Supplemental Material for

Strong Orbital Polarization in a Cobaltate-Titanate Oxide Heterostructure

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I. INTERFACE BETWEEN LaCoO3 and LaTiO3 LAYERS

Determining the interfacial structure of the heterostructure discussed in the manuscript is crucial to validate the strong orbital polarization observed in the cobaltate-titanate heterostructure. Especially for the $(LTO)_2/(LCO)_2$ superlattice, intermixing at the interface could lead to stabilization of the double-perovskite La₂TiCoO₆ phase, which would lead to contradictory behavior to the unidirectional charge transfer that leads to strong orbital polarization. Scanning transmission electron microscopy (STEM) measurements on the heterostructures serves as a local probe to image the interfacial character of the $[(LTO)_2/(LCO)_2] \times 10$ superlattice.

The HAADF STEM image shown in Fig. S1(a) shows that the crystalline structure is maintained throughout the entire film, without visible defects. In order to image the chemical composition of the superlattice, we measure an electron energy loss spectroscopy (EELS) spectrum on the selected region, indicated by the yellow dotted overlay. Fig. S1(b) shows

element-specific maps of La, Ti, Co, and Ti+Co, respectively, where one can see an atomically sharp interface between the cobaltate and titanate layers. Due to sample drift during the EELS data acquisition, each map is slightly distorted. It can be further visualized in Fig. S1(c), where the relative intensity of Ti and Co is plotted as a function of distance from top to bottom along the z-direction in the region selected in Fig. S1(b). If significant intermixing at the interface occurred between the LTO and LCO layers, the Ti and Co signals would be mixed more evenly throughout the layers as the intermixing drives the system towards La(Co,Ti)O₃, instead of the distinct Ti and Co signals that are observed. The La EELS map in Fig. S1(b) also shows an even electron density distribution of La throughout the region. A non-negligible degree of La vacancies would be visible as variations in the La EELS map or HAADF STEM image.



Figure S1. (a) HAADF STEM image of an $[(LTO)_2/(LCO)_2] \times 10$ superlattice. (b) Element-specific EELS map of the region specified by yellow box in figure (a). (c) Intensity of Ti and Co signal derived from the EELS map as a function of distance along the yellow arrow (c-axis) drawn in figure (b).

In addition, x-ray diffraction (XRD) and x-ray reflectivity (XRR) measurements along the (00L) direction reveal a sharp interface and are shown in Fig. S2. The XRD shows sharp superlattice peaks around (0 0 3/4) and (0 0 5/4), which indicates that the repeating unit consists of four atomic layers. The intensity of these superlattice peaks is sensitive to the quality of the

interface and would disappear in the case of a Co-Ti intermixed interface. The superlattice peak is also visible in the XRR plotted in the inset of Fig. S2 as a peak at a two-theta value near 5.2 degrees. The fit for the XRR using Rigaku GlobalFit is plotted with a black line and shows that the interfacial roughness is less than one unit cell. For comparison, we simulate the XRR spectra with large interfacial roughness, ~1nm, drawn with a blue line, which shows no superlattice peak and only finite thickness oscillations. Combining what we observe in STEM-EELS and the x-ray measurements, we conclude that the alternating behavior of two titanate and cobaltate layers is a global character, and that sharp interfaces occur throughout the film.



Figure S2. X-ray diffraction along the (00L) direction around the (001) Bragg peak for an $[(LTO)_2/(LCO)_2] \times 10$ heterostructure. The STO (001) peak and superlattice (SL) (001) peaks are indicated in the figure. The x-ray reflectivity (XRR) measurement is shown in the inset, with the fit drawn as a black line. The blue line shows the simulated XRR spectra with 1nm interfacial roughness.

II. EFFECT OF INTERFACIAL STRUCTURE ON THE ORBITAL POLARIZATION

As discussed in section I above, maintaining a sharp interface between the titanate and cobaltate layers is crucial in realizing the orbital polarization in the heterostructure. We use first principles calculations to study the effect of interfacial structure on the orbital polarization to further address that the electronic structure discussed in the manuscript arises from the (LTO)₂/(LCO)₂ superlattice free of interfacial intermixing. Theoretical calculations show that the intermixing of Ti and Co at the interface reverses the direction of the orbital polarization, opposite from what is shown in the experiment. We begin with the ideal $(LTO)_2/(LCO)_2$ superlattice on the STO substrate considered in the main text (Fig. S3(a)), choose one Co, and switch its position with its nearest neighbor Ti across the interface. The resulting system is relaxed to its ground state (Fig. S3(b)). The in-plane and out-of-plane hole occupancies are computed across all Co atoms in this system and the resulting r value (Eq. (1) in the main text) is r = 1.004, compared to r = 0.868 for the layered (LTO)₂/(LCO)₂ superlattice. Note that r = 1indicates no orbital polarization with equal hole occupancies in in-plane and out-of-plane orbitals. This is a significant change outside the experimental uncertainties in the measurement of r. We conclude that the observed orbital polarization is consistent with only a small degree of intermixing across the interface.



Figure S3. $(LTO)_2/(LCO)_2$ superlattice with (a) ideal interface and (b) intermixed interface.

III. STRUCTURAL MEASUREMENT AND ANALYSIS

The atomic structures of oxide thin films and heterostructures are determined from an analysis based on high-resolution synchrotron x-ray diffraction measurements along the crystal truncation rods (CTRs). The measurements are made at room temperature using a six-circle diffractometer at the beamline 33-ID-D at the Advanced Photon Source, US. The CTRs are measured along the specific directions in reciprocal space defined by the crystallographic axes of the SrTiO₃ substrate. The measured intensities are further analyzed to yield a real-space three-dimensional electron density map (EDM) through the Coherent Bragg Rod Analysis (COBRA) thin film phase retrieval method [42, 43].

Fig. S4(a) and S4(b) shows CTRs measured for the LCO thin film and the single-repeat $(LTO)_2/(LCO)_2$ heterostructure, which is used in obtaining the EDM in Fig. 2(a) and 2(b), respectively, in the main text. The EDM of the heterostructure in Fig. 2(b) shows some discrepancy between the apical and planar oxygen, which may be due to the disorder (asymmetry) in the oxygen octahedral distortion present in the system.



Figure S4. Measured crystal truncation rods (blue circles) and the fits (red line) for (a) the LCO thin film and (b) the single-repeat $(LTO)_2/(LCO)_2$ heterostructure. The indices in each plot refer to the (h, k, l) measured for each CTR.

To test the validity of our value of $U_{Co} = 2.5 \text{eV}$ for describing LCO, we test different magnetic configurations of bulk LCO on an STO substrate within GGA+U. We consider 4 different magnetic configurations – ferromagnetic (FM), A-type antiferromagnetic (A-AFM), C-type antiferromagnetic (C-AFM) and G-type antiferromagnetic (G-AFM). We also consider various Co spin configurations: only high-spin Co, only low-spin Co, and 3 different types of mixture of high-spin and low-spin Co atoms (A-type, C-type, and G-type). We confirm that the FM with G-type order of high- and low-spin Co atoms is the ground state. Table 1 shows the relative energies of the different phases. The calculated r value (Eq. (1) in the main text) for this system is r = 1.157.

Configuration	E (meV/Co)
NM	0.0
FM + G-OO	-141.8
A-AF + G-OO	-127.2
C-AF + G-OO	-127.2
G-AF + G-OO	-127.2
FM.HS	57.3
A-AF.HS	111.9
C-AF.HS	15.7
G-AF.HS	-91.2

Table 1. Energies of different magnetic configurations of bulk LaCoO₃ on STO substrate relative to the energy of the nonmagnetic state.