Theoretical Investigation of Al K-edge X-ray Absorption Spectra of Al, AlN and Al$_2$O$_3$

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High-resolution X-ray absorption spectra of Al, AlN and Al$_2$O$_3$ are measured at the Al K-edge, which have revealed a chemical shift in the threshold energy and significant differences in the spectral fine structures among the three compounds. In order to interpret the chemical shift and the fine structures of these spectra, first-principles calculations using the full-potential linearized augmented plane wave method within the density functional theory are carried out, taking into account the core-hole effect. The resultant theoretical spectra quantitatively reproduce both the chemical shift and the spectral fine structures of the experimental ones. The dependence of the theoretical spectra on the supercell size is also examined.

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1. Introduction

Measurements of the X-ray absorption near-edge structure (XANES) and the electron-energy-loss near-edge structure (ELNES) facilitate efficient analysis of the electronic structure of condensed matter, because these experimental methods are particularly sensitive to changes in the chemical state. Combined use of a transmission electron microscope (TEM) and ELNES can provide information on the chemical state of solid-state materials with a very high spatial resolution. On the other hand, XANES generally has better energy resolution and a lower detection limit than ELNES. For instance, a chemical state analysis of an ultra-dilute dopant at a level of several atomic ppm has been successfully performed with the XANES technique by using a third-generation synchrotron radiation source.1)

A number of attempts to reproduce the fine structures of the XANES and ELNES spectra have been achieved by using first-principles calculations. First-principles calculations based on the density function theory (DFT) were first applied for analyzing X-ray absorption spectra in the late 1970s.2) In the last two decades, various calculation methods such as a multiple-scattering approach,3–5) a periodic band structure calculation method6–8) and a molecular orbital method with model clusters9–13) have been adopted to explain the characteristic features of the XANES/ELNES spectra. However, most of these methods only provide qualitative agreement with experimental data. Recently, a first-principles band structure calculation using an orthogonalized linear combination of the atomic orbitals (OLCAO) method14) was successfully used to reproduce the experimental spectral fine structures quantitatively.15,16)

Various Al K-edge XANES spectra of Al compounds have been extensively studied both experimentally and theoretically. A high-resolution experimental Al K-edge XANES spectrum of metallic Al was obtained17) using the total electron yield (TEY) and the total fluorescence yield (TFY) methods for the measurements. It was reported that differences in the spectral fine structures were observed between TEY and TFY, but no theoretical interpretation was presented.17) Experimental XANES spectra of AlN were reported,16) and the experimental fine structure was quantitatively explained by using the OLCAO method. Mention was made in that report of a striking core-hole effect on the theoretical estimation of the XANES/ELNES spectra.16) The fine structure of Al$_2$O$_3$ has also been obtained experimentally18–20) and theoretically explained by using the multiple-scattering method. However, to the best of our knowledge, these materials have not been examined systematically using the same calculation method to investigate the experimental chemical shifts and differences in spectral fine structures. In this work, we measured high-resolution Al K-edge XANES spectra of Al, AlN and Al$_2$O$_3$ as representative examples of metallic, semiconducting and insulating Al compounds, respectively, in order to investigate the validity of our calculation method for analyzing XANES/ELNES spectra. We carried out the first-principles calculations taking the core-hole effects into account. Experimental chemical shifts and spectral fine structures of these compounds were successfully reproduced by our present calculations.

This type of calculation using the supercells within the full-potential linearized augmented plane wave (FP-LAPW) method was reported by Radtke et al.21) for an analysis of N K-edge ELNES spectra of AlN, in which they employed a small supercell consisting of 32 atoms. However, no discussion was presented concerning the dependence of the theoretical spectral shapes on the supercell size Therefore, this dependence was also examined in this work by varying the supercell size.
2. Experimental and Calculation Procedures

High-resolution X-ray absorption spectra at the Al K-edge were measured using the BL1A beamline at the Ultraviolet Synchrotron Orbital Radiation Facility (UVSOR) of the Institute for Molecular Science in Okazaki, Japan. All the X-ray absorption spectra were collected by the total electron yield (TEY) method. The incident photon beam was monochromatized using a KTP (2θ = 1.0954 nm) double-crystal monochromator. Commercially available high purity Al foil and wurtzite and corundum types of AlN and Al$_2$O$_3$ powders were attached to the first photocathode of the electron multiplier using adhesive carbon tape. The crystal structures and contaminants of the samples employed here were checked by X-ray diffraction (XRD) measurements, which revealed the presence of only small amounts of contaminants.

In order to interpret the experimental Al K-edge XANES spectra of Al, AlN and Al$_2$O$_3$, first-principles DFT calculations were carried out by using the FP-LAPW $^{22,23}$ package, WIEN2k. $^{24}$ The generalized gradient approximation (GGA-PBE) $^{25}$ was employed as an effective-exchange-correlation functional. The muffin-tin radius, $R_{MT}$, was set to 2.7 Bohr for Al of metallic Al, while that of Al, N and O of AlN and Al$_2$O$_3$ was 1.7 Bohr. The product of the muffin-tin radius and the maximum reciprocal space vector $K_{\text{max}}$, i.e., the plane-wave cutoff, $R_{MT}K_{\text{max}}$, was fixed at 7.0. For Al 1s and 2s, electrons were treated as the core states, while only 1s was the core state for O and N. Cell parameters, number of atoms and the k-point sampling meshes for the calculated models are shown in Figs. 1(a)–(c). The experimental XANES spectrum of metallic Al has a broad continuous peak as is typical of metallic materials and was mainly composed of three peaks, labeled as A, B and C as shown in Fig. 1(a). In the spectra of AlN and Al$_2$O$_3$, seven peaks, labeled as D to I for AlN and as K to Q for Al$_2$O$_3$, were found in the present energy range as shown in Figs. 1(b) and (c), respectively. The threshold energy increased in the order of Al, AlN and Al$_2$O$_3$, which is a so-called chemical shift as shown in Figs. 1(a)–(c). The spectra calculated by using $4 \times 4 \times 4$, $3 \times 3 \times 2$ and $2 \times 2 \times 1$ supercells for Al, AlN and Al$_2$O$_3$, respectively, are shown in Figs. 1(d)–(f) in comparison with the experimental ones. The transition energy was calculated from the difference in the total electronic energy between the ground and core-hole states. The theoretical spectra shown in Figs. 1(d)–(f) showed the same tendency as the experimental chemical shift, although the absolute transition energy for each compound was slightly overestimated by approximately 0.9 eV.

3. Results and Discussion

The observed Al K-edge X-ray absorption spectra of Al, AlN and Al$_2$O$_3$ are shown in Figs. 1(a)–(c). The experimental XANES spectrum of metallic Al has a broad continuous peak as is typical of metallic materials and was mainly composed of three peaks, labeled as A, B and C as shown in Fig. 1(a). In the spectra of AlN and Al$_2$O$_3$, seven peaks, labeled as D to I for AlN and as K to Q for Al$_2$O$_3$, were found in the present energy range as shown in Figs. 1(b) and (c), respectively. The threshold energy increased in the order of Al, AlN and Al$_2$O$_3$, which is a so-called chemical shift as shown in Figs. 1(a)–(c). The spectra calculated by using $4 \times 4 \times 4$, $3 \times 3 \times 2$ and $2 \times 2 \times 1$ supercells for Al, AlN and Al$_2$O$_3$, respectively, are shown in Figs. 1(d)–(f) in comparison with the experimental ones. The transition energy was calculated from the difference in the total electronic energy between the ground and core-hole states. The theoretical spectra shown in Figs. 1(d)–(f) showed the same tendency as the experimental chemical shift, although the absolute transition energy for each compound was slightly overestimated by approximately 0.9 eV.

### Table 1. Cell parameters, number of atoms in the supercell and k-point sampling meshes for the calculated models. $\Gamma$ means $\Gamma$ point sampling only.

<table>
<thead>
<tr>
<th></th>
<th>Cell parameters (nm)</th>
<th>Number of atoms</th>
<th>k-mesh</th>
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<tr>
<td></td>
<td>$a$</td>
<td>$b$</td>
<td>$c$</td>
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<td>Al</td>
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<tr>
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<tr>
<td></td>
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<td>0.9339</td>
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<tr>
<td></td>
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<tr>
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<td></td>
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</table>
and Al$_2$ peaks were chosen for AlN and Al$_2$O$_3$ theoretical peak energies is plotted in Fig. 2. The first intense spectra, the relationship between the experimental and calculated chemical shift between the experimental and calculated energies is shown in Fig. 2. The second peak was chosen for metallic Al, because the first peak was too broad to determine the peak energy.

4 eV ($\Delta E/E = +0.3\%$). In order to compare and evaluate the chemical shift between the experimental and calculated spectra, the relationship between the experimental and theoretical peak energies is plotted in Fig. 2. The first intense peaks were chosen for AlN and Al$_2$O$_3$, whereas the second one was plotted for metallic Al, since the first intense peak (peak A) in its spectrum was too broad to determine the precise peak energy. As shown in Fig. 2, fairly good linearity was obtained between the experimental and calculated peak energies. This means that the first-principles DFT calculations can predict the chemical shift of the XANES spectra for the system examined here.

With our present calculation method, a three-dimensional periodic boundary condition is always necessary. Hence, interactions between core-holes appear, when core-holes are introduced. To investigate the influence of the interactions between core-holes, we performed calculations in which the supercell size was varied. The spectral line shapes of the experimental and theoretical XANES spectra are compared in Fig. 3. As seen in these figures, the experimental spectral fine structures were well reproduced by the present calculations, when the largest supercells were employed, i.e., 4 x 4 x 4, 3 x 3 x 2 and 2 x 2 x 1 supercells for Al, AlN and Al$_2$O$_3$, respectively. In the case of metallic Al, the agreement between the experimental and calculated spectral profiles was slightly improved by increasing the supercell size. The previous report mentioned that the XANES profile of metallic Al mainly originated from Al oxides and/ or hydroxides when it was measured by the TEY method, which was the main reason why the spectral profiles differed between the TEY and TFY methods. However, our first-principles results for pure metallic Al agreed well with the experimental data, although the present experimental line shapes showed spectral features similar to those described in the previous report.

From the results of our present calculations, it is concluded that the main component of the present Al K-edge spectrum of metallic Al measured by the TEY method was bulk metallic Al. In the case of AlN, peak E was missing in the theoretical spectra obtained with the 3 x 3 x 1 supercell, although this supercell provided better agreement with the experimental data than the smaller 2 x 2 x 1 supercell. The 3 x 3 x 2 supercell successfully reproduced the whole fine structure, including peak E. The experimental spectrum of Al$_2$O$_3$ was well reproduced even when the 1 x 1 x 1 cell was used. However, a larger supercell, i.e., the 2 x 2 x 1 supercell consisting of 120 atoms, provided a better chemical shift than the 1 x 1 x 1 cell. From the results of this investigation using different supercell sizes, the largest supercells of those examined here provided the best agreement with the experimental results in all three cases, which suggests that the supercell size should be chosen as large as possible to reduce core-hole interactions.

A detailed first-principles analysis of AlN using the OLCAO method was reported, which gave a quantitative reproduction of the experimental fine structure. Both the OLCAO and WIEN2k codes are based on the all-electron first-principles methods. Hence, the theoretical spectra given by these two methods are usually almost the same as in the case of AlN. However, these two codes offer different advantages based on their algorithms and implementations, e.g., 1) OLCAO requires a shorter computational time than WIEN2k and 2) fully relativistic calculations can be performed with the WIEN2k code.

In conclusion, high-resolution X-ray absorption spectra of Al, AlN and Al$_2$O$_3$ at the Al K-edge were measured and their spectral fine structures were quantitatively reproduced by using first principles DFT calculations that took the core-hole effect into consideration. The chemical shifts of these materials were also systematically interpreted on the basis of the present calculations. Our calculation method was shown to be valid for analyzing the XANES spectra of metallic, semiconducting and insulating compounds of Al.
This type of first-principles calculation can be a powerful tool for systematic and quantitative analysis of XANES/ELNES spectra.

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REFERENCES