

## Tensile-strain-dependent spin states in epitaxial LaCoO<sub>3</sub> thin films

In transition metal compounds, charge, spin, and orbital degrees of freedom induced by a strong electron correlation realize various physical phenomena such as superconductivity, metal-insulator transition, and charge ordering [1]. The perovskite-type cobalt oxide LaCoO<sub>3</sub> is one of the most interesting materials because of its various electron degrees of freedom. Since the spin state of LaCoO<sub>3</sub> is sensitive to the crystal field, a spin crossover from the low-spin (LS) to high-spin (HS) state occurs upon increasing the temperature [2]. Epitaxial strain can also affect the spin states, and ferromagnetism is observed in LaCoO<sub>3</sub> thin films at lower temperatures ( $\leq 85$  K) [3-5]. In previous studies, the spin states of thin films were considered by the orderings of 3d electrons on the basis of resonant X-ray diffraction [3-5]. However, direct observations of the electronic structures are important to clarify the spin states. Since it is difficult to determine the spin states by conventional techniques such as X-ray absorption spectroscopy (XAS), we performed resonant inelastic soft X-ray scattering (RIXS) with the Co  $2p \rightarrow 3d \rightarrow 2p$  process ( $L$  edge) [6]. RIXS is one of the most powerful techniques for clarifying the spin states by observing the  $d-d$  excitations.

LaCoO<sub>3</sub> epitaxial thin films (30 nm thickness) were fabricated on LSAT(110) and LSAT(111) [(LaAlO<sub>3</sub>)<sub>0.3</sub>(SrAl<sub>0.5</sub>Ta<sub>0.5</sub>O<sub>3</sub>)<sub>0.7</sub>] substrates by pulsed laser deposition. The same substrates with different orientations enable us to observe the pure strain effects on XAS and RIXS spectra. The lattice constant of the LSAT substrate is 3.868 Å, whereas that of the LaCoO<sub>3</sub> bulk is 3.804 Å, indicating that tensile strains are applied to the LaCoO<sub>3</sub> epitaxial thin films grown on the LSAT substrates. The magnitudes of the tensile strains from the LSAT(110) and LSAT(111) substrates are 1.0% and 0.5%, respectively (strains are defined as the ratio of the cubic root of the unit cell volume) [3,4]. The XAS and RIXS experiments were performed at SPRING-8 BL07LSU HORNET [7]. The RIXS measurements were performed with soft X-rays from 770 to 810 eV (Co  $L_{3,2}$  edge). In this range of X-ray energies, the energy resolution is  $\sim 300$  meV. A charge-coupled device (CCD) detector was set at 90° relative to the incident X-ray with horizontal polarization to suppress elastic scattering (see inset in Fig. 1(b)).

Co  $L_{3,2}$  edge XAS spectra measured with the total electron yield (TEY) mode are shown in Fig. 1(a). The peaks at approximately 779 and 794 eV correspond to the Co  $L_3$  and  $L_2$  edges, respectively. Although

the magnitude of the strain is different between LSAT(110) and LSAT(111), the XAS spectra are similar. To investigate the strain effect on the electronic structures from  $d-d$  excitations, we performed RIXS measurements. We selected energies of A:  $L_3 - 2.9$  eV, B:  $L_3 - 1.5$  eV, C:  $L_3 - 1.0$  eV, D:  $L_3$ , E:  $L_3 + 1.7$  eV, and F:  $L_2$  as the excitation energies. The RIXS spectra of the LaCoO<sub>3</sub> thin films are shown in Fig. 1(b). These spectra are normalized with the intensity of the highest

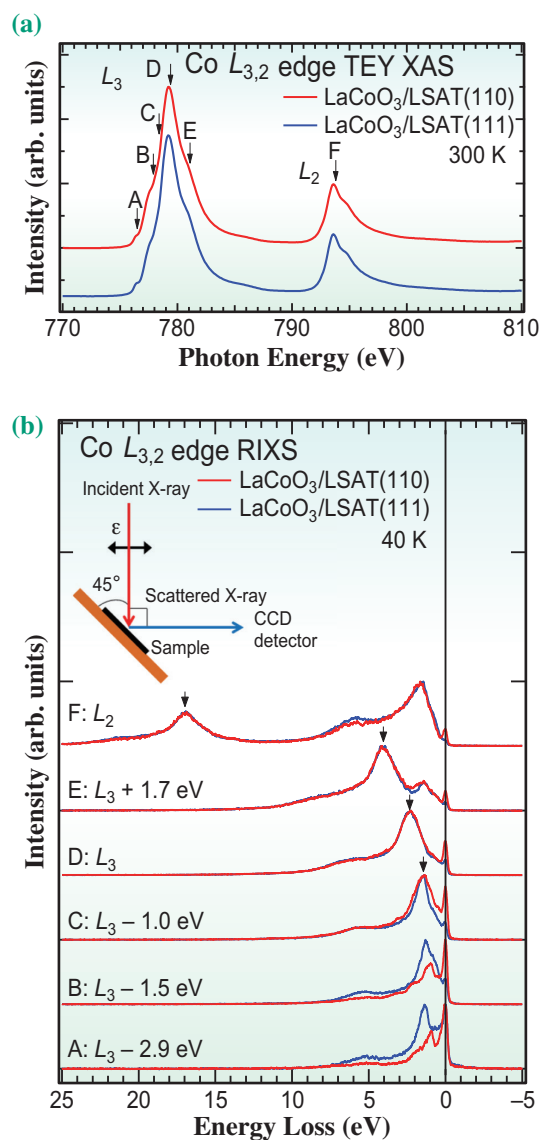


Fig. 1. Co  $L_{3,2}$  edge (a) TEY XAS and (b) RIXS spectra of LaCoO<sub>3</sub> thin films grown on LSAT (110) and LSAT(111) substrates. All RIXS spectra are normalized by the intensity of the highest peak. The inset shows a schematic diagram of the experimental setup of RIXS.

peak. The thick solid line shows the center of the elastic scattering peaks, whereas the arrows indicate the fluorescence peaks. Other peaks from 0 to 4 eV correspond to the  $d-d$  excitations. In the spectra with the energies of A and B, the peaks of  $d-d$  excitations can be clearly observed. The  $d-d$  excitations are markedly different between the thin films on LSAT(110) with 1.0% tensile strain and LSAT(111) with 0.5% tensile strain, indicating that the spin states of  $\text{LaCoO}_3$  change with the magnitude of the tensile strain. On the other hand, in the spectra excited by higher energies (C, D, E, and F), the peaks of  $d-d$  excitations are not clear owing to the overlapping with the larger fluorescent peak. Then, we selected the excitation energy A:  $L_3 - 2.9$  eV and analyzed the spectra by impurity Anderson model calculations in  $O_h$  and  $D_{2h}$  local symmetries.

The experimental RIXS spectra excited with A:  $L_3 - 2.9$  eV (776.5 eV) measured at 40 and 300 K and the theoretical spectra with several electronic states are shown in Fig. 2. The peaks observed at approximately 0.3 eV are assigned to the excitations from the HS ground states. On the other hand, the

peaks observed at 1.3 eV correspond to the excitations from the LS ground states. However, the peaks at 1.0 eV in  $\text{LaCoO}_3/\text{LSAT}$  (110) cannot be explained by either the LS or HS state with  $O_h$  symmetry. From the comparison with the theoretical spectra, the peak for the HS state is shifted to 1.0 eV by lowering the symmetry from  $O_h$  to  $D_{2h}$ , indicating that the spin state of  $\text{LaCoO}_3/\text{LSAT}(110)$  consists of the HS states with different local symmetries, i.e., a mixture of  $O_h$  and  $D_{2h}$  symmetries.

In this study, we performed RIXS measurements and revealed that the spin states of Co ions were different between the bulk crystal and thin film crystals. Although it is difficult to observe the strain effects on the spin states by conventional XAS measurements, a clear difference can be observed by RIXS.

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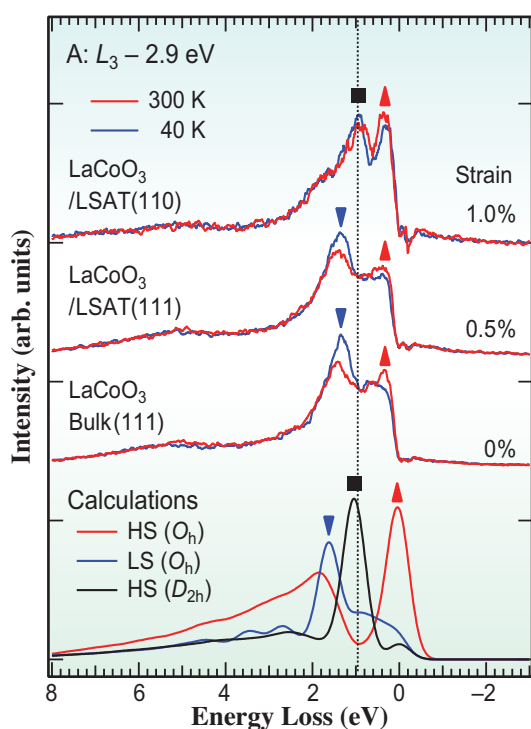


Fig. 2. Experimental RIXS spectra excited with A:  $L_3 - 2.9$  eV (776.5 eV) measured at 40 and 300 K and the theoretical spectra in  $O_h$  and  $D_{2h}$  symmetries.

### References

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