# Collapse of the simple localized $3d^1$ orbital picture in Mott insulator

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The orbital degree of freedom of electrons greatly influences the physical properties of materials such as magnetic order and unconventional superconductivity. An orbital is a minimal unit of "shape," and the orbital state can be unraveled by observing the spatial anisotropic distribution of electrons. However, it is difficult to experimentally extract the orbital information in a crystal because of various technical problems. Here, the Ti-3*d* orbital state in perovskite-type oxides RTiO<sub>3</sub> (R = Y, Sm, and La) is directly determined by a core differential Fourier synthesis (CDFS) method using synchrotron x-ray diffraction. The valence electron-density distribution, including information on the anisotropy and the hybridization between atomic orbitals, can be extracted from the CDFS analysis. Our study not only demonstrates the relationship between the magnetic- and orbital-ordered states called the Kugel-Khomskii model, but also provides a nontrivial picture of the orbital state reconstructed by the orbital hybridization.

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## I. INTRODUCTION

The degree of freedom (DOF) of an electronic orbital, which responds to the crystal electric field, is the minimal unit of "shape" by localized valence electrons in a crystal, and an important parameter determined using Neumann's principle [1], which describes the relationship between anisotropic physical properties and crystallographic point groups. For example, the magnetic and orbital ground states are coupled by the Kugel-Khomskii model [2]. However, some series of systems show quantum phase transitions between different ground states despite the same point group. In this case, determining the quantum parameters of electronic orbitals at local magnetic sites is crucial.

In a crystalline material, among three DOFs of electrons (charge, spin, orbital), the charge and spin can readily react to external electric and/or magnetic fields. However, directly observing the orbital is difficult, although it greatly influences material anisotropic physical properties [3], such as unconventional superconductivity [4–7] and giant magnetoelectric

effect [8-10]. If the electron orbital can be directly observed, for example, it will provide an experimental research guideline for an electron nematic phase [11], where it is difficult to extract the nematicity from the structural information. The orbital state in materials has been studied by several experimental methods including polarized neutron diffraction [12], resonant x-ray scattering [13,14], and multipole analysis using x-ray diffraction (XRD) [15]. Most recently, a Co orbital-ordered state at the surface in CeCoIn<sub>5</sub> was observed by scanning tunneling microscope [16], and orbital imaging in Ni ions was achieved by nonresonant inelastic x-ray scattering [17]. However, in these methods, the measurable substances are limited and/or the results may depend on the model constructed by the analysts. Therefore, an experimental measurement or calculation tool is required that can easily determine the orbital state without the assumed model.

Here, we focus on determining the orbital-ordered state of an  $RTiO_3$  series, where R is a rare-earth element. The  $Ti^{3+}-3d^1$  orbital-ordered state in a  $TiO_6$  octahedron is characterized by an electron localized in the  $t_{2g}$  orbitals as a Mott insulator by strong electron correlations. Although the space group in this system is common (*Pnma*), the ground state systematically changes from antiferromagnetic (AFM) to ferromagnetic (FM) as the ion size of R decreases, as summarized in phase diagrams [18,19]. In the  $RTiO_3$  series, various theoretical studies on the orbital and magnetic ground states have been performed by assuming a localized  $Ti^{3+}-3d^1$  orbital [20–23]. This series is a typical material for verifying (i) the spatial resolution required for direct observation of the orbital

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state, and (ii) the dynamic range for extracting information of one electron from all in the unit cell. However, despite various experiments on the orbital state of  $RTiO_3$  [12–15,24,25], few quantum parameters have been reported for substances other than  $YTiO_3$ .

For RTiO<sub>3</sub> system, the crystal electric field around Ti<sup>3+</sup> changes because the combined Jahn-Teller-type and GdFeO<sub>3</sub>-type distortions change with the ion radius of R [20,22,26]. The Ti-3d orbital-ordered state is greatly affected by the distortions. Also, the significance of the Ti-O hybridization in this system is pointed out [23,27]. However, all experimental results were analyzed based on only a localized 3d orbital model [12–15,24,25], in which the bonding/covalent electrons between the Ti and O orbitals were not considered.

To fully understand the physical properties in this system, information on the spatial distribution of the valence electron density (VED) is indispensable. Recently, we proposed an electron-density (ED) analysis method called core differential Fourier synthesis (CDFS) [28] using synchrotron XRD. Using this method in an organic charge-transfer salt, we succeeded in the direct observation of the VED distribution formed by molecular orbitals as well as the determination of the charge-ordering state [28]. The CDFS based on the high-resolution data obtained from short-wavelength synchrotron x ray is extremely effective for observing not only spatially extended molecular orbitals but also atomic orbitals localized in one atom. In this paper, we revealed the Ti-3d orbital-ordered state in  $RTiO_3$  (R = Y, Sm, and La) from the localized VED distribution with a spatial resolution of  $\sim 0.1$  Å. Furthermore, through point-charge-model and density-functional-theory (DFT) calculations, it is verified that the CDFS method indeed extracts essential orbital information.

#### **II. METHODS**

## A. XRD experiments

The XRD experiments were performed on the BL02B1 beamline at the synchrotron facility SPring-8 in Japan [29]. A helium-gas-blowing device was employed to cool the sample to 25 K. A two-dimensional imaging plate, which had a dynamic range of  $\sim 10^6$ , was used as the detector. The incident energy of synchrotron x rays was E = 35 keV. For the crystal structural analysis, we used original software for extracting the diffraction intensity [30]. Diffraction intensity averaging was performed using SORTAV [31]. Crystal structural and ED analysis were performed using JANA2006 [32]. Crystal structure and ED distribution figures were visualized by using VESTA [33].

#### **B. CDFS method**

The diffraction intensity  $I(\mathbf{K})$  obtained from the XRD experiment can be described as a Fourier transform of the ED  $\rho(\mathbf{r})$  using the scattering vector  $\mathbf{K}$  [Eq. (1)],

$$I(\mathbf{K}) = S \left| \int_{\text{all}} \rho(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d\mathbf{r} \right|^2.$$
(1)

Here, *S* is a scaling factor. The integration range  $[\int_{all} in Eq. (1)]$  corresponds to the range in which x rays can interfere

in the crystal. In the case of a crystal, it can be described as Eq. (2) using Laue functions L(s), L(t), L(u), where  $K = sa^* + tb^* + uc^*$ ,

$$I(\mathbf{K}) = S L(s)L(t)L(u) \left| \int_{\text{unit cell}} \rho(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d\mathbf{r} \right|^2 \propto |F_{\text{obs}}(\mathbf{K})|^2.$$
(2)

Here,  $|F_{obs}(\mathbf{K})|$  is the absolute value of the experimentally observed crystal structure factor. As is well known, if the number of unit cells N in a crystal is sufficiently large, the Laue function becomes  $N^2$  only when s, t, u are integers, and when  $\mathbf{K} = (s, t, u) \neq (h, k, l)$  (h, k, l are integers),  $I(\mathbf{K}) = 0$ . In principle, the ED distribution can be reproduced by the inverse Fourier transform of diffraction intensity according to

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{K}}^{\infty} F_{\text{obs}}(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{r}},$$
(3)

if the infinite diffraction data was observed. However, there are generally three problems when calculating the ED. (i) To extract the VED with anisotropic information, a sufficiently wide dynamic range of intensity is required. (ii)  $|F_{obs}(\mathbf{K})|$  is obtained from the experimental diffraction intensity because of the relationship of  $I(\mathbf{K}) \propto |F_{obs}(\mathbf{K})|^2$ . In this case,  $|F_{obs}(\mathbf{K})|$ does not include information of the phase term  $P = e^{i\phi(\mathbf{K})}$ as  $F_{obs}(\mathbf{K}) = |F_{obs}(\mathbf{K})|P = |F_{obs}(\mathbf{K})|e^{i\phi(\mathbf{K})}$ , which is necessary for the calculation of  $\rho(\mathbf{r})$ . This phase retrieval problem has been studied in various fields such as x-ray imaging [34,35], surface x-ray diffraction [36], and x-ray holography [37]. (iii) Because the number of the  $F_{obs}(\mathbf{K})$  data is finite, the mathematical truncation effect appears prominently in the ED distribution.

Concerning (i), the number of electrons of Ti- $3d^1$  responsible for the orbital-ordered state is one per formula unit. On the other hand, the number of electrons of YTiO<sub>3</sub> is 85 per formula unit. If  $I(\mathbf{K})$  is simplified to be proportional to the square of the number of electrons, it is necessary to have a dynamic range that can accurately extract the  $1/85^2 = 1/7225$  to  $10^{-4}$  of the measured maximum intensity. The important point is that  $10^{-4}$  signal information should be observed with sufficient signal-to-noise S/N ratio. This requirement is sufficiently fulfilled by using the current synchrotron radiation facility, in which the dynamic range of  $10^6$  is guaranteed.

Concerning (ii), since the phase term can be assigned from the calculated crystal structure factor

$$F_{\rm cal}(\mathbf{K}) = \sum_{j} f_j T_j e^{-i\mathbf{K} \cdot \mathbf{r}_j}$$
(4)

using  $P = F_{cal}(\mathbf{K})/|F_{cal}(\mathbf{K})|$ , Eq. (3) can be rewritten as

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{K}}^{\infty} |F_{\text{obs}}(\mathbf{K})| P e^{i\mathbf{K} \cdot \mathbf{r}}.$$
 (5)

Here,  $r_j$  is the *j*th atomic position,  $T_j$  is the *j*th atomic displacement parameter, and  $f_j$  is the *j*th atomic scattering factor, which is described as

$$f_j(\mathbf{K}) = \int_{\text{atom}} \rho_j(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d\mathbf{r}.$$
 (6)

For example, Fig. 1 shows the atomic scattering factor of Ti as a function of  $\sin \theta / \lambda$  [38]. Here,  $\lambda$  is the wavelength



FIG. 1. Atomic scattering factor of Ti [38]. Black, blue, and orange lines indicate the contribution of the total, core, and valence electrons, respectively.

of the incident x ray, and  $\theta$  is the XRD angle. While the contribution of the core electrons extends to the high-angle region, the contribution of the valence electrons exists only in the low-angle region  $(\sin \theta / \lambda \leq 0.5 \text{ Å}^{-1})$ . When calculating the ED, it is necessary to determine  $F_{cal}(K)$  with high accuracy to obtain the correct phase term *P*. For this purpose, the structural refinement is performed using only the high-angle I(K) (the so-called high-angle analysis), where the contribution of the spatially spread valence electron is very small. In this study, the high-order terms of anharmonic atomic displacement parameters were not considered, because we measured the crystal at an extremely low temperature.

Concerning (iii), the truncation effect of the Fourier synthesis can be suppressed by using the CDFS method. The equation of the inverse Fourier transform by the CDFS method is described as

$$\rho_{v}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{K}} \left\{ \left| |F_{\text{obs}}(\mathbf{K})| P - \left| \sum_{j} f_{j}^{\text{core}} T_{j} e^{-i\mathbf{K} \cdot \mathbf{r}_{j}} \right| P^{\text{core}} \right] e^{i\mathbf{K} \cdot \mathbf{r}} \right\} + \frac{n_{v}}{V}. \quad (7)$$

Here,  $f_j^{\text{core}}$  is the *j*th atomic scattering factor with only the core electrons contribution, which corresponds to the blue line in Fig. 1.  $P^{\text{core}}$  is the phase term with only the core electrons contribution calculated as  $P = F_{\text{cal}}^{\text{core}}(\mathbf{K})/|F_{\text{cal}}^{\text{core}}(\mathbf{K})|$ .  $n_v$  is the total number of valence electrons contained in the unit cell. It is noted here that the 000 Bragg reflection intensity cannot be observed experimentally. When ignoring the second term  $n_v/V$  in Eq. (7), the total number of electrons in the unit cell becomes zero. Therefore, the VED distribution data are corrected by adding the  $n_v/V$  term.

In general,  $(\sin \theta / \lambda)_{\text{max}}$  measured experimentally is  $\sim 2.5 \text{ Å}^{-1}$  ( $d_{\min} \sim 0.2 \text{ Å}$ ) even when using the short-wavelength x ray obtained at the synchrotron radiation facility. In Fig. 1, a nonzero value remains in  $f_{\text{Ti}}(=f_{\text{Ti}}^{\text{core}})$  at  $\sin \theta / \lambda =$ 

 $2.5 \text{ Å}^{-1}$ . Therefore, even if the short-wavelength x ray is used, the mathematical truncation effect cannot be avoided from the calculation using Eq. (5). On the other hand, in Eq. (7), the inverse Fourier transform is performed on the term obtained by subtracting the core electron contribution from  $|F_{obs}(\mathbf{K})|$ , which contains the contribution of all electrons. Because most of the contribution of the remaining  $f_{Ti}^{valence}$  exists only in  $\sin\theta/\lambda \leq 0.5 \text{ Å}^{-1}$ , it is possible to extract the VED with little truncation effect of the Fourier synthesis by the CDFS analysis. It is noted that, in this study, the structural model  $F_{cal}(\mathbf{K})$  [Eq. (4)] used to calculate the phase term does not consider the anisotropic VED. Therefore, in the peculiar case such that the orbital state that breaks the site symmetry in the unit cell is realized, the phase recovery using a measurement method which is different from the diffraction experiment is necessary. At present, this problem is an open question, and we think it is an issue for the future.

XRD data must satisfy the following three conditions to perform the CDFS analysis. Condition 1: a dynamic range of at least six digits or more, and statistical accuracy to guarantee this range, to obtain the spatial distribution of one electron that dominates the orbitals with respect to the total number of electrons in the asymmetric unit; condition 2: measurements of the high-angle diffraction intensity corresponding to the high real-space resolution, for reconstructing an ED that can represent the spatial spread of the orbitals by the inverse Fourier transform; and condition 3: 100% completeness of the measured reciprocal-lattice space. An experiment satisfying the above conditions was performed on the BL02B1 beamline at SPring-8 [29]. In the present experiment, the resolution limit was  $d_{\min} = 0.25 \text{ Å} [(\sin \theta / \lambda)_{\max} = 2.0 \text{ Å}^{-1}]$  and the completeness (the ratio of measured regions in the independent reciprocal-lattice space regions) was almost 100% that allowed the CDFS analysis.

## C. DFT calculation

The DFT calculations for ferromagnetic YTiO<sub>3</sub> were carried out using the full-potential linearized augmented plane-wave method [39] as implemented in the HiLAPW code and using the structural parameters determined in the present XRD experiment (see Tables S1 and S2 in Supplemental Material Sec. 1 [40]). The muffin-tin sphere radii were set to 1.2 Å for Ti, Y and 0.8 Å for O. The Brillouin zone was sampled with  $10 \times 10 \times 10$  k-point mesh. The local-density approximation plus Hubbard U (LDA + U) method [41] was employed to account for the on-site 3*d*-3*d* Coulomb interaction. The spin-orbit interaction is neglected in our calculations because Ti is a light 3*d* transition metal. The Slater integrals used were  $F_0 = 4 \text{ eV}$ ,  $F_2 = 7.719 \text{ eV}$ , and  $F_4 = 4.383 \text{ eV}$  [20] that corresponded to U = 4 eV and J = 0.864 eV.

#### **III. RESULTS**

## A. Structural analysis

First, we focus on YTiO<sub>3</sub> (FM transition temperature is  $T_c = 30$  K), which is the most experimentally investigated for the orbital state in this series [12,13,15,24,25]. The structural analysis results using a single crystal of YTiO<sub>3</sub> at 25 K (FM



FIG. 2. (a) Crystal structure of YTiO<sub>3</sub> at 25 K (ferromagnetic phase). (b) Valence electron-density distribution, which is calculated by the diffraction data in  $0 \text{ Å}^{-1} \leq \sin \theta / \lambda \leq 2.0 \text{ Å}^{-1}$ , around Ti with internal coordinates (1/2, 1/2, 1/2) obtained from the CDFS analysis (isosurface level:  $3.2e/\text{Å}^3$ ). (c) Schematic illustration of the Ti<sup>3+</sup>-3d<sup>1</sup> orbital-ordered state in YTiO<sub>3</sub> system and the theoretical valence electron-density distribution of the  $C_1|yz\rangle + C_2|zx\rangle$  orbital ( $C_1 = 0.8$  and  $C_2 = 0.6$ ).

phase) are shown in Tables S1–S3 in Supplemental Material Sec. 1 [40]. Only high-angle reflections  $(0.6 \text{ Å}^{-1} \leq \sin \theta / \lambda \leq 2.0 \text{ Å}^{-1})$ , to which valence electrons of oxygen do not contribute [38], were used to refine structural parameters with high accuracy (see Sec. II for details of the high-angle analysis). Figure 2(a) shows the crystal structure of YTiO<sub>3</sub> at 25 K. The *R* value of the high-angle analysis was  $R_1(I > 3\sigma) = 1.96\%$  (number of unique reflections: 5823). The obtained structural parameters show agreement (within 1.5%) with previous reports of XRD at 127 K (within 1.5%) [42] and neutron diffraction at 40 K (within 0.6%) [24]. In the TiO<sub>6</sub> octahedron, the Jahn-Teller-type distortion is realized, in which two of the six O's move away from Ti along the *z*-axis direction and four O's approach Ti in the *xy* plane.

In the simple  $3d^1$  picture, the 3d orbital state of Ti can be described as a linear combination of  $d_{yz}$ ,  $d_{zx}$ , and  $d_{xy}$  according to Eq. (8):

$$\varphi(\mathbf{r}) = C_1 |yz\rangle + C_2 |zx\rangle + C_3 |xy\rangle,$$
  
(|C\_1|<sup>2</sup> + |C\_2|<sup>2</sup> + |C\_3|<sup>2</sup> = 1). (8)

When a crystal structure is obtained from the experiment, the quantum parameter of the orbital can be extracted by calculating the crystal field from the structural parameters. For calculating the crystal field, it is convenient to calculate each ion as a point charge. However, to calculate the anisotropy of the crystal field with high accuracy, it is necessary to perform convolution calculations of the point charge far away from the required crystal field. In this case, the accuracy of the structural parameters used for the calculation is very important. In fact, the crystal structure of SmTiO<sub>3</sub> [26] used in calculations of Mochizuki *et al.* [22] is not in good agreement with our results (described later), where their Ti-O(ii) bond length [labeled in Fig. 6(a)] differs from our result by 0.013 Å.

To avoid the truncation effect of the calculation range, the Q-mode method [43] or Ewald's method [44] are known. In this study, to extract the quantum parameters  $C_1$ ,  $C_2$ , and  $C_3$  of the Ti-3d orbital with high accuracy, we performed the point-charge model calculation using Ewald's method [44], in which the structural parameters obtained by the high-angle analysis are used. Detailed calculation conditions and the definition of the quantization axes are shown in Supplemen-

tal Material Secs. 4 and 3 [40], respectively. We obtained that  $C_1 = 0.7852$ ,  $C_2 = 0.6137$ , and  $C_3 = -0.0828$ , which are qualitatively consistent with the results of previous reports [12,13,15,21,24,25].

## **B. CDFS analysis**

To extract information on the Ti-3d orbital from the VED distribution, the CDFS analysis was performed in YTiO<sub>3</sub>. Figure 2(b) shows the VED distribution around Ti with internal coordinates (1/2, 1/2, 1/2) obtained from the CDFS analysis, which simply subtracts the contribution of the core electrons from the whole ED distribution using Eq. (7). When using the CDFS analysis, the resolution of the expressible ED distribution must be limited by the maximum value of  $(\sin \theta / \lambda)_{\text{max}}$  of the diffraction data. Figure 3 shows the VED distribution [sectional view of the (121) plane] around Ti calculated by the diffraction data with a different  $(\sin \theta / \lambda)_{max}$ range. Although the valence electron contribution  $f_{Ti}^{valence}$  exists only in  $\sin \theta / \lambda \leq 0.5 \text{ Å}^{-1}$  in the atomic scattering factor of Ti (Fig. 1), the anisotropy of the VED distribution is hardly observed at  $(\sin \theta / \lambda)_{\text{max}} = 1.0$ , and  $1.5 \text{ Å}^{-1}$ . On the other hand, the anisotropy of the VED distribution can be observed clearly at  $(\sin \theta / \lambda)_{max} = 2.0 \text{ Å}^{-1}$ . Because the CDFS method



FIG. 3. (a)–(c) Valence electron-density distributions of the ( $\overline{1}21$ ) plane on Ti with internal coordinates (1/2, 1/2, 1/2) in YTiO<sub>3</sub>, which are calculated by the diffraction data in  $0 \text{ Å}^{-1} \leq \sin \theta / \lambda \leq 1.0 \text{ Å}^{-1}$ ,  $0 \text{ Å}^{-1} \leq \sin \theta / \lambda \leq 1.5 \text{ Å}^{-1}$ , and  $0 \text{ Å}^{-1} \leq \sin \theta / \lambda \leq 2.0 \text{ Å}^{-1}$ , respectively.



FIG. 4. (a) Density of states of the Ti-4s and Ti-4p orbitals in YTiO<sub>3</sub>. (b), (c) Density of states of the Ti-3d orbitals. The zero energy refers to the highest occupied level. (d) Valence electron-density distribution around Ti obtained from the DFT calculation, which corresponds to valence electrons occupying the orbitals below the Fermi level (E = 0 eV).

is based on the inverse Fourier transform, how much fine waves can be represented to express the VED distribution depends on how high-order Fourier series terms can be included in the calculation. In other words, even if most of the contribution of  $f_{\text{Ti}}^{\text{valence}}$  is included in the reflections of  $\sin \theta/\lambda \leq 0.5 \text{ Å}^{-1}$ , the information on higher-order reflections up to  $(\sin \theta/\lambda)_{\text{max}} = 2.0 \text{ Å}^{-1}$  is essential to reproduce the anisotropy of the 3*d* orbital. Therefore, to observe the anisotropy of the ED distribution around Ti, short-wavelength x rays and a diffraction system that can measure the highresolution diffraction data are indispensable.

The VED distribution around Ti has a characteristic butterflylike shape reflecting the  $t_{2g}$  orbital [Fig. 2(b)]. In the simple  $3d^1$  picture of this system [Fig. 2(c)], the  $t_{2g}$  orbitals split into two  $|yz\rangle$ ,  $|zx\rangle$  orbitals and one  $|xy\rangle$  orbital due to the Jahn-Teller-type distortion in a TiO<sub>6</sub> octahedron. Furthermore, the orbital-ordered state shown as  $C_1|yz\rangle + C_2|zx\rangle$ , which corresponds to the VED distribution with butterflylike shape, is realized by the exchange interaction with surrounding orbitals. However, a closer observation of Figs. 2(b) and 3(c) reveals that the VED remains positive at the center of Ti, which is originally a node of the d orbitals [Fig. 2(c)]. This result is supposed to vanish in the simple  $3d^1$  picture. The VED observed from the CDFS analysis may include the spatial distribution of bonding/antibonding electrons such as molecular orbitals [28]. Ignoring the ED in the central part, the butterflylike VED can be fitted by Eq. (8). When the evaluation function s, defined as Eq. (9), is minimized, the quantum parameters are  $C_1 = 0.7902$ ,  $C_2 = 0.6092$ , and  $C_3 = 0.0668$ ,

$$s = \frac{\sum_{\boldsymbol{r}} |\rho(\boldsymbol{r}) - |\varphi(\boldsymbol{r})|^2|}{\sum_{\boldsymbol{r}} |\rho(\boldsymbol{r})|}.$$
(9)

These values show good agreement with Ewald's method calculation. It is noted that the *s* value obtained here, s = 0.435, is relatively large. This result reflects the nonvanishing ED at the center of Ti. The linear combination of the  $t_{2g}$  orbitals alone cannot fully explain the whole image of the ED

obtained from the CDFS analysis, particularly concerning the high ED around the center of Ti.

#### C. Electronic structure

The important point here is that we do not assume any orbital model when performing the CDFS analysis. As the contribution of the core electrons of each atom is simply subtracted from the total ED information, this method extracts the valence electrons including bonding/covalent electrons, without any bias of the model. For this reason, complementary interpretation using first-principles calculations rather than model calculations is extremely effective. Thus, we performed a DFT calculation. Figures 4(a)-4(c) show the partial density of states (DOS), where the energy E = 0 refers to the highest occupied level. The 3d states mainly reside around E = 0 eV. In particular, the states immediately below E =0 eV that form a sharp peak with a narrow bandwidth of 0.62 eV [Fig. 4(c)] consist exclusively of spin-up  $t_{2g}$  states and host the  $3d^1$  orbital ordering. These orbital-ordered states produce a butterflylike VED as observed in the CDFS analysis [Fig. 2(b)]. In contrast, in the deeper energy region [Fig. 4(a)], relatively large 4s and small 4p DOS's of both spins are seen around E = -7.0 and -6.0 eV, respectively. This clearly suggests that the covalency between Ti-4s and O-2s/2p orbitals is not negligible [23,27,45]. These 4s-like electrons produce a spherical density distribution peaked at the center of Ti, which corresponds well to the high density around the Ti nucleus found in the CDFS analysis [Fig. 3(c)]. It may be worth adding that a small number of the  $e_g$  states  $(d_{3r^2-r^2})$  and  $d_{x^2-y^2}$ ) of both spins are occupied in the deep energies around E = -5.5 eV [Fig. 4(b)], where the O-2*p* states are dominant. These occupied  $e_g$  states are there to form  $pd\sigma$  bonding states, and to produce a density distribution around Ti that spreads towards the O atoms (see Fig. S8 in Supplemental Material Sec. 5 [40] for details). Because this ED is low, however, it is difficult to recognize its trace from the total VED in the CDFS analysis results.



FIG. 5. (a) Crystal structure of  $RTiO_3$  in the *ac* plane of y = 0. (b)–(d) Difference of the orbital arrangements in YTiO<sub>3</sub> at 25 K (ferromagnetic phase) (isosurface level:  $3.2e/Å^3$ ), SmTiO<sub>3</sub> at 30 K (antiferromagnetic phase) (isosurface level:  $3.2e/Å^3$ ), respectively. Valence electron-density distributions around Ti obtained from the CDFS analysis in the y = 0 plane are shown. The size of the valence electron-density distribution obtained by the CDFS analysis is represented twice as large. The pink dot lines show the *a*-glide plane.

Figure 4(d) shows the VED distribution around Ti obtained from the DFT calculations. The ED corresponding to the 4s states exists at the center of Ti, which is surprisingly similar to the result of the CDFS analysis [Fig. 3(c)]. As the bare 4s orbital is more spatially spread than the 3d orbital, the VED localized at the center of Ti corresponds to the rich-density area of electrons in the bonding orbital formed by the hybridization between the Ti-4s and O-2s/2p orbitals. From the perspective of ligand field theory [46], which is well applied to transition-metal complex compounds, it is natural to anticipate that the Ti orbitals are covalently bonded to surrounding ligand orbitals and some of the electrons occupy the bonding orbitals. However, in real space it is not obvious where the electrons occupying the bonding orbitals exist. Furthermore, the orbital-ordered state in this system is realized not only by the hybridization but also by the complex combined Jahn-Teller-type and GdFeO<sub>3</sub>-type distortions [20,22,26]. The CDFS analysis clearly shows this nontrivial picture.

## **D.** Orbital arrangements

Figures 5(b)-5(d) show the orbital arrangements of Ti in YTiO<sub>3</sub> at 25 K (FM phase), in SmTiO<sub>3</sub> at 30 K (AFM phase), and in LaTiO<sub>3</sub> at 30 K (AFM phase), respectively, obtained from the CDFS analysis. Although the space group is common (*Pnma*) in  $RTiO_3$  (R = Y, Sm, and La), each shape and arrangement of the VED distributions is different depending on the orbital-ordered states. The directions in which the ED distribution extends differ between neighbor sites in YTiO<sub>3</sub> (FM phase), whereas the directions are uniform in SmTiO<sub>3</sub> and LaTiO<sub>3</sub> (AFM phase). The former looks like the antiferro-orbital-ordered state, and the latter looks like the ferro-orbital-ordered state. These orbital arrangements depend not only on the quantum parameters but also on the relationship between their parameters and the direction of the symmetry operation (a-glide plane). Our results are in good agreement with the Kugel-Khomskii model [2], which predicts the ferromagnetic and antiferromagnetic interactions working on the antiferroic and ferroic orbital orders, respectively.

## **IV. DISCUSSION**

From the results of our structural analysis, the quantum parameters of SmTiO<sub>3</sub> are calculated as  $C_1 = 0.7665$ ,  $C_2 =$ 0.5635, and  $C_3 = 0.3081$  by the point-charge model calculation using Ewald's method [44]. These values are not in good agreement with the previous report [22], where  $C_1 = 0.73$ ,  $C_2 = 0.64$ , and  $C_3 = 0.24$ , due to the different precision of the crystal structure used in the calculations, as described above. On the other hand, we determined the quantum parameters  $C_1 = 0.9300$ ,  $C_2 = -0.0403$ , and  $C_3 = 0.3653$  of Ti in SmTiO<sub>3</sub> from the VED distribution [Fig. 5(c)] using Eq. (9), where s = 0.49. Furthermore, as the VED distribution of Ti in LaTiO<sub>3</sub> can no longer be represented by the linear combination of the 3d orbitals [Fig. 5(d)], the quantum parameters could not be extracted from the VED. These complex VED distributions of R = Sm and La may be related to the fact that there are few experimental reports on the quantum parameter in the RTiO<sub>3</sub> system, except in the case of R = Y.

To investigate the origin of the complex orbital-ordered states, the crystal structures in the TiO<sub>6</sub> octahedron in R = Y, Sm, and La were investigated. The change in volume of the  $TiO_6$  octahedron is less than 0.3%, regardless of the type of R, indicating that there are almost no changes in the valence of Ti ions. The O-Ti-O angles in the TiO<sub>6</sub> octahedron change significantly with the changes in R [Fig. 6(b)]. Of the three Ti-O bonds in the TiO<sub>6</sub> octahedron, the Ti-O(iii) bond length changes the most (~1.4%) with changes in R [Fig. 6(c)]. These structural changes correspond to the changes in the crystal field around Ti. It is necessary to confirm whether the Ti-O covalency depends on R in the RTiO<sub>3</sub> system. Unfortunately, as the CDFS analysis is based on the inverse Fourier transform of finite data [Eq. (7)], it is difficult to discuss the absolute value of the obtained ED. Therefore, the ratios of the number of electrons within the ionic radius of each of Ti and O  $(\text{Ti}^{3+}: 0.67 \text{ Å}; \text{O}^{2-}: 1.35 \text{ Å})$  [47] were compared in R = Y, Sm, and La [Fig. 6(d)]. These ratios increase in the order of R = Y, Sm, and La. This result corresponds to the fact that more electrons move from O to Ti, that is, the hybridization



FIG. 6. (a) a TiO<sub>6</sub> octahedron at Ti with internal coordinates (1/2, 1/2, 1/2). O atoms are labeled with (i)–(iii) in the ascending order of the Ti-O bond length. (b) Change in the O-Ti-O angles in the TiO<sub>6</sub> octahedron. (c) Change in the Ti-O bond length. (d) Change in the ratio of the number of electrons around Ti and O atoms.

is stronger in the order of R = Y, Sm, and La, which is consistent with the previous report using x-ray photoemission spectra [27]. Due to the stronger Ti-O hybridization, the VED distribution in R = Sm and La may be further away from the simple  $3d^1$  model than that in R = Y.

In our results for YTiO<sub>3</sub>, the Ti-O bonding orbital consists of not only the 4s orbital but also the  $e_g$  orbitals (Fig. S8 [40]). The quantum parameters of the 3d orbital could be determined relatively easily in the case of YTiO<sub>3</sub> because the contribution of the hybridized orbital with O is presumed to be mainly for the spherical Ti-4s orbital. The anisotropy of the spatial distribution of electrons in the Ti-O bonding orbitals changes according to the nature of the Ti-O hybridization, which can affect the crystal field of its own Ti-3d orbitals. In fact, in the case of LaTiO<sub>3</sub>, because the ED around the center of Ti is very thin [Fig. 5(d)], the contribution of the 4s orbital seems to be small. The strong Ti-O hybridization in LaTiO<sub>3</sub> [Fig. 6(d)] may suggest the anisotropy of the hybridized orbitals. The complex VED distributions of Ti in R = Sm and La obtained from the CDFS analysis cannot be described by the simple combination of the *d* orbitals [Figs. 5(c) and 5(d)]. In the present study, it has not been possible to describe the VED distribution that reflects the whole orbital state in R = Sm and La by the DFT calculations.

## V. SUMMARY

We revealed the orbital-ordered state, including the Ti-O hybridization, in the RTiO<sub>3</sub> system directly from the VED distribution obtained from the CDFS analysis using synchrotron radiation x rays. The CDFS method can determine the orbital state regardless of the physical properties and can be applied to almost all elements without the need for difficult experiments or analysis techniques if a high-stability top-up operation mode and high-resolution/short-wavelength x-ray source are used. In particular, because the CDFS analysis is based on the inverse Fourier transform equation [Eq. (7)], the bias introduced by analysts is minimal. Only the quality of the XRD data and the accuracy of the structural analysis are reflected in the results. Our results may signal a breakthrough in the study of orbital states in materials. The CDFS analysis will provide a touchstone for a complete description of the electronic state by first-principles or other theoretical calculations.

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