

論文の内容の要旨

X-ray spectroscopy study of electronic states in transition metal compounds controlled by crystal structures (遷移金属化合物の結晶構造により制御された電子状態の X 線分光による研究)

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In transition metal compounds, strong electron correlations generate charge, spin, and orbital degrees of freedom and realize various unique physical phenomena such as charge ordering [1]. Perovskite-type cobalt oxide is one of the most intriguing materials due to its various electron degrees of freedom.

One typical example is perovskite-type LaCoO_3 with Co^{3+} . The spin state of LaCoO_3 is considered to take LS state with $e_g^0 t_{2g}^6$, intermediate-spin (IS) state with $e_g^1 t_{2g}^5$, or HS state with $e_g^2 t_{2g}^4$. The population of HS state gradually increases as the temperature increases from around 100 K and the HS state becomes dominant above 500 K [2]. Although the spin state and its temperature dependence of LaCoO_3 bulk have already been studied by using various experimental and theoretical approaches [3-9], the spin states have not been completely determined yet. Especially, the spin states in the intermediate temperature region remain controversial, *i.e.* the mixed HS/LS state or the IS state. Epitaxial strain can also influence the spin states as observed for ferromagnetism in LaCoO_3 thin films at lower temperatures ($\lesssim 85$ K) [10-17]. It is indicated that the ferromagnetism originates from the spin-state, orbital, and spin orderings [15-17]. However, the spin states of strained LaCoO_3 thin films were not yet decided. Therefore, we had an interest in clarifying the electronic structures of LaCoO_3 thin films and their epitaxial strain dependence by using resonant soft x-ray scattering (RIXS), one of the most powerful techniques to clarify the complicated spin states. The Co $L_{3,2}$ edge RIXS experiments were performed at BL07LSU HORNET of SPring-8. We confirmed that the spin states of LaCoO_3 thin films on $(\text{LaAlO}_3)_{0.3}(\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3)_{0.7}$: LSAT substrates can be changed by the magnitude of the tensile strains from the substrates. By comparing the d - d excitations with the theoretical calculations, we estimated the spin states of LaCoO_3 thin films with different tensile strains. Figure 1 shows the comparison between the experimental RIXS spectra and the linear combinations

of theoretical spectra. The estimated ratio in $\text{LaCoO}_3/\text{LSAT}(111)$ with 0.5% tensile strain is $\text{HS}(O_h) : \text{LS}(O_h) = 1 : 2$ and is consistent with resonant x-ray diffraction study. On the other hand, the obtained ratio of spin states in $\text{LaCoO}_3/\text{LSAT}(110)$ with 1.0% tensile strain is $\text{HS}(O_h) : \text{HS}(D_{2h}) = 1 : 1$, indicating a strain induced unique spin state.

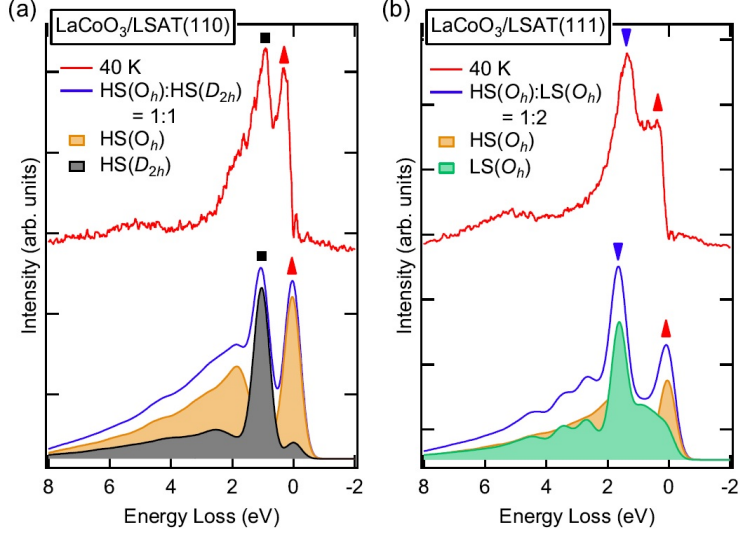


Figure 1: Comparison between the experimental RIXS spectra and the linear combinations of theoretical spectra in (a) $\text{LaCoO}_3/\text{LSAT}(110)$ and (b) $\text{LaCoO}_3/\text{LSAT}(111)$. The triangles, squares, and inverted triangles indicate the main peaks of the $\text{HS}(O_h)$, $\text{HS}(D_{2h})$, and $\text{LS}(O_h)$ ground states, respectively.

We are also interested in higher Co valence compounds such as $\text{SrCoO}_{3-\delta}$ whose Co valence is close to 4+. Brownmillerite-type ($Ima2$) $\text{SrCoO}_{2.5}$ has Co^{3+} with $d^6: e_g^2 t_{2g}^4$ [18]. The magnetic structure was reported to be antiferromagnetism with $T_N = 537$ K. Although it is difficult to insert the oxygen in $\text{SrCoO}_{2.5}$, SrCoO_3 bulk single crystal was synthesized by treating $\text{SrCoO}_{2.5}$ at a high pressure (6.5 GPa) and a high temperature (1023 K) with KClO_4 [19]. In SrCoO_3 , the valence of Co is 4+ and the crystal structure is cubic perovskite-type ($Pm\bar{3}m$). The material exhibit ferromagnetism with $T_C = 305$ K. On the other hand, $\text{SrCoO}_{3-\delta}$ thin films can be synthesized under lower pressure and temperature than bulk by Jeon *et al.* [20]. They postannealed $\text{SrCoO}_{2.5}$ thin films at 400°C for 5 min in O_2 (600 Torr) and obtained $\text{SrCoO}_{3-\delta}$ thin films. Direct synthesis of $\text{SrCoO}_{3-\delta}$ was also reported in $\text{O}_2 + \text{O}_3$ (5%) [21]. Then, we wonder if we can synthesize $\text{SrCoO}_{3-\delta}$ thin films by annealing $\text{SrCoO}_{2.5}$ in $\text{O}_2 + \text{O}_3$ and control the value of $3 - \delta$ by epitaxial strains from the substrates. For the evaluation of $\text{SrCoO}_{3-\delta}$, we used synchrotron x-ray, one of the most powerful tools to investigate the electronic and crystalline structures directly. In this study, we performed the x-ray diffraction (XRD), hard x-ray photoemission spectroscopy (HAXPES), soft x-ray absorption spectroscopy (XAS), x-ray magnetic circular dichroism (XMCD), and superconducting quantum interference device (SQUID) measurements of $\text{SrCoO}_{3-\delta}$ thin films on STO and LSAT substrates. The XRD, HAXPES, and XAS results indicate that the metallic $\text{SrCoO}_{3-\delta}$ thin films have a cubic perovskite-type crystal structure with higher Co valence than 3+, meaning the oxygen injection by ozonization. Although the results of the thin films on STO with 2.0% tensile strain and LSAT with 1.0% tensile strain

are not so different in XRD, HAXPES, and XAS, the XMCD signal of $\text{SrCoO}_{3-\delta}/\text{LSAT}$ is two times stronger than that of $\text{SrCoO}_{3-\delta}/\text{STO}$ as shown in Fig. 2. The XMCD results mean that the physical properties of $\text{SrCoO}_{3-\delta}$ can be controlled by the strain.

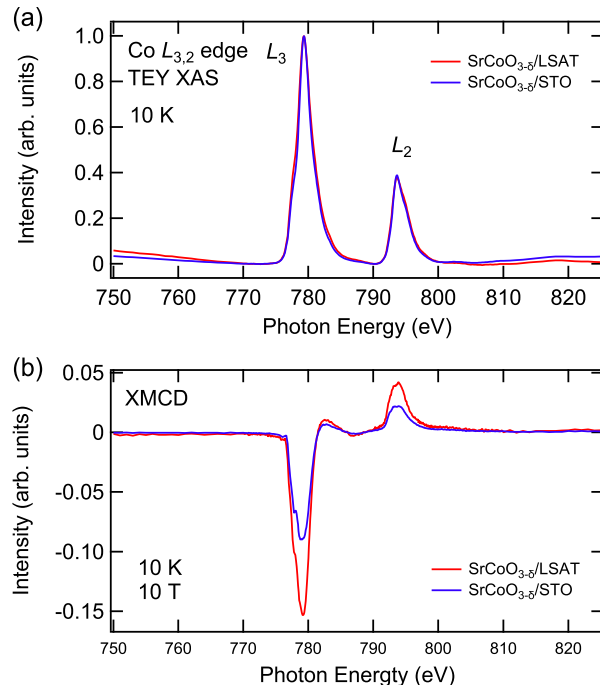


Figure 2: (a) Co $L_{3,2}$ edge TEY XAS spectra of $\text{SrCoO}_{3-\delta}$ thin films on LSAT and STO substrates. (b) XMCD spectra measured at 10 K and 10 T (out of plane direction).

In addition to the static states mentioned above, we also concerned with the photo-induced dynamics of the electronic structures, *i. e.* the interaction between the electronic structures and light. Then, we constructed an equipment for time-resolved x-ray absorption spectroscopy (Tr-XAS) and time-resolved resonant soft x-ray scattering at BL07LSU of SPring-8 [22]. In the first step of the time-resolved measurements, we focused on the valence fluctuation materials such as Eu compounds which show the valence fluctuation between Eu^{2+} with $J = 7/2$ and Eu^{3+} with $J = 0$. $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$ is one of the most suitable materials because it shows the large valence change (valence transition) by external stimuli such as temperature. Although the valence transition by temperature, pressure, and magnetic field were already reported [23–28], the photo-induced valence transition is not well understood. Therefore, we performed Tr-XAS and investigated the photo-induced valence dynamics in $\text{EuNi}_2(\text{Si}_{0.21}\text{Ge}_{0.79})_2$ by using our own equipment. Figure 3 shows the time-resolved XAS change at the energy for Eu^{2+} (1129.6 eV) and Eu^{3+} (1131.5 eV) obtained by PEY mode. We successfully observed the photo-induced valence variation between Eu^{2+} to Eu^{3+} . From the laser fluence dependence measurements of XAS change, the XAS change looks proportional to the fluence, indicating that the photo-induced valence change is different from temperature-induced one. We also clarified the timescale of change, *i. e.* τ_{change} is faster than 50 ps and that of recovery τ_{recovery} is slower than 1 ns. Since the valence of Eu does not completely recover even 10 ns later from the laser excitation, a

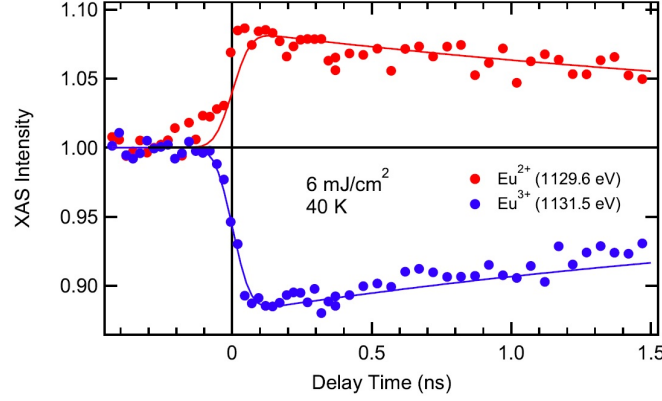


Figure 3: Time-resolved XAS change at the energy for Eu^{2+} (1129.6 eV) and Eu^{3+} (1131.5 eV) obtained by PEY mode. Dots and lines show the experimental results and the fitting ones. The measurements were performed at 40 K under the 1.5 eV laser irradiation with the fluence $\sim 6 \text{ mJ/cm}^2$. Delay time is defined as the time difference between the synchrotron x-ray bunch and the laser pulse. Dotted lines denote delay time = 0.

metastable state excited by photon may exist.

As describe above, the electronic structures in $3d$ and $4f$ electron systems are sensitive to external stimuli and can be controlled by applying various stimuli such as strain and photo irradiation. In the thin films, applying tensile strain, which is not realized by pressure, is considered to be important for finding novel physical properties. The photo-induced state also considered to lead to emergent physics such as photo-induced superconductivity. Therefore, the ultrafast interaction between the novel physical properties controlled by strain and photon should open the door of new physics.

References

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