ Phosphors such as Ce³⁺-doped Y₃Al₅O₁₂ (YAG)⁴ and Eu²⁺-doped Sr_xCa_{1-x}AlSiN₃ (SCASN)⁵ have been widely used for this purpose. Phosphors doped with transition-metal (TM) ions also can be good candidates for white light generation. For example, red phosphors based on Mn⁴⁺-doped fluorides have been recently put into commercial use.⁶ However, since these phosphors require a special surface treatment to suppress the degradation due to high temperature and high humidity, other red phosphors activated by Mn⁴⁺ are still desired. In order to clarify the properties of Mn⁴⁺-activated phosphors, extensive experimental researches⁷ and a systematic semi-empirical ligand-field analysis⁸ have been performed. In this work, we aimed to develop a first-principles approach to predict the crystal-field and Racah parameters of transition metal ions in optical materials to assist in the search for new phosphor hosts.

In order to predict the properties of TM ions in crystals, first-principles calculations are quite useful. For example, the multiplet energy levels of ruby (Cr³⁺ doped α -Al₂O₃) were calculated based on the configuration-interaction (CI) calculation program called the discrete variational multi-electron (DVME) program.⁹ However, since the simple CI calculation tend to overestimate the multiplet energies, we introduced two corrections based on the discrete variational (DV)-X α molecular orbital (MO) calculations in order to obtain good agreement with the experimental results. One is the configuration-dependent correction (CDC) which corrects the average energy of each configuration (configuration center) and the other is the correlation correction (CC) which corrects the multiplet splitting of each configuration.

The origin of the overestimation of the multiplet energies in the case of simple CI calculation is considered to be the underestimation of the electron correlation due to the finite number of the Slater determinants used as the basis functions.

In this work, we calculated the crystal-field and Racah parameters of ruby based on first-principles calculations using the relationship between the ligand-field theory and the MO theory, and investigated the validity of the one-electron DV-X α calculation and the many-electron DVME calculation for evaluation of these parameters.

Relationship Between the Ligand-Field Theory and the MO Theory

When a 3d transition metal ion is placed under octahedral crystal field, the 3d levels split into t_{2g} and e_g levels. For simplicity these levels will be denoted as t_2 and e in this paper. The energy separation Δ between these levels is called the crystal-field parameter. If the TM ion has N electrons occupying d levels, the electronic configuration can be classified as $t_2^{N-n}e^n$ where n is the number of electrons occupying e levels. Based on the matrix elements of the ligand-field theory,¹⁰ Sambe and Felton¹¹ derived an equation on the average energy of each configuration (configuration center) $E_{\text{LFT}}(t_2^{N-n}e^n)$ as,

$$E_{\text{LFT}}(t_2^{N-n-1}e^{n+1}) - E_{\text{LFT}}(t_2^{N-n}e^n) = \Delta + \frac{8}{3} \left(n - \frac{3N+1}{8} \right) K, \quad [1]$$

where K is a parameter expressed by the Racah parameters B and C ,

$$K = \frac{C}{2} - B. \quad [2]$$

Based on the assumption equating the above configuration centers in the ligand field theory with the average energies of the corresponding configurations in the hyper Hartree-Fock theory, they also derived the following equation connecting the spin-restricted MO energies with the crystal-field and Racah parameters,

$$\epsilon_e(n) - \epsilon_t(n) = \Delta + \frac{8}{3} \left(n - \frac{3N+1}{8} \right) K, \quad [3]$$

where $\epsilon_t(n)$ and $\epsilon_e(n)$ are the MO energies of t_2 and e orbitals calculated for $t_2^{N-n}e^n$ configuration. Therefore, by calculating MO energies for two different values of n , the values of Δ and K can be determined. Especially for calculation of Δ , it is convenient to set $n = \bar{n} \equiv (3N+1)/8$ since in this case Δ can be simply expressed as the orbital energy difference,

$$\Delta = \epsilon_e(\bar{n}) - \epsilon_t(\bar{n}), \quad [4]$$

in the $t_2^{N-\bar{n}}e^{\bar{n}}$ configuration. By inserting Δ into Eq. 3 for another value of n , K can be also calculated as,

$$K = \frac{3}{8n-3N-1} [\epsilon_e(n) - \epsilon_t(n) - \Delta]. \quad [5]$$

It should be emphasized that Δ is not the separation between t_2 and e levels in the ground state nor the Slater's transition state¹² as assumed by most first-principles calculations, however, it corresponds to the separation between t_2 and e levels in a certain configuration with $n = \bar{n}$.

In order to determine the values of B and C , we need another relationship between B and C . In the case of $N = 3$, the spin-flip transition energy within t_2^3 configuration from $S_z = 3/2$ to $S_z = 1/2$

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Table I. The values of various parameters for ruby estimated by the DV-X α calculations, together with the values obtained by parameter fitting based on the peak positions in the observed absorption spectra of ruby reported by Fairbank et al.¹⁷

	Δ (eV)	K (eV)	E^{SF} (eV)	B (eV)	C (eV)	γ
Experimental (Fairbank et al.)	2.250	0.1060	2.040	0.07997	0.3720	4.651
DV-X α ($n = 0$)	2.268	0.006238	1.9630	0.1153	0.2430	2.108
DV-X α ($n = 1$)	2.268	0.006703	1.9630	0.1151	0.2436	2.116
DV-X α ($n = 2$)	2.268	0.007232	1.9630	0.1149	0.2442	2.126
DV-X α ($n = 3$)	2.268	0.007796	1.9630	0.1147	0.2449	2.136

can be used for this purpose.⁹ In this case, the initial state corresponds to $^4A_2(S_z = \frac{3}{2})$ while the final state corresponds to four states, $^4A_2(S_z = \frac{1}{2})$, $^2T_2(S_z = \frac{1}{2})$, $^2E(S_z = \frac{1}{2})$, and $^2T_1(S_z = \frac{1}{2})$. If we neglect the interaction between t_2^3 configuration and the other configurations, the energies of 4A_2 , 2T_2 , 2E , and 2T_1 can be expressed using the Racah parameters as $-15B$, $-6B + 3C$, $-6B + 3C$, $5C$, respectively. Considering the weight of the degeneracy, the average spin-flip transition energy $E_{\text{LFT}}^{\text{SF}}$ can be expressed as,

$$E_{\text{LFT}}^{\text{SF}} = \frac{10}{3} (3B + C). \quad [6]$$

Since this spin-flip transition corresponds to the transition from $t_2 \uparrow$ to $t_2 \downarrow$, the transition energy can be also calculated as the spin-unrestricted MO energy difference $\epsilon_{t_2\downarrow}^{TS} - \epsilon_{t_2\uparrow}^{TS}$ in the Slater's transition state with $t_2 \uparrow^{2.5} t_2 \downarrow^{0.5}$ configuration. Thus we obtain,

$$\epsilon_{t_2\downarrow}^{TS} - \epsilon_{t_2\uparrow}^{TS} = \frac{10}{3} (3B + C), \quad [7]$$

as the relationship connecting the spin-unrestricted MO energies and the Racah parameters. This approach is similar to that by Ohnishi and Sugano¹³ but slightly modified to include the $^4A_2(S_z = \frac{1}{2})$ state as the final state of the transition.¹⁴

Model Cluster for Ruby

A model cluster consisting of 63 atoms was constructed based on the crystal structure of $\alpha\text{-Al}_2\text{O}_3$.¹⁵ Then by substituting the central Al^{3+} ion by Cr^{3+} ion, a $\text{CrAl}_{14}\text{O}_{48}$ model cluster for ruby was constructed for first-principles electronic state calculations. In order to reproduce the effective Madelung potential, several thousand point charges were located at the atomic positions outside the cluster.

Estimation of Crystal-Field and Racah Parameters Based on DV-X α Method

The MO calculations were performed using the DV-X α method. The MOs were constructed as a linear combination of the numerically generated atomic orbitals (NAOs). The NAOs were refined flexibly in each iteration and optimized for the chemical environment. The details of this program have been described by Adachi et al.¹⁶ The NAOs used in the calculation were 1s, 2s, 2p for oxygen, 1s, 2s, 2p, 3s, 3p, 3d for aluminum and 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p for chromium. The number of sampling points for numerical integration was 100,000 for the central

chromium ion, 10,000 for the six first-neighbor oxygen ions, and 1,000 for the other ions.

In the case of $N = 3$, $\bar{n} = 1.25$. Therefore, we performed the DV-X α calculation of ruby in the $t_2^{1.75} e^{1.25}$ configuration. The value of Δ calculated from Eq. 4 was 2.2685 eV. In order to calculate K , we also performed MO calculations of ruby for $n = 0, 1, 2, 3$. The values of $\epsilon_e(n) - \epsilon_t(n)$ for $n = 0, 1, 2, 3$ were 2.2477 (eV), 2.2640 (eV), 2.2829 (eV), and 2.3049 (eV), for which the values of K calculated from Eq. 5 were 0.006238 (eV), 0.006703 (eV), 0.007232 (eV), and 0.007796 (eV), respectively. Although the K value changes depending on n , the variation is small and the results are considered to be consistent.

In order to determine the values of B and C , we also calculated the spin-flip transition energy $E_{\text{DVX}\alpha}^{\text{SF}} = \epsilon_{t_2\downarrow}^{TS} - \epsilon_{t_2\uparrow}^{TS}$. Since the value of $E_{\text{DVX}\alpha}^{\text{SF}}$ calculated by the spin-unrestricted DV-X α method was 1.9630 eV. Therefore, from Eqs. 2 and 7, the values of B and C were calculated for each value of n . The values of the parameters Δ , K , $E_{\text{DVX}\alpha}^{\text{SF}}$, B , C , and $\gamma (= C/B)$ are summarized in Table I, together with the values obtained by fitting to the experimental values reported by Fairbank et al.¹⁷ The value of B ranges from 0.1147 (eV) to 0.1153 (eV) which are comparable to the free ion value (0.1138 eV)¹⁰ and much larger than the experimental value (0.0800 eV). Therefore, it seems that the nephelauxetic effect is not taken into account properly in these calculations. Moreover, the value of γ ranges from 2.108 to 2.136 which are too small compared to the value obtained from the experimental data (4.651). The calculated multiplet energy levels using the obtained parameters Δ , B , and C are listed in Table II. Although the multiplet energies depend on the value of n , the variation is very small. Compared to the experimental values reported by Fairbank et al., the energies of doublets are underestimated. On the other hand, despite the large discrepancy of parameters such as B and γ from the experimental values, the energies of quartets are in reasonable agreement with the experimental values.

Estimation of Crystal-Field and Racah Parameters Based on DVME Method

The CI calculations were performed using the DVME method. In the case of ruby, $10C_3 = 120$ Slater determinants constructed with the 10 MOs mainly consisting of chromium 3d orbitals were used as the basis functions. The multiplet energies were obtained by diagonalizing the many-electron Hamiltonian.

Table II. The multiplet energy levels of ruby (eV) calculated using Δ and K obtained by the spin-restricted DV-X α calculation, and $\Delta E_{\text{DVX}\alpha}^{\text{SF}}$ obtained by the spin-unrestricted DV-X α calculation, together with the peak positions in the observed absorption spectra of ruby reported by Fairbank et al.¹⁷

	2E (R)	2T_1 (R')	2T_2 (B)	4T_2 (U)	$^4T_{1a}$ (Y)	$^4T_{1b}$ (Y')
Experimental (Fairbank et al.)	1.79	1.85	2.60	2.23 (σ)	3.01 (σ)	4.84 (σ)
	1.79	1.85	2.61	2.28 (π)	3.11 (π)	4.84 (π)
		1.88	2.65			
Theoretical ($n = 0$)	1.541	1.665	2.362	2.268	3.341	5.193
Theoretical ($n = 1$)	1.541	1.665	2.363	2.268	3.340	5.192
Theoretical ($n = 2$)	1.542	1.666	2.364	2.268	3.339	5.190
Theoretical ($n = 3$)	1.543	1.666	2.365	2.268	3.338	5.188

Table III. The multiplet energy levels of ruby (eV) calculated using Δ , K , and $E_{\text{DVME}}^{\text{SF}}$ obtained by the DVME calculations, together with the peak positions in the observed absorption spectra of ruby reported by Fairbank et al.¹⁷

	${}^2\text{E (R)}$	${}^2\text{T}_1 \text{ (R')} $	${}^2\text{T}_2 \text{ (B)}$	${}^4\text{T}_2 \text{ (U)}$	${}^4\text{T}_{1a} \text{ (Y)}$	${}^4\text{T}_{1b} \text{ (Y')}$
Experimental (Fairbank et al.)	1.79	1.85	2.60	2.23 (σ)	3.01 (σ)	4.84 (σ)
	1.79	1.85	2.61	2.28 (π)	3.11 (π)	4.84 (π)
		1.88	2.65			
Theoretical	2.107	2.206	3.188	2.639	3.716	5.828

Table IV. The values of various parameters for ruby estimated by the DV-X α calculation, DVME calculation, and their combination, together with the values obtained by parameter fitting based on the peak positions in the observed absorption spectra of ruby reported by Fairbank et al.¹⁷

	Δ (eV)	K (eV)	E^{SF} (eV)	B (eV)	C (eV)	γ
Experimental (Fairbank et al.)	2.250	0.1060	2.040	0.07997	0.3720	4.651
DV-X α ($n = 1$)	2.268	0.00624	1.9630	0.1153	0.2430	2.108
DVME	2.639	0.110	2.541	0.108	0.437	4.034
DVME + DV-X α	2.268	0.110	1.9630	0.0737	0.348	4.993

Since all the CI matrix elements are calculated in the DVME calculation, each configuration center can be directly calculated from the average of the diagonal CI matrix elements corresponding to that configuration. Therefore, we can insert the configuration center calculated by the DVME method $E_{\text{DVME}}(t_2^{N-n}e^n)$ instead of $E_{\text{LFT}}(t_2^{N-n}e^n)$ in Eq. 1 in order to calculate the crystal-field and Racah parameters.

If we define,

$$\Delta E_{\text{DVME}}(n) = E_{\text{DVME}}(t_2^{N-n-1}e^{n+1}) - E_{\text{DVME}}(t_2^{N-n}e^n), \quad [8]$$

then

$$\Delta E_{\text{DVME}}(n+1) - \Delta E_{\text{DVME}}(n) = \frac{8}{3}K. \quad [9]$$

Thus K can be calculated by,

$$K = \frac{3}{8} [\Delta E_{\text{DVME}}(n+1) - \Delta E_{\text{DVME}}(n)] \quad [10]$$

By setting the energy of $E_{\text{DVME}}(t_2^3e^0)$ to be zero, the calculated relative values of $E_{\text{DVME}}(t_2^2e^1)$, $E_{\text{DVME}}(t_2^1e^2)$, $E_{\text{DVME}}(t_2^0e^3)$ are 2.4189 (eV), 5.1318 (eV), 8.1387 (eV), respectively. The calculated values of K were 0.1102 (eV) for all cases of $n = 0, 1, 2$, indicating that the results are consistent for all configurations.

In order to determine the values of B and C , we also calculated the average spin-flip transition energy within t_2^3 configuration from $S_z = 3/2$ to $S_z = 1/2$. By performing the CI calculation only within the t_2^3 configuration, the average transition energy $E_{\text{DVME}}^{\text{SF}}$ of the transitions from ${}^4\text{A}_2(S_z = \frac{3}{2})$ to four states, ${}^4\text{A}_2(S_z = \frac{1}{2})$, ${}^2\text{T}_2(S_z = \frac{1}{2})$, ${}^2\text{E}(S_z = \frac{1}{2})$, and ${}^2\text{T}_1(S_z = \frac{1}{2})$ was calculated. The calculated $E_{\text{DVME}}^{\text{SF}}$ can be inserted instead of $E_{\text{LFT}}^{\text{SF}}$ in Eq. 6 to calculate the values of B and C . Since the value of $E_{\text{DVME}}^{\text{SF}}$ calculated from the CI calculation was 2.5415 eV. Therefore, from Eqs. 2 and 6, the values of B and C were obtained as 0.1084 (eV) and 0.4373 (eV), respectively. Therefore, the value of B is comparable to the free ion value (0.1138 eV) and much larger than the experimental value (0.0800 eV). On the other hand, the calculated value of γ is 4.034 which is reasonable compared to the value obtained by the DV-X α calculation in the previous section. The calculated multiplet energy levels using the obtained parameters Δ ,

B , and C are listed in Table III. In this case, both doublets and quartets are significantly overestimated.

Combination of DV-X α and DVME Methods

The values of the parameters Δ , K , E^{SF} , B , C , and $\gamma (= C/B)$ obtained by the DV-X α calculation ($n = 1$) and those obtained by the DVME calculation are summarized in Table IV, together with the values obtained by fitting to the experimental values reported by Fairbank et al.¹⁷ Compared to the values obtained from the experimental data, Δ is evaluated better by the spin-restricted DV-X α calculation, K is evaluated better by the DVME calculation, and E^{SF} is evaluated better by the spin-unrestricted DV-X α calculation. Therefore, we combined these parameters to obtain an appropriate set of parameters. The calculated values of B and C are 0.0737 (eV) and 0.368 (eV), respectively. In this case, the value of B is comparable to the experimental value (0.07997 eV) and much smaller than the free ion value (0.1138 eV). Therefore, it seems that the nephelauxetic effect is described properly. The value of γ is 4.993 which is also reasonable compared to the experimental value (4.651). The calculated multiplet energy levels using the obtained parameters Δ , B , and C are listed in Table V. Although the energies of doublets are slightly underestimated, the agreement between the theoretical values and the experimental values are significantly improved.

Since K is a parameter related to the configuration centers, the fact that K is evaluated better by the spin-restricted DV-X α calculation indicates that the spin-restricted DV-X α calculation is appropriate for the correction to the configuration centers in the DVME calculation. Similarly, since the spin-flip transition energy E^{SF} is related to the multiplet splitting in each configuration, the fact that E^{SF} is evaluated better by the spin-unrestricted DV-X α calculation indicates that the spin-unrestricted DV-X α calculation is appropriate for the correction to the multiplet splitting of each configuration in the DVME calculation. These results provide a theoretical basis for the configuration-dependent corrections and the correlation corrections introduced in the previous calculations.⁹

Table V. The multiplet energy levels of ruby (eV) calculated using Δ obtained by the spin-restricted DV-X α calculation, K obtained by the DVME calculation, and $E_{\text{DV-X}\alpha}^{\text{SF}}$ obtained by the spin-unrestricted DV-X α calculation, together with the peak positions in the observed absorption spectra of ruby reported by Fairbank et al.¹⁷

	${}^2\text{E (R)}$	${}^2\text{T}_1 \text{ (R')} $	${}^2\text{T}_2 \text{ (B)}$	${}^4\text{T}_2 \text{ (U)}$	${}^4\text{T}_{1a} \text{ (Y)}$	${}^4\text{T}_{1b} \text{ (Y')}$
Experimental (Fairbank et al.)	1.79	1.85	2.60	2.23 (σ)	3.01 (σ)	4.84 (σ)
	1.79	1.85	2.61	2.28 (π)	3.11 (π)	4.84 (π)
		1.88	2.65			
Theoretical	1.661	1.721	2.535	2.268	3.039	4.872

Conclusions

The crystal-field and Racah parameters of ruby were evaluated based on first-principles calculations using the relationship between the ligand-field theory and the molecular orbital theory. It is found that the combination of Δ obtained by the spin-restricted DV-X α calculation, K obtained by the DVME calculation, and E^{SF} obtained by the spin-unrestricted DV-X α calculation provide the appropriate set of the ligand-field parameters.

These results clarified the hidden problems in the DVME calculations and justified the configuration-dependent correction based on the spin-restricted DV-X α calculation and the correlation correction based on the spin-unrestricted DV-X α calculation introduced in the previous DVME calculations⁹ by providing a theoretical basis for these corrections.

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