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

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Abstract

The electronic structure of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ ($x \leq 0.10$) has been investigated by high-resolution soft-X-ray emission spectroscopy (SXES) spectra in the Ti 2p energy region. At the t_{2g} -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.

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1. Introduction

It is well known that filling control system $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ 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 predom-

inantly 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 $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ 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 ~ 1.5 eV. The relative intensity of these bands strongly depends on La doping. Recent investigations have

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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 $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ ($x = 0-0.10$). 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 $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.05, 0.10$) were synthesized by melt-quenching stoichiometric mixture of La_2O_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_2O_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 $\text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3$. The spectra are derived from the

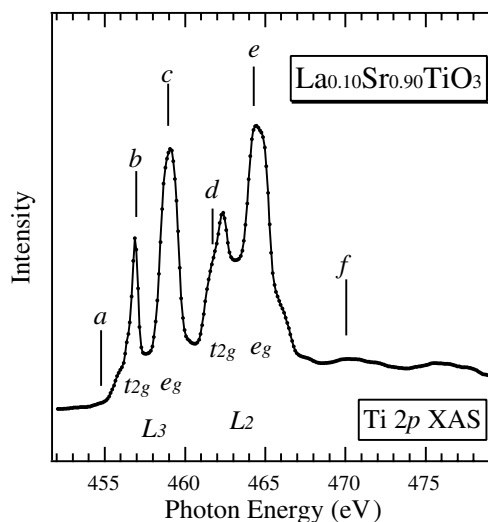


Fig. 1. Ti2p XAS spectra of $\text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3$. The numbers indicate the photon energies, where the Ti2p SXES spectra were measured.

two parts of L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) [7,14]. They are split into the t_{2g} and e_g states by the octahedral ligand field. Here, note that the energy position of the t_{2g} subband does not depend much on the La doping. However, the intensity of t_{2g} subband increases by La doping, indicating that the doped electrons enter into the bottom of occupied Ti 3d band. The vertical bars, which are labeled from a to f, indicate the selected photon energies for resonant SXES measurements.

Fig. 2 shows the Ti2p SXES spectra of $\text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3$ excited at each point of Fig. 1. It is well known that the Ti2p emission reflects the Ti 3d 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 Ti 3d \rightarrow 2p fluorescence spectrum. This spectrum provides evidence indicating that the Ti 3d state hybridizes with the O 2p state in the valence band. Four dashed lines (A, B, C and D peaks) show the fluorescence bands. As reference, the PES spectrum of $\text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3$

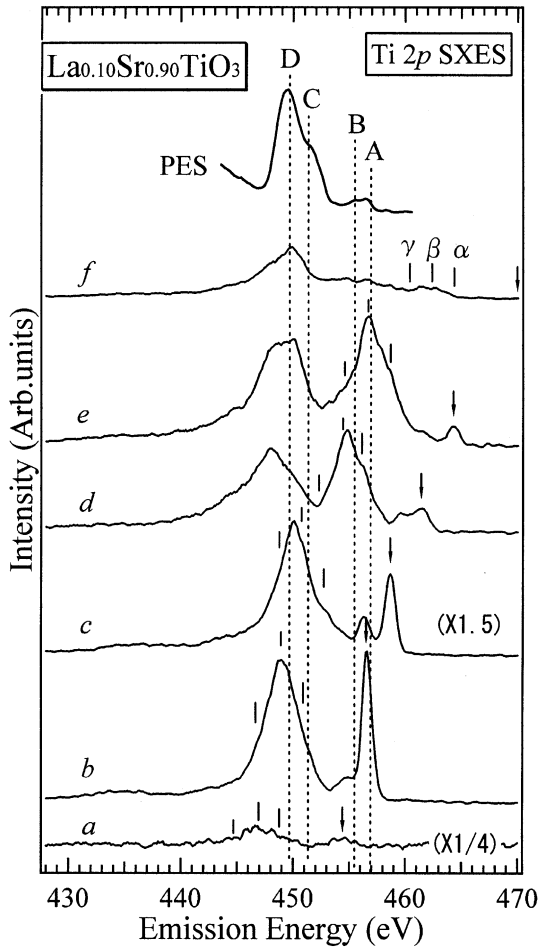


Fig. 2. Ti 2p SXES spectra of $\text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3$ excited at various photon energies indicated in Fig. 1. Arrow shows the energy position of the excitation photon energy. Vertical lines show the energy positions of Ti 3d \rightarrow 2p fluorescence. As reference, the PES spectrum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

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 α , β and χ 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

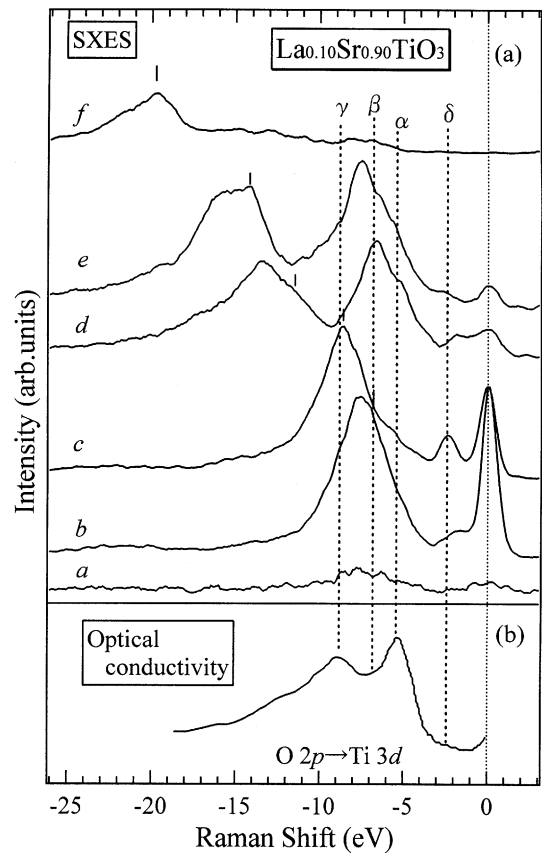


Fig. 3. (a) Ti 3d \rightarrow 2p SXES and (b) optical conductivity spectra of $\text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3$ presented as the relative emission energy to the elastic scattering. The optical conductivity spectrum is taken from [3].

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 O 2p state to unoccupied Ti 3d state. Thus, the α peak corresponds to the transition from the non-bonding band to the t_{2g} subband, and the β peak corresponds to the transition from the bonding band to the t_{2g} subband of Ti 3d. The χ 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 t_{2g} -resonance in $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ ($x = 0-0.10$). The intensity is normalized at the Ti 3d \rightarrow 2p fluorescence peak. Comparing each spectrum, one notes that the intensities of the elastic peak (δ_1) as well as the δ_2 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 δ_1 indicates the Drude peak overlapping with elastic peak because the resolution of the experimental system is ~ 0.6 eV. Therefore, the δ_2 peak corresponds to the d–d transition between two coherent bands. On the other hand, the PES spectra of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ show two features at ~ 1.5 eV and E_F in the band gap below the E_F that are attributed to Ti 3d states [6,11]. In the case of t_{2g} 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 δ_2 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 δ_2 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].

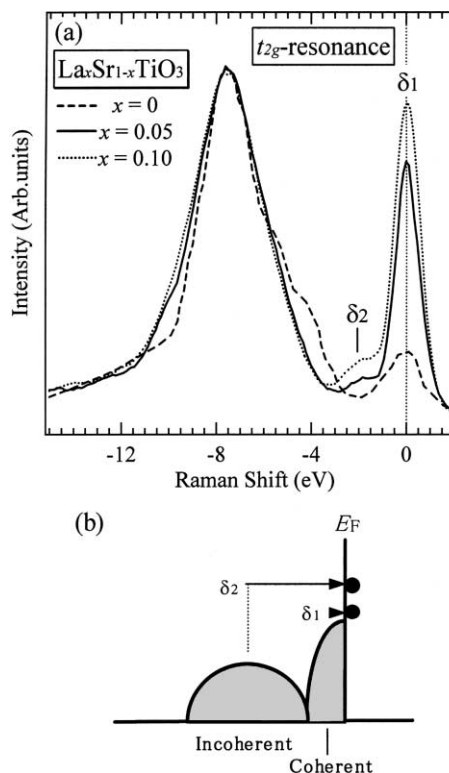


Fig. 4. (a) t_{2g} -Resonance SXES spectra as a function of La doping of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$. This t_{2g} spectrum for $\text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3$ is spectrum b in Fig. 3. (b) Schematic diagram of the d–d transition observed at SXES spectra.

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 t_{2g} -resonance SXES spectra of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ for $x < 0.10$. This Raman shift corresponds to the magnitude of the effective $U_{dd}/2$.

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