Anomalous magnetism in strained La$_{1-x}$Sr$_x$CoO$_3$ epitaxial films (0 ≤ x ≤ 0.5)

H. W. Yang$^1$, H. R. Zhang$^{1,2*}$, Y. Li$^1$, S. F. Wang$^2$, X. Shen$^1$, Q. Q. Lan$^1$, S. Meng$^1$, R. C. Yu$^1$, B. G. Shen$^1$ & J. R. Sun$^1$

$^1$Beijing National Laboratory for Condensed Matter & Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China, $^2$College of Physics Science and Technology, Hebei University, Baoding 071002, Hebei Province, People’s Republic of China.

Spin state controlling has always been a focus of intensive studies due to its importance for novel effect exploration and information technology. Complex oxides with competitive mechanisms are suitable objects of study for this purpose due to their susceptibility to external stimuli. Perovskite cobaltate La$_{1-x}$Sr$_x$CoO$_3$ is one of such oxides. Combined effects of lattice strains and hole-doping have been studied for the LSCO films with 0 ≤ x ≤ 0.5. It is found that the lattice strain, either tensile or compressive, destabilizes the ferromagnetic (FM) state of the epitaxial films, leading to a nonmagnetic state that extensively exists in a doping window embedding deep into the range of the FM phase in bulk counterparts. Density functional theory calculations reveal a distinct spin state transition due to the combined effects of lattice distortion and hole-doping, explaining the unique magnetic behaviors of LSCO.
The Co $\text{O}_6$ octahedra, whereas others ascribed them to oxygen deficient regions and argued that the HS $\text{Co}^{2+}$ ions sandwiching the dark stripes are responsible for the ferromagnetism in LCO. In any cases, the ferromagnetism disappears by the incorporation of minor Sr ions.

**Combined effects of lattice strain and hole doping.** Figs. 3a and 3b show the temperature-dependent magnetization, $M-T$, of the (001)-LSCO films with $t=50$ nm, measured with an applied field of 0.05 T in field-cooling mode. Similar to the previously reported results, the tensile LSCO/STO films of $x=0$ and $x \simeq 0.3$ are in FM state at low temperatures, and the Curie temperature, defined by the inflection point in the $M-T$ curve, varies between 80 and 205 K. Fascinatingly, the FM character is greatly weakened in the intermediate doping range of 0.05 < $x$ < 0.2. As shown by the amplified $M-T$ curves in Fig. 3a, the steep cliff for $x=0$ declines when $x=0.05$, and

![Figure 1](https://www.nature.com/scientificreports/) Crystal structure of the (001)-LSCO($x=0.2$)/STO films of different thicknesses. (a) and (b) X-ray reciprocal space maps around the (-103) Bragg reflections of the LSCO/STO films with the thicknesses of 50 nm (a) and 100 nm (b). The inset plot is the topography of a 50-nm-thick LCO/STO film. Image size is 1 $\mu$m × 1 $\mu$m. (c) Lattice parameter of the LSCO/STO films, deduced from reciprocal space maps. Dashed line indicates the lattice constant of bulk LSCO.

![Figure 2](https://www.nature.com/scientificreports/) (a) High angle annular dark-field (HAADF) image of the LCO/STO film with a thickness of 50 nm. (b) HAADF image of a 7-nm-thick LSCO($x=0.1$)/STO film. Periodical dark stripes in the LCO film but not the LSCO film can be clearly seen.
disappears completely when \( x = 0.2 \). The strong-to-weak crossover of the magnetic character is clearly shown by Fig. 3c: Different from the typical FM behavior of the films with \( x = 0, 0.3 \), and 0.5, the \( M-H \) curves for \( x = 0.1 \) and 0.2 are essentially NM in nature. According to Fig. 3e, the saturation magnetization, \( M_s \), is only \( \sim 0.06 \mu_B/Co \) for \( x = 0.1 \) and \( \sim 0.04 \mu_B/Co \) for \( x = 0.2 \). These values are much lower than the corresponding bulk ones (dashed line in Fig. 3e). This implies that, by simply applying lattice strain, we can realize not only the NM→FM transition of LCO but also the FM→NM transition of LSCO for \( x < 0.2 \). Obviously, the intertwined strain and doping effects make the FM state unstable. The magnetization rises again when \( x \) exceeds 0.3, and approaches a saturation value. The magnetic behavior of the LSCO/LAO film is relatively simple. It is weakly FM for \( x < 0.1 \) and strongly FM for \( x \geq 0.2 \) (Fig. 3b). The \( M_S \) grows monotonically from \( \sim 0.1 \) to \( \sim 1.2 \mu_B/Co \) as \( x \) increases from 0 to 0.5, without any anomalies in the intermediate doping range (Figs. 3d and 3f). One thing deserving special attention is that the magnetization of the film is fairly lower than that of the bulk values even when \( x > 0.3 \), indicating the robustness of the strain effect.

To verify the unique strain effect in tensile films, thermal magnetization is measured for differently relaxed films. As a consequence of lattice strain, as shown in Fig. 4a, the magnetization of the LCO/STO film shows a monotonic decrease with \( t \) when \( t > 40 \) nm. \( M \) of the 20-nm-thick film is abnormally low \( M \sim 0.22 \mu_B/Co \), probably due to interfacial effect. In contrast, the FM state of the LSCO\((x=0.2)\)/STO film is increasingly enhanced by increasing \( t \). As shown in Fig. 4b, the magnetization is nearly zero for \( t=20 \) nm, and remains low until film thickness exceeds 50 nm. However, it undergoes a 50-fold growth from \( t=50 \) nm to 200 nm. Obviously, with the release of lattice strain, the FM order is deteriorated in LCO but rebuilt in LSCO.

To quantify the strain effect, the \( M_s-\sigma \) dependences are studied, where \( \sigma \) is out-of-plane strain defined by \( (d_{Co})/c_0 \) with \( d=c \) for (001)-films and \( d_{110}/c_2 \) for (110)-films. In Fig. 4c we present the representative \( M_s-\sigma \) relations for the LCO and LSCO\((x=0.2)\) films. From a first sight, all data of the LCO films collapse into a master curve, ascending monotonically from \( \sim 0.1 \) to \( \sim 0.9 \mu_B/Co \) as \( \sigma \) decreases from \( \sim 0.82\% \) to \( \sim 1.77\% \). According to this \( M_S-\sigma \) relation, the \( M_S \) increasingly increases towards the low \( \sigma \) limit, and \( M_S \) values well beyond 1 \( \mu_B/Co \) are available if further strain is achievable. In contrast, the LSCO films exhibit a much more complex behavior: With the increase of \( \sigma \), \( M_S \) first increases and then decreases, yielding a local maximum of \( \sim 1 \mu_B/Co \) around \( \sigma = 0 \). Different from LCO, 1 \( \mu_B/Co \) is the highest value that can be invoked by simply adjusting lattice strains. Assuming that all of the Co\(^{3+} \) ions are in the LS state while half Co\(^{3+} \) ions in the IS and half Co\(^{3+} \) ions in the LS state, a simple calculation gives \( M_S=0.2 \times 1+2 \times 0.4=1 \mu_B/Co \), where the Lander’s \( g \)-factor has been set to 2.

Based on the data in Figs. 3 and 4, we obtained the phase diagrams in Fig. 5. Figs. 5a and 5c show the phase distribution on the \( T-x \) plane for the LSCO/STO and LSCO/LAO films, respectively. Presence of a NM window (0.1< \( x < 0.2 \)) in the former films and the enhanced FM character with \( x \) in the latter films can be clearly seen. Sandwiched by these two figures is a mapping of \( M_S \) on the \( \sigma-x \) plane (Fig. 5b), derived from the \( M_S-\sigma \) relations of different Sr contents. The most remarkable feature is the existence of a downwards curved NM strip, where \( M_S \) is low (blue-colored region). It demonstrates the depression of lattice strain on the FM state. Take the case of tensile strain as an example (it corresponds to out-of-plane compressive strain). The NM window can even go deep into the doping range (\( x>0.2 \)) where the DE prevails in bulk LSCO. From this phase diagram, we would expect a magnetic switching whenever a deviation from strain-free state occurs for LSCO of \( x > 0.1 \). The increased magnetization at the

**Figure 3 | Doping effect on magnetism for the LSCO films grown on different substrates with a constant thickness of 50 nm.** (a) and (b) Thermal magnetizations of the LSCO/STO (a) and LSCO/LAO (b) films, recorded in the warming process after field cooling the films to 10 K. The applied field is 0.05 T. (c) and (d) Isothermal magnetizations of the LSCO/STO (c) and LSCO/LAO (d) films, recorded at 10 K. (e) and (f) Saturation magnetizations as functions of Sr content, deduced from the \( M-H \) curves in (c) and (d), respectively. Red/green symbols represent the observed/calculated results. Data of the bulk LSCO (extracted from Ref. 1) are shown in (e) by a dashed line.
lower left counter of this $\sigma$-$x$ plane is an exception, where the SE prevails.

**Ab initio calculation of magnetic property.** To get a further understanding of the distinctive doping effects, we performed *ab initio* calculations on the magnetic property of LSCO within the framework of density functional theory. As shown by the green symbols in Figs. 3e and 3f, the calculated magnetic moments satisfactorily reproduce the trends in the experimental data, i.e., the dramatic reduction of $M_s$ in intermediate doping range in LSCO/STO and the monotonic $M_s$ growth in LSCO/LAO, indicating that the theoretical model has captured the main features of the strained effect.

To quantify structural features, we analyzed the atomic configurations around Sr in the supercells. For the LCO/STO film, the CoO$_6$...
polyhedron deviates considerably from the octahedral symmetry. Due to the presence of tensile strains, in-plane and out-of-plane Co-O bonds are significantly different. As illustrated in Fig. 6a, two CoO$_6$ octahedra in the supercell of LCO are elongated while other two compressed along the z-axis. A direct calculation indicates that the Co$^{3+}$ ion in the more severely elongated O$_6$ cage is in the HS state (marked by light cyan color) while other three Co$^{3+}$ ions are in the LS state. This ratio is lower than that deduced from the data of x-ray absorption spectroscopy but well agrees with the observation that $M_S \approx 1 \mu_B$/Co. The distortion of the CoO$_6$ octahedron has influenced the electronic population of the $t_{2g}$ and $e_g$ levels, stabilizing the HS state. As established, the SE between HS-LS HS Co$^{3+}$ ions gives rise to the FM order in tensile LCO film.

Fig. 6b presents the projected density of states for 3$d$ orbitals at a LS Co$^{3+}$ site (left panel) and a HS Co$^{3+}$ site (right panel) of the LCO/STO film. As expected, spin-up and spin-down states display different densities for HS Co$^{3+}$ but similar densities for LS Co$^{3+}$. As shown in Fig. 5c, the two elongated CoO$_6$ polyhedrons at $x=0$ disappear after the doping of $x=0.125$. According to the 1:3 HS to LS Co$^{3+}$ ratio, on average each La$^{3+}$ in LCO/STO will have two HS Co$^{3+}$ and six LS Co$^{3+}$ neighbors. Due to their large CoO$_6$ cell volume, the two HS Co$^{3+}$ ions (marked by light cyan color) will be the first ones to be affected by Sr, being transited into LS Co$^{3+}$ and LS Co$^{3+}$, respectively. Here Co$^{3+}$ and Co$^{3+}$ appear as LS ions to vacate space for Sr$^{2+}$ that is larger than La$^{3+}$. After a simple calculation, we obtain an equation for magnetization, $M_S = (1-7x) \mu_B$/Co. According to this equation, HS Co$^{3+}$ ions will completely disappear at $x \approx 0.15$, which is exactly in the middle of the NM window. With the help of lattice strain, the incorporation of Sr has promoted the population of Co$^{3+}$ in the LS state. This is in sharp contrast to the doping effect on bulk LCO, which transits LS Co$^{3+}$ into IS Co$^{3+}$. Obviously, doping effect has gained new features in the presence of lattice strain. Due to the clamping of the substrate, Sr affects not only the transited Co$^{3+}$ ion but also a neighboring HS Co$^{3+}$ ion, greatly depressing both the SE and the DE.

**Figure 6** (a) Schematic diagram of the distorted CoO$_6$ polyhedrons in LCO/STO. Number besides octahedron indicates its sequence in supercell. Light cyan marks the CoO$_6$ octahedron in the HS state. After the incorporation of Sr, the two HS Co$^{3+}$ in elongated CoO$_6$ octahedra (light cyan) are transited into a LS Co$^{3+}$ and a LS Co$^{3+}$ state, respectively. Meanwhile, the CoO$_6$ octahedra reshape to accommodate the structure deformation thus resulted. (b) Projected density of states for 3$d$ orbitals at a LS Co$^{3+}$ site (left panel) and a HS Co$^{3+}$ site (right panel) for the marked CoO$_6$ octahedra in (a). Dashed line marks the Fermi energy. The positive and negative densities of states are for spin up and spin down, respectively. (c) Cell volume of the CoO$_6$ octahedra in the supercells and the magnetic moment of the Co ions in the O$_6$ cages, numbed in sequence. "M" and "V" denote magnetic moment and cell volume, respectively.
interactions. When x is high, the strain effect is partially overcome by enhanced DE. Due to cooperative lattice distortions, Sr doping now favors an IS state rather than simply depresses the spin state of Co$^{3+}$, causing a magnetic upturn of the $M_\text{s}$-$x$ curve (Fig. 1e).

For the LCO/LAO film, the Co$\text{O}_x$ polyhedron is nearly perfectly octahedral. This implies a high degeneracy of the $t_{2g}$ orbitals and the $e_g$ orbitals, thus the Co$^{3+}$ ions are mainly in the LS state. It explains the low $M_\text{s}$ of LCO/LAO. Our LCO/LAO film shows a finite $M_\text{s}$, probably due to the presence of cation vacancies which give rise to native Co$^{4+}$ ions. The introduction of Sr at least will transit a LS Co$^{3+}$ to a LS Co$^{4+}$ (see the case of when $x = 0.125$ in the bottom panel of Fig. 6c), assigning Co ions magnetic moments. Consequently, $M_\text{s}$ grows monotonically with $x$. We note that the Jahn-Teller-like distortion of the Co$\text{O}_x$ octahedron in LSCO/10 is $x = 0.125$ is obviously weaker than that in corresponding LSCO/STO: the in-plane and out-of-plane Co-O bond ratio is $\sim 1$% for LSCO/STO and $\sim 5$% for LSCO/STO. It may explain the weakness of the strain effect in LSCO/STO.

In conclusion, tensile strain favors the FM state of LCO but strongly destabilizes the FM state of LSCO, and even generates a NM window that embeds deep into the doping range of the FM phase in bulk counterparts. Ab initio calculations indicate that, with the help of lattice strain, the introduction of Sr triggers a high to low spin state transition for the Co$^{3+}$ ions. This, together with strain-induced enhanced Jahn-Teller distortions, weakens the FM coupling between Co$^{3+}$ and Co$^{4+}$, leading to the NM window. Compared with tensile strain, the effect of compressive strain is slightly worse, thanks to reduced Jahn-Teller distortion.

Methods

Sample fabrication. L$\text{a}_{1-x}\text{Sr}_x\text{CoO}_3$ films with a Sr content between 0 and 0.5 were grown respectively on (001) and (110)-oriented LaAlO$_3$ and SrTiO$_3$ substrates ($3 \times 5 \times 0.5$ mm$^2$) using pulsed laserablation technique ($\lambda = 248$ nm). Thefluence of the laser pulses was $1.5 \pm 1$ cm$^{-2}$, and the repetition rate was $1 \text{ Hz}$. In deposition process, the substrate was kept at $800 \text{ C}$ and the oxygen pressure at $50 \text{ Pa}$. The film thickness, $t$, varies between $20 \text{ nm}$ and $200 \text{ nm}$, determined by the deposition time. After deposition, the films were in-situ annealed for $15 \text{ min}$ in an $O_2$ pressure of $1 \text{ bar}$ before cooling down to the ambient temperature.

Structural and magnetic characterizations. Morphology of the film was analyzed by the atomic force microscopy (Seiko SPI 3800N) at the ambient conditions. The crystal structure of the films was determined by a Bruker diffractometer equipped with thin film accessories (D8 Discover, $\lambda = 1.5406 \text{ A}$). High-resolution aberration-corrected scanning transmission electron microscopy (STEM) investigation was carried out on a JEM-ARM200F microscope with double $C_2$ correctors for the condenser lens and objective lens. The available point resolution is better than $0.08 \text{ nm}$ at an operating voltage of $200 \text{ kV}$. The high angle annular dark-field (HAADF) images were acquired at acceptance angles of $70-150 \text{ mrad}$. Magnetic measurements were conducted on a Quantum Design vibrating sample magnetometer (VSM-SQUID) in the temperature interval from $3 \text{ K}$ to $300 \text{ K}$.

Density functional theory calculations. The projected augmented plane-wave (PAW) pseudo-potentials were used, as implemented in the Vienna ab-initio Simulation Package (VASP). To accurately describe exchange and correlation interactions, the local spin density approximation (LSDA) + U method$^{2,3}$ was employed with the effective Hubbard parameter of $U_{\text{eff}}=3.8 \text{ eV}$ for Co in LCO, and $U_{\text{eff}}=3.3 \text{ eV}$ for Co in Sr doped LCO, referring to Ref. 19. The supercells adopted in the calculation are $2a_{\text{BN}} \times 2a_{\text{BN}} \times 2a_{\text{BN}}$, $2a_{\text{BN}} \times 2a_{\text{BN}} \times 4a_{\text{BN}}$, $2a_{\text{BN}} \times 2a_{\text{BN}} \times 4a_{\text{BN}}$, and $2a_{\text{BN}} \times 2a_{\text{BN}} \times 2a_{\text{BN}}$ for the Sr concentration of $0.125$, $0.2$, $0.3$, and $0.5$, respectively, where $a_{\text{BN}}$ is the bulk lattice constant of the perovskite unit cell. A brief description of the calculation procedure is as follows. First, a stable and strain-free structure is established for LSCO through optimizing the total energy of the system, and the resulted lattice was expanded along in-plane direction to fit the experimental one. Second, the resulting lattice was subjected to an adjustment along out-of-plane direction to get an energy minimum. For this state, the electronic and magnetic structures are calculated.

Acknowledgments

This work has been supported by the National Basic Research of China (Grant Nos. 2011CB921801, 2012CB921403, and 2013CB921701) and the National Natural Science Foundation of China (Grant Nos. 11074285, 51372064, and 11134007).

Author contributions

J.R.S. conceived and designed the experiments, analyzed and interpreted the data. H.W.Y. and H.R.Z. prepared the samples, performed the structural and magnetic measurements and acquired data with S.F.W., J.C.R. and L.W. H.W.Y. and J.C.R. conducted the first-principle calculation. The AFM characterizations of the sample were made by Y.L. The transmission electron microscope analysis was conducted by X.S., Q.Q.L. and H.R.Z. prepared the sample, performed the structural and magnetic measurements.

Additional information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Yang, H.W. et al. Anomalous magnetism in strained Lao.5Sr0.5CoO3 epitaxial films ($0 \times 0 \times 0.5$). Sci. Rep. 4, 6206; DOI:10.1038/srep06206 (2014).
