Prediction of emission energy of Cr$^{3+}$ in oxides based on first-principles calculations and machine learning

Tsubasa Hori, Kazuyoshi Ogasawara
School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen Sanda, Hyogo 669-1337 Japan
fye08548@kwansei.ac.jp

Abstract. The first-principles calculations of the energies of the emission level ($^2E_g$) of Cr$^{3+}$ in 10 oxide crystals were performed using the first-principles configuration-interaction calculations. In order to improve the accuracy of the prediction, a machine learning model was created by using the results of the first-principles calculations and the experimental $^2E_g$ energies as the training data. The predicted values using this model showed good correlation with the experimental values, where the correlation coefficient is 0.92. The obtained predicted model indicated that the Cr 3d component of $t_{2g}$ molecular orbital is the most important quantity for prediction of the $^2E_g$ energy.

1. Introduction
Transition-metal ions with d$^3$ electronic configuration such as Cr$^{3+}$ and Mn$^{4+}$ are utilized as emission centers in various luminescent materials such as ruby (Cr$^{3+}$-doped alumina) [1] or alexandrite (Cr$^{3+}$-doped chrysoberyl) [2]. Since it is difficult to investigate the multiplet energy levels of Cr$^{3+}$ in a wide variety of crystals experimentally, the theoretical prediction of the emission energy is indispensable for the efficient development of novel Cr$^{3+}$-doped luminescent materials. In the high field environment, the emission of octahedrally coordinated Cr$^{3+}$ occurs from $^2E_g$ state. Since both this state and the ground state belong to the same ($t_{2g}$)$^3$ electronic configuration, the Stokes shift due to the structural relaxation in the excited state is negligibly small. Therefore the $^2E_g$ energy calculated in the ground state can be regarded as the emission energy. In this study, we predicted the multiplet energy of the emission level ($^2E_g$) of Cr$^{3+}$ in oxides by first-principles calculations based on the discrete variational multi-electron (DVME) method [3] using relatively small clusters consisting of seven atoms. In order to improve the accuracy of the prediction, we also performed a machine learning modeling using the Waikato environment for knowledge analysis (WEKA) [4].

2. Computational Methods
2.1. First-principles calculation
We performed the first-principles calculations of the multiplet energies of Cr$^{3+}$ in oxides using the discrete variational multi-electron (DVME) method [3], which is a configuration-interaction (CI) calculation program based on the discrete-variational Xα (DV-Xα) molecular orbital (MO) method. We considered 10 oxide crystals listed in Table 1. In these crystals the impurity Cr$^{3+}$ ions occupy the Al sites coordinated with six O$^{2-}$ ions. Therefore, we constructed 7-atom clusters centred at Al$^{3+}$ ion based on the crystal structures of the host crystals [6-15]. Then the model clusters for Cr$^{3+}$ in oxides
were constructed by substituting Cr$^{3+}$ for Al$^{3+}$. The space group, lattice constants, the symmetry of the model clusters are summarized in Table 1.

Table 1. Crystal structure data considered in this work and the symmetry of the model cluster.

| Host crystal          | Space group | Lattice constant / Å | Symmetry (7 atomic cluster) |
|-----------------------|-------------|----------------------|------------------------------|
| Al$_2$O$_3$ [6]       | R3cH        | a=b=4.7589, c=12.9919 | C$_3$                        |
| Al$_2$SiO$_5$ [7]     | Pnmm        | a=7.719, b=7.587, c=5.533 | C$_2$                        |
| Y$_3$Al$_5$O$_{12}$ [8]| la$\bar{3}$d | a=b=c=12.004         | C$_i$                        |
| YAl$_3$(BO$_3$)$_4$ [9]| R32H        | a=b=9.295, c=7.243   | C$_i$                        |
| YAIO$_3$ [10]        | Pbnm        | a=5.172, b=5.327, c=7.361 | C$_i$                        |
| GdAl$_3$(BO$_3$)$_4$ [11]| R32H     | a=b=9.031, c=7.257   | C$_i$                        |
| MgAl$_2$O$_4$ [12]   | Fd$\bar{3}$m | a=b=c=8.081          | C$_i$                        |
| CsAl(MoO$_4$)$_2$ [13]| P$\bar{3}$m1 | a=b=5.551, c=8.037   | D$_{3d}$                     |
| KA1(MoO$_4$)$_2$ [14] | P$\bar{3}$m1 | a=b=5.545, c=7.070   | D$_{3d}$                     |
| NaMgAl(MoO$_4$)$_5$ [15]| P$\bar{1}$ | a=6.874, b=6.931, c=17.575 | C$_i$                        |

2.2. Machine learning

The machine learning was performed using the software developed in the University of Waikato known as WEKA (Waikato Environment for Knowledge Analysis) [31]. The predictive model of $^2$E$_g$ energy was created based on the linear regression algorithm. As the attributes, the theoretical $^2$E$_g$ energy obtained by the first-principles calculations, the crystal field splitting 10$D_q$, the Cr 3d compositions of the $t_{2g}$ or $e_g$ MOs were considered.

3. Results

The correlation between the theoretical $^2$E$_g$ energy obtained by the first-principles calculation and the experimental ones is shown in Figure 1. The correlation coefficient is 0.52 and the theoretical values are significantly overestimated. The main cause of the poor correlation is the small size of the model clusters while the main cause of the overestimation is underestimation of the electron correlation due to the finite number of the Slater determinants in the CI calculation. The accuracy of the first-principles calculation can be improved by using larger clusters and introducing some corrections such as configuration-dependent correction (CDC) and correlation correction (CC) [3]. However, in this work, we tried to improve the accuracy of the prediction by creating a machine learning model.

![Figure 1](image_url)  
**Figure 1.** Correlation between the theoretical $^2$E$_g$ energies of Cr$^{3+}$ in oxides obtained by the first-principles calculations and the experimental ones [16].
Using the experimental $^{2}E_g$ energies of Cr$^{3+}$ in oxides [16] as the training data, we obtained the predictive model of the $^{2}E_g$ energies of Cr$^{3+}$ in oxides ($y$) as,

$$y = 1.2983a - 8.7732b - 1.6185c + 8.5079,$$

(1)

where $a$ is the theoretical $^{2}E_g$ energy obtained by the first-principles calculation, $b$ and $c$ are the Cr 3d orbital component of $t_{2g}$ and $e_g$ MOs, respectively. In this model, $10Dq$ is not included since consideration of $10Dq$ did not improve the accuracy of the prediction. The correlation between the predicted $^{2}E_g$ energy using Eq (1) and the experimental ones [16] is shown in Figure 2. In this case, the correlation coefficient is 0.92. Therefore, the correlation is significantly improved compared to the simple CI calculations using small clusters.

Figure 2. Correlation between the predicted $^{2}E_g$ energies of Cr$^{3+}$ in oxides using the machine learning model and the experimental ones [16].

Figure 3. Relationship between the theoretical $^{2}E_g$ energies and the Cr 3d components of $e_g$ orbitals obtained by the first-principles calculations.

4. Discussion

In order to investigate the physical meaning of Eq. (1), we have investigated the correlation between the theoretical $^{2}E_g$ energy and the Cr 3d orbital component of the MOs mainly consisting of Cr 3d orbitals. The relationship between the theoretical $^{2}E_g$ energy and the Cr 3d orbital component of $e_g$ MO is shown in Figure 3. Although the correlation is not good, it should be noted that the data could be classified into three groups, namely, oxides, borates, and molybdates. They clearly appear in different regions in this map. This fact indicates that the Cr 3d orbital component of $e_g$ MO is a good quantity to correct the computational errors depending on the group. The relationship between the theoretical $^{2}E_g$ energy and the Cr 3d orbital component of $t_{2g}$ MO is also shown in Figure 4. There is a relatively high correlation between these quantities. This is due to the fact that the $^{3}E_g$ energy is mainly determined by
the Coulomb repulsion among electrons within the \((t_{2g})^3\) configuration. In Eq. (1), the coefficient of the Cr 3d orbital component of \(t_{2g}\) MO \((b)\) is much larger than that of the theoretical \(2E_g\) energy \((a)\), indicating that it is the better quantity to predict the actual \(2E_g\) energy.

5. Conclusion

First-principles calculations of \(2E_g\) energy of \(\text{Cr}^{3+}\) in 10 oxides were calculated based on simple CI calculations using small clusters. The correlation coefficient between the calculated \(2E_g\) energies and the experimental ones was 0.52, indicating poor correlation. In order to improve the accuracy of the prediction, we created a machine learning model of the \(2E_g\) energy, using the results of the first-principles calculations and the experimental \(2E_g\) energies as the training data. The correlation coefficient between the predicted \(2E_g\) energies using this model and the experimental ones is 0.92, indicating significantly improved predictive capability. The obtained predictive model indicated that the Cr 3d component of \(t_{2g}\) MO is the most important quantity to predict the actual \(2E_g\) energy while the Cr 3d component of \(e_g\) MO is also effective for corrections of computational errors depending on the groups of the host crystals.

Acknowledgement

Supports from Kwansei Gakuin University are gratefully acknowledged.

References

[1] T. H. Maiman, Nature, **187**, 493 (1960).
[2] J. C. Walling, O. G. Peterson, H. P. Jenssen, R. C. Morris, and E. Wayne O’Dell, *IEEE J. Quantum Electron.*, **16**, 1302 (1980).
[3] K. Ogasawara, T. Iwata, Y. Koyama, T. Ishii, I. Tanaka, and H. Adachi, *Phys. Rev. B* **61**, 143 (2000).
[4] I. H. Witten, E. Frank, M. A. Hall, and C. J. Pal, *Data Mining: Practical Machine Learning Tools and Techniques* (Elsevier, Amsterdam, 2000).
[5] H. Adachi, M. Tsukada, C. Satoko, *J. Phys. Soc. Jpn.*, **45**, 875 (1978).
[6] G. F. Imbush and R. Kogelman, *Optical Spectroscopy of Electronic Centers in Solids*, in: W. A. Yen and P. M. Selzer (Eds.), *Laser spectroscopy of solids, Top. Appl. Phys. Vol. 49* (Springer, Berlin, 1981).
[7] J. Qin, C. Rudowicz, Y. M. Chang, and Y. Yeung, *Phys. Chem. Minerals*, **21**, 532 (1994).
[8] D.-P. Ma and J.-R. Chen, *Commun. Theor. Phys.*, **44**, 165 (2005).
[9] M. G. Brik, A. Majchrowski, L. Jaroszewicz, A. Wojciechowski, and I. V. Kityk, *Philos. Mag. B*, **90**, 4569 (2010).
[10] M. Sugiyama, T. Yanagida, D. Totsuka, Y. Yokota, Y. Futami, Y. Fujimoto, and A. Yoshikawa, *J. Cryst. Growth*, **362**, 157 (2013).
[11] G. Wang, H. G. Gallagher, T. P. J. Han, and B. Henderson, *J. Cryst. Growth*, **183**, 272 (1996).
[12] A. R. Molla, C. R. Kesavulu, R. P. S. Chakradhar, A. Tarafder, S. K. Mohanty, J. L. Rao, B. Karmakar, and S. K. Biswas, *J. Alloys Compd.*, **583**, 498 (2014).
[13] G. J. Wang, L. Z. Zhang, Z. B. Lin, and G. F. Wang, *J. Alloys Compd.*, **489**, 293 (2010).
[14] G. J. Wang, X. F. Long, L. Z. Zhang, G. F. Wang, S. Polosan, and T. Tsuboi, *J. Lumin.*, **128**, 1556 (2008).
[15] K. Hermanowicz, *J. Lumin.*, **109**, 9 (2004).
[16] M. G. Brik, S. J. Camardello, A. M. Srivastava, N. M. Avram and A. Suchockie, *ECS J. Solid State Sci.*, **5** (1) R3067-R3077 (2016).