Electron correlation energy of La$_x$Sr$_{1-x}$TiO$_3$ by high-resolution soft-X-ray emission spectroscopy

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Abstract

The electronic structure of La$_x$Sr$_{1-x}$TiO$_3$ ($x \leq 0.10$) has been investigated by high-resolution soft-X-ray emission spectroscopy (SXES) spectra in the Ti2p energy region. At the $t_2$g-resonance SXES spectra, the d–d transition whose Raman shift is about 2.2 eV corresponds to the magnitude of the half intra-atomic Coulomb energy ($U_{dd} = 2$). The magnitude does not change in $x \leq 0.10$. This fact is consistent with the results obtained from the effective mass and the electronic specific heat.

1. Introduction

It is well known that filling control system La$_x$Sr$_{1-x}$TiO$_3$ changes from a Mott–Hubbard insulator (LaTiO$_3$) with a d$^1$ configuration at $x = 0$ to a band insulator (SrTiO$_3$) with a d$^0$ configuration at $x = 1$ by varying the d-band filling number [1,2]. According to the classification scheme of Zaanen, Sawatzky, and Allen, the insulating d$^1$ (Ti$^{3+}$) compound is Mott–Hubbard type insulator and the band gap is formed between states of predominantly Ti 3d character. They reported that the electronic specific heat and the effective mass $m^*$ deduced from the Drude model increase with increasing $n$ for the large d-band filling region ($x > 0.5$), while those are constant in small d-band filling region ($x < 0.5$) [1–4]. This fact indicates that the electron correlation effect is important when $x > 0.5$, while it is not so important when $x < 0.5$.

The electronic structure of La$_x$Sr$_{1-x}$TiO$_3$ has been extensively studied by photoemission spectroscopy (PES) [5–11]. The PES spectra have two features in the band gap below the Fermi level ($E_F$) that correspond to the coherent band at $E_F$ and to the incoherent band at binding energy of $\sim 1.5$ eV. The relative intensity of these bands strongly depends on La doping. Recent investigations have
proposed that the spectroscopic data yield spectral weight transfer between the coherent and incoherent bands [11]. However, it is difficult to determine the electron correlation energy by PES technique due to the surface effect.

In this study, we present high-resolution soft-X-ray emission (SXES) and X-ray absorption spectra (XAS) of La$_x$Sr$_{1-x}$TiO$_3$ ($x = 0–0.10$). SXES spectra reflect the electronic structure of the bulk compared with photoelectron spectra, because the mean free path of a soft-X-ray is very long compared with that of the electron [12]. The observed Raman scattering provides useful information about electronic structure [12–17]. This purpose of this study is to determine experimentally the magnitudes of the electron correlation energy ($U_{dd}$) in the bulk state through the study of d–d transition.

2. Experimental

Single crystals of La$_{1-x}$Sr$_x$TiO$_3$ ($x = 0.05, 0.10$) were synthesized by melt-quenching stoichiometric mixture of La$_2$O$_3$, TiO$_2$ and SrO powders in a floating-zone furnace. Special attention was paid to synthesis of the samples with $x$ close to 0 including the sample LaTiO$_3$. Careful precalcining of La$_2$O$_3$ (source of La) and a fairly strong reducing condition (40% H$_2$/Ar) prevented the La deficiencies and extra oxygen. The single crystals were examined using X-ray diffraction.

SXES and XAS spectra were measured using a soft-X-ray spectrometer installed at the undulator beamline BL-2C (in Photon Factory) [16], at the high energy accelerator organization. Synchrotron radiation was monochromatized using a varied-line spacing plain grating whose average groove density is 1000 lines/mm. The spectra were measured at depolarized configuration. The energy resolution was smaller than 0.4 eV at $h\nu = 450$ eV. The bottom axis was calibrated by measuring the 4f core level of Au.

3. Results and discussion

Fig. 1 shows the Ti2p XAS spectra of La$_{0.10}$Sr$_{0.90}$TiO$_3$. The numbers indicate the photon energies, where the Ti2p SXES spectra were measured.

Fig. 2 shows the Ti2p SXES spectra of La$_{0.10}$Sr$_{0.90}$TiO$_3$ excited at each point of Fig. 1. It well known that the Ti2p emission reflects the Ti3d partial density of states [12]. An arrow shown in each spectrum is attributed to elastic scattering of the excitation photon. The elastic peak is enhanced at the excitation energy corresponding to the t$_{2g}$ absorption peak of L$_3$. Then, the peak intensity decreases with increasing the excitation energy.

The SXES spectrum f is an off-resonance spectrum attributed to the normal Ti3d $\rightarrow$ 2p fluorescence spectrum. This spectrum provides evidence indicates that the Ti3d state hybridizes with the O2p state in the valence band. Four dashed lines (A, B, C and D peaks) show the fluorescence bands. As reference, the PES spectrum of La$_{0.10}$Sr$_{0.90}$TiO$_3$
is also shown above the fluorescence spectrum. It is striking that the energy positions of fluorescence spectrum are in a good agreement with those of the PES spectrum. Therefore, we can estimate that the A and B peaks correspond to the bonding state and nonbonding state of the valence band, and the C and D peaks correspond to the coherent band and incoherent in the band gap energy region.

Four features shown with vertical bars \( \alpha \), \( \beta \) and \( \chi \) represent the energy positions that have energy separation of 5.5, 6.8 and 9.2 eV, respectively, from the excitation energy. They shift as the excitation energy is varied. These features are attributed to the soft-X-ray Raman scattering, that is, inelastic scattering. The soft-X-ray Raman scattering that is excited in the L\(_3\) absorption spectral region overlaps with the Ti 3d \( \rightarrow \) 2p fluorescence.

Fig. 3(a) shows the SXES spectra of \( \text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3 \), where the abscissa represents the Raman shift that is the energy shift from the elastic scattering. The Ti 3d \( \rightarrow \) 2p fluorescence peaks shift to the higher energy as the excitation energy increases. On the other hand, it is reported that the elementary excitation of the Raman scattering is

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**Fig. 2.** Ti 2p SXES spectra of \( \text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3 \) excited at various photon energies indicated in Fig. 1. Arrow shows the energy position of the excitation photon energy. Vertical lines show the energy positions of Ti 3d \( \rightarrow \) 2p fluorescence. As reference, the PES spectrum of \( \text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3 \) in the valence band region is shown above the fluorescence spectrum.

**Fig. 3.** (a) Ti 3d \( \rightarrow \) 2p SXES and (b) optical conductivity spectra of \( \text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3 \) presented as the relative emission energy to the elastic scattering. The optical conductivity spectrum is taken from [3].
the valence band transition. Therefore, the Raman scattering can be compared with the optical conductivity spectrum, as shown in Fig. 3(b). The spectrum is composed of two parts: a Drude-like photoresponse near 0 eV due to the charge carrier and interband transitions observed at energies larger than 3 eV. The Raman scatterings observed at the SXES spectra are in good agreement with the optical conductivity spectrum [3], which accords to the charge-transfer (CT) transition from O2p state to unoccupied Ti3d state. Thus, the α peak corresponds to the transition from the nonbonding band to the t2g subband, and the β peak corresponds to the transition from the bonding band to the t2g subband of Ti3d. The γ peak corresponds to the transition from the nonbonding band to e_g subband.

Fig. 4(a) shows the SXES spectra as a function of doping at the t2g-resonance in La_{x}Sr_{1−x}TiO_{3} (x = 0–0.10). The intensity is normalized at the Ti 3d → 2p fluorescence peak. Comparing each spectrum, one notes that the intensities of the elastic peak (δ₁) as well as the δ₂ peak in the band gap increase with increasing La doping. In the optical conductivity spectra, the intensity at E_F increases with increasing La doping, indicating the Drude photoresponse [3]. The increasing of intensity at δ₁ indicates the Drude peak overlapping with elastic peak because the resolution of the experimental system is ~0.6 eV. Therefore, the δ₂ peak corresponds to the d–d transition between two coherent bands. On the other hand, the PES spectra of La_{x}Sr_{1−x}TiO_{3} show two features at ~1.5 eV and E_F in the band gap below the E_F that are attributed to Ti3d states [6,11]. In the case of t2g bands, there is typically no large band splitting so that the contribution to the Raman scattering is due to the half electron correlation energy (U_{dd}/2). From the previous information we suggest, the δ₂ corresponds to the d–d transition between coherent and incoherent bands as shown in Fig. 4(b). This is in a good agreement with the result estimated from the analysis of Ti 2p core level PES spectra. The δ₂ peak does not shift much by doping. On one hand, the U_{dd} does not depend on La doping in this doping region. This fact reflects the results of the effective mass and the specific heat [1–4].

4. Conclusion

We have studied the soft-X-ray scattering due to the CT transition and compared the SXES spectra with the optical conductivity spectrum in VUV region. The Raman scattering, which is attributed to the d–d transition between the incoherent and the coherent bands, was directly observed in the t2g-resonance SXES spectra of La_{x}Sr_{1−x}TiO_{3} for x < 0.10. This Raman shift corresponds to the magnitude of the effective U_{dd}/2.

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