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Electronic structure for the metal–insulator transition in $La_{1-x}Sr_xTiO_3$ probed by resonant soft-X-ray emission spectroscopy

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Abstract

The electronic structure of doped Mott-insulator $La_{1-x}Sr_xTiO_3$ has been studied by resonant soft-X-ray emission spectroscopy (SXES). At the t_{2g}-resonance SXES spectra, the d–d transition whose Raman shift is about 2.0 eV reflects the magnitude of half on-site Coulomb energy (U_{dd}). The U_{dd} does not change much around the metal–insulator transition at $x = 0.05$ in $La_{1-x}Sr_xTiO_3$. This result is thought to be in accord with the prediction of dynamical-mean-field theory.

Keywords: $La_{1-x}Sr_xTiO_3$; SXES; d–d transition; On-site Coulomb energy (U_{dd})

$La_{1-x}Sr_xTiO_3$ 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 $x = 1$ [1]. For a wide range of x values in between ($0.05 < x < 1$), the series exhibits a paramagnetic metallic phase. The enhancement of electronic specific heat (γ), which is proportional to the conduction electron effective mass (m^*), is expected for correlated metals near a metal–insulator (M–I) transition at $x = 0.05$, though that is not expected for M–I transition at $x = 0.95$ [1–4]. Therefore, the M–I transition is believed to be controlled by the relative magnitudes of the on-site Coulomb energy (U_{dd}) and the one-electron bandwidth (W); the system is metallic when $U_{dd}/W < 1$ and is an insulator when $U_{dd}/W > 1$.

In this paper, we present soft-X-ray emission spectroscopy (SXES) spectra of $La_{1-x}Sr_xTiO_3$ [5,6]. In small d-band filling region ($x \leqslant 0.90$), we reported that the Raman scattering of the t_{2g}-resonance SXES spectra, which is attributed to d–d transitions between the lower Hubbard and the quasiparticle bands, reflects the magnitude of the effective $U_{dd}/2$. By using this technique, we estimate experimentally the effective U_{dd} near the M–I transition at $x = 0.05$.

SXES measurements were carried out at the undulator beamline BL-2C at the Photon Factory

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(PF) of the High Energy Accelerator Organization (KEK). Synchrotron radiation was monochromatized using a varied-line spacing place grating whose average groove density is 1000 lines/mm. The SXES spectra were measured with soft-X-ray emission spectrometer. The energy resolution was higher than 0.4 eV at $h\nu = 450$ eV.

Fig. 1(a) shows the Ti 2p X-ray absorption spectrum of $LaTiO_3$. The spectrum consists of two parts derived from the spin–orbit split of L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) states. They are further split into the t_{2g} and e_g states by the octahedral ligand field. The vertical bars, which are labeled from *a* to *e*, indicate the selected photon energies for resonant SXES measurements.

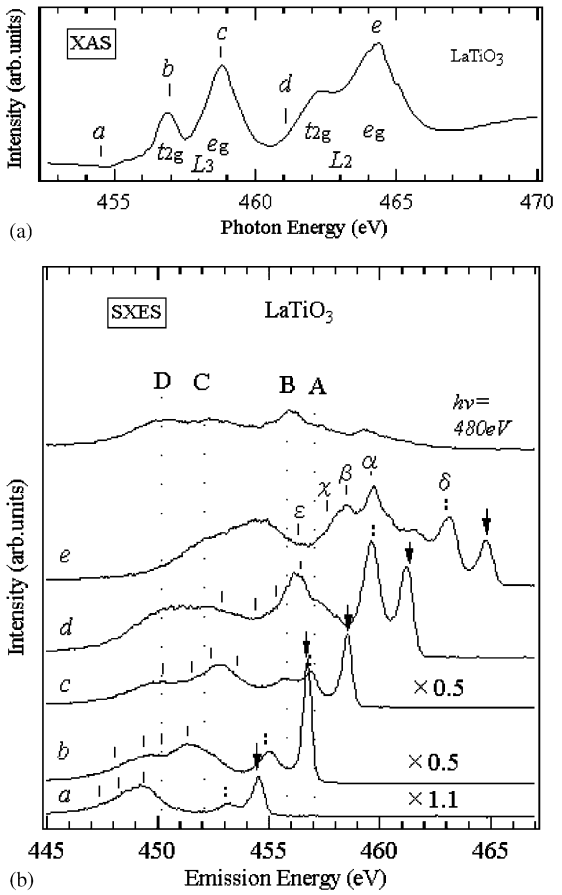

Fig. 1. (a) Ti 2p X-ray absorption spectrum of $La_{0.90}Sr_{0.10}TiO_3$. (b) Ti 2p SXES spectra excited at various photon energies indicated in (a). Vertical dashed lines indicate the energy positions of the excitation photon energy and Ti $3d \rightarrow 2p$ fluorescence.

Fig. 1(b) shows the Ti 2p SXES spectra of $LaTiO_3$. An arrow shown in each spectrum is attributed to elastic scattering of the excitation photon. The SXES spectrum excited at $h\nu = 480$ eV is an off-resonance spectrum attributed to the normal Ti $3d \rightarrow 2p$ fluorescence spectrum. This spectrum indicates 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 band. These energy positions of fluorescence spectrum are in a good agreement with those of the PES spectrum [5–7]. Therefore, we can estimate that the D and C peaks correspond to the bonding and nonbonding states of the O 2p valence band, and the A and B peaks correspond to the quasiparticle band and lower-Hubbard band in the band gap energy region.

Four features shown with vertical bars α, β, χ, and ε represent the energy positions that have energy separation of 5.2, 6.2, 7.2, and 8.3 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 [5,6]. The soft-X-ray Raman scattering that is excited in the L_3 absorption spectral region overlaps with the Ti $3d \rightarrow 2p$ fluorescence. The SXES spectrum *a* excited at below the Ti 2p threshold show an apparent feature at a lower energy than the elastic scattering.

Fig. 2(a) shows the t_{2g}-resonance SXES spectra of $LaTiO_3$ (insulating) and $La_{0.90}Sr_{0.10}TiO_3$ (metallic), where the abscissa is the Raman shift from the elastic scattering. The elastic scattering peak is located at 0 eV. These intensities are normalized by the beam current value and measurement time. As reference, the optical conductivity spectra are also shown in Fig. 2(b). Four Raman scattering peaks denoted by α, β, χ, and ε can be compared with the optical conductivity spectra [3], since the elementary excitation of the Raman scattering is the valence band transition. Four Raman scattering peaks are in good accordance with the optical conductivity spectra. This fact indicates that these Raman scattering peaks are attributed to a charge-transfer transition from the O 2p state to the unoccupied Ti 3d state [5,6]. On the other hand,

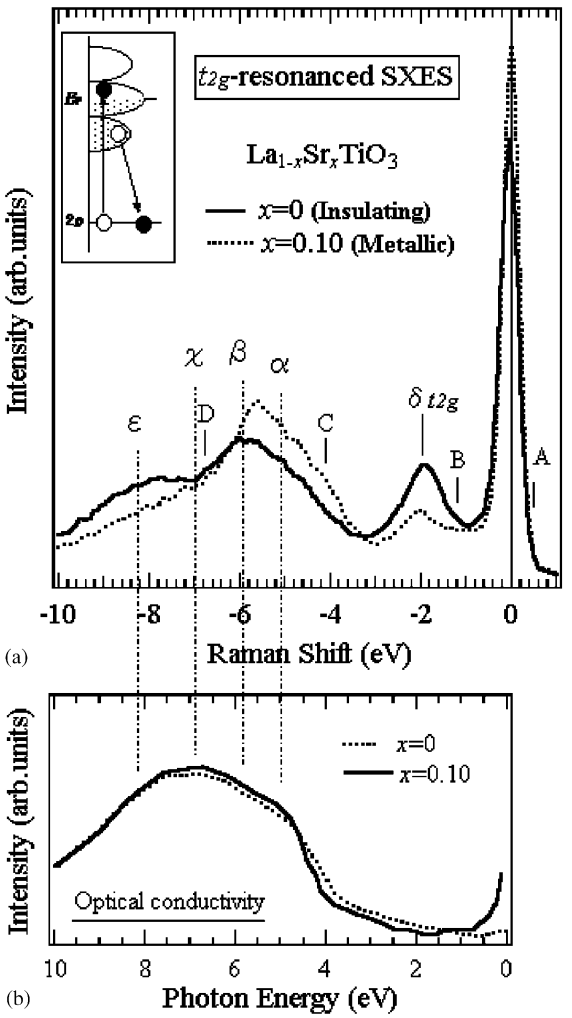

Fig. 2. (a) t_{2g}-resonance SXES spectra and (b) optical conductivity spectra of $La_{1-x}Sr_xTiO_3$ ($x = 0, 0.10$).

comparing each SXES spectrum, the intensity at 0 eV is lower in $LaTiO_3$, indicating the Drude photorespone shown in the optical conductivity spectra. Furthermore, the intensity of the δt_{2g} peak in the band gap decreases with Sr doping, which has been already observed in the PES study [6,7]. 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 U_{dd}. That is, the Raman scattering of the δt_{2g} peak at $\sim$2.0 eV corresponds to the d–d transition from the lower Hubbard band to the unoccupied quasiparticle band. Therefore, we can estimate the half U_{dd} ($U_{dd}/2$), so that we can experimentally know that the effective U_{dd} does not depend on the Sr dopant concentration. The magnitude of U_{dd} is in good agreement with the energy separation of lower- and upper-Hubbard bands observed by PES and inverse-PES spectra [6].

In conclusion, we have studied the electronic structure near the M–I transition in $La_{1-x}Sr_xTiO_3$ using SXES. The Raman scattering of the t_{2g}-resonant SXES spectra indicate features due to the d–d transitions corresponding to the $U_{dd}/2$. The U_{dd} does not change much around M-I transition at $x = 0.05$ in $La_{1-x}Sr_xTiO_3$. This result is considered to be in accord with the prediction of dynamical-mean-field theory [8].

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References

[1] M. Imada, A. Fujimori, Y. Tokura, Rev. Mod. Phys. 70 (1999) 1039.
[2] Y. Tokura, Y. Taguchi, Y. Okada, Y. Fujishima, T. Arima, K. Kumagai, Y. Iye, Phys. Rev. Lett. 70 (1993) 2126.
[3] Y. Fujishima, Y. Tokura, T. Arima, S. Uchida, Phys. Rev. B 46 (1992) 11167.
[4] Y. Taguchi, T. Okuda, M. Ohashi, C. Murayama, N. Mohri, Y. Iye, Y. Tokura, Phys. Rev. B 59 (1999) 7917.
[5] T. Higuchi, T. Tsukamoto, M. Watanabe, M.M. Grush, T.A. Callcott, R.C. Perera, D.L. Ederer, Y. Tokura, Y. Harada, Y. Tezuka, S. Shin, Phys. Rev. B 60 (1999) 7711.
[6] T. Higuchi, D. Baba, T. Takeuchi, T. Tsukamoto, Y. Taguchi, Y. Tokura, A. Chainani, S. Shin, Phys. Rev. B 68 (2003) 104420.
[7] A. Fujimori, I. Hase, H. Namatame, Y. Fujishima, Y. Tokura, H. Eisaki, S. Uchida, K. Takegahara, F.M.F. de Groot, Phys. Rev. Lett. 69 (1992) 1796.
[8] H. Kajueter, G. Kotliar, G. Moeller, Phys. Rev. B 53 (1996) 16214.