Systematic First-Principles Calculations of Charge Transfer
Transitions of Transition Metal Ions (Sc$^{3+}$, Ti$^{3+}$, V$^{3+}$, Cr$^{3+}$, Mn$^{3+}$, Fe$^{3+}$) in $\alpha$-Al$_2$O$_3$ with Structural Optimization

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Abstract. In order to calculate the LMCT energies for various trivalent TM ions in $\alpha$-Al$_2$O$_3$ using realistic model clusters, we performed structural optimization using the CASTEP code and constructed the optimized TMO$_6^{69-}$ and TMAl$_1$O$_6^{30+}$ clusters (TM = Sc$^{3+}$, Ti$^{3+}$, V$^{3+}$, Cr$^{3+}$, Mn$^{3+}$, Fe$^{3+}$). We obtained the LMCT energies of TM ions by first-principles many-electron calculations using the DVME method. It was found that the differences between the LMCT energies of the optimized clusters and those of the relaxed clusters based on the crystal radii originate from the difference in the multiplet splitting of the LMCT states. The results also indicated that the LMCT energies of transition metal ions in $\alpha$-Al$_2$O$_3$ can be calculated using small clusters composed of the central TM ion and the first-neighbor oxygen ions.

1. Introduction

The position of the impurity level within the band gap is very important in optical materials. It can be estimated by calculating the charge transfer transition energy from the valence band to the impurity levels (Ligand to Metal Charge Transfer: LMCT). Recently, we successfully reproduced the LMCT energies and their experimental trend of transition metal (TM) ions in $\alpha$-Al$_2$O$_3$ using the discrete variational multi-electron (DVME) method [1] considering the configuration-dependent correction
(CDC) and the lattice relaxation (LR) based on the Shannon’s crystal radii [2]. We also clarified that the LMCT energy is very sensitive to the bond length. In this work, in order to calculate the LMCT energies for various trivalent TM ions in α-Al₂O₃ using more realistic model clusters, we performed structural optimization using the Cambridge Serial Total Energy Package (CASTEP) code [3-5] and constructed the optimized TMO₆⁻ and TMAl₁₃O₆³⁺ clusters (TM = Sc³⁺, Ti³⁺, V³⁺, Cr³⁺, Mn³⁺, Fe³⁺).

We obtained the LMCT energies of TM ions in α-Al₂O₃ by first-principles many-electron calculations using the DVME method for both the relaxed clusters based on the Shannon’s crystal radii and the optimized cluster based on the CASTEP, and compared the results.

2. Computational Method

We constructed a 7-atom cluster with C₃ symmetry consisting of the central aluminum ion and the first-neighbor oxygen ions, and a 20-atom cluster in which the second-neighbor aluminum ions were added, based on the crystal data of α-Al₂O₃ (#ICSD 73724). [6] Then we substituted various trivalent TM (Sc, Ti, V, Cr, Mn, Fe) ions for the central aluminum ion. The effective Madelung potential was considered by setting point charges on the atomic sites around the cluster. The lattice relaxation was considered in two ways. One is the method to estimate the relaxed bond lengths based on the Shannon’s crystal radii [7, 8]. The other is a method based on the structural optimization using the CASTEP code. The optimized lattice constants of α-Al₂O₃ by the CASTEP calculation are \( a = 4.806 \) Å and \( c = 13.119 \) Å. In this calculation, the Vanderbilt ultrasoft pseudopotentials [9] were used and the Generalized Gradient Approximation (GGA) exchange-correlation potential proposed by Perdew, Burke, and Ernzerhof (PBE) were considered [10]. The procedure employed here is similar to those used in Ref. 11.

In this work, we suppose that the LMCT occurs only from the first-neighbor ions to the TM ion. The CI calculation of the LMCT energies requires to consider the ground configuration and the excited configuration after LMCT. The number of 2p orbitals is 18 because there are 6 oxygen ions around the TM ion. Therefore we considered \( 3d^n2p^{36} \) configuration as the ground configurations and \( 3d^{n+1}2p^{35} \) configuration as the excited configuration. The \( 3d^{n}2p^{36} \) configuration includes the excited states of the d-d transition. Then, the LMCT energy was obtained by the energy difference between the lowest multiplet energy within the \( 3d^{n}2p^{36} \) configuration and the lowest multiplet energy within the \( 3d^{n+1}2p^{35} \) configuration. In calculations using the CI approach, multiplet energies are generally overestimated because of the finite number of Slater determinants. However, this overestimation can be corrected nonempirically by introducing the configuration-dependent correction (CDC) in which a correction term estimated from one-electron calculation is added to the diagonal elements of the many-electron Hamiltonian [1].
3. Results and discussion

The LMCT energy diagram calculated by the DVME method with CDC together with the experimental data [12,13] is shown in Fig. 1. The trend from Sc to V was reproduced better by calculations using the optimized clusters. Although the differences in the LMCT energies of Cr, Mn, and Fe between the relaxed clusters based on the crystal radii and the optimized clusters based on the CASTEP are small, they are relatively large for Sc, Ti, and V. These energy differences are due to the difference in the average TM-O bond lengths between the cluster models of the two approaches. The differences in the average TM-O bond lengths of Sc, Ti, and V are 0.58 Å, 0.16 Å and 0.11 Å, respectively, while those of Cr, Mn, and Fe are less than 0.1 Å.

Fig. 1. LMCT energy diagram of trivalent transition metal ions in α-Al₂O₃ calculated by the DVME method with CDC together with the experimental data [12,13]. Left figure shows the LMCT energies using 7-atom clusters while right figure shows the LMCT energies using 20-atom clusters.

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Fig. 2 shows the cluster size dependence of the LMCT energies between 7-atom cluster and 20-atom cluster. Left figure shows the LMCT energies calculated using the optimized clusters based on the CASTEP while right figure shows the LMCT energies calculated using the relaxed clusters based on the Shannon’s crystal radii.

Fig. 2 shows the cluster size dependence of the LMCT energy diagrams where the results of 7-atom clusters and those of 20-atom clusters are compared. The CDC were also considered in these
calculations. The differences between the LMCT energies of the 7-atom cluster and those of the 20-atom cluster are small in both the calculation using the optimized clusters based on the CASTEP and that using the relaxed clusters based on the Shannon’s crystal radii. The reason can be explained by the difference in the barycenters of the 3d\textsuperscript{n}2p\textsuperscript{36} and 3d\textsuperscript{n+1}2p\textsuperscript{35} configurations and the multiplet splitting of the LMCT state. The MO energy diagram of VO\textsubscript{6}\textsuperscript{9-} and VAl\textsubscript{13}O\textsubscript{630+} calculated by the DV-X\alpha method is shown in Fig. 3.

![MO energy diagram of VO\textsubscript{6}\textsuperscript{9-} and VAl\textsubscript{13}O\textsubscript{630+}](image)

Fig. 3. MO energy diagram of VO\textsubscript{6}\textsuperscript{9-} and VAl\textsubscript{13}O\textsubscript{630+} calculated by the DV-X\alpha method. Blue and red lines are V 3d levels and oxygen 2p levels, respectively.

In this diagram the highest energy of the t\textsubscript{2g} orbital of V\textsuperscript{3+} is set at 0 eV. The energy differences between t\textsubscript{2g} level and the highest oxygen 2p level of the 20-atom clusters are smaller than those of the 7-atom clusters. When the energy differences between t\textsubscript{2g} level and the highest oxygen 2p level are large, the difference of the barycenters of the 3d\textsuperscript{n}2p\textsuperscript{36} and 3d\textsuperscript{n+1}2p\textsuperscript{35} configurations is large. Then the LMCT energy is expected to be larger. On the other hand, the splittings of the oxygen 2p levels of the 20-atom clusters are smaller than those of the 7-atom clusters. When the splitting of the oxygen 2p levels is large, the multiplet splitting of the LMCT state is large. Then the LMCT energy is expected to be smaller. The results indicated that the LMCT energies of the 7-atom and the 20-atom clusters are almost the same due to the cancelation of these two effects. As a result, the LMCT energies of transition metal ions in α-Al\textsubscript{2}O\textsubscript{3} can be calculated using small clusters composed of the central TM ion and the first-neighbor oxygen ions.

4. Conclusion
We performed structural optimization using the CASTEP code and constructed the optimized clusters. We obtained the LMCT energies of TM ions in α-Al\textsubscript{2}O\textsubscript{3} by first-principles many-electron calculations using the DVME method. The decreasing trend from Sc to V was improved in the results based on the CASTEP compared to the results based on the Shannon’s crystal radii. On the other hand, the energy
differences between the 7-atom clusters and the 20-atom clusters are small. These results indicated that the LMCT energies of transition metal ions in $\alpha$-$\text{Al}_2\text{O}_3$ can be calculated by calculations using small clusters composed of the central TM ion and the first-neighbor oxygen ions.

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