

Atomic-resolution study of oxygen vacancy ordering in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ thin films on SrTiO_3 during in situ cooling experiments.

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Oxygen vacancy ordering has been the focus of attention in transition metal oxides owing to the observed influence of vacancy ordering on the magnetic and transport properties. The Brownmillerite structure, which is known to exist in oxygen deficient $\text{SrCoO}_{3-\delta}$, alters the ferromagnetism in SrCoO_3 to antiferromagnetism in $\text{SrCoO}_{2.5}$. [1] The alternating oxygen octahedral and tetrahedral structure changes the Co spin state ordering and thus the magnetic properties. [2] This Brownmillerite structure is also found in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (LSCO) thin films grown on SrTiO_3 (STO) and LaAlO_3 (LAO) substrates. For these thin films, interfacial strain from the substrate is considered to intensify charge disproportionation into Co^{4+} and $\text{Co}^{2+}/\text{Co}^{3+}$ and then form oxygen vacancy ordering. [3] STO also undergoes antiferrodistortive phase transition at 105 K from cubic to tetragonal due to the rotation of the TiO_6 octahedra. [4] The coupling between the rotated TiO_6 octahedra and CoO_6 octahedral at the LSCO/STO interface can distort the CoO_6 octahedral and further tune Co spin-state ordering in oxygen deficient LSCO thin film.

In this contribution, we focus on the atomic-resolution characterization of oxygen vacancy ordering in LSCO epitaxial thin films grown on STO using aberration-corrected scanning transmission electron microscopy (STEM), electron energy-loss spectroscopy (EELS) and in situ cooling experiments. Thin films grown on LAO substrate are used as a reference sample to distinguish the effects of interfacial strain and the STO structural phase transition at low temperature. Here, we utilize the aberration-corrected JEOL ARM200CF equipped with a Gatan Image Filter (GIF) spectrometer to acquire atomic-resolution EELS maps of the oxygen vacancy ordering in the LSCO thin film at both room temperature (300 K) and liquid nitrogen temperature (90 K). We will also utilize electron magnetic circular dichroism measurements at 90 K to measure the local magnetic moment. The in situ cooling experiments are conducted using a Gatan 636 liquid nitrogen double tilt cooling holder.

Figure 1a) shows oxygen vacancy ordering of LSCO films grown on STO. The O *K*-edge EELS signal from dark layer and bright layers of the oxygen vacancy ordered domains during in situ cooling experiment to 90 K is shown in Figure 1b). The oxygen *K*-edge pre-peak appears to split into two peaks in the bright layers, while in dark layer, only one peak appears with an energy between the two peaks. This observation is in good agreement with previous DFT calculations for the octahedral and tetrahedral structures in $\text{SrCoO}_{2.5}$. [2] The Co *L*-edge spectra (Figure 1c) show the difference in Co valence state in the bright and dark layers, respectively. Figure 2a) shows the LAADF image of LSCO/STO tilted by 8° off [100] zone axis to satisfy the requirement of EMCD in the three-beam geometry for convergent beam diffraction (Figure 2b). [5] The resulting EMCD signal at 90 K is shown in Figure 2c) showing a significant difference in the Co *L*-edge ratios between plus and minus position. This suggests the presence of strong magnetic moments in the ordered domains. We will present further analysis and comparison with reference data from LSCO thin films grown on LAO which exhibit different magnetic properties compared to films grown on STO. [6]

References:

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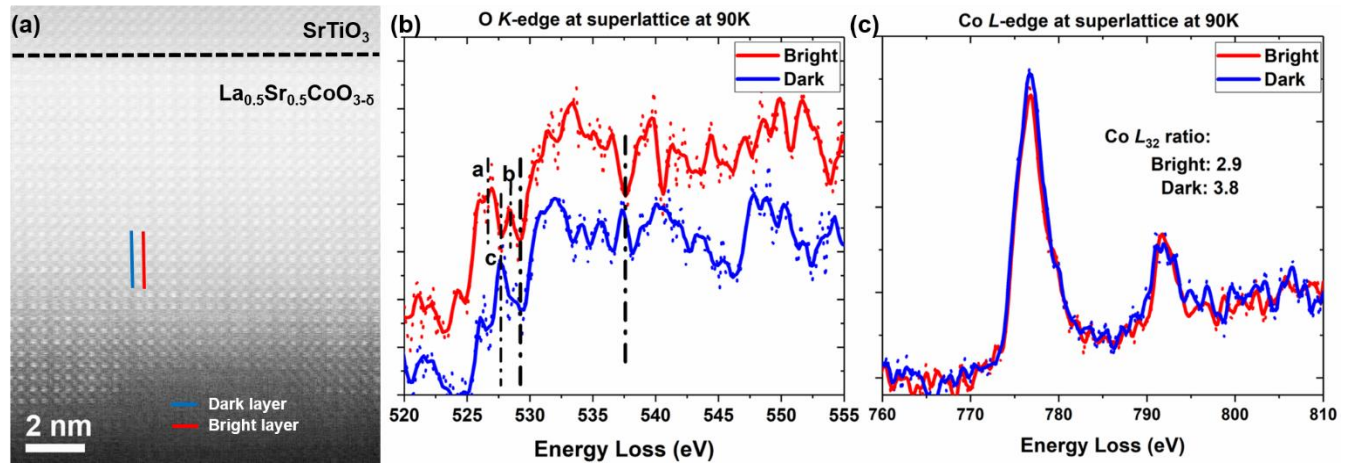


Figure 1. (a) HAADF image of LSCO on STO at 90 K (filtered), bright layer and dark layer is marked in image. (b) O K-edge at bright layer and dark layer at low temperature is showing separately. (c) Corresponding Co L-edge at low temperature reflects the different Co valence state between dark and bright layer.

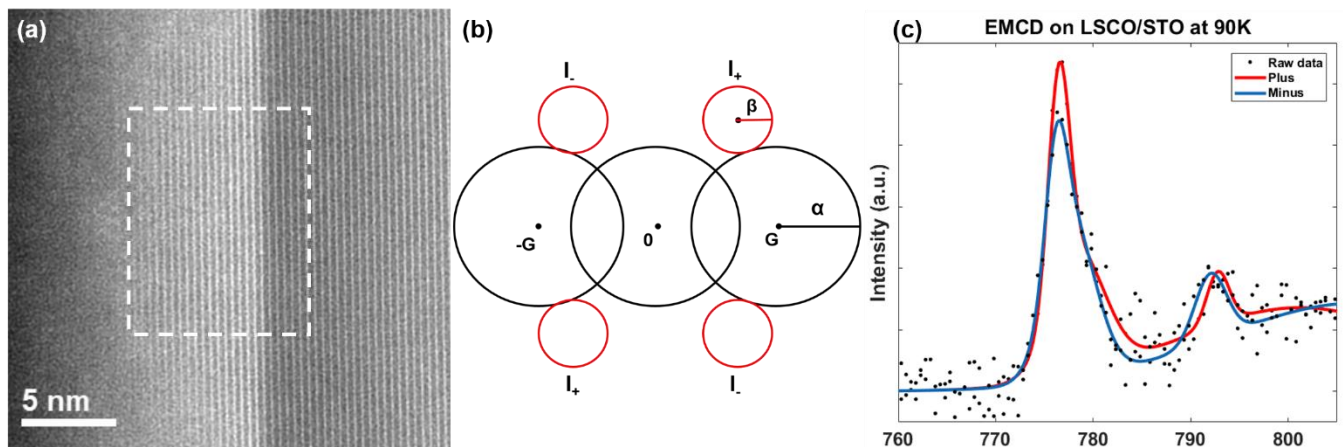


Figure 2. (a) LAADF image of LSCO on STO tilted by 8° off [100] at 90 K (filtered). (b) Schematic setup of EMCD in the three beam condition for convergence angle α , red circles mark the plus/minus position of EELS aperture in the three-beam setup, β is collection angle. (c) EMCD acquired from area (a) at 90 K.