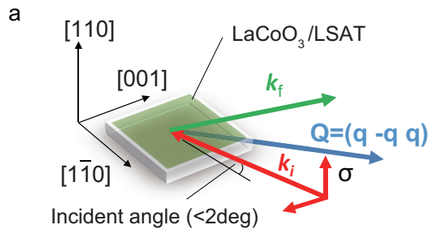
Surface Ordering of Electron Degrees of Freedom in $LaCoO_3$ Thin Film

The surface of condensed matter, accompanied by translational and inversion symmetry breaking, occasionally triggers emergent phenomena, and thus has attracted much attention for a long time. It has been known that the phase transition at the surface sometimes occurs at a different temperature from that of the bulk. The surface melting of orbital order, where the transition temperature at the surface is lower than that of the bulk, has been actually observed for the orbital order in a layered perovskite manganite [1]. In this study, conversely, we discovered unprecedented surface freezing and bulk melting of electronic order in a tensile-strained epitaxial perovskite-type $LaCoO_3$ thin film.

Perovskite-type cobalt oxide $LaCoO_3$, containing Co^{3+} ion with six 3*d* electrons ($3d^6$), is known to show the spin-state transition or spin-crossover by variation of temperature or application of a magnetic field, and has been attracting much attention in these decades. At the lowest temperature, $LaCoO_3$ is a non-magnetic insulator with the low-spin (LS, $t_{2g}^6e_g^0$, $S = 0$) state of Co^{3+}. With increasing temperature, it undergoes an insulator to metal transition at about 500 K concomitantly with the spin-crossover transition to the high-spin (HS, $t_{2g}^4e_g^2$, $S = 2$) state. In the intermediate temperature region, it has been highly controversial whether the spin-state of Co^{3+} is a mixed state of HS and LS, or the intermediate-spin (IS, $t_{2g}^5e_g^1$, $S = 1$) state. The spin state of Co^{3+} ion is sensitive to distortion and the size of CoO_6 octahedron. Indeed, $LaCoO_3$ thin film, where the lattice constants expand compared to the bulk crystal, exhibit the non-LS state of Co^{3+} ion even at the lowest temperature, giving rise to ferromagnetism. For example, $LaCoO_3$ thin film grown on $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) substrate shows spontaneous magnetization below $T_S = 95$ K. Recently, we have determined that the spin-state and orbital order of Co^{3+} ion show up with modulation vector $q_o = (q_o, -q_o, q_o)$ with $q_o = 1/4$ below $T_O = 115$ K; therefore the magnetic moment arises from ferromagnetic order [2]. Since the electronic state is strongly sensitive to the lattice symmetry, the orbital order near the surface might be influenced by the surface effect.

In order to elucidate the surface state of $LaCoO_3$ thin film, we have developed a novel technique of surface sensitive grazing-incident resonant soft X-ray diffraction (GI-RSXS), utilizing the soft X-ray diffractometer installed at BL-16A. The technique makes it possible to probe the super-lattice of electronic order in the depth of a few nm beneath the surface. With this method, we have investigated the surface state of electronic orders, i.e. spin-state, orbital, and spin, in $LaCoO_3$/LSAT(110) thin film (**Fig. 1a**). **Figure 1b** shows an X-ray absorption spectrum (XAS) measured by partial fluorescence yield (FY) at the reflection condition. The absorption peaks at around 777 eV and 791 eV are assigned to the Co L_3- and L_2-edge, respectively. **Figure 1c** shows resonant scattering spectra at (q, q, q) with $q \sim 1/4$. Hereafter, we call the three peaks at the Co L_3-edge as P1, P2 and P3 in increasing order of energy.



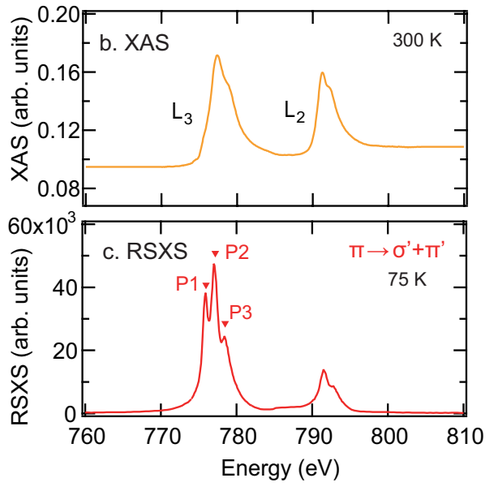


Figure 1: **(a)** Schematic drawing of the grazing-incident resonant soft X-ray scattering (GI-RSXS). The diffracted soft X-rays (k_f) were observed with the incident soft X-rays (k_i) being in the grazing angle condition. The scattering plane was tuned nearly parallel to the sample surface. **(b)** XAS and **(c)** RSXS spectra at the Co $L_{2,3}$-edge of $LaCoO_3$/LSAT(110) thin film.

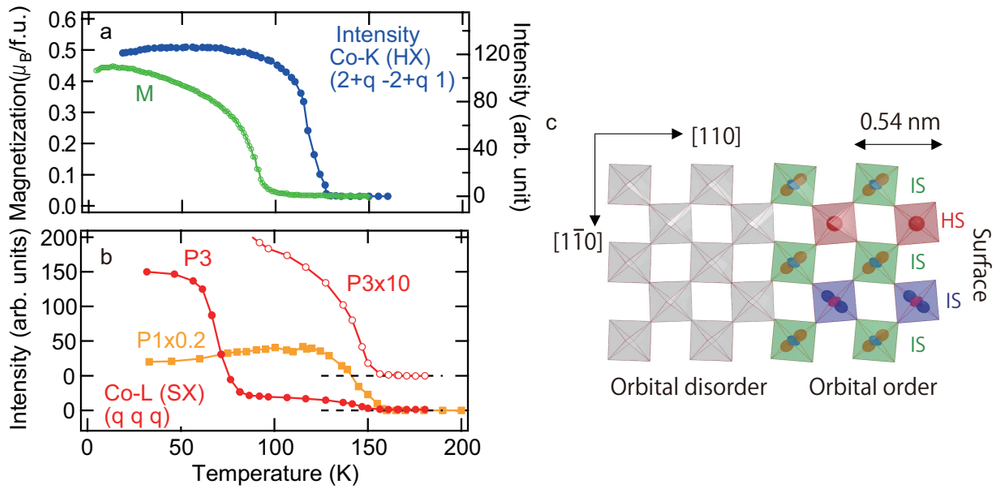


Figure 2: Temperature dependence of **(a)** Magnetization (M) and intensity of super-lattice peaks at ($2 + q$, $2 - q$, q) with $q = 1/4$ measured by hard X-ray diffraction (HX), **(b)** Intensities of super-lattice peaks at (q, $-q$, q) for P1 and P3 of GIRSXS (SX). **(c)** Schematic picture of the surface freezing and bulk melting of orbital order.

Figure 2b shows the temperature dependence of the GI-RSXS peak intensities for P1 and P3 in comparison with that of magnetization and intensity of orbital order observed by resonant X-ray scattering at the Co-K edge (HX) in **Fig. 2a**. The phase transition temperature of orbital order observed by the GI-RSXS method was revealed to be 155 K (P1 and P3), which was 30 K higher than that in the bulk determined by bulk-sensitive hard X-ray diffraction (HX). The results suggest a coexistence of orbital order phases with different transition temperatures in the present thin film. By taking into account the probing depth, it is reasonable that the resonant peaks of GI-RSXS come from the electronically ordered states emerging at the surface, where the transition temperature becomes higher than that of the bulk, that is, surface freezing and bulk melting of orbital order (**Fig. 2c**) [3].

The origin of the observed surface freezing of orbital order is elucidated by considering the reconstruction of electronic order at the surface with broken symmetries. If the lattice reconstruction at the surface occurs so as to stabilize the Jahn–Teller distortion, it could stabilize the orbitally-active intermediate-spin state of Co^{3+} ion and thus the orbital order at the surface.

REFERENCES

[1] S. B. Wilkins, X. Liu, Y. Wakabayashi, J.-W. Kim, P. J. Ryan, H. Zheng, J. F. Mitchell and J. P. Hill, *Phys. Rev. B* **84**, 165103 (2011).
[2] J. Fujioka, Y. Yamasaki, H. Nakao, R. Kumai, Y. Murakami, M. Nakamura, M. Kawasaki and Y. Tokura, *Phys. Rev. Lett.* **111**, 027206 (2013).
[3] Y. Yamasaki, J. Fujioka, H. Nakao, J. Okamoto, T. Sudayama, Y. Murakami, M. Nakamura, M. Kawasaki, T. Arima and Y. Tokura, *J. Phys. Soc. Jpn.* **85**, 023704 (2016).

BEAMLINES

BL-3A, BL-4C and BL-16A

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