Tunable Ferromagnetism in LaCoO₃ Epitaxial Thin Films

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1. Introduction

Ferromagnetic insulators (FM-Is) are essential components in dissipation-less spintronic devices with highly suppressed leakage currents.[1,2] They generate pure spin currents by filtering charges and introducing spins into adjacent nonmagnetic layers via the magnetic proximity effect.[1–8] However, FM-Is are scarce in nature compared to more conventional FM metals because the general superexchange mechanism in insulators promotes antiferromagnetic (AFM) ordering.[9–12] Iron yttrium garnet (YIG), α-Fe₂O₃, spinel CoFe₂O₄, EuS, EuO, and strained EuTiO₃ thin films are some examples of FM-I materials.[13–19] Epitaxially strained LaCoO₃ (LCO), e.g., deposited on SrTiO₃ (STO), (LaAlO₃)₀·₇(Sr₂AlTaO₈)₀·₃ (LSAT), or YAlO₃ substrates, is an emerging FM-I with a Curie temperature above the liquid N₂ temperature (Tₘ ≈ 80 K).[20,21]

Long-range FM ordering in epitaxial LCO thin films is facilitated by strain-induced lattice distortions. Although bulk LCO is nonmagnetic with a rhombohedral crystal structure, the tensile strain in the thin film is known to induce monoclinic and tetragonal phases, resulting in the spin-ordered state.[20,22,23] The large and facile modification of the crystalline symmetry originates from the ferroelastic nature of LCO, which favors the formation of twin-domain structures under mechanical pressure or epitaxial strain.[24–31] Such twin-domain structures have been observed as dark stripe patterns in high-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) imaging.[20,23,32,33] Detailed microstructure analyses using HAADF STEM on (100)-oriented LCO thin films enable classification of basic lattice units into compressed- (c-unit), tensile-stretched- (t-unit), and bulk-units (b-unit).[23] Among these, c-units with coexisting low (LS) and high spin (HS)-states of the Co spin configuration were found to be responsible for the FM phase. It should be noted that the FM phase, characterized by Tₘ, in the (100)-oriented LCO thin film was mostly unchanged. As summarized in Table 1, the reported values of Tₘ of (100)-oriented LCO thin films are mostly in the range of 80–85 K,[20,34–45] despite the large difference in the degree of epitaxial strain. (Note that Tₘ might decrease further below 80 K, if the crystalline quality is not ideal.[43] Such unsusceptible behavior in Tₘ suggests that the magnetically active c-units are highly resilient against orthogonal stress, again taking advantage of the ferroelastic nature of LCO.[21]

Modifications in the crystallographic orientation lead to disparate lattice symmetry, offering extra tunability in the functional properties of epitaxial thin films. Even though an identical film/substrate system is used, implying the same degree of nominal epitaxial strain, the structural symmetry of the thin film can be modulated by the crystallographic orientation of the substrate, leading to stress that is not orthogonal to the lattice. For instance, the FM Tₘ of epitaxial SrRuO₃

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thin films can be increased from 147 to 157 K as the crystallographic orientation changes from (100) to (111), respectively because of the reduced spin dimensionality within the trigonal symmetry. [46] In epitaxial La$_0.7$Sr$_0.3$MnO$_3$ thin films, (110) and (111)-oriented thin films exhibit larger spin moments than (100)-oriented thin films. [47] As the crystallographic orientation of LaAlO$_3$ thin films on KTaO$_3$ substrates changed from (100) to (110) or (111), emergent superconductivity was observed. The superconducting critical temperatures could be further modulated between the (110) and (111)-oriented thin films, with the values of 1 and 2 K, respectively. [48–50] Because the crystallographic orientation determines the structural symmetry of the lattice unit, it is expected to modify the robust FM-I phase of LCO epitaxial thin films as well. This strategy would provide fundamental insight into the structure–property relationship of LCO, which would not have been possible using only (100)-oriented thin films with different strain states, but the same type of orthogonal stress. Indeed, studies on LCO thin films with crystallographic orientations other than (100) are highly limited and report inconsistent $T_C$ values, as shown in Table 1, and a systematic comparison among the thin films with different orientations has not been conducted thus far.

In this study, we demonstrate a large modulation of the FM phase in LCO epitaxial thin films, including the substantial tuning of $T_C$ by tailoring the structural symmetry via crystallographic orientation control. We fabricated LCO thin films on (100)-, (110)-, and (111)-oriented STO substrates using pulsed laser epitaxy (PLE). The structural quality and crystallographic symmetry of the thin films have been determined by X-ray diffraction (XRD) measurements and HAADF STEM imaging. The FM phases for the (100)-, (110)-, and (111)-oriented LCO thin films have $T_C$s of 81.5, 90.2, 76.1 K, respectively. The large modulation of the FM $T_C$, i.e., $\approx 18\%$ enhancement in the (110)-oriented thin film compared to the (111)-oriented one, captures the effectiveness of the crystallographic symmetry control on the lattice units. The physical origin of the $T_C$ enhancement was investigated by characterizing the microscopic lattice units, electronic structure measurements, and theoretical calculations. In particular, the reduced crystal-field splitting energy and enhanced Co–O charge transfer in the (110)-oriented thin film led to the considerably enhanced FM properties.

### 2. Results and Discussion

The global lattice structures of the LCO thin films (30 nm) were characterized using XRD to reveal the systematic crystallographic orientation dependence. Figure 1a shows the XRD

| $T_C$ [K] | $H$ [Oe] | Substrate | Orientation | Thickness [nm] | Reference |
|----------|---------|-----------|-------------|----------------|-----------|
| 43.2     | 200     | LAO       | (100)       | 100            | Phys. Rev. B 77, 014434 (2008) |
| 69.2     | 200     | SLAO      | (100)       | 100            |           |
| 71.6     | 200     | SLGO      | (100)       | 100            |           |
| 76.0     | 200     | LSAT      | (100)       | 100            |           |
| 77.6     | 200     | STO       | (100)       | 100            |           |
| 80/87    | 200     | LSAT      | (100)       | 8/50           | Phys. Rev. B 79, 024424 (2009) |
| 86       | 2000    | STO       | (100)       | 100            | Eur. Phys. J. B 76, 215 (2010) |
| 75       | 2000    | LAO       | (100)       | 100            |           |
| 85       | 2000    | LSAT      | (100)       | 100            |           |
| 87       | 2000    | PMN-PT    | (100)       | 100            |           |
| 84       | 2000    | SLAO      | (100)       | 100            |           |
| 80       | 2000    | STO/LSAT  | (100)       | 20-90          | J. Appl. Phys. 105, 07E503 (2009) |
| 76-83    | 50      | LAO       | (100)       | 30-95          | J. Appl. Phys. 109, 07D771 (2011) |
| 75.9/81.2| 50      | STO/LSAT  | (100)       | 15             | Phys. Rev. B 91, 144418 (2015) |
| 80       | 1000    | STO/LSAT  | (100)       | 30             | Nano Lett. 12, 4966 (2012) |
| 94       | 1000    | LSAT      | (110)       | 60             | Phys. Rev. Lett. 111, 027206 (2013) |
| 24       | 1000    | LSAT      | (111)       | 60             | Phys. Rev. B 92, 195115 (2015) |
| 92/90    | 500     | STO/LSAT  | (110)/(100) | 35/38          |           |
| 85       | 500     | STO/LSAT  | (100)       | 30             | AIP Advances 8, 056317 (2018) |
| 85       | 500     | STO       | (100)       | 12             | PNAS 115, 2873 (2018) |
| 78       | 500     | STO       | (100)       | 70             | Curr. Appl. Phys. 28, 87 (2021) |
| 50       | 500     | STO       | (111)       | 80             | Phys. Status Solidi B 259, 2100424 (2021) |
| 76.1-90.2| 1000    | STO       | (100), (110) and (111) | 30 | This work |
θ–2θ scans for the LCO thin films epitaxially grown on the (100)-, (110)-, and (111)-oriented STO substrates. Fine thickness fringes are commonly observed along with the corresponding LCO peaks (Figure 1a; Figure S1a,b, Supporting Information), indicating consistent crystalline phases with atomically smooth surfaces and interfaces. Atomic force microscopy images show atomically smooth surfaces of the epitaxial LCO thin films with low surface roughness of <1 u.c. (Figure S2, Supporting Information). Figure 1b shows the XRD reciprocal space maps around the (103), (120), and (212) Bragg reflections for the LCO thin films with the (100), (110), and (111) orientations, respectively. Despite the difference in the crystallographic orientations, all films were fully strained to the substrates. Although the nominal lattice mismatch between the thin film and the substrate is identical, it is important to note that the degree of strain still differs owing to symmetry modification. The difference in the degree of strain is shown in Figure 1c, in terms of the pseudocubic unit cell volume (V_u.c.) and out-of-plane strain (ε_{oop}), High-resolution HAADF STEM images for LCO thin films grown on d) (100), e) (110), and f) (111) STO substrates. Dark stripe patterns are observed in all crystallographic orientations of the LCO thin films. Two distinct regions are marked with white horizontal lines. Region I near the interface is a “uniform region” without the dark stripe patterns. Region II away from the interface contain the dark stripe patterns.

**Figure 1.** Crystal structures of epitaxial LCO thin films with various crystallographic orientations: a) XRD θ–2θ scans of epitaxial LCO thin films (#) grown on STO substrates with different orientations. b) XRD reciprocal space maps (RSM) of the (100)-, (110)-, and (111)-oriented LCO thin films, shown around the (103), (120), and (212) Bragg reflections of the STO substrates, respectively. Crystallographic orientation-dependent c) unit cell volume (V_u.c.) and out-of-plane strain (ε_{oop}). High-resolution HAADF STEM images for LCO thin films grown on d) (100), e) (110), and f) (111) STO substrates. Dark stripe patterns are observed in all crystallographic orientations of the LCO thin films. Two distinct regions are marked with white horizontal lines. Region I near the interface is a “uniform region” without the dark stripe patterns. Region II away from the interface contain the dark stripe patterns.

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The LCO thin films commonly exhibit a coherent alignment of the atomic columns without any defects and/or misfit dislocations at the interfaces. Interestingly, distinctive dark stripe patterns (with ≈3 u.c. periodicity) were observed, above a certain thickness of the interfacial layer. We carefully exclude the presence of oxygen vacancy ordering at the dark stripe patterns by electron energy loss spectroscopy (EELS) measurements (Figure S3, Supporting Information). While the dark stripe patterns have been frequently recognized for the high-quality (100)-oriented LCO thin films,[20,23,32,33] we report similar patterns in (110)- and (111)-oriented thin films for the first time. The LCO thin films can be categorized into two regions considering the dark stripe pattern, i.e., Region I (near the interface) and Region II (above the interface).[20] Region I is free of the dark stripe patterns, suggesting a conventional fully strained state. The thickness of Region I is the thickest for the (110)-oriented thin film, and the thinnest for the (111)-oriented thin film, consistent with the fact that the (110)-oriented thin film has the largest deviation in V_u.c. from the bulk value (55.604 Å³). On the other hand, Region II presents twin-domain structures due to the ferroelastic relaxation of the LCO thin film, as mentioned earlier. For more detailed structural analyses, we measured the distance of La columns in Region II along the two orthogonal axes perpendicular to the electron-beam direction in the HAADF STEM images (Table S1, Supporting Information). The lattice structure of magnetically active c-units,[21] is distorted differently depending on the substrate orientations, suggesting that the robust structure can be tuned by symmetry constraints. The volume of c-unit is the largest in the (110)-oriented LCO thin film, while it is the
smallest on the (111)-oriented film, which is consistent with the XRD results.

The FM ordering in the LCO thin films is strongly coupled to the crystallographic symmetry. Figure 2a shows the temperature-dependent magnetization, M(T), of the LCO thin films under field-cooled (FC, 1000 Oe) cooling along the in-plane direction. A clear FM transition with a sudden upturn of M(T) is observed at 81.5, 90.2, and 76.1 K for the (100)-, (110)-, and (111)-oriented LCO thin films, respectively. The inset of Figure 2a shows the linear extrapolation of M(T) for the T_C determination. The magnetic-field-dependent magnetization, M(H), measured at 2 K, demonstrates a clear FM hysteresis loop, as shown in Figure 2b. The values of saturation magnetization (M_s) and remanent magnetization (M_r) are summarized in Figure 2c,d, respectively, exhibiting consistent orientation-dependent trends with T_C (Figure 2e). Indeed, a substantial enhancement in ferromagnetic properties, i.e., T_C (≈18%), M_s (≈36%), and M_r (≈49%), is observed, by comparing the (110)-oriented thin film to the (111)-oriented one. The same trend was observed from the Curie–Weiss (C–W) law fitting of the M(T) curves, in terms of the effective ratio of the HS-state (Figure S4, Supporting Information).[29] Within the prevailing spin configuration model of LCO epitaxial thin films,[23,29,33,51] in which the LS- and HS-states coexist, the effective ratios of HS-state are 68.4%, 69.5%, and 52.2%, respectively, for the (100)-, (110)-, and (111)-oriented LCO thin films. X-ray photoelectron spectroscopy results consistently support that the (110)-oriented LCO thin film exhibits the largest HS state ratio (Figure S5, Supporting Information).[29]

The electronic structures of LCO thin films provide a microscopic mechanism for FM modulation with distinctive crystallographic symmetries. In particular, we performed spectroscopic ellipsometry to capture minute changes in the electronic band structures of the LCO thin films. The real part of the optical conductivity, σ_1(ω), of bulk LCO,[20,52] below 4 eV, σ_1(ω) consists of two Lorentz oscillators centered at ≈1.5, and ≈3.0 eV, labeled as the β (d-d transition within Co 3d orbitals, brown dotted lines) and γ peaks (charge transfer transition, O 2p → Co 3d, green dotted lines), respectively, as shown in Figure 3b.[52] The quantitative values of the peak positions (ω) and spectral weights (SW) of the β and γ peaks are summarized in Figure 3c,d. The (110)-oriented LCO thin film exhibited a lower ω for both the β and γ transitions compared to those of the (100)- and (111)-oriented thin films. In addition, the (110)-oriented thin film showed a larger SW value for both the β and γ transitions compared to those of the (100)- and (111)-oriented thin films.

The strongly intertwined electronic structure and FM properties of the LCO epitaxial thin films modulated by crystallographic orientation are illustrated in Figure 4. When we consider an HS configuration within LCO, which is necessary for the FM ordering, the net spin moment can be evaluated from the energy states of the electron orbitals within the atomic picture. In particular, this tendency can be qualitatively captured by taking into account the energy cost (Δ) of the spin-state transition from an LS to HS configuration. A larger spin moment, and hence stronger FM behavior, is expected for a smaller Δ. Δ can be defined as, Δ = Δ_CF − Δ_AH − W/2, where Δ_CF and Δ_AH are the crystal-field splitting and Hund energies, respectively, and W is the bandwidth.[29] Thus, the competition between Δ_CF, Δ_AH, and W determines Δ. Both the bond length (r_CO−O average distance between Co and O ions) and bond angle (θ, Co–O–Co angle) influence Δ and the energy scales,[51,53,54] in which Δ_CF = r_CO−O^−5 and W = r_CO−O^−3.5cos(π − θ).[29,55] Apparently, Δ_CF has a stronger dependence on r_CO−O, and hence, is a dominant factor for determining Δ. For the CoO_6 octahedra, Δ_CF is determined by the energy difference between the Co t_2g and e_g states, as depicted in Figure 4a. Because Δ_AH is directly related to ω_B and partially related to ω_F, the observation of the lowest ω_F and ω_B in the (110)-oriented LCO thin film (Figure 3c) indicates that the film has the lowest Δ_AH, leading to a stronger FM spin ordering (small Δ, Figure 2).[55,56] We can directly infer this insight from the lattice structure, as the (110)-oriented...
LCO thin film has the largest $V_{\text{u.c.}}$ among the films studied (Figure 1c,d; Table S1, Supporting Information). We further note that the charge transfer transition from the O 2p to Co 3d orbitals, depicted by $SW_{\text{t}}$, is the largest for the (110)-oriented LCO thin film. We expect that (110)-oriented LCO thin film to have $\theta$ value closer to 180° than the other orientations, as it has the largest $V_{\text{u.c.}}$, that would lead to a stronger charge transfer between Co and O orbitals. It has been reported that a stronger charge transfer transition leads to enhanced magnetic ordering in LCO thin films. In general, the facile spin and charge transfer between Co 3d and O 2p orbitals introduces a strong FM superexchange interaction. 

The total and partial density of states (DOS) calculated by ab-initio density functional theory (DFT) calculations consistently support the modulation in $\Delta_{\text{CF}}$ and charge transfer between the Co and O orbitals, as shown in Figure 4b. We used the experimental lattice parameters obtained from the HAADF STEM analyses (Table S1, Supporting Information) for the calculations. Previously, it was found that the rocksalt-type HS/LS-FM order within the $c$-unit is responsible for the magnetic properties of epitaxially strained LCO. Therefore, we used the rocksalt-type HS/LS-FM order, which is the most stable state regardless the crystallographic symmetry (Table S2, Supporting Information). The modulated optical transitions $\beta$ (brown arrow) and $\gamma$ (green arrow) from the DFT calculations are systematically reproduced, as shown in the inset of the bottommost panel of Figure 4b. As the crystallographic orientation changes from (111) to (100) to (110), the separation between the Co–O hybridized states and the Co 3d states increases on the order of 0.1 eV, which is consistent with the results of $\sigma_{\text{t}}(\omega)$ shown in Figure 3.

Recently, diffusion Monte Carlo calculations showed that the magnetic ground state of the LCO thin film highly depends on the La–La distance, with the rocksalt-type HS/LS-FM order becoming the most stable state at a specific compressive strain. In terms of the exchange mechanism, this order mainly results from correlation superexchange, which refers to the magnetic interaction whereby two electrons of $O^{2-}$ mediate the exchange coupling between neighboring HS and LS Co$^{3+}$. More specifically, the double occurrence of AFM superexchange coupling along the HS Co$^{3+}$ $d_{x^2-y^2}$ – $O^{2-}p_{\sigma}$ – LS Co$^{3+}$ $d_{x^2-y^2}$ – $O^{2-}p_{\sigma}$ – HS Co$^{3+}$ $d_{x^2-y^2}$ pathway could facilitate the FM ordering (Figure S6, Supporting Information). In this mechanism, the net spin moment of LS Co$^{3+}$ $d_{x^2-y^2}$ (which would be empty in the ideal LS Co$^{3+}$ configuration) may be a descriptor for the superexchange interaction strength because it reflects the spin-polarized charge transfer from neighboring $O^{2-}p_{\sigma}$ orbitals.

To quantitatively assess the spin-polarized charge transfer, we analyzed the eigen occupations of the $d$ orbital density matrix of the HS and LS Co$^{3+}$ stabilized as the HS/LS FM order in the $c$-units of (100), (110), and (111)-oriented LCO thin films (Table 2). The eigen occupations are fictitious auxiliary physical quantities, which often provide important insights into the orbital states of the transition metal ions. The HS Co$^{3+}$ was confirmed to have an HS $d_{\text{t}}$ orbital configuration with all majority-spin orbitals and the minority-spin $d_y$ orbital fully occupied, but the other minority-spin orbitals almost empty. The result for LS Co$^{3+}$ shows that the three lower-energy $d$ orbitals, i.e., $d_{xy}$, $d_{yz}$, and $d_{zx}$, are almost fully occupied, which is consistent with LS Co$^{3+}$. In contrast, the two higher-energy $d$ orbitals (the $e_g$ orbitals), i.e., $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals, are expected to be empty in the ideal LS Co$^{3+}$ orbital configuration, but as mentioned above, they are partially occupied because of the spin-polarized charge transfer from $O^{2-}$. Interestingly, the net spin moment of LS Co$^{3+}$ $d_{x^2-y^2}$ estimated by the difference between the eigen occupations of its majority- and minority-spins, was the largest (0.1562) in the LCO with the (110) orientation. This DFT calculation result directly implies that the spin-polarized charge transfer, which determines the superexchange interaction strength, occurs more actively in the (110)-oriented LCO thin films than in the (100)- or (111)-oriented films. In addition, local magnetic moments of HS Co$^{3+}$ within the HS/LS-FM order are summarized in Table S3 (Supporting Information). Upon comparison, the local magnetic moment
was the largest in the c-unit stabilized the (110)-orientation, followed by that in the (100)- and (111)-orientations, which also matches with experimental results.

3. Conclusion

We studied an unexpectedly large modulation of ferromagnetic properties, including a sizable increase in $T_C$, in crystallographic orientation dependent-LCO thin films. By systematically controlling the crystallographic symmetry, we obtained LCO thin films with various structural parameters. The clear FM phases strongly coupled to the crystallographic symmetry demonstrated that the (110)-oriented LCO thin film exhibited highly enhanced FM properties. Optical spectroscopy and DFT calculations revealed that LCO thin films with small $\Delta_{CF}$ and large spin-polarized charge transfer between the Co 3d and O 2p orbitals facilitate FM ordering in the (110)-oriented LCO thin film. This study implies that the symmetry constraint is an efficient tuning parameter for the exchange interaction strength in epitaxial LCO thin films, in which ferromagnetism is highly robust against conventional strain due to its ferroelastic nature.

4. Experimental Section

Epitaxial Thin Film Growth: High-quality LCO epitaxial thin films were fabricated using PLE on conventionally HF-treated STO substrates with various orientations [(100), (110), and (111)]. An excimer KrF laser ($\lambda = 248$ nm, IPEX864; Lightmachinery) with a fluence of 0.9 J cm$^{-2}$ and a repetition rate of 2 Hz was used. The thin films were synthesized at 500 °C under an oxygen partial pressure of 100 mTorr. Each set of thin films with distinctive orientations (with the same number of laser shots) was simultaneously fabricated.

Atomic and Crystal Structure Characterization: The crystalline structure and lattice parameters of the LCO thin films were characterized using high-resolution XRD (PANalytical X'Pert Pro). HAADF STEM measurements were performed on a Nion UltraSTEM200 microscope operated at 200 kV. The microscope was equipped with a cold field emission gun and a corrector of third- and fifth-order aberrations for sub-angstrom resolution. The collection inner half-angle for the HAADF STEM was 65 mrad. Cross-sectional TEM specimens were prepared via Ar ion milling after conventional mechanical polishing.

Surface Characterization: Atomic force microscopy measurements were performed using a commercial system (Park Systems, NX10) to examine the surface topography and roughness.

Magnetization Measurements: A magnetic property measurement system (MPMS3; Quantum Design) was used to characterize the in-plane magnetic properties of the thin films. The temperature-dependent magnetization, $M(T)$, was measured from 300 to 2 K under a...
Table 2. Orbital occupations of the HS and LS states for LCO thin films: A summary for occupations of $t_{2g}$ ($d_{x^2}$, $d_{y^2}$, and $d_{z^2}$) and $e_g$ orbital ($d_{x^2−y^2}$ and $d_{z^2−r^2}$) for HS and LS states.

|         | HS       | LS       | Difference |
|---------|----------|----------|------------|
| $e_g$   |          |          |            |
| (100)   | $3z^2−r^2$ | 1.0211   | 0.2333    | 0.7878     |
|         | $x^2−y^2$ | 1.0635   | 0.4318    | 0.6317     |
| $t_{2g}$ | $xy$     | 0.9726   | 0.9721    | 0.0005     |
|         | $yz$     | 0.9943   | 0.2213    | 0.7730     |
|         | $zx$     | 0.9932   | 0.2175    | 0.7757     |
| (110)   | $3z^2−r^2$ | 1.0215   | 0.2304    | 0.7911     |
|         | $x^2−y^2$ | 1.0601   | 0.4279    | 0.6322     |
| $t_{2g}$ | $xy$     | 0.9733   | 0.9730    | 0.0003     |
|         | $yz$     | 0.9932   | 0.2154    | 0.7778     |
|         | $zx$     | 0.9920   | 0.2167    | 0.7753     |
| (111)   | $3z^2−r^2$ | 1.0250   | 0.2318    | 0.7932     |
|         | $x^2−y^2$ | 1.0725   | 0.4331    | 0.6394     |
| $t_{2g}$ | $xy$     | 0.9732   | 0.9727    | 0.0005     |
|         | $yz$     | 0.9957   | 0.2333    | 0.7624     |
|         | $zx$     | 0.9957   | 0.2332    | 0.7625     |

magnetic field of 1000 Oe. The magnetic field-dependent magnetization, $M(H)$, was measured at 2 K.

Chemical Composition Characterization: X-ray photoelectron spectroscopy (XPS; AXIS SUPRA, KRATOS Analytical) with Al Kα radiation was used to study the chemical state and composition of the LCO thin films. All the X-ray photoelectron spectra were calibrated using the C 1s bonding peak (284.5 eV). The Co 2p and valence states of the LCO thin films were deconvoluted using Gaussian–Lorentz curves.

Optical Spectroscopy: The optical conductivity of the LCO thin films was measured using spectroscopic ellipsometry (J. A. Woollam Co., Inc.). A wavelength range from mid-infrared to UV (0.6–6.2 eV) with incident angles of 60° and 65° was used. A three-layer model analysis (surface roughness (50% of material and 50% of voids), LCO, and STO layers) to obtain dielectric functions and optical conductivities of the thin films was employed.

Theoretical Calculations: Ab-initio DFT calculations were performed using the Vienna ab-initio simulation package (VASP) code. The Perdew–Burke–Ernzerhof plus Hubbard correction (PBE + U) was used for the exchange-correlation functional, in which the double-counting interactions were corrected using the full localized limit (FLL). The values used for the on-site direct Coulomb parameter (U) and the anisotropic Coulomb parameter (J) were 4.5 and 1.0 eV, respectively. A plane wave basis set at a cutoff energy of 600 eV was used to expand the electronic wave functions, and the valence electrons were described using projector-augmented wave potentials. All atoms were relaxed by the conjugate gradient algorithms until none of the remaining Hellmann–Feynman forces acting on any atoms exceeded 0.02 eV Å⁻¹.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
crystallographic orientation, ferromagnetic insulators, ferromagnetic ordering, perovskite LaCoO₃, pulsed laser epitaxy

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