Coercivity enhancement driven by interfacial magnetic phase separation in SrTiO$_3$(001)/Nd$_{0.5}$Sr$_{0.5}$CoO$_3$

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Thin-film perovskite cobaltites have been found to exhibit coercivity values enhanced by almost 2 orders of magnitude in comparison to bulk. In this paper, we have investigated this unexplained coercivity enhancement in detail, focusing on epitaxial SrTiO$_3$(001)/Nd$_{0.5}$Sr$_{0.5}$CoO$_3$ films, which display coercivity values up to 40 kOe at low temperatures. Thickness-dependent (10–800 Å) magnetometry and magnetotransport studies demonstrate that nanoscopic magnetic phase separation occurs in the interface region of Nd$_{0.5}$Sr$_{0.5}$CoO$_3$ [consistent with recent work on SrTiO$_3$(001)/La$_{1-x}$Sr$_x$CoO$_3$], which is responsible for the degradation in magnetic and electronic properties in the very-thin-film limit. The coercivity is shown to be intimately related to the existence of this (70-Å-thick) interfacial phase-separated layer, leading us to advance an explanation for the coercivity enhancement in terms of the pinning of domain walls by interfacial nanoscopic ferromagnetic clusters and a crossover to single domain clusters at very low thickness. Simple estimates of the magnetocrystalline anisotropy (from the maximum coercivity), cluster dimensions (from the superparamagnetic blocking temperature), multidomain to single domain crossover point, and domain-wall width, provide quantitative support for this picture.

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I. INTRODUCTION

The investigation of complex oxide heterostructures has undergone dramatic expansion in recent years, driven by exciting prospects from both the fundamental and the applied perspectives. Much of the scientific interest has focused on the ability to stabilize novel nonequilibrium ground states (either at interfaces or due to epitaxial strain), or to obtain film properties distinctly different from bulk. Due to the extraordinary functionality of the materials, potential technological applications arise in very diverse areas, such as solid oxide fuel cells (SOFCs), catalysis, ferroelectric random access memory (RAM), spintronics, and, indeed, oxide electronics, in general. Given the importance of heterointerfaces in these applications, the well-known issue of degradation in desired properties at interfaces with dissimilar oxides becomes a significant challenge.

Magnetic complex oxides, such as the intensively studied perovskite manganites provide a perfect example via two, likely closely related, experimental observations. The first comes from oxide magnetic tunnel junctions (MTJs), such as (001)-oriented LSMO/STO/LSMO trilayers [La$_{1-x}$Sr$_x$MnO$_3$ = LSMO and SrTiO$_3$ = STO]. In these MTJs, the anticipated high-conduction electron-spin polarization in LSMO and the close lattice match to STO, lead to exceptionally high tunneling magnetoresistance (TMR) at cryogenic temperatures. The TMR decreases rapidly with increasing temperature however [even well below the Curie temperature ($T_C$)] , an effect that was linked to the difficulty of maintaining high, thermally stable, magnetization and spin polarization at LSMO surfaces and interfaces. The second observation comes from single ferromagnetic (F) metallic manganite films (e.g., $x \approx 0.3$ LSMO) deposited on single crystalline insulating perovskite substrates, such as STO(001). Even in this close to ideal situation, degradation in magnetization and conductivity is consistently observed in the very-thin-film limit [e.g., Refs. 9–12], being substantially stronger than what would be expected from conventional finite-size effects.

Recently, we investigated this issue of degradation in magnetic and electronic properties in very thin films, using the doped perovskite cobaltite La$_{1-x}$Sr$_x$CoO$_3$ (LSCO) as a model system. This is a material that has generated considerable interest from the fundamental magnetism perspective [primarily due to phenomena, such as spin-state transitions and magnetoelectronic phase separation (MEPS) e.g., Ref. 14], at the same time being of interest for applications in catalysis, spintronics, and as electrodes in SOFCs, and ferroelectric RAM. In bulk form, this system exhibits the well-known MEPS phenomenon. Nanoscopic hole-rich F clusters form in a semiconducting non-F matrix, as evidenced by a number of techniques, including neutron diffraction, Co nuclear magnetic resonance, small-angle neutron scattering (SANS), and inelastic neutron spectroscopy. As $x$ is increased, the clusters percolate at a critical doping level of $x_c = 0.17–0.18$, inducing a transition to a metallic long-range-ordered F ground state, which is reached at a critical doping level of $x = 0.22$, a homogeneous F phase is entered, i.e., the phase-separated regime ends, a fact that can be understood within a doping fluctuation model. $T_C$ eventually approaches room temperature deep in the F phase. Importantly, in the MEPS regime, this material was shown to be a natural analog to artificial systems formed by depositing F clusters in a non-F matrix, leading to an intercluster giant magnetoresistance (GMR)-type effect, directly analogous to intergranular GMR. Thus, this intercluster magnetotransport effect provides a simple probe of the existence of nanoscopic MEPS, a fact which played a key role in our recent study of the degradation in magnetization and conductivity in STO(001)/LSCO films. This system was found to enter a suppressed magnetization state below a thickness $t^*$ of about 80 Å at $x = 0.5$, coincident with a...
crossover from metallic-like to insulating-like transport. This crossover was found to be accompanied by the abrupt onset of large, negative, hysteretic, and isotropic magnetoresistance (MR), which was conclusively demonstrated to be of the intercluster GMR type. This provides strong, albeit indirect, evidence that the well-known degradation in electronic and magnetic properties actually occurs due to the formation of a thin magnetically phase-separated layer near the interface with STO(001), even at compositions that do not exhibit MEPS in bulk. This conclusion was verified via direct detection of the short-range F clusters using SANS. The interface-induced MEPS was then subsequently explained via the observation of subtle depthwise variations in Sr doping and O content. These variations were ascribed to intrinsic thermodynamic and structural effects, the formation of an O vacancy superstructure to accommodate lattice mismatch with the substrate being the most important.

During the course of the STO(001)/LSCO study described above, it was noticed, in agreement with other observations on LSCO and La$_1$-$_x$Ca$_x$CoO$_3$ (001) films, that the coercivity ($H_C$) is substantially enhanced over the bulk value. This is aptly demonstrated by Fig. 1(b), which displays 10-K hysteresis loops of an $x = 0.5$ LSCO bulk polycrystalline specimen, and an 800-Å-thick epitaxial film on STO(001). The bulk $H_C$ is 0.25 kOe, typical for polycrystalline samples of this composition. The film $H_C$, on the other hand, is 7 kOe, increasing up to 18 kOe at lower thicknesses. Thus, the coercivity is enhanced by a factor of almost 100 over the bulk value, the origin of this enhancement being unknown. In terms of executing a systematic study of this $H_C$ enhancement, Nd$_{1-x}$Sr$_x$CoO$_3$ (NSCO) is an attractive material due to the fact that, from the currently available data, it exhibits the largest bulk $H_C$ values in the Ln$_{1-x}$AE$_x$CoO$_3$ series (Ln and AE represent lanthanide and alkaline-earth ions, respectively). Bulk polycrystalline samples at $x = 0.3–0.5$ were found to exhibit $H_C$ values on the order of 2 to 3 kOe [see Fig. 1(a)], which was interpreted by Fondado et al. in terms of the orbital angular momentum ($L$) contribution of the Nd ions to the magnetocrystalline anisotropy, via the $L$-$S$ coupling. The data of Fig. 1(a) demonstrate that this indeed translates into very large $H_C$ values in thin-film $x = 0.5$ NSCO.

We find $H_C = 27$ kOe in the thick-film limit (i.e., 800 Å), increasing to almost 40 kOe at lower thickness, as discussed in detail below. Therefore, we view STO(001)/NSCO as an ideal system in which to study the fundamental physical origins of this extraordinary $H_C$ enhancement.

Thus, the object of this study is threefold. We wish to determine (a) if the STO(001)/NSCO system exhibits the same degradation in magnetic and electronic properties as LSCO(001) in the very-thin-film limit, (b) if so, whether this degradation can be related to the existence of a nanoscopic magnetically phase-separated layer detected via the characteristic intercluster magnetotransport, and (c) whether the observed $H_C$ enhancement is related in any way to this interface-induced MEPS. As discussed in detail below, the results confirm that the thickness dependence of the magnetic and transport properties is indeed strongly degraded in the very-thin-film limit, and that this is again related to the existence of interfacial MEPS. Most importantly, the $H_C$ enhancement is found to be intimately related to the formation of this phase-separated layer near the interface with STO(001). The thickness dependence of $H_C$ in fact leads us to advance pinning of domain walls at nanoscopic F clusters in the interface layer, and an eventual crossover to a single domain cluster regime as the origin of the coercivity enhancement. A simple quantitative analysis of the temperature- and thickness-dependent magnetometry data demonstrates self-consistency of this picture, providing further support for the model. Thus, the results provide a complete explanation for the very large $H_C$ values found in thin perovskite cobaltite films, further emphasizing the importance of subtle interfacial phenomena for the magnetic properties of these complex oxide films.

II. EXPERIMENTAL CONSIDERATIONS

NSCO films ($x = 0.5$ in all cases) were deposited on STO(001) substrates by reactive sputtering from 2-in. sintered ceramic targets prepared by a conventional solid-state reaction. Depositions were performed at a substrate temperature of 700 °C, a deposition rate of 1.8 Å/min (100 W of power), and O$_2$ and Ar partial pressures of 20 and 50 mTorr, respectively. The base pressure of the system was $1 \times 10^{-8}$ Torr. Postdeposition annealing for 2 h in flowing O$_2$ at 500 °C removed all traces of a CoO impurity phase from the x-ray diffraction patterns. Note that these conditions are very similar to those used for the STO(001)/LSCO system studied previously and that details on the optimization of those growth conditions are provided in Ref. 37. Structural characterization by high-resolution x-ray diffraction (including wide-angle diffraction, rocking curves, in-plane diffraction, and grazing incidence reflectivity) was performed using CuK$_\alpha$ radiation on a PANalytical X’pert system. Thickness and deposition rate determinations were done with x-ray reflectivity. Scanning transmission electron microscopy (STEM) observations were carried out in a VG Microscopes HB501UX dedicated STEM operated at 100 kV. This column is equipped with a Nion aberration corrector and...
a Gatan, Inc. Enfina electron energy loss (EELS) spectrometer. Co $L_{2,3}$ and Ti $L_{2,3}$ depth profiles were generated by integrating the intensities under the EELS edges after background subtraction (using a power-law fit). The chemical profiles were averaged laterally over approximately 20 nm in the direction parallel to the interface. Specimens for STEM were prepared by conventional methods, i.e., grinding, dimpling, and Ar-ion milling. Magnetometry measurements (10–300 K, fields up to 70 kOe) were performed in a Quantum Design superconducting quantum interference device system, while critical thickness ($t_{\text{crit}}$) with a factor of 2 smaller than that seen for STO(001)/LSCO at the STO (002) factor of 2 smaller than that seen for STO(001)/LSCO at the STO (002) (see below for more details). The leftmost vertical dotted line indicates the expected diffraction angle for a fully relaxed film, highlighting that, even at 800 Å, these films do not fully relax to the bulk lattice parameter. It is worth noting that the $t_{\text{crit}}$ we observe here for STO(001)/NSCO (i.e., 100 Å) is a factor of 2 smaller than that seen for STO(001)/LSCO at the same $x$ value and deposition conditions. This is qualitatively consistent with the increased lattice mismatch (2.43%) cf. the LSCO case (1.92%).

Additional data on the strain relaxation process is shown in Fig. 3, which plots the $t$ dependence of $c$, the (002)-rocking-curve FWHM, and the length scale $\Lambda$, extracted from the width of the (002)-wide-angle diffraction peak using Scherrer’s equation. As discussed previously for STO(001)/LSCO, these three quantities clearly reveal $t_{\text{crit}}$, which is indicated by the vertical dotted line at $t = 100$ Å. The $c$-axis lattice parameter [Fig. 3(a)] is approximately constant for $t < t_{\text{crit}}$, relaxing rapidly at higher thicknesses. This relaxation is also seen in the (002)-rocking-curve width [Fig. 3(b)] due to the increased mosaicity associated with the strain relaxation mechanism. In STO(001)/LSCO, this was directly related to a crossover from a two-dimensional (2D)-like to a three-dimensional growth mode. This strain relaxation is also evident in the $\Lambda(t)$ data, which deviate downward from $\Lambda = t$ at 100 Å. This occurs due to the fact that, below $t_{\text{crit}}$, the out-of-plane diffraction peak width is dominated by finite-size effects (the thickness in this case as the scattering vector is purely out of plane), with no contribution from the microstrain as the film is uniformly strained throughout its depth. Above $t_{\text{crit}}$ however $\Lambda(t)$ deviates below $\Lambda = t$ due to the microstrain contribution to the peak width that necessarily occurs in partially relaxed films.

Further characterization of the structure of these epitaxial STO(001)/NSCO films is provided by the Z-contrast STEM imaging shown in Fig. 4. Figure 4(a) displays a low magnification image of a 90-Å-thick film, demonstrating that the film is relatively smooth and continuous over long lateral

![Graph](image.png)
length scales (≈2500 Å). The higher magnification image of the interior of a 330-Å-thick sample [Fig. 4(b)] reveals the oxygen vacancy superstructure discovered previously in LSCO films,39 which leads to intensity modulation of alternate CoO2 planes. The formation of this tetragonal superstructure is confirmed by the fast Fourier transform shown in the inset to Fig. 4(b), which displays weaker features midway between the strong primary diffraction spots. Progressively higher magnification microscopy [Figs. 4(c) and 4(d)] reveals a sharp coherent interface in atomic resolution images. The extent to which the STO/NSCO interface is chemically abrupt is better assessed in Fig. 4(e), which plots the normalized and extent to which the STO/NSCO interface is chemically abrupt a sharp coherent interface in atomic resolution images. The LSCO films,39 which leads to intensity modulation of alternate the oxygen vacancy superstructure discovered previously in the interior of a 330-Å-thick sample [Fig. 4(b)] reveals higher magnification microscopy [Figs. 4(c) and 4(d)] reveals in the same film. An explicit scale bar is provided in (a); for (b)–(d) high-resolution images of the substrate-film interface and (c) and (d) high-resolution images of the substrate-film interface in the same film. An explicit scale bar is provided in (a); for (b)–(d) (atomic-resolution images) note the lattice parameters determined in the text. The inset to (b) is a fast Fourier transform of the image. Panel (e) shows a depth (z) profile of the normalized integrated EELS intensity for Co and Ti for the sample shown in (a). The dotted lines are fits to provide a simple characterization of the interface width as described in the text.

We begin our discussion of the magnetic and transport properties of these STO(001)/NSCO films with Fig. 5, which plots the temperature (T) dependence of the low field (H = 100 Oe) magnetization (M) and coercivity normalized to their 10-K values (top panel), electrical resistivity (ρ) in both 0- and 90-kOe magnetic fields (middle panel), and the 90-kOe MR, defined as [ρ(H) − ρ(0)/ρ(0)] (bottom panel). The data are shown for three representative thicknesses: 620, 120, and 55 Å. Starting with $M(T)$ [Hc(T) will be discussed below], from Fig 5(a), we see that the films exhibit bulklike F properties at large thicknesses (i.e., 620 Å). The observed $T_C$ is around 200 K, suppressed by about 20 K with respect to bulk polycrystals.36 This is a similar magnitude of suppression with respect to the bulk found in STO(001)/LSCO, which exhibits $T_C$ values suppressed by 15–20 K at the same $t$.13,37 Given the observation (Fig. 4) of an O vacancy superstructure, it is obvious that at least some level of O deficiency must be present, despite the cool in O2 and postdeposition anneal. It is worth pointing out that, based on the bulk phase diagram,36
an O deficiency of only 0.04, i.e., a chemical formula of Nd$_{0.5}$Sr$_{0.5}$CoO$_{2.96}$ would be sufficient to account for this reduction in $T_C$. Note that the lower $F$ ordering temperatures for NSCO cf. LSCO (at any particular $x$ value) are consistent with the narrower $e_g$-derived bandwidth expected from the reduced ionic size of Nd$^{3+}$ (1.27 Å) cf. La$^{3+}$ (1.36 Å). This results in a tolerance factor (TF) of about 0.970 [cf. 0.985 for LSCO (Ref. 40)], which drives the observed symmetry change from rhombohedral ($R$-$3c$)/cubic ($Pm$-$3m$) (Ref. 41) to orthorhombic ($Pnma$) (Refs. 34, 36 and 38) in bulk. The resultant decrease in the Co-O-Co bond angle from 180$^\circ$ then leads to the reduced double exchange bandwidth and $T_C$ in a simple picture. The other important feature present in $M(T)$ at $t = 620$ Å [Fig. 5(a)], is the clear decrease in $M$ below about 60 K, confirming that the ferrimagnetism induced by the antiferromagnetic ordering of the Nd$^{3+}$ ions with respect to the Co sub-lattice$^{38}$ is preserved in thin films. The Nd ordering temperature ($T_{\text{fem}}$) is 55–60 K, again slightly depressed in comparison to the 70-K bulk value.$^{36,38}$ As $t$ decreases to 120 Å [Fig. 5(b)] and 55 Å [Fig. 5(c)], the qualitative form of $M(T)$ is unaltered, but $T_C$ and $T_{\text{fem}}$ decrease (see below for more details).

The transport and magnetotransport properties are shown as a function of $t$ in the middle and lower panels of Fig. 5. At high $t$, the $\rho(T)$ curve in $H = 0$ [Fig. 5(d)] reveals a 300-K resistivity around 3 mΩ cm with negative $d\rho/dT$ over the entire measured temperature range. Application of $H = 90$ kOe leads to a negative MR, which peaks at $\approx -5.5\%$ near 160 K, i.e., somewhat below $T_C$. As $T \rightarrow 0$, the MR decreases, falling to only $-1\%$ at 5 K. Thus, the $M$ behavior at these high $t$ values is rather similar to bulk, where the negative MR peaks just below $T_C$ at values around $-5.5\%$. However, the increased $\rho$ in comparison to bulk [$\sim 0.3$ mΩ cm at 300 K for $x = 0.5$ (Ref. 36)], and the absence of a wide $T$ interval over which a metalliclike $T$ dependence (i.e., $d\rho/dT > 0$) is observed, is somewhat unexpected. In bulk polycrystalline samples, positive $d\rho/dT$ emerges below $T_C$ for $x \approx 0.30$. In the absence of additional data on the distortion of the CoO$_6$ octahedra in these strained thin films, we can only assume that effects such as increased O vacancy concentration (or other forms of increased disorder cf. bulk) are sufficient to induce a weakly semiconducting state in thin films. It should be noted that the lowering of the average $A$-site cation radius from La$^{3+}$Sr$_{0.5}$CoO$_3$ (TF = 0.985) to Pr$_{0.5}$Sr$_{0.5}$CoO$_3$ (TF = 0.975) to Nd$_{0.5}$Sr$_{0.5}$CoO$_3$ (TF = 0.970) leads to a decrease in the residual resistivity ratio $[\rho(300\text{ K})/\rho(0)]$, where $\rho(0)$ is the residual resistivity of $x = 0.5$ polycrystalline bulk samples from 3 (Ref. 14) to 1.7 (Ref. 36). Thus, it is clear that Nd$_{0.5}$Sr$_{0.5}$CoO$_3$ lies close to the boundary for the onset of localization of the electrons in the $e_g$-derived band. This is supported by observations on bulk Pr$_{1-x}$Ca$_x$CoO$_3$ at high $T$ ($T \approx 0.95$), where a regime with $d\rho/dT > 0$ over a wide $T$ interval does not occur.$^{43}$ In the context of the current paper, the behavior of $\rho(T)$ and MR($T$) at lower thicknesses is of more interest. As shown in Fig. 5(e), reducing $t$ to 120 Å only leads to a small increase in $\rho$ and a slightly stronger insulatinglike $T$ dependence. The peak in MR($T$) below $T_C$ is still present [Fig. 5(b)], although the low $T$ tail in the MR is significantly more pronounced than in the 620-Å-thick sample. At $t = 55$ Å [Fig. 5(f)], however, the increase in $\rho$ is much more dramatic; the low $T$ resistivity

FIG. 5. (Color online) Temperature dependence of the reduced magnetization (left axis) and coercivity (right axis) (top panel), resistivity in zero field and 90-kOe field (middle panel), and the magnetoresistance (bottom panel), defined as $[\rho(90\text{ kOe}) - \rho(0)]/\rho(0)$.

The data are shown for films with thicknesses of 620 Å (left panel), 120 Å (middle panel), and 55 Å (right panel).
is summarized in Fig. 6, which plots $T_C$ for polycrystalline samples exhibit of comparison to bulk properties, note that $x T_C$ in (c). The vertical dotted line marks the characteristic thickness $t^*$. Other dotted lines are guides to the eye.

increases by over an order of magnitude in comparison to $t = 120 \, \AA$, and a strongly insulating $T$ dependence is observed, with no clear anomaly in $\rho(T)$ at $T_C$. A similarly dramatic change occurs in the MR [Fig. 5(i)]. The small feature at $T_C$ is now dominated by the large low $T$ tail, the MR approaching $-60\%$ at the lowest $T$ measured. This greatly exceeds any MR observed in the long-range-ordered F metallic phase in bulk NSCO.36

The $t$ dependence of these magnetic and transport properties is summarized in Fig. 6, which plots $T_C$, $T_{\text{term}}$, the saturation magnetization [$M_S$, determined from 10-K $M(H)$ loops], and the MR at $T = 35 \, \text{K}$ and $H = 90 \, \text{kOe}$. For purposes of comparison to bulk properties, note that $x = 0.5$ bulk polycrystalline samples exhibit $T_C \approx 220 \, \text{K}$, $T_{\text{term}} \approx 70 \, \text{K}$, $M_S \approx 0.8 \, \mu_B/\text{Co}$, and MR ($T = 35 \, \text{K}$) $\approx 0$.36 The evidence for an abrupt crossover to a state below $t = 70 \, \text{Å}$ with suppressed $T_C$, suppressed $M_S$, and enhanced resistivity and low $T$ MR is quite clear. The rapid increase in 35-K MR, from $-6.5\%$ at $t = 75 \, \text{Å}$ to $-55\%$ at $t = 55 \, \text{Å}$ is particularly dramatic. Importantly, as in the STO(001)/LSCO case,13,37 this low $T$ MR exhibits all the characteristic signatures of the intercluster GMR-type effect discussed above,13,32 clearly distinguishing it from the more conventional MR effect found in the vicinity of $T_C$. Specifically, this low $T$ MR is found to be negative, hysteretic [with peaks in $\rho(H)$ at $H_C$], and isotropic with respect to the relative orientation of the injection current ($I$) and applied field. As an example, we find a 45-K negative MR of 37% in 90 kOe with $H$ perpendicular to $I$, compared to 36% with $H$ parallel to $I$ (in both cases, $H$ is in plane). As discussed above, this form of MR can definitively be assigned to the situation where isolated nanoscopic F clusters exist in a non-F matrix.13,32 In the case of STO(001)/LSCO, this was further substantiated by direct detection of these nanoscopic magnetic clusters via SANS measurements on multiply stacked films.13 Thus, we conclude that, below some thickness $t^*$ (70 Å, in this case), an interfacial MEPS layer is found, explaining the existence of suppressed $M_S$, enhanced $\rho$, and an intercluster MR effect. The only quantitative difference in comparison to the STO(001)/LSCO system is the slightly smaller $t^*$ of 70 Å cf. 85 Å (Ref. 13) (at $x = 0.5$). Given the extraordinary level of similarity with the case of STO(001)/LSCO, we assume that this interfacial MEPS layer has the same microscopic origin, i.e., deepwise variations in Sr and O concentrations, which can be traced back to the differences between bulk- and surface-dopant dissolution energies and tensile strain effects, respectively.13,22

As in the STO(001)/LSCO case, it is likely that the formation of O vacancies to accommodate lattice mismatch with the substrate is important.13 Thus, the formation of an O vacancy superstructure (Fig. 4) running perpendicular to the interface [as in STO(001)/LSCO] is significant. As a final comment on the data of Fig. 6, we should point out that $T_C(t)$ (which is discussed in more detail below) is in fact quantitatively similar in form to $T_C(t)$; when $T_C(t)/T_C (800 \, \text{Å})$ is compared to $T_{\text{term}}(t)/T_{\text{term}} (800 \, \text{Å})$, the curves are indistinguishable within the scatter of the data.

Having confirmed rapid degradation in electronic and magnetic properties below a thickness $t^*$ of 70 Å, and having established that this is due to nanoscopic interfacial MEPS as in STO(001)/LSCO, 10-K $M(H)$ loops were measured at multiple $t$ in order to determine whether $H_C(t)$ reflects the interfacial MEPS layer, as might be expected if this is intimately related to the anomalous $H_C$ enhancement. The results, shown in Fig. 7, indeed provide clear evidence for the importance of the characteristic thickness $t^*$. The coercivity is found to increase gradually from 19.5 kOe at 800 Å to ~30 kOe near $t^*$. Below, this $H_C$ increases much more rapidly, reaching a plateau near 38 kOe in the region between 45 and 20 Å, before dropping precipitously to 0 at even lower $t$. Therefore, we define three distinct regions (I, II, and III), as indicated in Fig. 7 and as shown schematically in Figs. 8(a)–8(c). Region III ($t > t^*$) corresponds to the situation where a continuous long-range-ordered F film with thickness ($t - t^*$) lies atop

![FIG. 6. (Color online) Thickness dependence of (a) the Curie and F-ordering temperatures, (b) the 10-K saturation magnetization, and (c) the 35-K 90-kOe magnetoresistance. Note the logarithmic scale in (c). The vertical dotted line marks the characteristic thickness $t^*$. Other dotted lines are guides to the eye.](image)

![FIG. 7. Thickness dependence of the 10-K coercivity. The data are divided into three thickness regions by the characteristic thicknesses $t^*$ and $t_{SP}$, marked by the vertical dotted lines. The dotted line through the data is a guide to the eye.](image)
the magnetically inhomogeneous nanoscopic phase-separated layer of thickness $t^*$. Region II, on the other hand ($t_{SP} \lesssim t \lesssim t^*$), corresponds to the situation where the entire film is composed of nanoscopic F clusters embedded in a non-F matrix. It will be shown below that these nanoscopic F clusters are single domain and, in this region, that they are thermally stable. Finally, in region I ($t < t_{SP}$), as discussed in more detail below, the nanoscopic F clusters become thermally unstable, i.e., superparamagnetism sets in, leading to the vanishing of $H_C$.

Measurements of $H_C(T)$ at various $t$ provide considerable additional insight. Such data are shown in Figs. 5(a)–5(c), where the right axis shows $H_C(T)$ normalized to its low $T$ value. Starting at $t = 620 \, \text{Å}$, i.e., deep into regime III of Fig. 7, we find that $H_C$ decreases monotonically with $T$, falling smoothly to 0 as $T \rightarrow T_C$. In fact, the form of $H_C(T)$ is very similar to that seen in bulk NSCO (Ref. 36) and LSCO (Ref. 44) at $x = 0.5$, the superlinear $T$ dependence being consistent with expectations for conventional Fss with strong irreversibility. Figure 5(b) shows that this behavior is preserved at $t = 120 \, \text{Å}$, i.e., a thinner film in region III. However, at $t = 55 \, \text{Å}$ (i.e., region II, $t < t^*$), very different behavior is observed. Specifically, $H_C$ drops very quickly with increasing $T$, vanishing at 45 K, i.e., well below the point at which $M(T)$ measured in $H = 100 \, \text{Oe}$ falls to 0. Measurements of $M(T)$ using a zero-field cooling protocol (not shown) reveal a small peak at a similar temperature (48 K). These observations, particularly the absence of hysteresis above some value of $T$, clearly indicate the onset of superparamagnetism in this very-thin-film regime with a blocking temperature $T_B$ of 45 K at $t = 55 \, \text{Å}$. Quite simply, the isolated nanoscopic F clusters in the magnetically phase-separated layer [Fig. 8(c)] become thermally unstable at very low $T$, leading to superparamagnetism. Thus, $T_B$ marks a transition from a high $T$ state where the cluster magnetizations fluctuate randomly on the time scale of the measurement to a low $T$ state where the individual cluster magnetizations freeze. It is worth noting that, in the case of the $t = 55$-Å film, $T_B$ lies very close to $T_{\text{ferri}}$. It is possible that the ordering of the Nd lattice provides additional magnetocrystalline anisotropy, thus contributing to the blocking transition. Low $T$ measurements on an even thinner film ($t = 12 \, \text{Å}$), reveal that $H_C$ vanishes at a lower blocking temperature of only 10 K.

Based on the above observations, we can advance a simple qualitative picture capable of explaining all of the observed phenomena, particularly $H_C(t,T)$. After discussion of this qualitative picture, we will present a simple quantitative analysis of the important magnetic parameters, demonstrating feasibility and self-consistency of the model. The basic picture is summarized schematically in Fig. 8. We propose that the nanoscopic short-range F clusters in the interfacial layer are single domain particles and are elongated in the film growth direction. (For simplicity, we will model them as cylindrical.) This morphology is the simplest scenario consistent with the observed data, in particular the decrease in $T_B$ with decreasing $t$, which necessarily requires that the single domain particles have a volume that increases with $t$. Qualitatively, the $H_C$ behavior observed in regions I–III can then be simply explained. Region III corresponds to a situation where the magnetization reverses via domain-wall motion in the long-range-ordered F overlayer. As $t \rightarrow t^*$, the thickness of this uniform layer decreases, providing two obvious driving forces for the $H_C$ enhancement with decreasing $t$; the influence of dimensional confinement on the motion of what are presumably Néel walls, and the domain-wall pinning potential created by the inhomogeneous nanoscopic phase-separated layer at the interface with the STO. We believe that both effects are likely active. The former is straightforward and leads to an increase in $H_C$ as $t \rightarrow t^{**}$ due to the increased energy barrier associated with the propagation of a Néel wall through a progressively thinner uniform F film. The second, i.e., the pinning of the domain walls45,46 by the phase-separated layer, is illustrated schematically in Figs. 8(d)–8(f). In essence, the total magnetic energy of the system is maximized when the domain walls in the long-range F overlayer align with the nanoscopic F clustered regions. Exact alignment of the domain wall with an F cluster would lead to the additional exchange energy cost associated with extending the domain wall through the F cluster to the interface with the STO(001) substrate. This is avoided (hence minimizing the total magnetic energy) by preferentially aligning the domain wall with the edge of the nanoscopic clusters or the non-F regions between the clusters, as shown in Fig. 8(d). Further motion of the domain wall then requires the additional input of energy required to switch the proximal F clusters, as shown in Fig. 8(e). The process is then repeated when the next F cluster is encountered [Fig. 8(f)]. In essence, the nanoscopic phase-separated layer generates a quasi-periodic 2D pinning potential for the long-range F overlayer, producing a situation where the domain wall executes a staggered motion due to sequential pinning/depinning transitions. This leads to an enhancement of $H_C$, which increases strongly as $t \rightarrow t^{**}$ (i.e., as the overlayer thickness approaches zero), as this is essentially an interface effect.

As $t$ is further decreased to the point where it falls below $t^*$ [i.e., the entry to region II, Fig. 8(b)], domain-wall motion is no longer possible, and the magnetization reversal in the single domain F clusters is forced to occur via rotation of

![FIG. 8. (Color online) (a)–(c) Schematics of the magnetic structure of films in regions III, II, and I, respectively. The dark regions are F ordered. (d)–(f) Schematics of the magnetic structure of a film in region III as a Néel wall propagates through the F overlayer.](image-url)
the magnetization of the individual isolated clusters. In this region, \(H_C\) is approximately constant (Fig. 7) until the cluster volume is reduced to the point where thermal stability of the nanoscopic cluster magnetization becomes an issue, i.e., the superparamagnetic regime (region I). In this very-thin-film regime, \(T_B\) decreases with decreasing \(t\), reaching 45 K at \(t = 55\, \AA\) [Fig. 5(c)], before eventually falling below 10 K, leading to the vanishing \(H_C\) seen in Fig. 7.

Simple quantitative estimates provide considerable support for this picture by demonstrating that the scenario is feasible given the known magnetic properties of the material and (b) that the model is self-consistent. The key magnetic parameters in the problem (e.g., the critical volume for superparamagnetism, the critical dimension for the single domain to multidomain crossover, the domain-wall width in the overlayer, etc.) require the knowledge of \(M_S\), the exchange stiffness (\(A\)), and the anisotropy constant (\(K\)). Given that we have detailed knowledge of \(M_S\), and that \(A\) can be estimated from mean-field theory, the central issue is the magnitude of \(K\).

The coercivity measured in region II provides a simple estimate of this magnetocrystalline anisotropy. Quite simply, we relate the maximum \(HC\) value measured in region II \(\langle H_{C\text{max}} \rangle\) to the anisotropy constant using the Stoner-Wohlfarth expression\(^{45}\) for coherent rotation of a single domain particle (the F clusters in this case),

\[
K_U = \frac{M_S H_{C\text{max}}^2}{2}. \tag{1}
\]

Note that we are explicitly assuming, for simplicity, that the magnetocrystalline anisotropy is uniaxial; \(K_U\) is the uniaxial anisotropy constant. Using 10-K values of \(M_S = 0.8\) \(\mu_B/Co\) and \(H_{C\text{max}} = 38.5\, \text{kOe}\), we obtain \(K_U = 2.5 \times 10^6\, \text{erg/cm}^3\) for STO(001)/NSCO and similar values for STO(001)/LSCO. Although the available data are limited, the agreement with other literature values is very reasonable. Specifically, Aarboðh et al.\(^{26}\) estimated the LSCO cluster anisotropy constant based on very simple arguments relating to the behavior of the bulk \(M(T)\) and obtained \(K_U \approx 0.3–1 \times 10^6\, \text{erg/cm}^3\). The more accurate methods of Mira et al.\(^{27}\) yielded \(K_U = 2.1 \times 10^6\, \text{erg/cm}^3\) at low \(T\) in x = 0.3 LSCO, in very good agreement with our value. This agreement is encouraging and confirms that the single domain Stoner-Wohlfarth-like picture is indeed applicable to the nanoscopic F clusters.

Additional quantitative information can be garnered from the data on the superparamagnetic blocking temperature \(T_B\). Assuming, as is typical, an attempted frequency on the order of 10\(^9\) Hz, the critical volume of 1 s is given by\(^{35}\)

\[
V_{SP} = \frac{4}{3} \pi R_{SP}^3 = \frac{4}{3} \pi \frac{6 k_B T}{K_U}. \tag{2}
\]

It is clear from Eq. (2) that \(T_B\) scales with \(V_{SP}\). Our data indicate \(T_B = 45\, \text{K}\) at \(t = 55\, \text{Å}\) and \(T_B = 10\, \text{K}\) at \(t = 12\, \text{Å}\), meaning that the ratio of the blocking temperatures (4.5:1) scales almost exactly with the thickness ratios (4.6:1), strong evidence that the cross-sectional area of the F clusters is independent of \(t\), i.e., the cylindrical geometry postulated above [Figs. 8(b) and 8(c)]. Inserting \(T_B = 45\, \text{K}\) and \(K_U = 2.6 \times 10^6\, \text{erg/cm}^3\) into Eq. (2), allows us to calculate the critical cluster radius for superparamagnetism \((R_{\text{clus}})\) from \(V_{SP} = \pi R_{\text{clus}}^3\). This generates a cluster radius of 20 \(\text{Å}\), remarkably consistent with the direct (SANS-based) measurements of the cluster dimensions just under the percolation threshold (i.e., \(x = 0.18\)) in bulk LSCO [around 23 \(\text{Å}\) (Ref. 23)]. This demonstrates that the superparamagnetism we observe in the very-thin-film limit is consistent with the expected length scales for the magnetic phase-separation effect in these systems. At this point, it is worth noting that the dimensions of these nanoscopic F clusters lie far below the expected single domain to multidomain crossover length scale, confirming that the assumption of single domain behavior is appropriate. In the large \(K_U\) limit (i.e., \(K_U \gg \mu_0 M_S^2\), easily satisfied in this case), the critical radius for the single domain to multidomain crossover in a spherical particle is given by\(^{45}\)

\[
R_{SD} = 9 (A K_U)^{1/2} / \mu_0 M_S^2, \tag{3}
\]

where \(\mu_0\) is the vacuum permeability. Performing a simple mean-field estimate of the exchange constant from \(T_C\), the lattice coordination number \((z)\) and the Co ion spin \((S)\),\(^{38}\) allows for estimation of \(A\) via \(A \approx \pi / (d)^2\), where \(d\) is the spacing between the Co ions. This gives \(A = 1 \times 10^{-12}\, \text{Jm}^{-1}\), which, when substituted into Eq. (3) yields \(R_{SD}\) in excess of 100 nm, i.e., much greater than the cluster dimensions. Thus, it is clear that the F nanoclusters in the magnetically phase-separated interfacial layer are indeed expected to be single domain.

It is also worth pointing out that the expected domain-wall widths in the F overlayer are on approximately the same scale as the size and spacing of the F clusters in the interfacial MEPS layer. In the thin-film limit (i.e., \(t < \delta\)), the Néel wall width is approximated by \(\delta \approx \pi (A/K_U)^{1/2}\), which yields \(\delta \approx 9\, \text{nm}\), a value that is expected to decrease with increasing \(t\) (Ref. 45). This is very comparable to the F-cluster diameter determined above (4 nm), and the cluster separation estimated from a simple comparison between the measured \(M_S\) at \(t = t^*\) and the bulk \(M_S\), which is on the order of 10 nm. These estimates confirm that the length scale describing the spatial variation of the 2D pinning potential is comparable to the expected domain-wall widths, meaning that strong pinning effects are indeed possible.

As a final comment on the coercive properties of these STO(001)/NSCO epilayers, it is worth pointing out that the nature of the magnetic anisotropy appears to be rather different than that seen in thin-film manganites. Figure 9 shows the 10-K in-plane angle \((\phi)\) dependence of \(H_C\) for a \(t = 800\, \text{Å}\) sample, i.e., the thick-film limit. Recall from Figs. 2 and 3 that these films remain significantly strained even at this thickness. Note that these data were simply extracted from anisotropie MR measurements of the type discussed in Ref. 37. Thus, they provide only \(H_C(\phi)\) rather than the remanence as a function of the angle, which is more direct. Nevertheless, the data apparently reveal the overall symmetry of the magnetocrystalline anisotropy, which appears to take the form of two biaxial anisotropies phase shifted by 45°. Specifically, \(H_C\) reaches weak minima at 0°, 90°, 180°, and 270°, in addition to stronger minima at 45°, 135°, 225°, and 315°. The weak minima correspond to the (100) family of directions for the STO(001) substrate, whereas, the strong minima correspond
to the (110) family. The simplest interpretation of these data is that the films possess a biaxial anisotropy with the easy axes along the pseudocubic NSCO (110) directions\(^4\) (producing the minima at 45\(^\circ\), 135\(^\circ\), 225\(^\circ\), and 315\(^\circ\)), in addition to a second substrate-imposed strain-induced biaxial anisotropy (producing the minima at 0, 90\(^\circ\), 180\(^\circ\), and 270\(^\circ\)). In fact, the solid line through the data in Fig. 9 is a simple model based on two biaxial anisotropies of differing magnitude. Although the existence of minima in \(H_{C}(\phi)\) at the easy axes is at first sight counterintuitive, \(H_{C}\) being lower along the easy axis than the hard axis has in fact been observed before in manganite thin films\(^5\), and, based on the form of \(H_{C}(\phi)\) determined in prior work on manganite films\(^5\), could even arise due to field misalignment. The essential difference between this situation and that seen in several prior studies on manganite films grown on STO is the existence of significant magnetocrystalline anisotropy intrinsic to the F. In the manganite case, the intrinsic anisotropy is so weak [\(K \sim 10^6\) erg/cm\(^3\)] (Ref. 52)] that the strain-induced\(^5\) or surface-step-induced\(^5\) contributions dominate. In the much more highly anisotropic cobaltites (\(K \sim 10^6\) erg/cm\(^3\)), the various contributions compete, the intrinsic anisotropy appearing to be the largest. Although these inferences are somewhat speculative, they do demonstrate that future studies using torque magnetometry\(^6\) and angle-dependent hysteresis loop measurements\(^5\) would be well worthwhile. As in the manganite case, it is likely that comparisons between (001)-oriented and (110)-oriented films will be needed to fully understand the behavior.\(^5\)\(^,5\)\(^2\)

As a final remark on the data, we note that future studies directed at understanding any possible relationship between the significant thin-film magnetocrystalline anisotropies and the O vacancy ordering are also worthwhile.

**IV. SUMMARY AND CONCLUSIONS**

To summarize, we have presented the results of a detailed study of the previously unexplained coercivity enhancement found to occur in thin-film perovskite cobaltites grown on STO(001) substrates. The STO(001)/Nd\(_{0.5}\)Sr\(_{0.5}\)CoO\(_3\) system was chosen for this study, and it was shown that it exhibited a rapid deterioration in magnetic and electronic properties below a thickness of approximately 70 Å, similar to STO(001)/LSCO. This deterioration is accompanied by the abrupt onset of large negative magnetoresistance at low temperatures, strong evidence that the degradation in magnetic and transport properties occurs due to interfacial magnetoelectronic phase separation on a nanoscopic scale. Detailed temperature- and thickness-dependent measurements demonstrate that the observed coercivity enhancement is intimately related to this interfacial phase separation. The data are interpreted within a simple picture where the coercivity increase with decreasing thickness is driven by a combination of the finite-size effect on Néel wall propagation in the continuous ferromagnetic overlayer and the 2D pinning potential provided by the nanoscopic ferromagnetic cluster array. Simple quantitative estimates of the key parameters provide strong support for the model and demonstrate self-consistency.

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