

## Direct determination of 3*d* orbital state in perovskite-titanate by synchrotron X-ray diffraction

The functions and physical properties of solid materials, such as magnetic order and unconventional superconductivity, are greatly affected by the orbital state of the outermost electrons (valence electrons) of the constituent atoms [1]. In other words, the minimal unit that determines the physical properties of a solid material is the orbital occupied by the valence electrons. Because the orbital state is responsible for the spatial anisotropy of physical properties, the orbital can also be regarded as the smallest unit of "shape." The orbital states in elements are basic knowledge that can be found in quantum mechanics or quantum chemistry textbooks. For example, it is known that the distribution of 3d electrons in transition elements have characteristic butterfly-type shapes (Fig. 1(c)). However, until now, it has been extremely difficult to observe the real-space distribution of such electron orbitals directly.

Using X-ray diffraction measurement, a complete electron density distribution can, in principle, be reproduced by performing the inverse Fourier transform on the 'infinite' number of diffraction intensities. However, in reality, because the number of reflections obtained by the X-ray diffraction experiment is 'finite', it is impossible to reproduce the complete electron density distribution owing to the mathematical truncation effects of the Fourier synthesis. We have found that this truncation effect can be minimized by focusing only on the valence electron term in the atomic scattering factor. Using SPring-8 **BL02B1**, which enables us to collect highintensity and high-resolution diffraction data, we succeeded in observing the butterfly-shaped spatial distribution of single-valence 3d electrons in the center of titanium in perovskite-type titanium oxide YTiO<sub>3</sub> (Fig. 1(a)).

To extract only valence electron information, it should be noted that the atomic scattering factor is formed by the sum of inner-shell and valence electrons. Although the contribution of the innershell electrons extends to the high-angle region, that of the valence electrons exists only in the lowangle region. We developed a new Fourier synthesis method in which data from each titanium ion's innershell electrons - which do not contribute to the compound's physical properties - are subtracted from the total electron distribution of each ion. The method is called core differential Fourier synthesis (CDFS) [2,3]. By CDFS, we succeeded in extracting the butterfly-shaped valence electron density distribution around a titanium ion with almost no truncation effect (Fig. 1(b)) and in determining the quantum parameters of the 3d orbital experimentally in YTiO<sub>3</sub>.

Notably, a closer look at the butterfly-shaped electron density revealed that a high density remained in the central region (inset of Fig. 1(b)), in contrast to free titanium atom in which electrons do not exist at the center because of the node of the 3d orbital (Fig. 1(c)). First-principles calculations confirmed this nontrivial orbital picture and reproduced the results of the CDFS analysis very well (Fig. 2(b)). It was found that the electron density at the center consists of the



Fig. 1. (a) Crystal structure of YTiO<sub>3</sub> at 25 K. (b) Valence electron density distribution around Ti with internal coordinates (1/2, 1/2, 1/2) obtained by CDFS analysis (isosurface level:  $3.2 e/Å^3$ ). (Inset) Sectional view of the plane (T21). (c) Schematic illustration of the Ti<sup>3+</sup>-3d<sup>1</sup> orbital-ordered state in YTiO<sub>3</sub> system and the typical valence electron density distribution of a  $t_{2e}$  electron.

valence electrons occupying the hybridized orbitals, which are mainly formed by the Ti-4*s* and O-2*s*/2*p* orbitals, generated by the bond between titanium and oxygen (Figs. 2(a,c)).

CDFS reveals the orbital states in materials regardless of the physical properties and can be applied to almost all elements without the need for difficult experiments or analytical techniques. The method requires neither quantum-mechanical nor informatic models, so bias introduced by analysts is minimized. The CDFS based on the high-quality data obtained by short-wavelength synchrotron X-ray is extremely effective for observing not only atomic orbitals localized in one atom but also spatially extended molecular orbitals [2,4]. The 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.



Fig. 2. (a) Density of states of the 4*s*, 4*p*, and 3*d* ( $t_{2g}$  and  $e_g$ ) orbitals of Ti in YTiO<sub>3</sub>. The zero-energy corresponds to the highest occupied level. (b) Valence electron density distribution around Ti, which corresponds to valence electrons occupying the orbitals below the Fermi level, obtained from the density-functional-theory calculation. (c) Schematic illustration of the orbital state including the Ti–O hybridization.

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