Atomic Imaging of Lattice and Electron Ordering in Tensile-Strained LaCoO3 Films

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Background

Strong multiple interactions between degrees of freedom (spin, orbital, charge, and lattice) in complex oxides give rise to rich electronic phase diagrams and thus to intriguing macroscopic functionalities, such as ferromagnetism, superconductivity, and multiferroicity [1, 2]. A famous example is LaCoO3 (LCO), in which unexpected ferromagnetism occurs in tensile-strained epitaxial LCO thin films, in contrast to paramagnetism in bulk LCO [3]. However, the underlying mechanism of emergent ferromagnetism and spin-state transitions remains controversial, with the tensile strain-induced ferroelastic deformation and oxygen vacancy ordering are known as two possible driving forces. Previous density functional theory (DFT) calculations on the ferromagnetism of tensile-strained LCO have shown that the tensile strain-induced changes in lattice constants are insufficient to stabilize the long-range ferromagnetic order [4]. Suppression of CoO6 octahedral rotations should be considered to modify the eg orbital order configuration and induce a spin-state transition to a ferromagnetic state. To date, no direct experimental evidence has been reported to support this theoretical prediction.

Methods

In this work, we systematically investigate the atomic and electronic structures, and their correlation with the spin-state transition and the ferromagnetic insulating state of high-quality LCO epitaxial films grown by pulsed laser deposition.

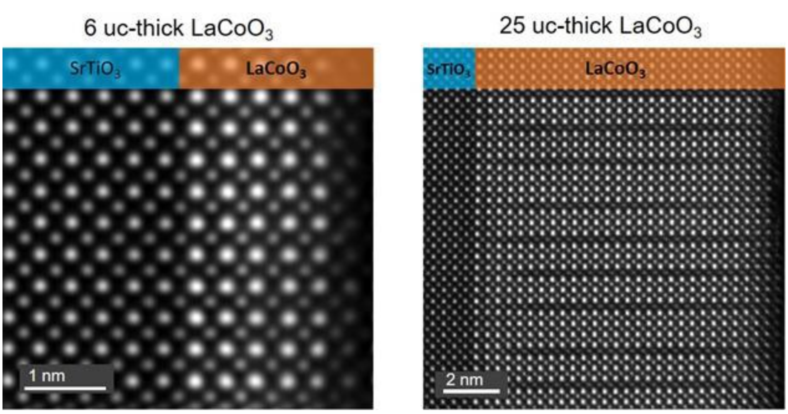
Results

Scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) were used to examine the 6 uc and 25 uc thick LCO films for comparison. High-angle annular dark-field STEM results support the appearance of dark stripes only in the 25-uc thick LCO film, showing well-ordered dark stripes with a period of ~ 3 uc in the interior part of the film (Fig. 1). EELS maps of the interface region show a sharp interface between LCO and STO without the formation of any misfit dislocations. Energy-loss near-edge structure analysis was performed to investigate the electronic structures of the LCO films at the atomic scale. In the dark stripes, the pre-peak of the O-K edge almost disappears, and the intensity of the O-K edge peaks is significantly reduced. Meanwhile, the peak positions of the Co-L2,3 edges shift to lower energies, and the Co-L3/L2 ratio is larger in the dark stripes than in the bright regions. These features fingerprint a reduction of the Co valence state in dark stripes due to the formation of oxygen vacancies. Quantitative analysis of annular bright-field STEM results reveals previously unreported long-range suppression of CoO6 octahedral rotations throughout 25-uc thick LCO epitaxial films, inducing an increase in the angle βCo-O-Co from bulk 163.5o to 172.5o. DFT calculations further unravel the underlying physical mechanism of the spin-state transition to induce an emergent and robust ferromagnetic insulating state.

Conclusion
This work provides new insights into how the interplay between degrees of freedom drives the ferromagnetic insulating state in tensile-strained ferroelastic LCO epitaxial films [5].

Fig. 1 STEM images of the LCO films with thicknesses of 6 uc and 25 uc, respectively.

Graphic:



Keywords:

EELS, STEM, LaCoO3, octahedral rotation

Reference:

1. R. Zhao et al. Nat. Commun. 13 (2022), 2364.
2. H. Wang et al. ACS Nano 14 (2020), 12697-12707.
3. N. Biskup et al. Phys. Rev. Lett. 112 (2014), 087202.
4. J.M. Rondinelli & N.A. Spaldin, Phys. Rev. B 79 (2009), 054409.
5. D. Li, H. Wang et al. Nat. Commun. 14 (2023), 3638.