

Middle-range-energy structures in Ti $L_{2,3}$ -edge x-ray absorption spectra of titanium oxidesSaki Imada^{1,*}, Yves Joly², and Frank M. F. de Groot³¹*Faculty of Electrical Engineering and Electronics, Kyoto Institute of Technology, Kyoto, Sakyo 606-8585, Japan*²*Université Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, F38042 Grenoble, France*³*Debye Institute of Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, Netherlands*

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The Ti $L_{2,3}$ -edge x-ray absorption spectra of various titanium oxides, including perovskite SrTiO_3 , rutile and anatase TiO_2 , and ilmenite CoTiO_3 , are analyzed with particular attention to the energy range beyond the near-edge/charge-transfer region and up to the oxygen K edge. We found that the spectral structure varies among materials and can be described using density functional theory without including the multielectron effects indispensable for describing near-edge and charge-transfer structures. We term the structures in this energy range the middle-range-energy structure and show that the distinct features are determined by the local atomic geometry around the target Ti atoms and, essentially, by the partial density of states of those atoms. Here, we demonstrate how to extract information from middle-range-energy structures by comparing them with *ab initio* calculations, and we propose this energy-range analysis as a new method for studying local atomic geometry, free of parameters describing multielectron effects.

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I. INTRODUCTION

X-ray absorption spectroscopy (XAS) is a powerful technique for studying the electronic and structural properties of materials. For $3d$ transition metals, the K edge and $L_{2,3}$ edge are commonly used. The K -edge absorption spectra are divided into two regions: the x-ray absorption near-edge structure (XANES), typically within the first 30–50 eV [1], and the following region up to several hundred eV, known as the extended x-ray absorption fine structure (EXAFS). Generally, the former is used to investigate local electronic states, while the latter is used to study local structures and, more specifically, atomic distances, Debye-Waller factors, and coordination numbers [2]. The K -edge absorption spectra are analyzed using first-principles electronic-structure methods, such as density functional theory (DFT)-based codes [3–5]. Although DFT is primarily a ground-state theory, it yields satisfactory results most of the time when a $1s$ core hole is included in the calculation with an extra electron set in the first unoccupied atomic state to obtain an “excited” density of states (DOS) and, subsequently, the spectrum. As such, $3d$ transition-metal K -edge XANES and EXAFS analyses have been conducted as standard procedures across all material classes.

At the $L_{2,3}$ edge of $3d$ transition metals, the structures in the near-edge region have attracted the most attention, despite multiplet and charge-transfer effects complicating their

interpretation [6,7], preventing DFT from interpreting the spectral shape correctly most of the time [8,9]. The reason is not that the DOS is calculated incorrectly, but that the spectral response of the x-ray absorption process is not proportional to it [6]. Two-particle calculations, such as time-dependent DFT and Bethe-Salpeter calculations [10], which are *ab initio* procedures, provide important improvements but do not capture all excitonic effects. To reproduce the spectral shape, theoretical efforts have employed multielectronic methods that capture intraatomic electron-electron interactions (multiplet ligand field theory) as well as configurational screening effects (charge transfer) [11]. As a result, various parameters describing multielectron correlations relevant to the materials’ functionalities can be obtained by comparing the calculated spectra with the data.

In contrast, the structure beyond the near-edge has rarely been studied. For example, in the Ti $L_{2,3}$ -edge absorption of Ti oxides, such as rutile and anatase TiO_2 , the near-edge structure extends about 13 eV from the edge energy, followed by the so-called charge-transfer satellites, about 12 eV beyond the end of the near-edge region, which have been investigated over the last 30 years [6,12–16]. In the meantime, the region beyond the charge-transfer structures, just 25 eV above the edge energy, has not been studied in detail. It should be noted that electron energy-loss spectra (EELS) are often measured for these materials over a wide energy range up to the oxygen K edge [17,18]. However, multiple-scattering effects of the primary electron (e.g., plasmons) make it difficult to observe weak structures, whereas the $L_{2,3}$ -edge XAS is free from these effects. Thus, based on the analogy to the K -edge absorption spectra mentioned above and given the advantages of $L_{2,3}$ -edge XAS over EELS, one can expect structural and possibly electronic information in the energy region beyond the near edge.

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TABLE I. Crystal parameters for calculations.

	Space group	Point group	Lattice constant (Å)
SrTiO ₃	$Pm\bar{3}m$	O_h	$a = b = c = 3.905$
Rutile TiO ₂	$P4_2/mnm$	D_{2h}	$a = b = 4.594, c = 2.959$
Anatase TiO ₂	$I4_1/amd$	D_{2d}	$a = b = 3.784, c = 9.615$
CoTiO ₃	$R\bar{3}$	C_3	$a = b = 5.056, c = 13.825$

This study investigates the Ti $L_{2,3}$ -edge absorption spectra of perovskite SrTiO₃, rutile and anatase TiO₂, and ilmenite CoTiO₃, whose near-edge structures are well studied [6,12,15,16,19–22], with particular attention to the energy range beyond the near-edge/charge-transfer region and up to the oxygen K edge (between 481 and 520 eV). We identified specific structures and found that the structures can be described using DFT without including the multielectron effects indispensable for describing near-edge and charge-transfer structures. We term the structure a middle-range-energy structure and demonstrate how to derive information, such as local atomic geometries around Ti and partial DOS (PDOS), from the structure using the FDMNES code.

The FDMNES code is based on single-particle DFT-LDA (local density approximation). It works in real space and can calculate electronic states in a free-potential shape, beyond the muffin-tin potential approximation, thanks to the finite-difference method [3,23]. A spectrum is calculated using a cluster of atoms within a sphere of a chosen radius, centered by default on the absorbing (target) atom. Since FDMNES can partially incorporate multielectronic effects via the time-dependent extension of DFT (TDDFT) in the linear-response limit [9], we also calculated the TDDFT spectra and compared them with the experimental spectra.

First, we will show the middle-range-energy structures of powder samples of SrTiO₃, rutile TiO₂, and anatase TiO₂, which are textbook cases of how near-edge structures change upon lowering the point symmetry around tetravalent Ti from O_h in SrTiO₃ to D_{2h} in rutile TiO₂ and D_{2d} in anatase TiO₂. The orientation dependencies will be discussed for single crystals of SrTiO₃ and rutile TiO₂. Then, we will present the case of ilmenite CoTiO₃, which is known to have a near-edge structure very close to that of SrTiO₃, as an interesting application of middle-range-energy structure analysis.

II. EXPERIMENT AND CALCULATIONS

Experiments were conducted at the C1 branch of BL27SU of SPring-8 [24] and BL4B of UVSOR [25] in Japan. We have investigated powders of SrTiO₃, rutile TiO₂, anatase TiO₂, and ilmenite CoTiO₃, as well as single crystals of SrTiO₃(100), SrTiO₃(111), rutile TiO₂(100), rutile TiO₂(001), and CoTiO₃(11–20). Total electron yield (TEY) signals were collected via the current drain at room temperature. The incoming light was normal to the surface, and the linearly polarized light was parallel to the surface. The TEY signal from the sample (I) was divided by the reference current (I_0), simultaneously measured using a collection mirror (BL27SU) and an Au mesh (BL4B) placed upstream of the analysis chambers. No further baseline correction was applied

in the graphs of this paper. Single-crystal samples of SrTiO₃ and rutile TiO₂ were tested both undoped and Nb doped (0.05 wt%), and it was confirmed that the spectral shapes were identical. Because the signal-to-noise ratios were better, the spectra of the Nb-doped samples are shown in this paper.

The theoretical spectra were calculated using the FDMNES code. The crystal parameters for the calculations are summarized in Table I. Using clusters with a target Ti atom at the center, the cluster-radius dependence of the spectra from 2 to 8 Å was tested. Self-consistent-field calculations were performed on the ground-state clusters. Then, the Ti $L_{2,3}$ spectra were calculated for the excited clusters using DFT and TDDFT approaches. Here, the excited-state cluster contains the target Ti atom with a $2p$ core hole and an excited electron in the lowest atomic unoccupied state. The ground-state PDOSs were also calculated after the self-consistent-field calculations. See the Supplemental Material [26] for

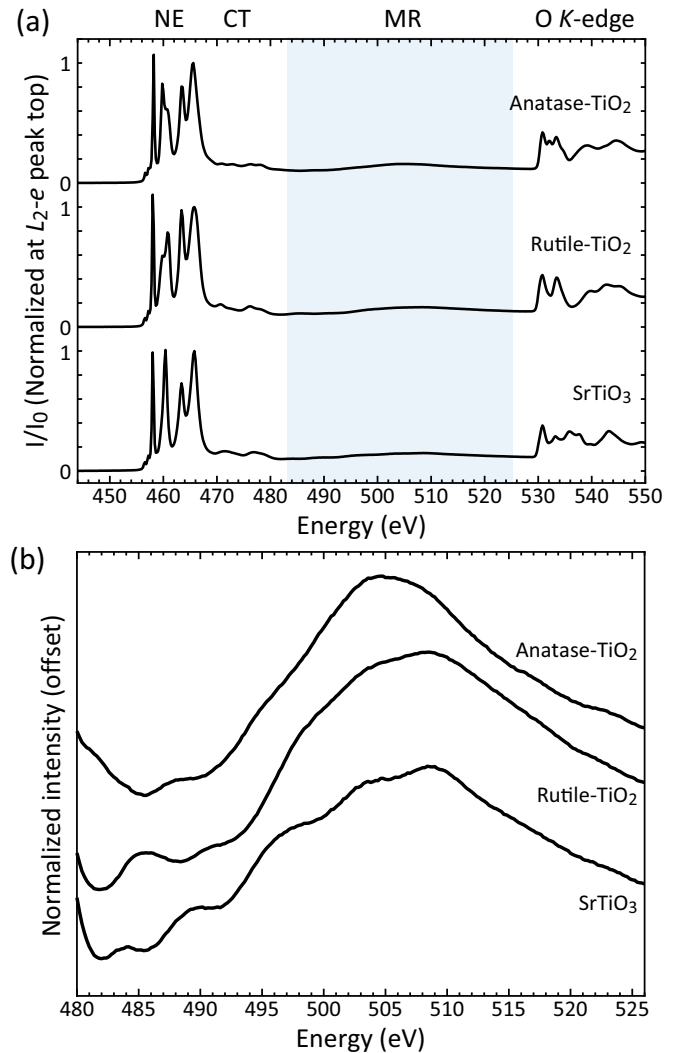


FIG. 1. Experimental spectra of anatase-TiO₂, rutile-TiO₂, and SrTiO₃ powders (a) in a wide energy range, including the near-edge (NE), charge transfer (CT), and middle-range-energy (MR) structures with O K -edge absorption structure. The spectra are normalized at L_{2-e} peak-top intensities. (b) The magnified spectra in the middle-range-energy region.

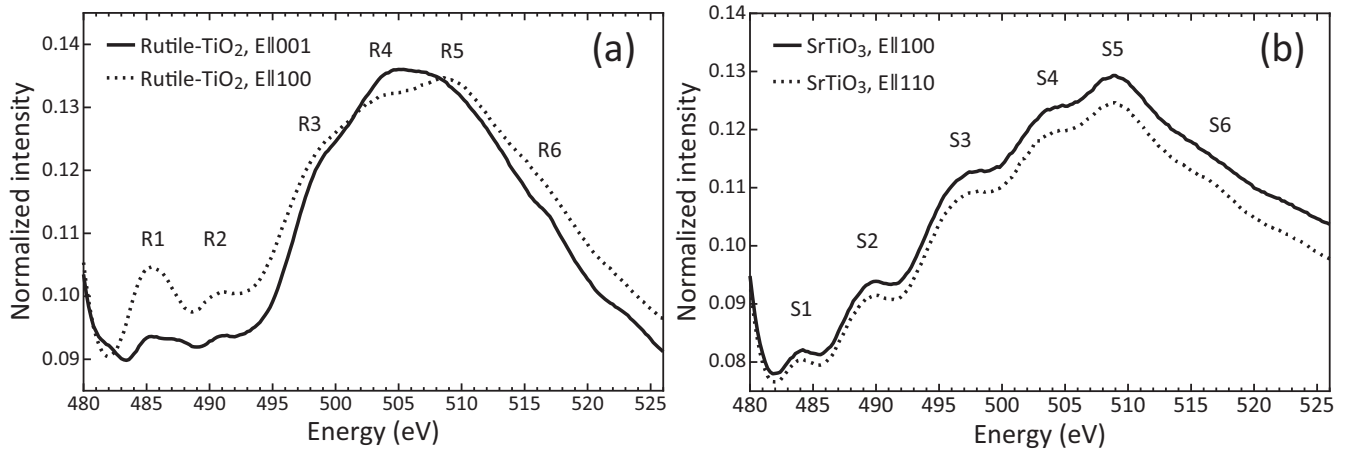


FIG. 2. Experimental Ti $L_{2,3}$ -edge spectra in the middle-range-energy region of single crystals. (a) Rutile TiO₂(001) for $E \parallel 100$, and rutile TiO₂(100) for $E \parallel 001$. (b) SrTiO₃(100) for $E \parallel 100$ and SrTiO₃(111) for $E \parallel 110$. The intensities are normalized at the L_{2-e} peak top.

representative input files for FDMNES calculations with the crystal information files, which can be downloaded from The Materials Project [27,28].

All spectra and PDOSs were calculated using the finite-difference method under the full potential. For comparison,

spectra for SrTiO₃ were calculated using the muffin-tin approximation, which is widely used in general codes, with and without multiple-scattering theory. Also, spectra for rutile TiO₂ were calculated using multiple-scattering theory in the muffin-tin approximation. See the Supplemental Material [26]

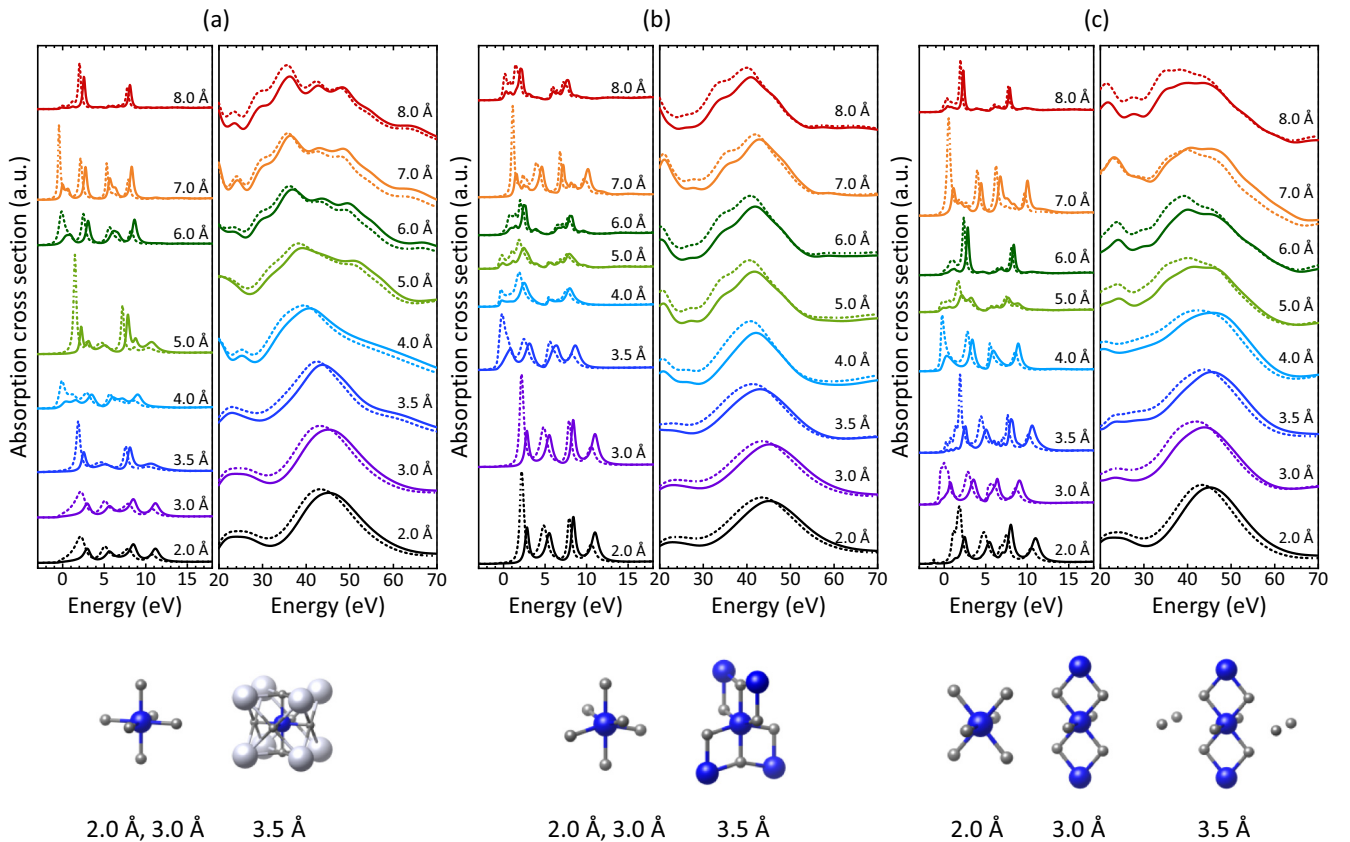


FIG. 3. Cluster-radius dependences of the calculated DFT (dashed line) and TDDFT (solid line) spectra for randomly oriented crystals of (a) SrTiO₃, (b) anatase-TiO₂, and (c) rutile-TiO₂. The left and right panels show the near-edge and middle-range-energy regions, respectively. The schematics are small cluster models.

for spectra calculated using methods other than the finite-difference method under the full potential.

III. RESULTS AND DISCUSSION

A. SrTiO_3 , anatase TiO_2 , and rutile TiO_2

Figure 1(a) shows the experimental spectra for anatase- TiO_2 , rutile- TiO_2 , and SrTiO_3 powders. The Ti $L_{2,3}$ near-edge, charge-transfer, and O K -edge structures exhibit typical shapes for these materials. The spectra in the middle-range-energy region are magnified in Fig. 1(b); it is clear that specific features are present for each material.

Orientation dependence was observed in the middle-range-energy structure of single-crystal rutile TiO_2 , as shown in Fig. 2(a). When the polarization of E is parallel to the 100 axis ($E \parallel 100$), the intensity of peak R1 is higher than that of peak R2, whereas peak R1 is as small as peak R2 for $E \parallel 001$. The relative intensities of R3, R4, and R5 differ between $E \parallel 100$ and $E \parallel 001$. In contrast, as shown in Fig. 2(b), an identical structure was observed for SrTiO_3 in the spectra for $E \parallel 100$ and $E \parallel 110$. These findings suggest that the middle-range-energy structures reflect crystal anisotropy.

To find the origin of the middle-range-energy structures, we performed the simulation using FDMNES. First, the cluster-radius dependencies were tested for randomly oriented crystals (i.e., powder samples). The near-edge structures are depicted in the left panels of Fig. 3. The DFT spectra (dashed lines) with $R = 2 \text{ \AA}$ of SrTiO_3 [Fig. 3(a)], anatase- TiO_2 [Fig. 3(b)], and rutile TiO_2 [Fig. 3(c)] exhibit four-peak structures, i.e., two L_3 and two L_2 peaks. At this radius, the clusters contain only the absorbing Ti atom and the surrounding six oxygen atoms. Thus, we observe the well-known crystal-field splitting between the e_g and t_{2g} states. At $R = 3 \text{ \AA}$, two more atoms are included in the area of calculation only in the rutile case. The resulting different electronic structure is responsible for the more complex peak feature.

The subsequent change in the theoretical spectral shape as the cluster radius increases to $8 \text{ \AA}$ similarly originates from changes in the target Ti's surroundings. It is important to note that the estimated Fermi levels also influence the near-edge spectral shape, because absorption begins at the Fermi level. The combined effects of the calculated electronic structure and Fermi levels result in a nonmonotonic change in the near-edge spectra as the cluster radius increases.

In TDDFT, an electron core-hole interaction intermixes the L_3 - and L_2 -edge spectra as a perturbation of the DFT case [8,9,29]. It means that TDDFT, at least in its simplest form, called time-dependent local density approximation (TDLDA), where the kernel is local [9], improves the so-called branching ratio of near-edge spectra (solid lines in the left panels of Fig. 3). It is nevertheless unable to reproduce excitonic features, such as the small leading peaks between 456 and 458 eV in the rising-edge region.

In contrast to the near-edge region, structural changes in the middle-range-energy region are gradual, as shown in the right panels of Fig. 3, where fine structures appear as the cluster radius increases. Across a wide range of cluster radii, the peak components of DFT spectra are retained in TDDFT

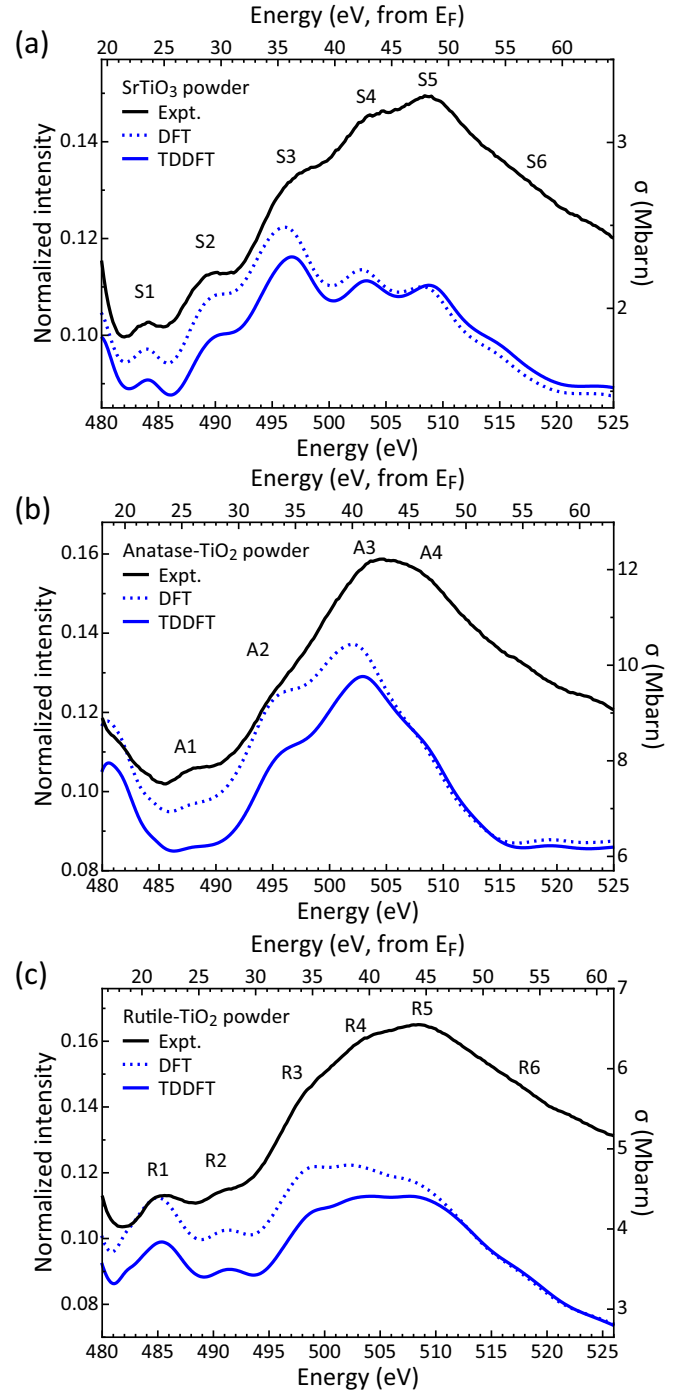


FIG. 4. Ti $L_{2,3}$ -edge DFT and TDDFT spectra in the middle-range-energy regions and experimental spectra of powder samples (a) SrTiO_3 , (b) anatase TiO_2 , and (c) rutile TiO_2 .

spectra, although the intensities are slightly different. Notably, the theoretical spectra reproduce the experimental ones beyond $6 \text{ \AA}$. The calculated spectra (cluster radius: $8 \text{ \AA}$) and the experimental spectra of SrTiO_3 , anatase- TiO_2 , and rutile- TiO_2 powders are compared in Figs. 4(a)–4(c). The theoretical and experimental spectra were aligned around peaks S3, A3, and R3, which are located in the middle of the energy region. For these three powder samples, all peaks appear in both the TDDFT and DFT spectra, with their relative peak energies

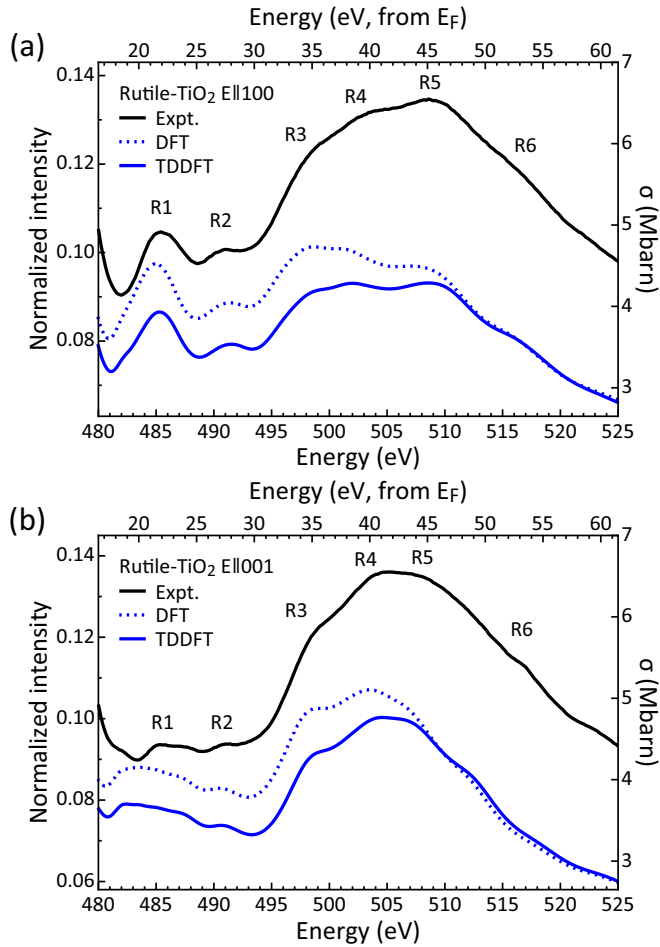


FIG. 5. Experimental spectra of single crystals and corresponding TDDFT and DFT spectra in the middle-range-energy region. (a) Rutile $\text{TiO}_2(001)$ for $E \parallel 100$, and (b) rutile $\text{TiO}_2(100)$ for $E \parallel 001$.

matching the experimental values. The peak intensities are more accurately reproduced in TDDFT spectra than in DFT spectra, implying that the core-hole interaction has a small effect in the middle-range-energy regions.

The orientation dependence of rutile TiO_2 was also calculated and compared with the data in Fig. 5. The peak intensity ratio R1 to R2 and the following structures of the experimental spectra are well reproduced in the calculated spectra.

Here, it is interesting to examine spectra calculated using multiple-scattering theory. At present, FDMNES offers the option to calculate a spectrum using multiple-scattering theory within the muffin-tin approximation. Figure S1 of the Supplemental Material [26] depicts the calculated spectra for SrTiO_3 for $E \parallel \{100\}$ using the muffin-tin approximation with [panel (a)] and without [panel (b)] multiple-scattering theory (MT-MST and MT, respectively). The cluster radii for the calculations were 8 Å. It should be noted that the spectra show less reproducibility in the number and/or energy separation of peaks than the full-potential finite-difference method (FP-FDM). It is apparent that the MT-MST spectra reproduced the intensity of the latter half of the MRE region; however, considering that the MT spectra show similar intensity to that

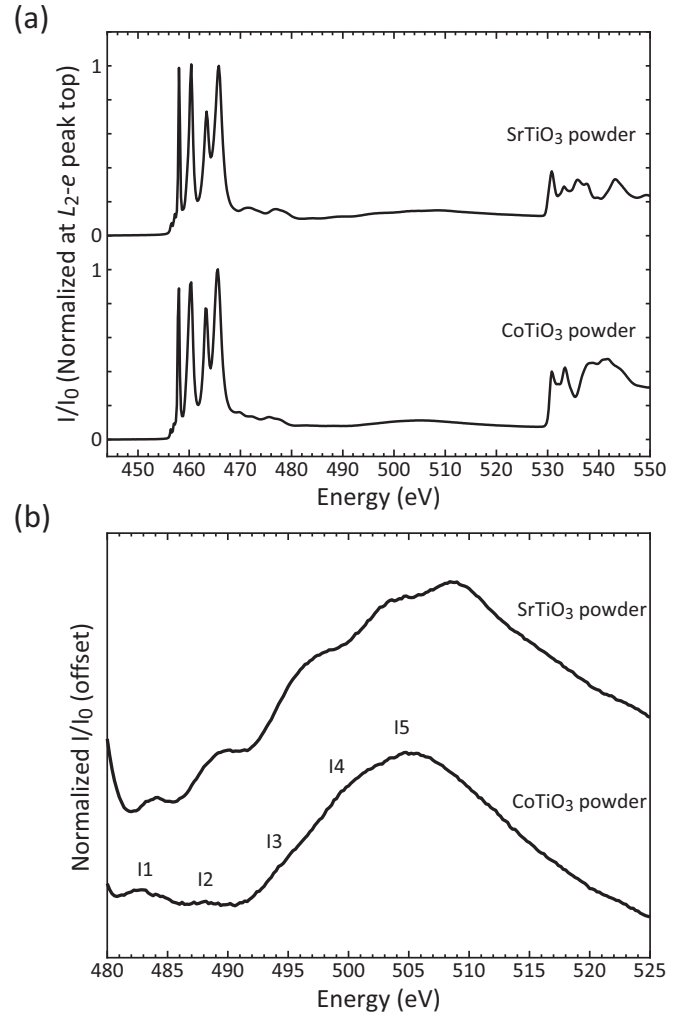


FIG. 6. Experimental spectra of ilmenite CoTiO_3 powder with SrTiO_3 powder in a wide energy range (a), and magnified spectra in the middle-range-energy region (b).

of the MT-MST ones, it can be said that it is not due to a multiple-scattering effect.

We also calculated the MT-MST spectra of rutile TiO_2 (8 Å in radii) for $E \parallel 100$ and $E \parallel 001$ (Fig. S2 in the Supplemental Material [26]). It is obvious that the FP-FDM spectra (Fig. 5) are reproduced much better than those of the MT-MST. This implies that FP-FDM is superior, especially for a low-symmetry material.

B. CoTiO_3 versus SrTiO_3

So far, it appears that the materials with different near-edge structures exhibit distinct middle-range-energy structures. Here, we present the case of ilmenite CoTiO_3 , which has been known to exhibit a SrTiO_3 -like near-edge structure [19,21,30]. Figure 6(a) displays the experimental spectra of the ilmenite CoTiO_3 powder compared with SrTiO_3 powder. In the near-edge region, CoTiO_3 powder exhibits a simple L_3 -edge “ e_g ” peak at around 460 eV, similar to that of SrTiO_3 . In contrast, in the middle-range-energy region [Fig. 6(b)], where SrTiO_3 exhibits five distinctive peaks (S1–S5), CoTiO_3 shows minor

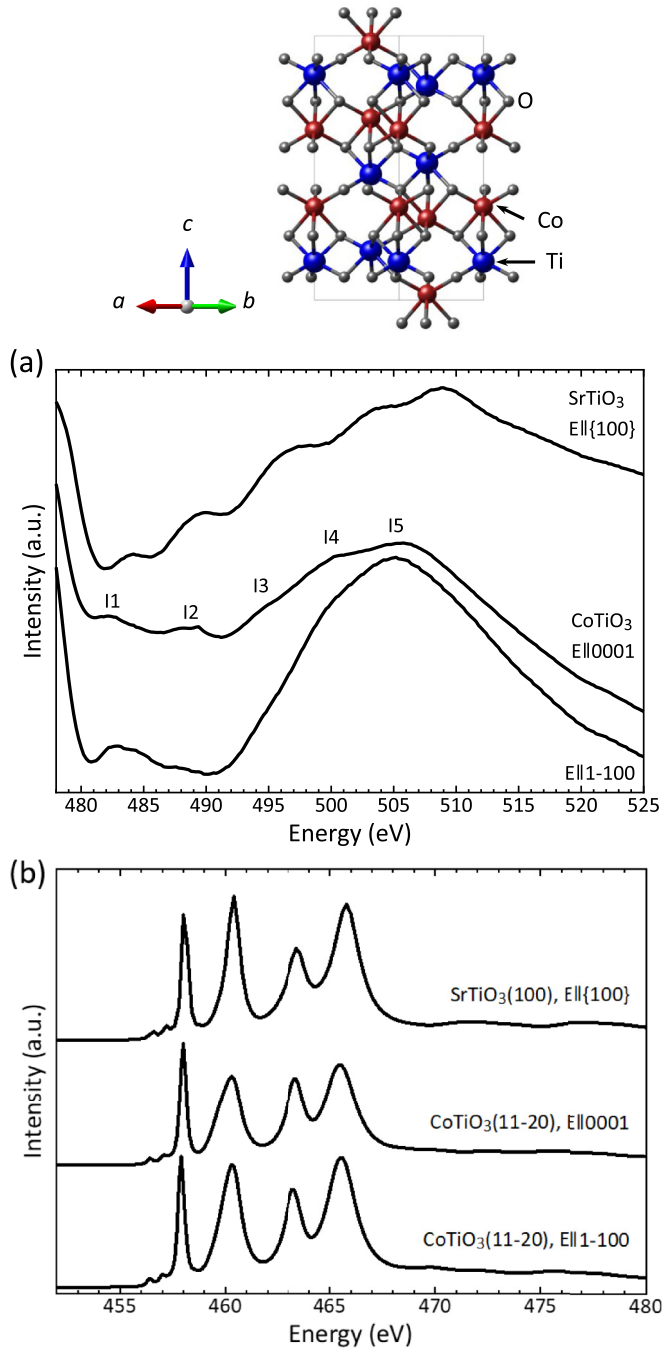


FIG. 7. Experimental spectra of ilmenite $\text{CoTiO}_3(11-20)$ single crystal with $\text{SrTiO}_3(100)$ single crystal in the middle-range-energy region (a) and in the near-edge region (b). The schematic shows that CoTiO_3 is illuminated at the top, drawn using VESTA [29].

structures at 483 and 488 eV (I1 and I2), followed by very small shoulders (I3 and I4) and a peak (I5) at 505 eV.

As illustrated at the top of Fig. 7, ilmenite CoTiO_3 has alternating bilayers of Ti and Co ions perpendicular to the c axis; thus, it is expected to exhibit different middle-range-energy structures depending on the polarization of the incident light parallel and perpendicular to the c axis. As shown in Fig. 7(a), the spectrum for $E \parallel 1-100$ shows a simple peak (I5) and a slight shoulder (I4) with almost flat structure in the

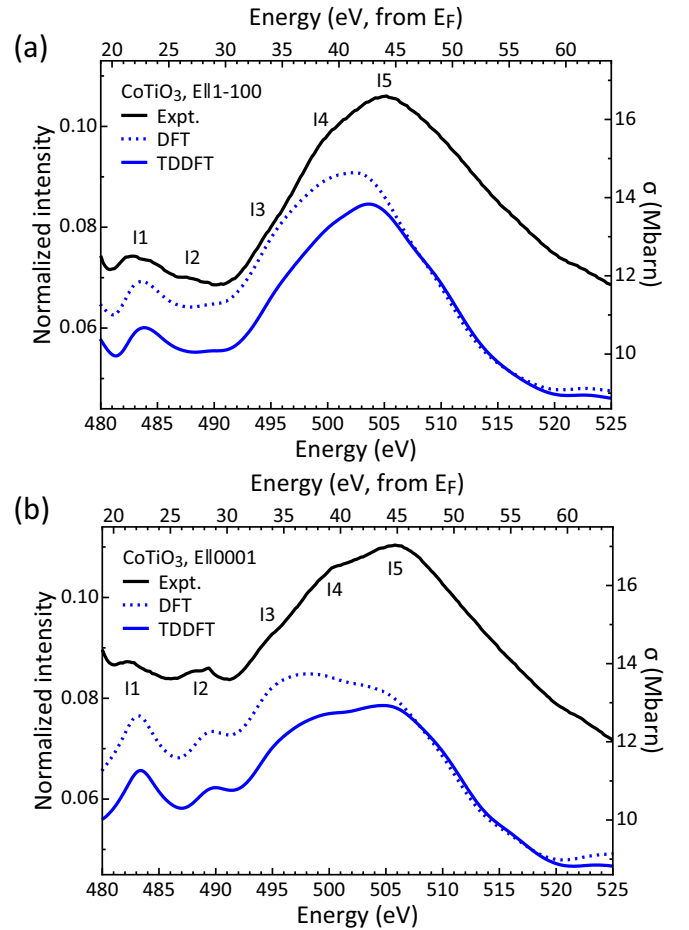


FIG. 8. Experimental spectra of $\text{CoTiO}_3(11-20)$ single crystal and corresponding TDDFT and DFT spectra in the middle-range-energy region for (a) $E \parallel 1-100$, and (b) $E \parallel 0001$.

I1 and I2 region, whereas that for $E \parallel 0001$ shows more distinctive structures, I2, I3, and I4, in contrast to the near-edge spectra [Fig. 7(b)] that show almost no polarization dependence. Figures 8(a) and 8(b) depict the calculated spectra (cluster radius 8 Å) compared with the experimental spectra for $E \parallel 1-100$ and $E \parallel 0001$, respectively, showing that the orientation dependence is reproduced. The slight discrepancy in the intensity of I1 will be discussed later.

The findings for ilmenite- CoTiO_3 versus perovskite- SrTiO_3 highlight the benefits of middle-range-energy structure analysis. Even when the near-edge spectra show no obvious differences between materials and/or measurement geometries, meaning that one cannot find local structural differences between the two using the near-edge spectra, the middle-range-energy spectra can provide information using an *ab initio* DFT approach.

C. Connection between the middle-range-energy structure and PDOS

We reduced the middle-range-energy structure to the PDOS of the materials. The first step is to decompose $L_{2,3}$ spectra into L_3 and L_2 spectral components. As described above, unlike a TDDFT spectrum, a DFT $L_{2,3}$ spectrum is the sum of the L_2 - and L_3 -edge spectra. The shape of the

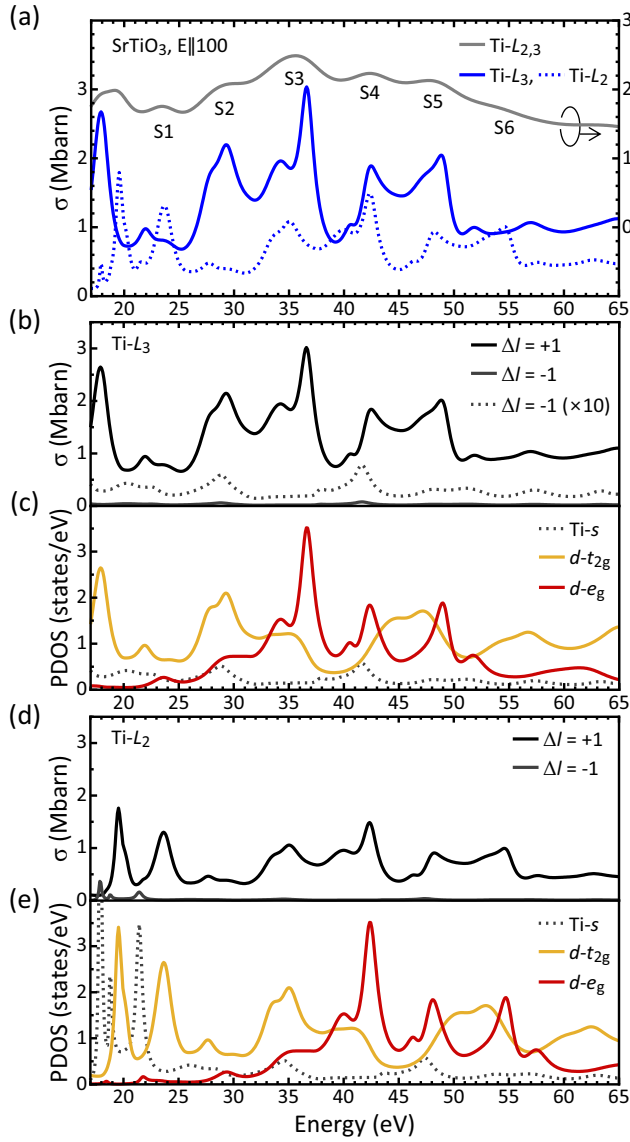


FIG. 9. Ti $L_{2,3}$, L_3 , and L_2 DFT spectra for SrTiO₃ (a), the L_3 DFT spectra divided into the elements for transitions from p to d ($\Delta l = +1$) and from p to s ($\Delta l = -1$) (b), and corresponding Ti PDOSs (c). The L_2 DFT spectra for $\Delta l = +1$ and $\Delta l = -1$ (d), and the Ti PDOSs shifted the energy to match the L_2 spectrum (e).

L_2 component (of the middle-range-energy structure) is very close to that of the L_3 , and its intensity is about half that of the L_3 when the $3d$ spin-orbit interaction is very small; that is the case of the $3d$ elements. Here, SrTiO₃ is discussed as an example. Figure 9(a) shows the DFT spectral components L_3 and L_2 with the convoluted $L_{2,3}$ spectrum for SrTiO₃. It was indicated that the L_2 component forms peak S1, the L_3 component forms peaks S2, S3, and S5, while S4 and S6 are mixtures of nearly equal amounts of L_2 and L_3 components.

The second step is to break the DFT L_3 and L_2 spectrum components down into transitions from p to d ($\Delta l = +1$) and from p to s ($\Delta l = -1$), since the edge is highly dipole dominated. As shown in Figs. 9(b) and 9(d), it appears that the transitions from p to d ($\Delta l = +1$) are the dominant source

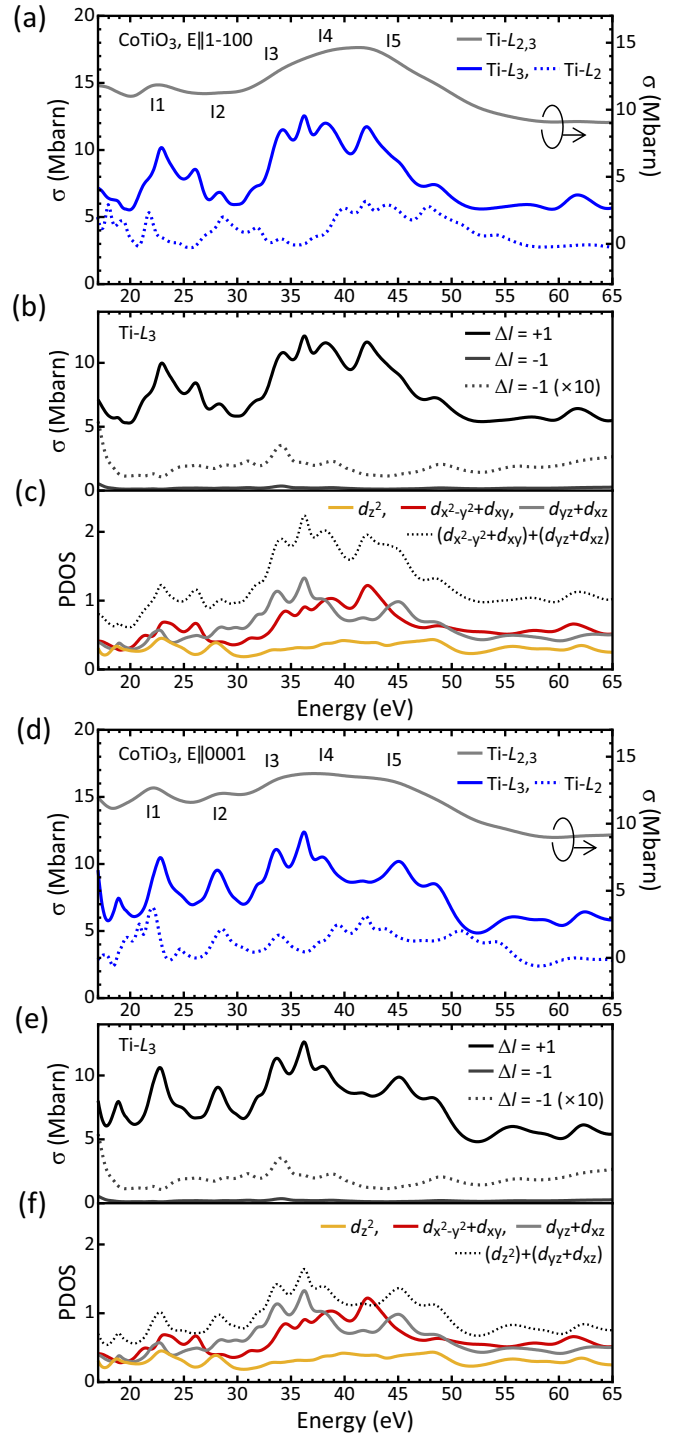


FIG. 10. (a) Ti $L_{2,3}$, L_3 , and L_2 DFT spectra for CoTiO₃ for $E \parallel 1-100$, (b) the L_3 DFT spectrum for p to d ($\Delta l = +1$) and from p to s ($\Delta l = -1$), and (c) Ti- d PDOS. (d) Ti $L_{2,3}$, L_3 , and L_2 DFT spectra for CoTiO₃ for $E \parallel 0001$, (e) the L_3 DFT spectrum for p to d ($\Delta l = +1$) and from p to s ($\Delta l = -1$), and (f) Ti- d PDOS.

in the middle-range-energy region for SrTiO₃. Figures 9(c) and 9(e) depict the absorber Ti PDOS of $d-t_{2g}$, and $d-e_g$ for the L_3 and L_2 , respectively. The energy axis for the PDOS for L_2 in Fig. 9(e) is shifted by 5.75 eV to match the L_2 spectral components. From these plots, we deduced that peak S1 is from $d-t_{2g}$ in L_2 , and peak S2 is mainly

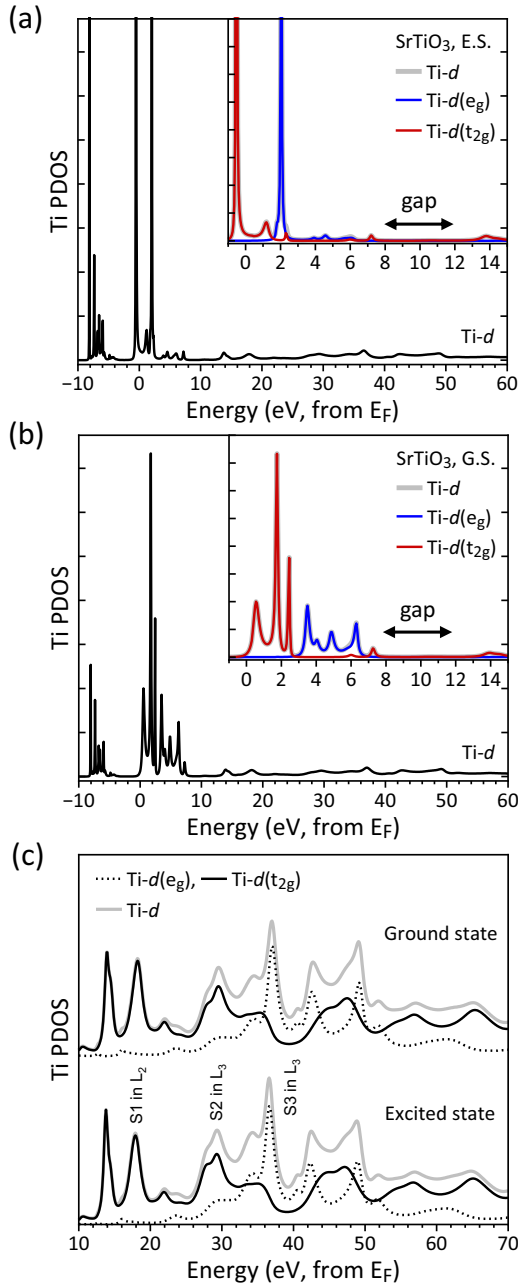


FIG. 11. The excited (a) and ground (b) states PDOSs of SrTiO₃. The insets are close-ups of the near-edge region. (c) The excited and ground states PDOSs in the middle-range energy region.

from $d-t_{2g}$ in L_3 , while peak S3 is from $d-e_g$ in L_3 . Peak S4 is a mixture of $d-e_g$ in L_3 and L_2 . Peak S5 is from $d-t_{2g}$ and $d-e_g$ in L_3 . Peak S6 is formed by almost every component.

The same procedures can be applied to spectra for an anisotropic single crystal. Figures 10(a) and 10(d) show the DFT $L_{2,3}$ spectrum with L_3 and L_2 spectral components of CoTiO₃ for $E \parallel 1-100$ and $E \parallel 0001$, respectively. Figures 10(b) and 10(e) depict corresponding L_3 spectral components and the spectra from p to d ($\Delta l = +1$) and from p to s ($\Delta l = -1$). Figures 10(c) and 10(f) are the Ti- d PDOSs. Similar to the case for SrTiO₃, the transitions from p to

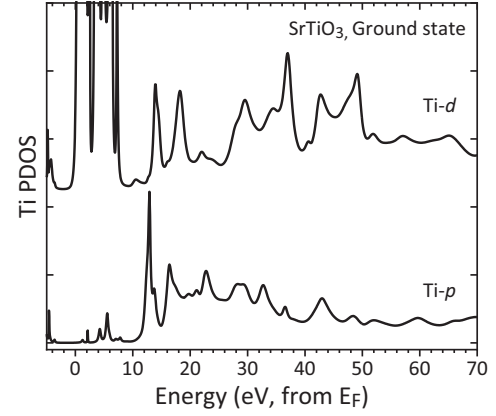


FIG. 12. The ground-state DOS of Ti- d and Ti- p of SrTiO₃.

d ($\Delta l = +1$) are the dominant source in the middle-range-energy region for CoTiO₃. Under the point symmetry C_3 around Ti, which we applied for the ilmenite structure (Table I), five $3d$ orbitals are categorized into two doublets ($d_{x^2-y^2}$, d_{xy}) and (d_{yz} , d_{xz}), and one singlet, d_{z^2} . The L_3 spectral component for $E \parallel 1-100$ is characterized by the Ti- $d_{x^2-y^2}$ and d_{xy} plus d_{yz} and d_{xz} [the dashed line in Fig. 10(f)], and that for $E \parallel 0001$ is characterized by the Ti- d_{z^2} plus d_{yz} and d_{xz} [the dashed line in Fig. 10(c)].

D. Comparison between excited and ground states

The excited state is calculated by placing a core hole in the $2p$ state and a screening electron in the $3d$ state. The Schrödinger equation is then solved again to obtain the excited PDOS shown in Fig 11(a). By comparison with the nonexcited PDOS in Fig. 11(b), we observe significant differences. Four points can be noted: (1) The large calculation radius, 8.0 Å, induces band spreading. (2) The ground-state Ti- d PDOS in the near-edge region has the common structure calculated in the literature [31], and is dramatically different from the excited PDOS. (3) A gap lies between 8 and 12 eV, in both the ground and excited states. (4) The PDOS structures above the gap show only a slight difference in some peak intensities between the ground and excited states [Fig. 11(c)]. Based on these findings, the Ti- d PDOS responsible for the middle-range-energy structures could be labeled as Ti-4 d PDOS, while that in the near-edge region is Ti-3 d PDOS. (Strictly, the quantum number n is valid only in the atoms at energy below the potential at infinity. In the continuum, n is no longer a good quantum number.)

E. Expected sensitivity of middle-energy-range $L_{2,3}$ edges in relation to K edges

Figure 12 shows Ti- d and Ti- p PDOSs in the ground state in the SrTiO₃ case. We see that in the middle energy range, the molecular orbital overlap is strong, leading to some resemblance between them. Given that the Ti- p PDOS is evidently closely related to the K -edge shape, this implies that the expected sensitivity to the atomic structure at the K edge and in the middle energy range of the $L_{2,3}$ edge can be of the same order. This must be true, although an $L_{2,3}$ -edge spectrum is a superposition of L_3 edge and L_2 edge.

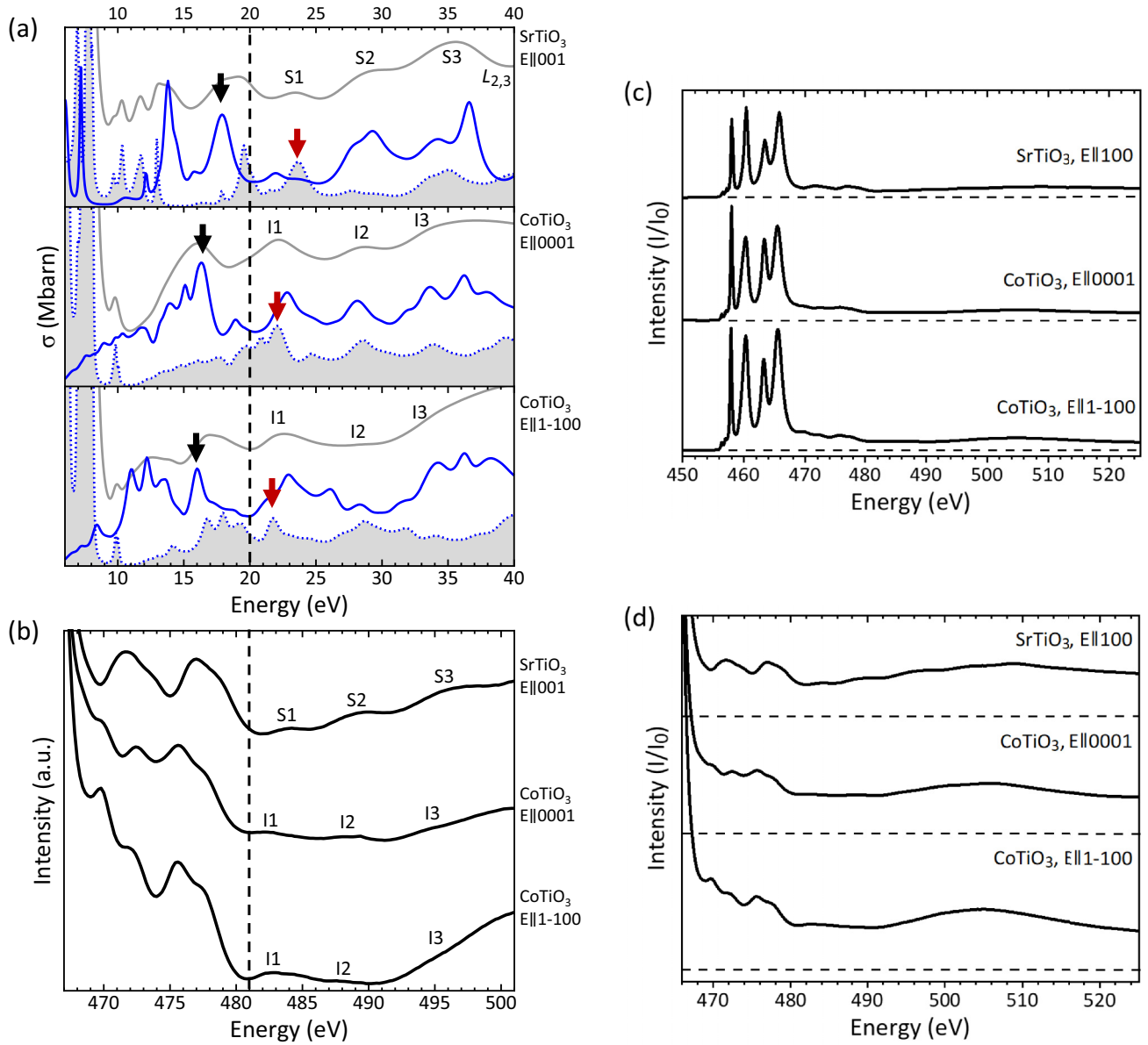


FIG. 13. (a) Ti $L_{2,3}$, L_3 , and L_2 DFT spectra of SrTiO₃ for $E \parallel 001$, CoTiO₃ for $E \parallel 0001$, and $E \parallel 0-100$ from the top. The red arrows indicate the L_2 components forming the first peak in the middle-range-energy region. The black arrows indicate the corresponding L_3 components. (b) The experimental spectra of SrTiO₃ for $E \parallel 001$, CoTiO₃ for $E \parallel 0001$, and $E \parallel 1-100$ in the charge-transfer and the first half of the middle-range-energy regions. Experimental spectra of SrTiO₃ and CoTiO₃ single crystals in the wide range (c) and close-up (d). The broken lines in (c) and (d) are baselines extended from the pre-edge region, as guides to the eye.

F. The PDOS components in the charge-transfer region

Finally, we discuss the Ti- d PDOS components in the charge-transfer region, in other words, the transient region between the near edge and the middle-range energy in these tetravalent Ti oxides. In the case of early transition metal oxides such as TiO₂, their charge-transfer satellites are positioned much higher above the multiplet states than those of late transition metal oxides such as CoO and NiO. The reason is that the effective hybridization in early transition metal oxides is very large, essentially due to the large number of empty $3d$ states [14].

Figure 13(a) shows the calculated $L_{2,3}$ spectra with the L_3 and L_2 spectral components for SrTiO₃ ($E \parallel 100$) and CoTiO₃

($E \parallel 0001$ and $E \parallel 1-100$) in the energy regions from the charge transfer and the first half of the middle-range-energy regions. The corresponding experimental spectra are shown in Fig. 13(b). Figures 13(c) and 13(d) show the experimental spectra in the near-edge, charge-transfer, and middle-range-energy structure regions. The red arrows in Fig. 13(a) indicate the L_2 components that form the first peaks in the middle-range-energy structures, such as S1 in the SrTiO₃ and I1 in the CoTiO₃ spectra. The corresponding L_3 components are about 5.75 eV closer to the Fermi level; that is, they appear in the charge-transfer region, as indicated by the black arrows. Because the intensity of L_3 components is about twice that of L_2 , it cannot be ignored when discussing the structure in the charge-transfer regions; the L_3 components can give

rise to peaks and/or substantial background intensities in the charge-transfer structure.

Inversely, the regions of the first peaks in the middle-range-energy structures can be affected by the charge-transfer transition. For example, peak I1 of CoTiO_3 for $E \parallel 0001$, which appears sharper in the calculated spectra than in the experimental spectra, is close to the charge-transfer structure and can overlap with the charge-transfer structure.

The charge-transfer structures of Ti oxides have been a focus of theoretical calculations incorporating multi-electron correlations [16,32,33]. Our findings, that is, the Ti-4d PDOS components may have intensity in the charge-transfer region, can give useful information to improve such studies.

IV. CONCLUSIONS

We investigated the middle-range-energy region of the Ti $L_{2,3}$ -edge absorption spectra of various titanium oxides, including the perovskite SrTiO_3 , rutile and anatase TiO_2 , and ilmenite CoTiO_3 , and identified specific features. The middle-range-energy structures can be described using DFT and TDDFT and are determined by the local atomic geometry around the target Ti atoms. This analysis, which can be carried out by extending the measurement energy range to

50–60 eV above the $L_{2,3}$ absorption edge and analyzing the middle-range-energy structures using a DFT-based code, can essentially be applied to other transition metals. This analysis, termed x-ray Absorption Middle-Range-Energy Structure, XAMRES, will allow us to explore the local atomic and electronic structures of transition metals and make $L_{2,3}$ -edge absorption spectroscopy a more powerful technique by performing it in conjunction with $L_{2,3}$ near-edge absorption analysis.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

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