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Core-hole effect on dipolar and quadrupolar transitions of $SrTiO_3$ and $BaTiO_3$ at Ti *K* edge

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Experimental pre-edge fine structures in the x-ray absorption spectra of $SrTiO_3$ and $BaTiO_3$ at Ti *K* edge are successfully reproduced within the framework of first-principles one-electron theory using the full-potential augmented plane wave plus local orbitals method. The importance of the following two points has been demonstrated: (1) proper inclusion of a Ti 1*s* core-hole using a large supercell, and (2) consideration of both dipolar and quadrupolar transitions. The core-hole effect is found to be more significant for quadrupolar transitions that form the first two peaks of the pre-edge structure, i.e., *p*1 to *p*2. They correspond to t_{2g} and e_g bands of the core-holed Ti. The other two peaks, *p*3 and *p*4, are found to be entirely due to the dipolar transition.

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I. INTRODUCTION

Near edge x-ray absorption fine structure (NEXAFS) has been widely used for the characterization of the electronic structures of condensed matters since it is sensitive to change in their local environment, such as chemical bondings and charges. A number of theoretical calculations to interpret the fine structures of NEXAFS spectra have been done using molecular orbital methods, band-structure methods, and multiple scattering methods.[1] However, the theoretical spectra do not always agree with the experimental spectra satisfactorily. Several factors contribute to the poor agreement. One of the most typical reasons is improper treatment of the interaction between a core-hole and an excited electron, i.e., the core-hole effect. The electronic structure at the final state of the x-ray absorption process is generally different from that of the initial state or the ground state. Since NEXAFS reflects the final state, proper inclusion of the core-hole effect is mandatory for reproducing experimental spectra by theoretical calculations. Recently, reproduction of experimental NEXAFS from many different kinds of crystals has been reported[2–8] by the first principles band-structure calculations within the density functional theory (DFT) using the orthogonalized linear combination of the atomic orbital (OLCAO) method[2] and the full-potential augmented plane wave plus local orbitals (APW+lo) method.[9] In these calculations, the core-hole was directly included in the self-consistent calculations. Interaction among core-holes was minimized using large supercells. Thereby the core-hole effect was included within the framework of one-electron theory. The method is more accurate than the widely used $Z+1$ approximation[10] in which the atomic number, *Z*, is increased by one to approximately introduce the core-hole effect.

NEXAFS spectra of 3*d* transition-metal (TM) compounds at TM *K* edge have been extensively studied both by experiment and theory.[11] Their pre-edge features, namely small peaks that appear approximately 10 eV below the major absorption edge [see Fig. 1(a)], are often used to identify local coordination of the TM atoms. Among them, experimental and theoretical data of Ti *K*-edge spectra of titanium oxides are most abundant. Vedrinskii *et al.*[12] discussed the pre-edge fine structures of $EuTiO_3$ and $PbTiO_3$ at Ti *K* edge by the multiple scattering method. Recently, Joly *et al.*[13] reported that the pre-edge feature in the Ti *K*-edge spectrum of rutile TiO_2 can be well reproduced by the finite difference method (FDM). They have obtained full-potential NEXAFS via fitting the spectra onto the experimental spectra, and computed both dipolar and quadrupolar transitions. Shirley[14] used the Bethe-Salpeter approach to compute the same edge of rutile TiO_2. He found that the inclusion of electron-hole interaction is essential for reproduction of the pre-edge feature.

Using band-structure calculations within the framework of first principles one-electron theory, however, no theoretical works have been reported on the pre-edge fine structures of any titanium oxides at the Ti *K* edge, to our best knowledge. If one can use a standard first principles band-structure method to reproduce experimental NEXAFS, it should be quite useful for researchers since one can correlate the NEXAFS results directly to the electronic structure that can be obtained via such calculations.

In the present study, we demonstrate successful results of the one-electron calculations for reproduction of the experimental pre-edge fine structures of $SrTiO_3$ and $BaTiO_3$ at Ti *K* edge NEXAFS. The core-hole effects are included in the manner as described above. Both contributions of dipolar and quadrupolar transitions are computed.

II. COMPUTATIONAL AND EXPERIMENTAL PROCEDURES

All calculations were made using the full-potential augmented plane wave plus local orbitals (APW+lo) package, WIEN2k.[15] The experimentally reported cubic ($Pm3m$) and tetragonal ($P4/mmm$) perovskite structures were examined for $SrTiO_3$ and $BaTiO_3$, respectively. A generalized gradient approximation proposed by Perdew *et al.*[16] was employed for the exchange-correlation functional. All electrons up to

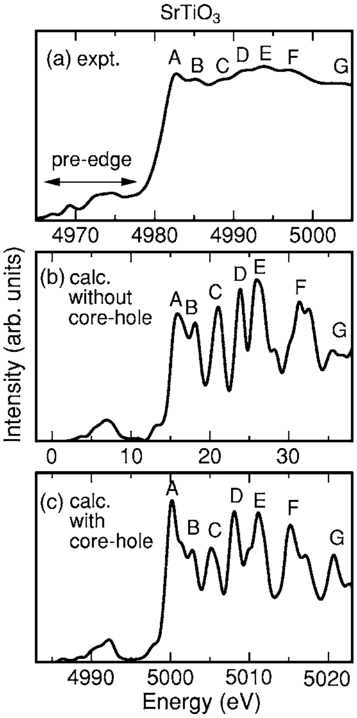

FIG. 1. Comparison of Ti *K*-edge NEXAFS spectra of $SrTiO_3$ between (a) experiment and calculations (b) without core-hole effect by unit-cell, and (c) with core-hole effect by supercell. The calculated spectra are the sum of dipolar and quaprupolar contributions. Note that the energies of calculated spectra are (b) the relative energy to the highest occupied band and (c) the calculated transition energy, respectively.

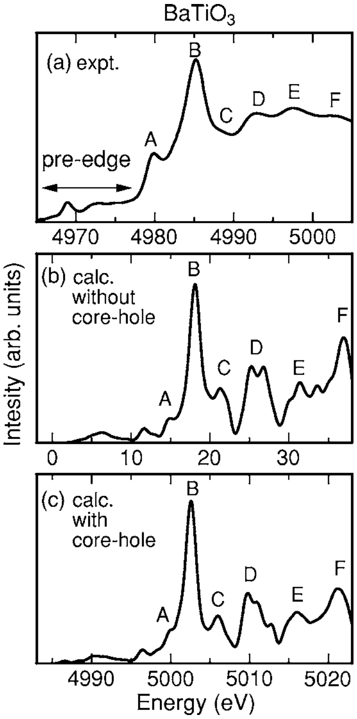

FIG. 2. Same view for $BaTiO_3$ as Fig. 1.

2*p*, 3*d*, and 4*d* were treated as core in the case of Ti, Sr, and Ba, respectively, while only 1*s* electrons were treated as core for O. The muffin-tin radii, R_{MT}, for Ti and O, and Sr and Ba were set to 1.8 and 2.0 Bohr, respectively. A product of the muffin-tin radius and the maximum reciprocal space vector K_{max}, i.e., the plane-wave cutoff, $R_{MT}K_{max}$ was fixed at 7.0 $(\mathrm{Bohr\,Ry}^{1/2})$ for all calculations. The relativistic effects were fully introduced for the core-electrons by solving the Dirac equation, while valence electrons were treated within the scalar relativistic approximations. Supercells consisting of 135 atoms were used in order to reduce the interactions among the core-holes due to the three-dimensional periodic boundary conditions within the band-structure calculations. The *k*-point sampling mesh was $3\times3\times3$ in the reciprocal space of the supercell for both $SrTiO_3$ and $BaTiO_3$. The theoretical spectral profile was obtained by a product of the radial part of the transition matrix element and the corresponding projected partial density of state, which was broadened with the Gaussian function of $\Gamma=1.0$ eV full width at half maximum. When the core-hole was introduced, transition energy was obtained by a difference in total electronic energies between ground and core-hole states.

High resolution x-ray absorption spectra at Ti *K* edge were measured by the transmission mode at the BL-12C in the Photon Factory, Tsukuba, Japan. The incident photon beam was monochromatized using a Si (111) double-crystal monochrometer and was irradiated perpendicularly onto the sample surface. Commercially available high purity powder prepared in the Soekawa Chemical Co., Ltd., was pressed into a pellet form, which was diluted by mixing with *h*-BN powder.

III. RESULTS AND DISCUSSION

Observed NEXAFS spectra of $SrTiO_3$ and $BaTiO_3$ at Ti *K* edge are shown in Figs. 1(a) and 2(a), respectively. Spectral fine structures here observed are almost the same as those in an earlier report.[17] These spectra can be separated into two parts, i.e., pre-edge and major absorption parts as pointed out in these figures. Pre-edge regions of the above two NEXAFS spectra are focused, which are shown in Figs. 3(a) and 4(a). At first, calculations were carried out at ground state, i.e., without core-hole effect. Resultant theoretical spectra are shown in Figs. 1(b) and 2(b) for $SrTiO_3$ and $BaTiO_3$, respectively. Although these calculations were carried out at ground state without core-hole effect, spectral features in major absorption regions were somehow reproduced. These results suggest that the core-hole effect is not so significant in the Ti *K*-edge x-ray absorption process through the electric dipole transitions in $SrTiO_3$ and $BaTiO_3$. This is contrary to many other systems that show significant core-hole effects.[2–8,18] However, the first pre-edge peak, peak *p*1, was missing in these theoretical spectra as shown in Figs. 3(b) and 4(b), and the intensities of the second one (*p*2) were much underestimated in both $SrTiO_3$ and $BaTiO_3$. In order to reproduce the "missing" pre-edge features in the ground state calculations, i.e., peak *p*1, the core-hole effect was introduced. In these calculations, one electron was removed from the Ti 1*s* and an additional electron was placed at the bottom in the conduction band. This state approximately corresponds to the final state of the Ti *K*-edge x-ray absorption process. Resultant

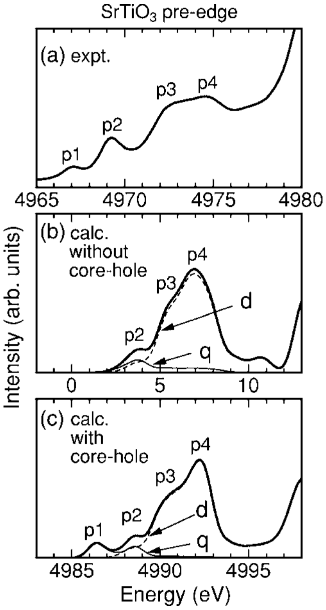

FIG. 3. View of pre-edge region for $SrTiO_3$. Thin dashed and solid lines are for dipolar (d) and quaprupolar (q) contributions, and thick solid line is the sum of these two.

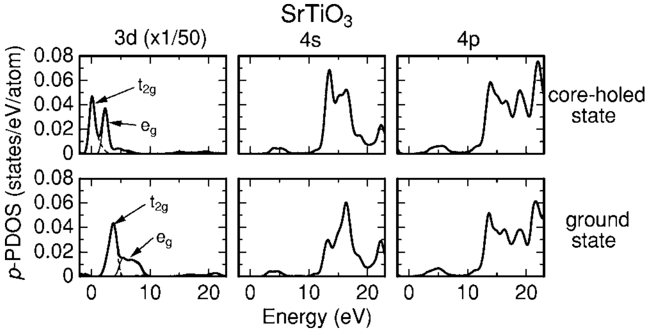

FIG. 5. (Top) Projected partial density of states (p-PDOS) of the core-holed Ti in $SrTiO_3$. (bottom) p-PDOS of Ti at the ground state. From left to right, $3d$, $4s$, and $4p$ components. $3d$ components are divided into t_{2g} (dashed) and e_g (solid) symmetries. Energies are relative ones to the highest occupied band.

theoretical spectra with core-hole effect are shown in Figs. 1(c) and 2(c) for $SrTiO_3$ and $BaTiO_3$, respectively, and the pre-edge regions are focused in Figs. 3(c) and 4(c). Whole spectral fine structures including both pre-edge and major parts are well reproduced by these calculations, though the intensities of $p2$ were still underestimated. It can be noted that energies of these x-ray absorption spectra are also well reproduced by the present calculations within the error of $\Delta E/E=0.4\%$, when the core-hole effect was taken into account. From these results shown in Figs. 3(c) and 4(c), the nature of the first pre-edge peak ($p1$) in both $SrTiO_3$ and $BaTiO_3$ can be ascribed to the quadrupolar transition from Ti $1s$ to $3d$. $p3$ and $p4$ are due to dipolar transitions from Ti $1s$ to $4p$. $p2$ is derived from the mixture of quadrupolar and dipolar transitions. It is interestingly noted that the first pre-edge peak ($p1$) appears only when the core-hole effects are included. As clearly seen in the difference between Figs. 3(b) and 3(c), and Figs. 4(b) and 4(c), peak energies from the quadrupolar contributions shift to lower energy by introducing the core-hole. This is quite reasonable, because $3d$ orbital is more localized to the Ti nucleus than $4p$ orbital in Ti. Hence the presence of core-hole on Ti $1s$ should affect the Ti $3d$ orbital more than $4p$.

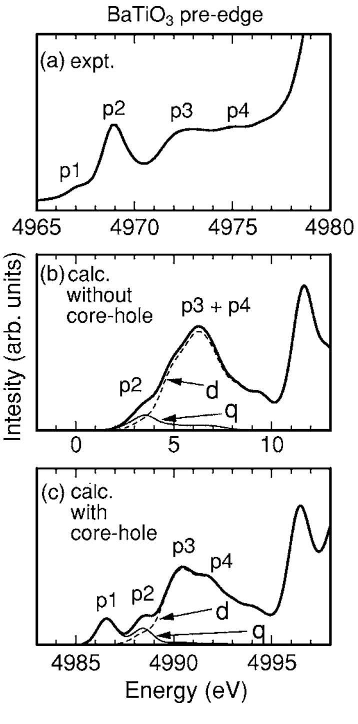

FIG. 4. Same view for $BaTiO_3$ as Fig. 3.

The theoretical NEXAFS was also calculated for the fictitious cubic structured $BaTiO_3$ with the same volume as that of the tetragonal one in order to examine the influence of the tetragonal distortion in $BaTiO_3$ on the NEXAFS profile. Resultant theoretical NEXAFS for cubic $BaTiO_3$ shows no significant difference from that for the tetragonal one, which suggests NEXAFS is not so sensitive to a change in this level of small distortion, i.e., $c/a=1.011$. The calculated result also confirms that the difference in spectral feature between $SrTiO_3$ and $BaTiO_3$ is not derived from the difference in symmetry of the crystal, but from the difference between unoccupied electronic structures of two compounds: They are mainly composed of either Ti+Sr orbitals or Ti+Ba orbitals.

In order to analyze the core-hole effect on each orbital component more specifically, projected partial density of states (p-PDOS) of Ti were computed. They are shown in Figs. 5 and 6 for $SrTiO_3$ and $BaTiO_3$, respectively. In this energy region, Ti s, p, and d components of the partial density of states should correspond mainly to $3d$, $4s$, and $4p$, respectively. As shown in these figures, the core-hole affects $3d$ and $4s$ components significantly, in which p-PDOSs do not only shift to lower energy but also they change their profiles. On the other hand, p-PDOS of $4p$ does not change so much, although a slight shift to lower energy appears. From the comparison of p-PDOS results between the states with or without core-hole, it is well confirmed that the influence of core-hole is more significant in quadrupolar transi-

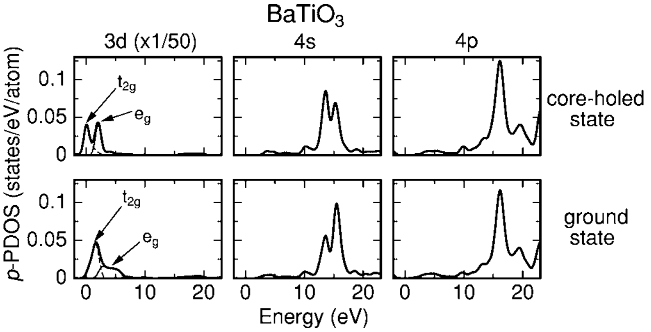

FIG. 6. Same view for BaTiO$_3$ as Fig. 5. Note that e_g and t_{2g} components are approximately denoted by the sums of d_{x2}, d_{y2}, and d_{z2}, and d_{xy}, d_{yz}, and d_{xz} in Ti 3d, respectively, assuming a pseudocubic structure.

tion than in dipolar transition. It is also noted that the origin of $p1$ is the quadrupolar transition of Ti $1s \rightarrow t_{2g}$. $p2$ is due to the mixture of quadrupolar transition of Ti $1s \rightarrow e_g$, and the dipolar contribution of Ti $1s \rightarrow 4p$. Using band-structure calculations with inclusion of the core-hole, assignments of NEXAFS peaks can be made in such a straightforward manner. It should also be emphasized that comparison of experimental or theoretical NEXAFS with ground state p-PDOS leads to a wrong interpretation. Such erroneous interpretations have been quite frequently made in literature.

IV. CONCLUSIONS

The first principles DFT calculations were carried out using the full-potential APW+lo method to interpret the pre-edge fine structures of the x-ray absorption spectra of SrTiO$_3$ and BaTiO$_3$ at Ti K edge. Theoretical spectra can quantitatively reproduce fine structures of the experimental Ti K-edge NEXAFS spectra of SrTiO$_3$ and BaTiO$_3$ including the pre-edge regions. It was found that the core-hole effect is more significant in quadrupolar transition rather than dipolar transition in the case of Ti K-edge NEXAFS. The origin of each pre-edge peak was also well-described by the present calculations; (a) the first pre-edge peaks ($p1$) are derived from quadrupolar transition of Ti $1s \rightarrow 3d$ (t_{2g}), (b) the second ones ($p2$) are the mixture of dipolar and quadrupolar transitions Ti $1s \rightarrow 3d$ (e_g) and Ti $1s \rightarrow 4p$, and (c) third and fourth peaks ($p3$ and $p4$) originate from the dipolar transitions of Ti $1s \rightarrow 4p$. From the present calculations, we have concluded that consideration of both quadrupolar transition and core-hole effects are essential for the quantitative reproduction of the Ti K-edge pre-edge fine structures. In other words, the pre-edge structures can be satisfactorily reproduced when the core-hole effects are properly taken into account by the band-structure calculations within the framework of one-electron theory.

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