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First-principles calculation of spectral features, chemical shift and absolute threshold of ELNES and XANES using a plane wave pseudopotential method

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Abstract

Spectral features, chemical shifts, and absolute thresholds of electron energy loss near-edge structure (ELNES) and x-ray absorption near-edge structure (XANES) for selected compounds, i.e. TiO₂ (rutile), TiO₂ (anatase), SrTiO₃, Ti₂O₃, Al₂O₃, AlN and β -Ga₂O₃, were calculated by a plane wave pseudopotential method. Experimental ELNES/XANES of those compounds were well reproduced when an excited pseudopotential, which includes a core hole, was used. In addition to the spectral features, it was found that chemical shifts among different compounds were also reproduced by correcting the contribution of the excited pseudopotentials to the energy of the core orbital.

1. Introduction

Electron energy loss near-edge structure (ELNES) and x-ray absorption near-edge structure (XANES) originate from the electronic transition from a core orbital to unoccupied bands [1–3]. Since the ELNES and XANES reflect the unoccupied partial density of states (PDOS) of a selected element, information concerning the local atomic environment and chemical bonding can be obtained by analysis of their spectral features. ELNES can be measured with transmission electron microscopy (TEM) or scanning TEM (STEM) with a spatial resolution at the sub-nanometer level [4–6]. Although XANES is inferior to ELNES in spatial resolution, XANES is superior in the detectable limitation. By combining a

synchrotron x-ray source with a highly sensitive multi-element solid state detector, the XANES signal from ultra-dilute dopants at a few ppm level can be obtained [7, 8]. Both ELNES and XANES are therefore powerful tools for modern materials' characterization.

In order to extract atomic and electronic structure information from the spectra, theoretical calculations are essential. Simulations of ELNES and XANES by different methods have been reported [9–20]. It has been well demonstrated that proper inclusion of a core hole, i.e. an electronic hole on a core orbital associated with the electron transition process, is essential to reproduce the experimental spectra [9–11]. Use of all-electron methods that include core orbitals, valence bands and conduction bands is a natural way to include the core-hole effect. Many previous studies

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including the theoretical calculation have employed such methods [9–18].

On the other hand, some have adopted pseudopotential methods in the calculation of XANES and ELNES [19–31]. Although core orbitals are not explicitly treated in the pseudopotential method, the core-hole effect can be taken into account in either of two ways: (1) use of the pseudopotential for the next heavier atom of the excited atom with an atomic number of Z . The method is often called the $Z + 1$ method [19–21] or (2) use of the pseudopotential specially designed for the excited atom with a core hole [22–31]. The first method is much more convenient since no supplementary work to generate the pseudopotential is required. However, the assumption cannot be verified all the time. As a matter of fact, the $Z + 1$ method cannot distinguish the core holes with different principal quantum numbers. It has been demonstrated that the $Z + 1$ approximation does not give the same results as calculations in which the core hole is correctly treated [13, 16, 19–21]. The second approach has successfully calculated ELNES and XANES [22–30]. This method is considered to have a great advantage as compared to all-electron calculations in that the plane wave pseudopotential method allows the efficient calculation of ELNES and XANES for large and complex systems, such as lattice imperfections and interfaces. On the other hand, although it has been demonstrated that the plane wave pseudopotential method can reproduce the spectral features [22–30], the ability to calculate the chemical shift and absolute threshold has not been limitedly discussed [31]. Hamann and Muller reported the way to calculate them but did not show the spectral features [31]. The calculation of the chemical shift is indispensable, especially for complex systems, because they usually include multiple sites for the element and it is often necessary to sum up the calculated spectra from the individual sites to compare with experiments. The theoretical transition energy is directly calculated by the all-electron method [13–18], while that by the plane wave pseudopotential method is not straightforward because core orbitals are not explicitly treated.

In this study, a method to calculate spectral features, chemical shift and absolute threshold by a plane wave basis pseudopotential method is reported. To demonstrate the validity of the present method, ELNES and XANES from AlN, TiO₂ (rutile), TiO₂ (anatase), SrTiO₃, Ti₂O₃ and β -Ga₂O₃ are systematically calculated. The results are compared with the results from all-electron calculations on the same systems.

2. Methodology

Theoretical ELNES/XANES can be obtained by computing the photoabsorption cross section (PACS) as described by Fermi's golden rule. It can be well approximated using matrix elements of the electric dipole transition between the core orbital and the unoccupied bands within a one-electron theory, except for the cases showing strong correlation among excited electrons and the core hole such as transition metal L_{2,3} ELNES/XANES [3]. In this study, K edges of TiO₂ (rutile), TiO₂ (anatase), Ti₂O₃, SrTiO₃, Al₂O₃, AlN and β -Ga₂O₃ are examined.

The core orbital was obtained from an all-electron calculation of an isolated atom. The excited pseudopotential was generated for the electronic configuration obtained by removing one electron from the corresponding core orbital. The final state wavefunctions were obtained adopting the excited pseudopotential for the excited atom in a supercell. The size of the supercell was chosen to be large enough to reduce artificial interactions between the excited atoms [12–18].

Plane wave basis pseudopotential calculations were performed within the generalized gradient approximation (GGA) using the CASTEP code [32]. Ultrasoft pseudopotentials were used and the plane wave cutoff energy (E_{cut}) was taken to be 400 eV. Monkhorst–Pack k -point density in reciprocal space, which is given by the number of k -points in the whole Brillouin zone multiplied by the real-space volume of the supercell, was set to approximately 5×10^3 points \AA^{-3} . The convergence of the calculations with both energy cutoff and k -point density was extensively tested. In order to compare with experimental spectra, the theoretical PACS was broadened using a Voigt function which is composed of Gaussian and Lorentzian functions with broadening factors of 0.2 eV and 0.4 eV, respectively. The details of the spectral calculation were described in [27].

In all-electron calculations, the theoretical transition energy (E_{TE}) can be evaluated from the total energy difference between the excited and ground states [3, 13–18]. In the pseudopotential method, the transition energy cannot be evaluated in such a straightforward manner since only valence electrons are included in the total energy. The contribution of the core electrons should also be evaluated. In the present study, we made the excited pseudopotentials by fixing all parameters, such as core radius, that are optimized for ground state pseudopotentials. Two potentials were generated by only changing the electronic configuration of the core orbitals. The theoretical transition energy was evaluated by the total energy difference between the excited and ground states, $\Delta E_{\text{valence}}$, by the pseudopotential calculation. In order to include a contribution of the core orbitals, a correction term, $\Delta E_{\text{core(atom)}}$, was used. E_{TE} is then obtained by the following equation:

$$E_{\text{TE}} = \Delta E_{\text{valence}} + \Delta E_{\text{core(atom)}}. \quad (1)$$

The subscript '(atom)' indicates that the value was obtained by the isolated atom calculation which is performed when generating the pseudopotentials. $\Delta E_{\text{core(atom)}}$ is obtained as follows:

$$\Delta E_{\text{core(atom)}} = \Delta E_{\text{All orbitals(atom)}} - \Delta E_{\text{valence(atom)}}. \quad (2)$$

$\Delta E_{\text{All orbitals(atom)}}$ is the total energy difference between the excited state and ground state obtained in the isolated atom calculation. $\Delta E_{\text{valence(atom)}}$ is the contribution of valence orbitals to the $\Delta E_{\text{All orbitals(atom)}}$. Since the $\Delta E_{\text{valence}}$ in equation (1) already includes the contribution of the valence band, $\Delta E_{\text{valence(atom)}}$ is necessarily subtracted from $\Delta E_{\text{All orbitals(atom)}}$ to avoid double-counting of the valence band contributions to the theoretical transition energy. Here, it should be noted that the chemical shift among different materials in this procedure is dependent only on $\Delta E_{\text{valence}}$

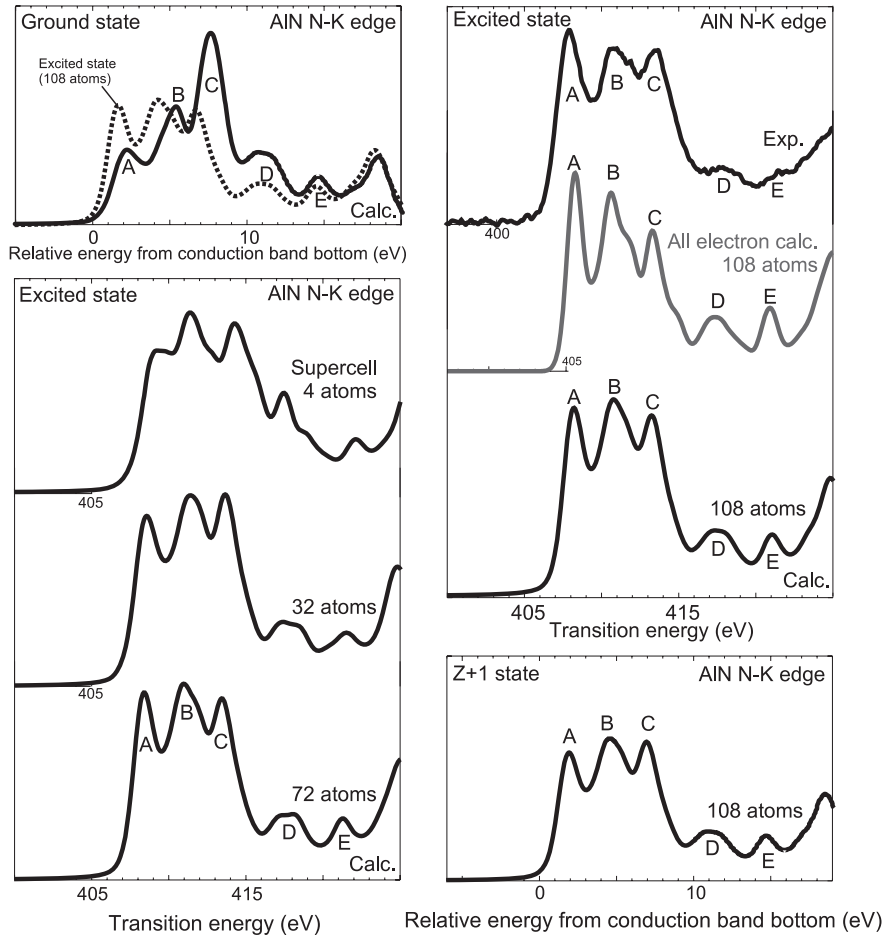


Figure 1. Dependence on supercell size of N K ELNES of wurtzite-AIN. Experimental spectrum taken from [15]. The ground state spectrum is compared with the excited state spectrum with the same vertical scale. The calculated spectra by the all-electron method, which is taken from [15], and that by the $Z + 1$ method are compared.

because $\Delta E_{\text{All orbitals(atom)}}$ is obtained by the isolated atom calculation. In this method, the core correction due to the presence of the core hole is included in the isolated atom calculation and the interactions between the core hole and prompted electrons are included as the interactions between the excited pseudopotential and the excited electron.

In order to confirm the convergence of the supercell size and the validity of the transition energy estimation, N K ELNES/XANES of wurtzite-AIN with different supercell sizes were calculated and compared with the result from the all-electron calculation as shown in figure 1. It is found that the calculated spectrum at the ground state (without core hole) is far from a satisfactory reproduction of the experimental spectrum. The calculated spectrum with the $Z + 1$ approximation is also shown. The $Z + 1$ calculation has been made by using a 108-atom supercell in which one N atom is substituted by an O atom. The number of O 1s electrons was two. Although the spectra by the $Z + 1$ method is not too different from that by the accurate core-hole method, this $Z + 1$ method cannot calculate the transition energy. On the other hand, by introducing a core hole in a sufficiently large supercell, the experimental spectrum can be reproduced by the present method. Similar to our previous report using all-electron methods [15], a supercell of more than

72 atoms is necessary to reproduce the experimental spectrum. In this study, we have employed 72–128-atom supercells for all crystals. Using such supercells, the distance of separation between the excited atoms in adjacent cells is approximately 10 Å. In addition to the spectral features, it is found that the theoretical transition energy is also satisfactorily reproduced. In the case of the N K edge of AIN, $\Delta E_{\text{valence}}$ and $\Delta E_{\text{core(atom)}}$ in equation (1) were calculated to be -152.82 and 559.35 eV, respectively, and then the theoretical transition energy E_{TE} becomes 406.53 eV. The error of the transition energy by the present method is 3 eV, which is less than 1% of the absolute transition energy. It is found that the accuracy of the present method is comparable to the all-electron method as shown in the figure. As mentioned above, the advantage of the present method is the efficiency. Although it depends on the case, from the author's experiences, this method is at least two times faster than that by the all-electron method.

3. Results and discussion

As the first set of examples, theoretical calculations of TiO₂ polymorphs were performed. Figure 2 shows the theoretical O K-XANES/ELNES for rutile-TiO₂ and anatase-TiO₂ in comparison to experimental spectra. An excited

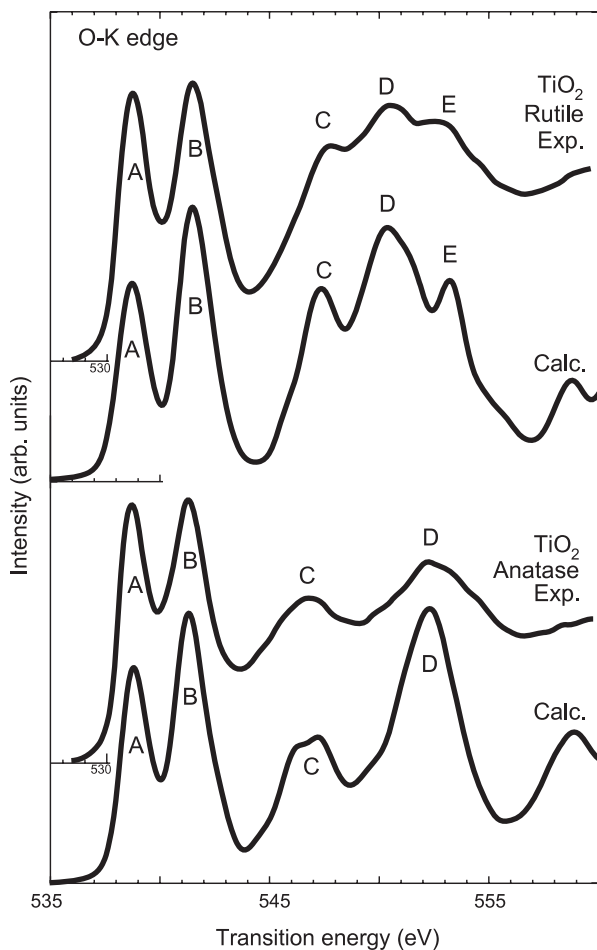


Figure 2. (Top and bottom) experimental [33] and calculated O K edge of TiO₂ polymorphs, rutile and anatase.

pseudopotential with a O 1s core hole was used. The theoretical spectra in figure 2 are aligned with the experimental spectra at the peak-top energy of peak A. Differences between the two spectra mainly appear in the region between 10 and 15 eV from the spectral threshold [33]. Rutile has three peaks, C, D and E, whereas anatase has two peaks, C and D. The difference between rutile and anatase is well reproduced by the present pseudopotential calculation when supercells of 72 and 108 atoms are used for rutile and anatase, respectively. It is also found that there is almost no chemical shift between rutile and anatase and it is reproduced by the present calculation.

Experimental and calculated Ti K-XANES/ELNES of Ti⁴⁺ compounds, rutile, anatase and SrTiO₃, and Ti₂O₃ are shown in figure 3 [8, 17]. The calculations were performed with 96-, 108-, 135- and 120-atom supercells with an excited pseudopotential with a Ti 1s core hole. Although the calculated spectra looks spikier compared with the experiments, it is probably due to the fact that a uniform broadening factor was employed in this study. Rutile has three distinct peaks B, C and D in the higher energy side, whereas a sharp peak C and a small peak B at the shoulder appear in anatase and SrTiO₃. Near the thresholds, these experimental spectra of Ti⁴⁺ compounds commonly exhibit pre-peaks A₁₋₄. The present calculation reproduces those pre-peak features except for the first pre-peak

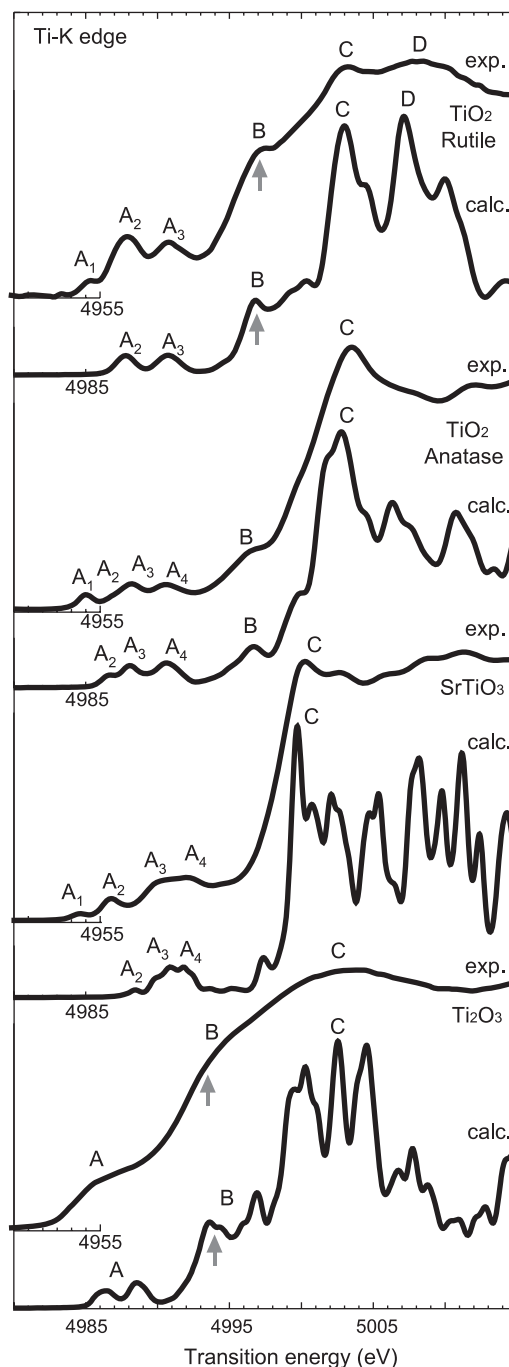


Figure 3. (Top to bottom) experimental [8, 17] and calculated Ti K edge of rutile-TiO₂, anatase-TiO₂ and SrTiO₃, and Ti₂O₃.

A₁. The absence of the peak A₁ can be ascribed to the fact that the electric quadrupole transition is not included in the present calculation. Yamamoto *et al* and Joly *et al* successfully reproduced the first pre-peak A₁ by including the quadrupole transitions in the calculation [17, 34]. However, the rest of the spectra, which originates from the dipole transition, is well reproduced. Contrary to those Ti⁴⁺ compounds, Ti₂O₃ has a broad profile and it shifts to the lower energy side. The chemical shift between the Ti⁴⁺ compound and Ti₂O₃ was measured by using peak B of rutile and Ti₂O₃, which are indicated by gray arrows in figure 3. It is found that

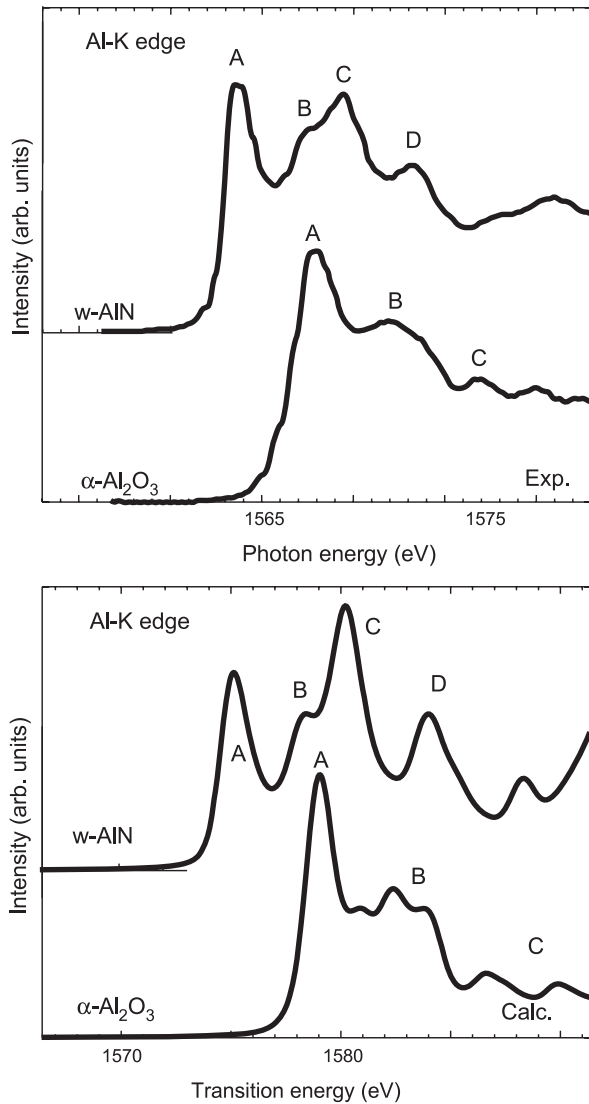


Figure 4. (Top and bottom) experimental [18, 35] and calculated Al K edge of wurtzite-AlN and α -Al₂O₃.

the calculated chemical shift, 3.21 eV, well reproduces the experimental chemical shift, 3.60 eV. The present calculation can reproduce not only the overall spectral features but also the chemical shift between Ti⁴⁺ and Ti³⁺ compounds.

In order to examine the chemical shift between compounds having the same valence states by the present method, Al K-XANES/ELNES of wurtzite-AlN and α -Al₂O₃ were calculated using 108- and 120-atom supercells, respectively. Mogi *et al* and Tatsumi *et al* reported similar calculations and found that the experimental chemical shifts are reproduced by using an all-electron method [18, 35]. The calculated spectra in the present work are compared with experiments in figure 4. It can be seen that these crystals exhibit different spectral features and they are well reproduced by the present calculation. Concerning the chemical shift, peak A of wurtzite-AlN is shifted towards lower energies of about 4.0 eV compared to peak A of α -Al₂O₃ in the experiment, which is in good agreement with the chemical shift in the calculation, 3.8 eV. As mentioned above, $\Delta E_{\text{core(atom)}}$ of both AlN and Al₂O₃ are identical values because they are calculated

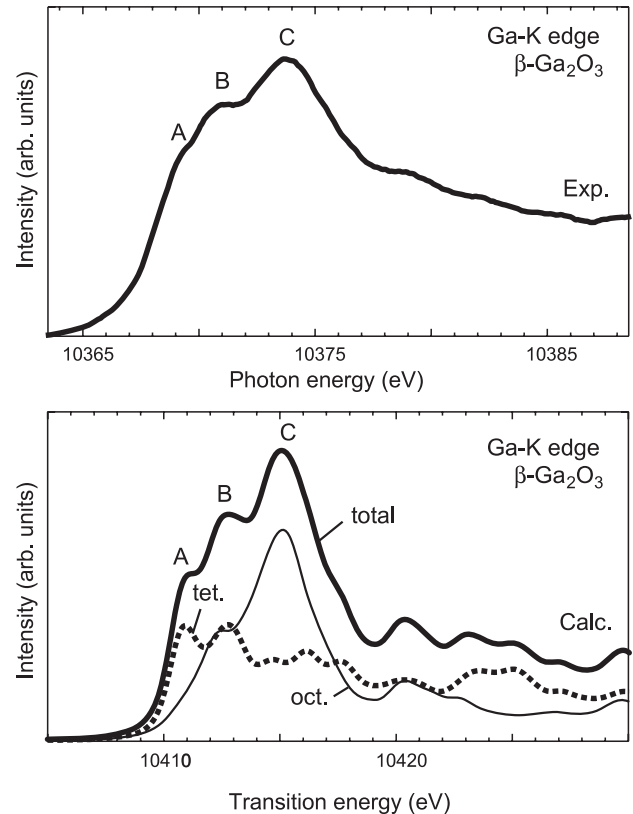


Figure 5. Experimental Ga K edge of β -Ga₂O₃ [7] and calculated spectrum.

by isolated Al atoms. Therefore, this chemical shift is caused by $\Delta E_{\text{valence}}$.

The accuracy of the chemical shift is important when multiple sites for the element are present in a sample. Then multiple calculated spectra for corresponding sites should be summed up with accurate alignment of their transition energies to make the theoretical spectra. Figure 5 shows experimental and calculated Ga K edges from β -Ga₂O₃, which has two cation sites, tetragonal and octahedral, with the ratio of 1:1. Individual spectra of those sites were separately calculated and were summed up with the alignment of the theoretical transition energy. It was found that the theoretical transition energies of those sites are very close to each other.

On the other hand, it can be seen that peaks A and B, which are located at the lower energy, are mainly composed of the tetragonal site, whereas the octahedral site contributes to the higher energy peak C. This difference can be ascribed to the local coordination of Ga at each site. For simplicity, isolated Ga³⁺ ions located at the center of an ideal octahedron and that of a tetrahedron are assumed. The p-orbitals, which are responsible for the K edge, cannot be hybridized with d-orbitals of the octahedral Ga³⁺, whereas p-d hybridization is allowed for the tetrahedral Ga³⁺ [36–38]. In the β -Ga₂O₃ crystals, those orbitals are more broadened because both sites are distorted from the ideal symmetries and are bonded with oxygens. However, the degree of the band dispersion of the d-orbital is expected to be broader in the tetrahedral site than that in the octahedral site due to the presence of the

p-d hybridization. The broader p-orbitals of the tetrahedral Ga can therefore contribute to the peaks in the lower energy side. These results correspond to those from an all-electron calculation [7]. In addition to the overall spectral profile, the energy differences among peaks A, B and C are well reproduced by the present calculation.

In this study, the contribution of the core orbital to the theoretical transition energy was obtained by the isolated atom calculation. From the results in figures 3–5, it is concluded that the approximation is reasonable to estimate the theoretical transition energy of those compounds at the K edge.

4. Summary

The plane wave pseudopotential method has been applied to obtain theoretical ELNES/XANES of TiO₂ (rutile), TiO₂ (anatase), Ti₂O₃, SrTiO₃, Al₂O₃, AlN and Ga₂O₃ at the K edges. Excited pseudopotentials with core holes were specially made to take into account the final state of the transition. Spectral features and chemical shift were well reproduced by the present calculations. The success of the computationally efficient method to calculate both spectral features and chemical shift of the ELNES/XANES in the first-principles manner paves the way for the computation of spectra for complex systems such as lattice imperfections and interfaces.

Finally, it should be mentioned that the present method is not immediately applicable for the calculation of the L_{2,3} edge of the transition metals, the M_{4,5} edge of the lanthanides and the K edge of very light elements. For those calculations, multi-electron interactions and exciton interactions must be considered rigorously. Such calculations are reported elsewhere [39–42].

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