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The La$_{1-x}$Sr$_x$CoO$_3$ (LSCO) thin films have attracted great attention in recent years because of their mysterious magnetic properties and potential applications to information technologies. Co ions in LSCO can exhibit three different spin states, i.e., high spin (HS) state ($t_{2g}^{5}e_{g}^{0}$, $S = 2$), intermediate spin (IS) state ($t_{2g}^{4}e_{g}^{1}$, $S = 1$), or low spin state (LS) ($t_{2g}^{5}e_{g}^{0}$, $S = 0$). Since the magnetic and transport properties of LSCO are closely related to spin state of the Co ions, great effort has been devoted to spin-state modification through, for example, introducing divalent ions, applying external pressures, or changing temperatures. The ground state of LaCoO$_3$ (LCO) is non-magnetic (NM). Recent studies showed that tensile strain drives the LCO film into a ferromagnetic (FM) state, since super-exchange (SE) interactions accompanying the interaction between HS Co$^{3+}$ and HS Co$^{3+}$ ions is proposed to be the driving force for the FM order. Just like that occurred in bulk LSCO. For the films with a x between 0 and 0.5, however, the combined tensile lattice strain and Sr-doping dramatically modifies the magnetic properties of LSCO thin films, resulting in a NM window around $x = 0.2$. This result demonstrates the potential for the artificial tuning of the magnetic exchanges in LSCO.

Obviously, the spin state of the Co ions is closely related to their local structure. Lattice strain and Sr-doping have effect by tilting, rotating, and distorting the CoO$_6$ octahedron. Therefore, an exploration for the correlation between the lattice distortion and the magnetism is a doubt conducive to tuning the spin states of Co ions, thus for controlling the magnetism of LSCO. For LCO/STO thin films, modulated dark stripes have been observed in atomic level STEM images. Although it is believed that the dark stripes bear a close relation to the magnetism of LCO, different scenarios for their effect were proposed. Some authors believed that the HS Co$^{3+}$ ions are responsible for the dark stripes, and it is the SE interaction between the HS and LS Co$^{3+}$ ions that gives rise to the FM order in the LCO thin films. In contrast, other authors attributed the dark stripes to oxygen vacancies, and believed that a SE-like hybridization between the HS Co$^{3+}$ and the LS Co$^{3+}$ ions yields the FM order. The ordering of the Co states may be relevant to the magnetism in this kind of film. As a consequence, the nature of the dark stripes and the origin of magnetism of LSCO thin films are still controversial. Recently, we found that the magnetism of LSCO/SrTiO$_3$ (STO) thin film first decreases ($x < 0.2$) and then increases ($x > 0.2$) with increasing $x$, indicating that the mechanism of magnetism depends strongly on $x$. A decrease in magnetization with increasing $x$ in the range of 0–0.1 is an interesting issue deserving further studies. The theoretical calculations clearly show that the elongated CoO$_6$ polyhedrons which are HS Co$^{3+}$ state at $x = 0$ disappear after the doping of $x = 0.125$. For the films with an intermediate $x$ between 0 and 0.5, however, no aberration corrected STEM images have been reported, though the magnetic properties change greatly in this doping range. Since the interactions between magnetic ions and the magnetic mechanism are different in the range of 0–0.1 and above 0.2, which are mentioned later, we just confine our studies for the doping range of 0–0.1 to investigate how the regular stripe-like superstructure in the LCO film evolves while the small amount of Sr ions is introduced.

In this work, we studied the microstructure and the electronic structure of LSCO ($0 \leq x \leq 0.1$) thin films grown on STO and LaAlO$_3$ (LAO) substrates, respectively, using the STEM and EELS techniques. A quantitative relation between the number of dark stripes and saturation magnetization is established for the LSCO films with different $x$, and the factors that determine the magnetism are discussed based on the STEM and EELS analyses. Our work may lead...
to a deep insight into the magnetism of the LSCO films, paving the way towards the designing of future devices using LSCO films.

Epitaxial LSCO (0 ≤ x ≤ 0.1) thin films were grown on (001)-orientated STO and LAO substrates, using pulsed laser ablation technique. The samples were investigated by high-resolution aberration-corrected STEM and EELS on a JEOL-ARM200F microscope. Figure 1(a) is an atomic-resolution HAADF-STEM image (along [010] orientation) of LCO/STO thin film. Similar to previously reported results, perpendicular dark stripes appear in the Co layers about 2–3 unit cells away from the LCO/STO interface, forming a regular superstructure with a periodicity of 3a₀ (a₀ is the unit cell parameter). The STEM image along [001] orientation and its selected area electron diffraction (SAED) show that the 3a₀ dark layers appear in both [100] and [010] directions. Based on the atomic spacing extracted from the experiment, we constructed a super-cell, which consists of three distorted CoO₆ octahedra, one is elongated while the other two are compressed along z-axis, as shown in Figure 1(b). Using this structure, we simulated the STEM image and insert it in Figure 1(a), which agrees well with the experimental one. The intensity of Co ions in the elongated octahedra of the simulated image reduces indicating that the lattice strain is conductive to the formation of the dark layers. Figure 1(c) is the intensity profile along the red line in Figure 1(a), showing a regular periodic interatomic spacing between neighboring La atoms and revealing that the average La-La interatomic distance across dark Co layers (0.456 nm) is obviously larger than the distance across the neighboring bright Co layers (0.356 nm). Figure 1(d) is the distribution of the La-La interatomic distance along the [100] direction, showing two Gaussian-like distributions located at 0.433 nm and 0.345 nm, respectively.

To get a deep insight into the mechanism for the magnetism in strained LSCO films, we further studied the influence of combined Sr-doping and lattice strain on the stripe-like superstructure. Figure 2 presents the typical HAADF-STEM images of the LSCO films with x = 0, 0.05, 0.1, grown on STO and LAO substrates, respectively. Fascinatingly, the numbers of dark Co layers are different as x varies. Figures 2(a)–2(c) are the HAADF images of the LSCO/STO films with x = 0.05, and 0.1, respectively. When minor Sr ions are introduced (x = 0.05), the originally perpendicular dark Co layers (Figure 2(a)) are disrupted and decreased in numbers. Meanwhile, the parallel dark Co layers appear to relax the local lattice strain induced by the synergistic effect of lattice strain and Sr doping (Figure 2(b)). When x increases to 0.1, the number of dark Co layers is further decreased in both directions, and the film becomes generally uniform as we expect, and only weak signatures of dark Co layers can be identified in the perpendicular direction. The La-La interatomic distance mappings of Figures 2(a)–2(c) clearly reflect the evolution of the microstructure with x. It can be concluded that the content of the dark Co layers decreases with the increasing x for the LSCO/STO films. For the LSCO/LAO films that exhibit compressive strain of 0.3%, the situation is relatively simple. As shown by the STEM images in Figures 2(d)–2(f), only a few dark Co layers parallel to the interface are observed, regardless of x. This result indicates that the dark stripe-like structure has a close relation to the lattice strain.

Since the orientation of [010] and [100] are equivalent for perovskite LSCO epitaxial thin films grown on substrates where the strain effects are the same in the two directions, the variation tendency of the number of dark Co ions can be approximately described by either of the two orientations. From the above HAADF images, the statistical percentage of dark Co ions (n) can be counted, and it exhibits a monotonic decrease as x (0 ≤ x ≤ 0.1) increases for LSCO/STO. To reveal its effect on magnetism, the magnetization (M) of the LSCO films is measured as a function of magnetic field (H) at a fixed temperature of 10 K. From the M-H curve, the saturation can be deduced. Fascinatingly, we found a close relationship between saturation magnetization and dark Co ions. As shown in Figure 3(a), corresponding to the decrease in the number of dark Co ions, the magnetization undergoes a concomitant reduction, and the two M-x and n-x curves coincide with each other very well. The percentage of dark Co layers of LSCO/STO thin films (shown by blue triangles) is 24% (x = 0), 12% (x = 0.05), and 4% (x = 0.1) in statistics, corresponding to the saturation magnetization (red squares) of 0.80 μB, 0.35 μB, and 0.07 μB, respectively. As a supplement, we would like to emphasize that this phenomenon is obtained not only for LSCO/STO but also for LSCO/LAO. Due to small compressive strain in LSCO/LAO, the percentage of dark Co layers are counted as only 1.4% (x = 0), 4.7% (x = 0.05), and 4.6% (x = 0.1) in statistics, respectively, as

![Fig. 1. Microstructure of LCO/STO thin film. (a) Experimental and simulated HAADF-STEM images of the LCO thin film along [010] orientation. The simulated HAADF image agrees well with the experimental one. (b) Crystal structure of the LCO/STO used in the simulation (including one elongated and two compressed octahedra). (c) Intensity profile measured along the [100] direction. (d) Distribution of the interatomic La-La distance along [100] direction.](image-url)
shown in Figure 3(b), corresponding to the measured weak magnetization of LSCO/LAO. These results strongly suggest that the dark Co ions could be responsible for the magnetism of LSCO films. It suggests that the dark Co ions should be HS or IS state.

To investigate the electronic structure of the stripe-like superstructure, O K edge, Co L near-edge structure spectra, and the average ratio of Co L3/L2 were carefully examined across the dark and bright Co ions (Figure 4). The results suggest that the higher spin state Co ions rather than oxygen vacancy is responsible for the occurrence of dark stripes as well as the magnetism, since only little difference in oxygen content was detected between dark and bright Co ions. It is known that the LS-HS transition is accompanied by a volume increase in the CoO6 octahedral. In our LCO/STO sample, the Co-O bond in the dark layer is increased as much as 0.4 Å (Figures 1(c) and 1(d)). The elongation of the CoO6 octahedral will certainly influence the electronic population of the t2g and eg levels, stabilizing HS Co3\(^{2+}\). This is consistent with the EELS results in Figure 4.

As a consequence, we conclude that high spin state of the dark Co ions is responsible for the magnetism of the LSCO films 0 ≤ x < 0.1. The SE between HS-LS-HS Co3\(^{2+}\) ions gives rise to the FM order of the LCO/STO film. Ab initio calculations reported by Yang et al.\(^{12}\) show that the substitution of larger radius Sr2\(^{2+}\) ions for smaller radius La3\(^{3+}\) ions will cause a transformation of HS Co3\(^{3+}\) to LS Co3\(^{3+}\) and LS Co3\(^{3+}\), reducing the population of the HS Co3\(^{3+}\) ions. Sr doping alters the spin state of Co ions via changing local lattice strains. This prediction is consistent with our experimental results. In the case of x = 0.05, the population of HS Co3\(^{3+}\) ions reduces, and thus, the double exchange (DE) interaction between Co3\(^{3+}\) and Co4\(^{2+}\) ions appears. Obviously, the DE does not compensate the reduction of the SE, and the magnetization of the LSCO/STO film is decreased. The

![FIG. 2. Atomic-resolution HAADF-STEM images of La1-xSr0.1CoO3(x ≤ 0.1) thin films (20 nm) on STO/LAO. (a) LaCoO3/STO, the dark layers appear as a superstructure of a periodicity of 3a0. (b) La0.95Sr0.05CoO3/STO, the regular periodic dark layers are destroyed and decreased. (c) La0.9Sr0.1CoO3/STO, periodic dark layers are hardly seen. (d) LaCoO3/LAO. (e) La0.95Sr0.05CoO3/STO. (f) La0.9Sr0.1CoO3/STO. Only few dark layers parallel to the interface are observed in the LSCO thin films grown on LAO substrates.](image)

![FIG. 3. The number of dark Co ions and the saturation magnetizations of LSCO as a function of Sr content: (a) STO substrate and (b) LAO substrate.](image)

![FIG. 4. Line scan EELS fine structures across the stripe patterns of LCO/STO thin films. The dotted black line and red line were obtained from the dark and bright Co layers, respectively. (a) O K-edges. (b) Co L2,3 edges. (c) The integrated intensities of O K edge. (d) The integrated intensity ratio of Co L3/L2.](image)
number of dark Co ions decreases with the increasing $x$ in the range of 0–0.1, and when $x$ approaches 0.1, HS Co$^{3+}$ ions almost disappear, with only a few dark Co layers surviving. Due to the low HS Co$^{3+}$ content and the lattice strain which depresses the DE, the magnetization reduces further.\textsuperscript{12} The magnetization exhibits an obvious upturn for further increasing $x$. In this case, the DE interaction is enhanced, partially overcoming the strain effect, and the magnetism has a totally different origin from that in $x \leq 0.1$.\textsuperscript{17} This indicates that the combined effects of lattice strain and Sr doping will cause a transition not only from LS to HS but also from HS to LS for Co$^{3+}$ ions. For the LSCO/LAO thin films, however, the Jahn-Teller distortion of the CoO$_6$ octahedron is weak since lattice strain is small. As a consequence, only minor Co ions are in the HS state; thus, the magnetism is weak.

In summary, the connection between dark Co ions and magnetism of strain-induced LSCO epitaxial films ($0 \leq x \leq 0.1$) is studied, and it is found that the variation tendency of the number of the dark Co ions is consistent with that of saturation magnetization of the films on both STO and LAO substrates. The number of dark Co ions can directly reflect the magnetic moment of the LSCO thin films ($0 \leq x \leq 0.1$). The dark Co ions are favored in Co$^{3+}$ HS state mainly on account of the lattice strain not oxygen vacancies. The mechanism of the FM of the LSCO thin films is as a result of the competition of DE, SE interactions of different spin states of Co ions induced by the lattice strain. Combining with lattice strain, Sr doping can change the LSCO thin film not only from NM to FM but also from FM to NM. Our results are helpful for a deep understanding of the origin of magnetism of LSCO thin films and pave the way for changing the magnetization of the LSCO thin film artificially, which is of great significance for the designing of the future devices using the LSCO materials.

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\textsuperscript{18}See supplementary material at http://dx.doi.org/10.1063/1.4937562 for more details of the analysis.

