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Strain-induced high-temperature perovskite ferromagnetic insulator

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Ferromagnetic insulators are required for many new magnetic devices, such as dissipationless quantum-spintronic devices, magnetic tunneling junctions, etc. Ferromagnetic insulators with a high Curie temperature and a high-symmetry structure are critical in integration with common single-crystalline oxide films or substrates. So far, the commonly used ferromagnetic insulators mostly possess low-symmetry structures associated with a poor growth quality and widespread properties. The few known high-symmetry materials either have extremely low Curie temperatures (≤ 16 K), or require chemical doping of an otherwise antiferromagnetic matrix. Here we present compelling evidence that the LaCoO$_3$ single-crystalline thin film under tensile strain is a rare undoped perovskite ferromagnetic insulator with a remarkably high Curie temperature (T$_C$) of up to 90 K. Both experiments and first-principles calculations demonstrated tensile-strain-induced ferromagnetism which does not exist in bulk LaCoO$_3$. The ferromagnetism is strongest within a nearly stoichiometric structure, disappearing when the Co$^{3+}$ defect concentration reaches around 10%. Significant impact of the research includes demonstration of a strain-induced high-temperature ferromagnetic insulator, successful elevation of the transition over the liquid-nitrogen temperature, and high potential for integration into large-area device fabrication processes.

Significance

Ferromagnetic insulators are highly needed as the necessary components in developing next-generation dissipationless quantum-spintronic devices. Such materials are rare, and those high-symmetry ones without chemical doping available so far only work below 16 K. Here we demonstrate a tensile-strained LaCoO$_3$ film to be a strain-induced high-temperature ferromagnetic insulator. Both experiments and first-principles calculations demonstrated that the tensile-strain-supported ferromagnetism reaches its strongest when the composition is nearly stoichiometric. It disappears when the Co$^{3+}$ defect concentration reaches around 10%. The discovery represents a chance for the availability of such materials, a high operation temperature, and a high epitaxial integration potential for making future devices.

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he realization of a dopant-free ferromagnetic insulator (FMI) is critical to the fabrication of versatile spintronic devices due to the potential for dopants acting as undesirable inelastic scattering centers. In low-symmetry magnetic materials, an FMI may be realized through charge ordering in which magnetic ions occupy different atomic sites. Unfortunately, integrating such low-symmetry FMIs (1–4) into film devices presents significant challenges due to large lattice mismatch between the film and commonly used substrates, which almost universally possess high-symmetry structures. In high-symmetry structures, however, magnetic ions likely occupy identical crystallographic sites so that charge-ordering-stabilized FMI states are highly disfavored. Thus, undoped high-symmetry FMIs remain extremely rare (5–7). In fact, chemical doping has always been a prerequisite for making high-symmetry FMIs such as the colossal magnetoresistance oxides (8–12) and magnetic semiconductors (13, 14). The two well-known undoped high-symmetry FMIs, EuS and strained EuTiO$_3$, exhibit low Curie temperatures of about 16 and 4 K, respectively (5, 7). Therefore, engineering an undoped, FMI with high symmetry and high transition temperature (T$_C$) is highly desirable.

Normalizing, realizing an FMI requires a nonzero energy cost (ΔE) associated with electron hopping from an occupied metal orbital to a nearby unoccupied metal orbital through the bridging ligand orbital, so that the “hops” remain virtual events (15–17). Recently, the diamagnetic perovskite LaCoO$_3$ has been suggested as a possible high-symmetry FMI candidate due to the near-degeneracy of various spin states of the Co$^{3+}$ ion, so that spin-state ordering may be readily achieved (18, 19). Such an ordering of the spin states, which may be induced through strain effects, was first theoretically proposed by Hsu et al. (20) and later by Demkov and coworkers (21) to explain the observed FM in the LaCoO$_3$ thin films (22, 23). However, previously fabricated LaCoO$_3$ thick films are susceptible to oxygen vacancy (O$_v$) ordering as observed in scanning transmission electron microscopy (STEM) studies (24–26). More recently, such O$_v$ ordering was reported to be critical for the observed FM in nanostochiometric LaCoO$_{3−δ}$ films (25, 26). Currently, the nature of the FMI state in LaCoO$_3$ films remains unresolved, and the roles of strain and O$_v$ remains hotly debated. In addition to resolving these questions, it is critical to elucidate whether the LaCoO$_3$ film can in fact yield an...
undoped, high-temperature FMI with the high symmetry which enables high-quality growth.

In this work, we fabricated nearly stoichiometric LaCoO$_3$ films through pulsed-laser deposition under a maximal oxygen pressure of 25 Pa, which resulted in layer-by-layer growth. Details of the sample information can be found in Materials and Methods and SI Appendix, section I. We also fabricated various LaCoO$_3$ thin films in which the Co$^{2+}$ concentration was systematically varied by tuning the oxygen pressure and film thickness. The latter increases the Co$^{2+}$ defect density when the thickness is reduced below 10 unit cells (u.c.). Further experiments and first-principles calculations demonstrated that the film with minimal Co$^{2+}$ under tensile strain exhibited the strongest FM state. The observed FM eventually disappears for Co$^{2+}$ concentrations above ~10%. These results indicate that LaCoO$_3$ films under tensile strain may represent the unusual case of a high-symmetry undoped FMI with a $T_C$ above liquid nitrogen temperature.

In Fig. 1A, we show magnetization and resistivity vs. temperature measurements for a 30-u.c. LaCoO$_3$ film grown under 25-Pa oxygen pressure on (001) SrTiO$_3$ substrate. The FM transition for this film appears at about 85 K. The resistivity increases with decreasing temperature from 390 to 70 K. Below 70 K, the resistance is over the measurement limit. A high-angle annular dark-field (HAADF) image, shown in Fig. 1B, was taken along the (010) direction by an aberration-corrected STEM. Long-range-ordered dark stripes associated with Co$^{2+}$ state (25) or La-La elastic interactions (24) were not observed in either the present HAADF images or a variety of images taken in different areas and directions of the film, although we occasionally observed short, randomly distributed stripes in some areas (SI Appendix, section II). Co and Ti L-edge electron energy-loss spectroscopy (EELS), shown in Fig. 1C, reveals that the film-substrate interface is very sharp. Furthermore, the thickness oscillation fringes in the X-ray diffraction shown in Fig. 1D and the atomic force microscopy image in Fig. 1E both demonstrate the high quality of the fabricated LaCoO$_3$ film.

To further examine the nature of the observed FMI, we intentionally introduced controlled levels of oxygen vacancies into the film by reducing the oxygen growth pressure and by reducing the film thickness, yielding LaCoO$_{3-x}$ films. The corresponding reductions in $T_C$ and magnetization are shown in Fig. 2A. We found that reducing the oxygen pressure causes $T_C$ to decrease and a dramatic reduction occurs between 10 and 15 Pa. X-ray diffraction analyses in Fig. 2B show that by reducing the oxygen pressure the out-of-plane lattice constant increases dramatically, in agreement with a previous report (27). All films discussed in this paper are coherently strained to their substrates, either SrTiO$_3$ or (LaAlO$_3$)$_3$(Sr$_2$TaAlO$_6$)$_3$ (LSAT). We define an effective strain by $\varepsilon_{\text{eff}} = 1 - c/a$. In Fig. 2C the effective strain was found to match the $T_C$ variation extremely well. Thus, reducing the oxygen pressure is associated with a reduction in $T_C$ and magnetization which we attribute to a reduction in the effective tensile strain and increased nonstoichiometry.

Reducing the film thickness (at a constant growth pressure of 15 Pa) allows the $T_C$ to be tuned more systematically while the effective strain remains relatively constant at ~3.5% in thicker films and ~3.3% in the 5-u.c. film. To probe the Co valence, we measured the Co L-edge and K-edge using soft X-ray absorption (XAS) and X-ray absorption near-edge structure (XANES) as shown in Fig. 2D and E, respectively. In a LaCoO$_3$ film under tensile strain, Co$^{4+}$ ions may exist in either the low-spin $t_{2g}^6e_g^{0}$ state (LS, $S = 0$) or the high-spin $t_{2g}^5e_g^2$ state (HS, $S = 2$) (19). The introduction of O$_{\delta}$s, however, could stabilize Co$^{2+}$ HS states ($S = 1.5$) with an orbital occupancy of $t_{2g}^2e_g^2$ (26, 28, 29). Quantitative XAS spectral analysis using atomic multiplet plus the crystalline-field calculation (30, 31) was performed to extract the individual concentrations of the three spin states (more details in SI Appendix, section III). Additionally, the Co valence was quantitatively analyzed by comparing the measured XANES spectra to the reference spectra with a well-determined Co valence in a pseudocubic structure (32). The dependences of $T_C$ and Co valence (both from the XAS and XANES) on the layer thickness are shown in Fig. 2F. Both decrease drastically as the thickness is reduced.

![Image](https://www.pnas.org/ cgi/doi/10.1073/pnas.1707817115)

**Fig. 1.** FMI state in a nearly stoichiometric LaCoO$_3$ film under tensile strain. (A) Temperature dependences of the magnetization and resistivity of a 30-u.c. LaCoO$_3$ film grown on (001) SrTiO$_3$ at p(O$_2$) = 25 Pa. The magnetization was measured by a superconducting quantum interference device (SQUID) along the in-plane direction with a 500-Oe field after field cooling. (Inset) Schematic of the LaCoO$_3$/SrTiO$_3$ heterostructure. (B) Cross-section STEM-HAADF image of the film taken along the (010) direction. (C) Ti and Co layer-by-layer distributions across the interface measured by STEM-EELS. (D) Synchrotron XRD measurement of the (00L) peaks. (E) Atomically flat LaCoO$_3$ surface with terraces measured by atomic force microscopy.
below 10 u.c. The coincidence of $T_C$ and Co valence transitions suggests that the introduced nonstoichiometry suppresses the FM.

Since the oxygen K edge is very sensitive to changes in the valence of the transition metal, we performed its STEM-EELS measurements to double check the Co valence obtained from XAS and XANES. We studied three representative samples on SrTiO$_3$ substrates (more details in SI Appendix, section II), including a thick film (30 u.c., 25 Pa), a thin film (7 u.c., 15 Pa), and a poorly oxygenated thick film (30 u.c., 1 Pa). The average oxygen K-edge spectra in Fig. 2G show that the 7-u.c. film exhibits a very weak preedge peak likely due to rich concentrations of O$_{v}$. From the line-by-line scans in the well-oxygenated 30-u.c. film, we do not observe clear trends of this prepeak weakening as the layer approaches the interface. To improve the signal quality and enable better comparison, we average the spectra of the top 10 layers, middle 10 layers, and interfacial 10 layers of the 30-u.c. films. We observe that the middle block has a slightly stronger prepeak than the surface and interfacial blocks, as shown in Fig. 2H.

To better understand the interplay between strain, off-stoichiometry, and FM in LaCoO$_3$, we performed first-principles density-functional theory (DFT) calculations, the details of which are shown in Materials and Methods. Consistent with previous investigations, the ground state of the strained LaCoO$_3$ is FM for $a = 3.905$ Å due to the high concentrations of HS Co$^{3+}$ and FM coupling between the nearest HS and LS Co$^{3+}$ (20, 21). Our calculations show that the FM in LaCoO$_3$ will indeed be suppressed by increasing the O$_{v}$ density. Such O$_{v}$s introduce extra electrons which generate HS Co$^{2+}$ atoms containing half-occupied $e_g$ orbitals which support antiferromagnetic (AFM) superexchange between half-occupied orbitals, which decreases the magnetization. LaCoO$_3$ films with three different O$_{v}$ concentrations were investigated using $2\sqrt{2} \times 2\sqrt{2} \times 4$ (1O$_{v}$/32Co), $2\sqrt{2} \times 2\sqrt{2} \times 4$ (1O$_{v}$/16Co), and $2\sqrt{2} \times 2\sqrt{2} \times 2$ (1O$_{v}$/8Co) u.c. (Fig. 3). Stoichiometric LaCoO$_3$ without O$_v$ was also explored using three structural models discussed above, all yielding similar results. One can see that when the concentration is only 1O$_{v}$/32Co (9.4% Co$^{2+}$), the magnetization only decreases slightly from 2 $\mu_B$/Co to 1.6 $\mu_B$/Co. This is because the AFM coupled HS Co$^{2+}$ atoms
only affect the local magnetic state. When the concentration increases to 1Ov/16Co (12.5% Co\textsuperscript{3+}), the magnetization decreases dramatically to 0.2 \(\mu_B/Co\) as the two Co\textsuperscript{2+} atoms introduce a long-range AFM coupling into the u.c. (more details in SI Appendix, section IV). For an even higher concentration of 1Ov/8Co (25% Co\textsuperscript{3+}), the magnetization is close to zero. This behavior may be well described by a step function with an inflection point near a Co\textsuperscript{2+} concentration of 10\%, in excellent agreement with our experimental results. The O\textsubscript{v}-ordered LaCoO\textsubscript{3} thin films have been studied by Bişkap et al. (25). Here we studied films with O\textsubscript{v} concentrations much less than that of the previous work. Although details did not agree, both studies showed fewer magnetizations in O\textsubscript{v}-occupied films than O\textsubscript{v}-free films.

In addition to the studies of films on SrTiO\textsubscript{3} described above, we have performed similar experiments using LaCoO\textsubscript{3} films grown on (001) LSAT substrates with varied thicknesses, and found similar results. In Fig. 4, we summarize the \(T_C\) of all three thin-film groups, in addition to examples of films in the literature (23, 24, 26), as a function of effective strain and Co valence to create a phase diagram. Higher \(T_C\)s are associated with the phase region with tensile strain and the lowest O\textsubscript{v} concentrations. Away from this region, \(T_C\) is sharply reduced or the films are nonmagnetic. The universality and substrate-independent reproducibility of these trends supports the validity and generality of this study. Therefore, the experimental findings strongly suggest that tensile strain of nearly stoichiometric LaCoO\textsubscript{3} thin films results in a high-temperature FMI.

Relative to other examples of undoped high-symmetry FMIs, the LaCoO\textsubscript{3} Curie temperature is surprisingly high. A detailed understanding of this behavior is not yet clear and will require further exploration. One possible explanation is the larger overlap between the Co 3d and oxygen 2p orbitals. In other FMIs such as EuS, the FM originates in localized 4f electrons at the Eu sites and their orbital overlapping with the S 2p orbital or Eu 5d orbital (33, 34). On the other hand, our theoretical calculations show that the Co 3d orbital is much broader than the Eu 4f orbital and the superexchange interaction in LaCoO\textsubscript{3} films (21) is more than one order magnitude larger than that in the Eu chalcogenides (34). The availability of an undoped high-symmetry and high-\(T_C\) FMI is an important step toward bringing quantum-spintronic devices into the practical operation regime. Our results here indicate that the tensile-strained LaCoO\textsubscript{3} thin film is a much better technological candidate than previous low-temperature FMIs, thanks to the material’s high \(T_C\) of nearly 90 K, its high cubic symmetry, and the ability to fabricate high-quality films over large areas on conventional substrates. The realization of such an FMI provides a solid foundation for the growth and design for next-generation device fabrication.

Materials and Methods

Sample Fabrication Using High-Pressure Reflective High-Energy Electron Diffraction Assisted Pulsed-Laser Deposition. Three groups of (001) LaCoO\textsubscript{3} thin films (summarized in SI Appendix, Table S1) were grown using a Pascal pulsed-laser deposition system assisted with double-differential pumped reflective high energy electron diffraction (RHEED). The SrTiO\textsubscript{3} substrates were etched in buffered hydrofluoric acid and annealed at 930 °C in flowing oxygen to obtain the uniform TiO\textsubscript{2} termination. All films were grown at 750 °C. The laser energy density was about 1.5 J/cm\textsuperscript{2} and the frequency was 1 Hz. The thickness of LaCoO\textsubscript{3} films was controllably monitored in situ by RHEED oscillations, and later certified by ex situ X-ray reflectivity measurements. The lattice structures of films were measured by Synchrotron X-ray diffraction (XRD), carried out on BL14B1 (10 keV) at Shanghai Synchrotron Radiation Facility, 1W1A (10 keV) at Beijing Synchrotron Radiation Facility and 33-BM-C (22 keV) at Advanced Photon Source in Argonne National Laboratory.

XAS and XANES. Co L-edge XAS measurements were performed on BL6.3.1.2 at the Advanced Light Source of Lawrence Berkeley National Laboratory and BL128-a at the National Synchrotron Radiation Laboratory of University of Science and Technology of China (USTC). XAS spectra were recorded in the total electron yield (TEY) and total fluorescence yield (TFY) mode simultaneously. The intensities were normalized to a reference signal recorded simultaneously on a gold mesh. The energy scale was calibrated by using metallic Co foil as reference. For the XAS TEY method, the penetration depth in the LaCoO\textsubscript{3} film was between 10 and 20 u.c. The measurements of Co K-edge XANES spectroscopy were carried out at room temperature at the beamline BL14W1 of the Shanghai Synchrotron Radiation Facility and 1W18-XAFS of Beijing Synchrotron Radiation Facility. The signals were collected in the TFY mode at 45° with respect to the X-ray incident beam direction. Standard cobalt and iron metal foils were employed for energy calibration and fluorescence filtering, respectively. Each spectrum was collected at least three times to minimize the error.

First-Principles DFT Calculation. The electronic and magnetic properties of LaCoO\textsubscript{3} films on SrTiO\textsubscript{3} substrates with different amount of O\textsubscript{v} were elucidated using first-principles DFT calculations, as implemented in Vienna Ab initio Simulation Package (VASP). The ion-electron interactions are described...
by the projector-augmented wave method. We use the generalized gradient approximation (GGA) with PW91 functional. Static local electronic correlations are added using the GGA exchange-correlation potential in the GGA+U method with $U = 5.27$ eV and $J = 1.47$ eV (Co$_{54}$) asseo et al. (21) did. In our calculations, all of the atomic positions are relaxed until the force on each atom is less than 0.01 eV/Å, and all of the self-consistent electronic calculations are converged to $10^{-6}$ eV per cell. To study the O$_2$ effect on the magnetic solution in LaCoO$_3$ film on SrTiO$_3$. $2\sqrt{2}\times 2\times 2$, $2\sqrt{2}\times 2\times 4$, and $2\times 2\times 2\times 4$ supercells were used by introducing one O$_2$ per supercell. We used the experimental lattice constant of SrTiO$_3$ $a = 3.905$ Å to fix the in-plane lattice constant of the LaCoO$_3$ film. With this lattice constant, a 3.5% tensile strain is applied to the LaCoO$_3$ film.

**STEM.** Specimens for STEM characterization were prepared by focused ion beam along the pseudocubic (101) direction of films on SrTiO$_3$ substrates. Specimens along (100), (110), (1-10) directions of the 30-μc film on SrTiO$_3$ substrate grown with P(O$_2$) = 25 Pa were also measured which are also absent of long-range O$_2$ order. Spherical-aberration-corrected HAADF images were acquired on a JEOL ARM200F microscope operating at 200 kV. For HAADF images, the convergence angle was about 23 mrad, and the inner and outer angles of the detectors was 90 and 370 mrad, respectively. The experimental STEM images were low-pass filtered. The intensity of every atomic column in the HAADF images was approximately proportional to $Z^{1.7}$ ($Z$ is the atomic number).

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