Manganese-based La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) compounds with the ABO$_3$-type perovskite structure exhibit a profuse variety of structural, electronic, and magnetic phases.\textsuperscript{1}$\La_{0.67}\Sr_{0.33}\MnO_3$ is a metallic ferromagnet at room temperature\textsuperscript{2} with unusual physical properties, such as colossal magnetoresistance (CMR)\textsuperscript{3} and almost total spin polarization (95% at 4 K)\textsuperscript{4} lending it significant potential for applications in spintronic devices. Bulk La$_{0.67}$Sr$_{0.33}$MnO$_3$ possesses a slightly distorted perovskite structure with a high Curie point $T_C = 370\;K$ and a saturation magnetization $M_S$ of 3.7 $\mu_B$/Mn.\textsuperscript{1} In thin films, strain originating from lattice/substrate mismatch plays a fundamental role in defining the structural and electronic properties of La$_{0.67}$Sr$_{0.33}$MnO$_3$. The small lattice mismatch between LSMO and SrTiO$_3$ (STO) (0.83%) is favorable for the epitaxial growth of thin films of LSMO.\textsuperscript{5}

Magnetic anisotropy can be an extremely sensitive probe of structural attributes in complex materials. While La$_{0.67}$Sr$_{0.33}$MnO$_3$ single crystals exhibit a uniaxial anisotropy in the (100) plane,\textsuperscript{6} films grown epitaxially on STO (001) develop an in-plane biaxial strain state with lower anisotropy in the orthogonal [100]/[010] directions relative to higher anisotropy in the [110] direction in the temperature range 20 K $\leq T \leq 300\;K$.\textsuperscript{7,8} Although the magnetocrystalline anisotropy energy of La$_{0.67}$Sr$_{0.33}$MnO$_3$ films has been widely studied as a function of temperature and film thickness,\textsuperscript{7,12} very little work has been done on the magnetic response of films in the explicit [100]/[010] crystallographic directions. In addition, there has been very little work on the magnetic properties as a function of A-site disordering in epitaxial films. Thermodynamically synthesized La$_{1-x}$Sr$_x$MnO$_3$, characterized by random site population of La$^{3+}$ and Sr$^{2+}$ cations in the perovskite A lattice site, allows the B-site cations to exhibit a mixed Mn$^{3+}$/Mn$^{4+}$ valence state. Current state-of-the-art synthesis techniques such as ozone-assisted molecular beam epitaxy allow control of the A-site disorder by interlayering layers of LaMnO$_3$ (LMO) and SrMnO$_3$ (SMO) to create ordered artificial or “digitally layered” analogues of La$_{1-x}$Sr$_x$MnO$_3$.\textsuperscript{13–15} represented as [(LMO)$_n$(SMO)$_m$)$_{x}$, where $n$ indicates the number of constituent integer layers and $m$ refers to the number of repeating units. In this manner, the correlations between spin, charge, and orbital degrees of freedom at the layer interface may be systematically investigated for their potential to generate novel states of matter.

In the present study, we employ magnetic measurements to investigate an unexpected and persistent asymmetry in the temperature dependence of the magnetization along the orthogonal [100] and [010] in-plane directions of La$_{0.67}$Sr$_{0.33}$MnO$_3$. This asymmetry signals a reduction in the in-plane symmetry of the film below room temperature and challenges the general assumption in the literature that La$_{0.67}$Sr$_{0.33}$MnO$_3$ films retain in-plane cubic anisotropy at all temperatures. This phenomenon is observed in both the A-site-ordered and -disordered films, with a more robust effect evident in the disordered sample. This easy-plane uniaxial magnetic anisotropy is tentatively attributed to symmetry modifications along the in-plane directions [100] and [010] stemming from a dominant Mn$^{3+}$ configuration and associated out-of-plane $d_{3z^2-r^2}$ bonding characterizing the LSMO-STO interface, as reported recently by Lee et al. with hypothesized origins in both charge imbalance and strain effects.\textsuperscript{16}

Films of composition La$_{0.67}$Sr$_{0.33}$MnO$_3$ were epitaxially grown on STO (001) substrates with a low-angle vicinal cut of 0.22° using ozone-assisted molecular beam epitaxy. Details regarding the growth are reported elsewhere.\textsuperscript{14,15} The films possess a nominally tetragonal structure with $c/a < 1$ and are confirmed to be epitaxially strained in the basal (ab) plane to the STO substrate ($\delta_{\text{STO}} = 3.905\;\text{Å}$). The nominal thicknesses, lattice parameters, and corresponding calculated strain values for the two film types at room temperature are reported in Table I. Bulk strain ($\epsilon_B$) and biaxial strain ($\epsilon^*$) values are calculated using the analytical model proposed by Milis et al.\textsuperscript{17} and indicate that both films exhibit small but finite stress. The difference in the thicknesses of the two films (A-site-ordered $= 30\;\text{nm}$ and A-site-disordered $= 50\;\text{nm}$) leads to a difference in calculated bulk strain value $\epsilon_B$, with the A-site-ordered film experiencing less bulk strain than the A-site disordered film. However, as

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TABLE I. Lattice parameters and corresponding strain values of the randomly alloyed film and the digitally synthesized superlattice of La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.33$). The bulk lattice parameter value of $a = 3.87\text{Å}$ was used to calculate the strain.

<table>
<thead>
<tr>
<th>Lattice parameter ($\text{Å}$) and strain (%)</th>
<th>Thickness (nm)</th>
<th>in-plane ($a=b$)</th>
<th>out-of-plane ($c$)</th>
<th>Bulk strain</th>
<th>Biaxial strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random Alloy ($\text{La}<em>{0.67}\text{Sr}</em>{0.33}\text{MnO}_3$)</td>
<td>50</td>
<td>3.90 (0.77)</td>
<td>3.84 (−0.78)</td>
<td>0.25</td>
<td>0.78</td>
</tr>
<tr>
<td>Digital superlattice [(LaMnO$_3$)$_2$(SrMnO$_3$)$<em>1$]$</em>{25}$</td>
<td>30</td>
<td>3.91 (1.02)</td>
<td>3.85 (−0.52)</td>
<td>0.51</td>
<td>0.77</td>
</tr>
</tbody>
</table>

shown in Table I, the $e^*$ values are the same for both films. These calculations imply that development of the in-plane magnetization should be the same for both films at room temperature.

A Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer was used for magnetic characterization of the LSMO films. The development of magnetization ($M$) as a function of temperature ($T$) in the range $10 \text{ K} \leq T \leq 400 \text{ K}$ at applied fields $H = 25, 50, 100, \text{ and } 250 \text{ Oe}$ was studied in the orthogonal in-plane crystallographic directions [100] and [010] in both zero-field-cooled (ZFC) and field-cooled (FC) conditions. The Curie temperature $T_C$ was determined from the derivative of the cooled (ZFC) and field-cooled (FC) conditions. The Curie temperature $T_C$ was determined from the derivative of the temperature dependent magnetization, $M(T)$ as a function of temperature at $H = 100 \text{ Oe}$ for A-site disordered random-alloy and A-site -ordered superlattice of composition $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.33$) with magnetic field applied in the in-plane easy direction of magnetization.

FIG. 1. Derivative of the temperature dependent magnetization, $M(T)$ as a function of temperature at $H = 100 \text{ Oe}$ for A-site disordered random-alloy and A-site -ordered superlattice of composition $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.33$) with magnetic field applied in the in-plane easy direction of magnetization.

FIG. 2. Field-cooled temperature-dependent magnetization at $H = 25, 50, 100, \text{ and } 250 \text{ Oe}$ for A-site disordered random-alloy and A-site -ordered superlattice of composition $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.33$) with magnetic field applied in the in-plane crystallographic directions [100] and [010]. The measured magnetization ($M$) is normalized to the saturation magnetization $M_s$ as measured at 20 K. Arrows indicate applied field at which in-plane cubic anisotropy is restored.
surface normal direction, the distribution of the orbital anisotropy in Mn$^{3+}$ state relative to Mn$^{2+}$ likewise is not uniform. Tensile strain that arises due to lattice mismatch between the film and the STO substrate favors $d_{3z^2-r^2}$ orbital configuration at the interface. However, owing to phase segregation of Mn$^{3+}$ near the STO-film interface, $d_{3z^2-r^2}$ orbitals are energetically favored relative to the $d_{x^2-y^2}$ orbitals at the interface. The reconstructed $d_{3z^2-r^2}$ orbital configuration typically signals compressive strain in the La$_{0.67}$Sr$_{0.33}$MnO$_3$ lattice along the in-plane $a$, $b$-axis. It must be noted that during film synthesis, a single layer of SMO followed by a double layer of LMO was first deposited on the STO substrate. Given the rigorous conditions of the digital synthesis MBE deposition technique and the order of heterostructuring in the A-site ordered superlattice, in most likelihood the concentration of Mn$^{3+}$ near the STO-film interface is smaller in the A-site-ordered superlattice than in the A-site-ordered random alloy. Thus, lowering of symmetry is less pronounced in the ordered superlattice.

Magnetization asymmetry along the orthogonal in-plane [100] and [010] directions may also be attributed to lattice modulations that help relieve stress originating from the strain mismatch between the LSMO and the underlying STO substrate. Biaxial lattice modulations aligned along [100] and [010] directions have been observed experimentally by Vigliante et al. and Gebhardt et al. in La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.1, 0.125$) films of nominal thickness $t \sim 50$ nm deposited on STO (001) substrates. It is also interesting to note similar conclusions reached in previous reports of asymmetric magnetic anisotropy measured along in-plane orthogonal directions authored by Krebs et al. on single-crystal (001) Fe films deposited on GaAs substrates and by Chen et al. on Co$_2$MnAl deposited epitaxially on GaAs. In all of these studies, the observed asymmetry in magnetic anisotropy is attributed to strain in the film-substrate interface that fosters inequivalence in the orthogonal bonding directions and lends a uniaxial anisotropy contribution to the existing cubic anisotropy.

In conclusion, we have established that epitaxial thin film samples of composition La$_{0.67}$Sr$_{0.33}$MnO$_3$ with thickness $t \leq 50$ nm deposited on single-crystal cubic SrTiO$_3$ (001) substrates show clear evidence of uniaxial in-plane magnetic anisotropy in orthogonal directions below room temperature, a result which signals a reduction in in-plane cubic symmetry. The structural origin of the symmetry reduction remains unclear; however, future work aimed at structural characterization of La$_{0.67}$Sr$_{0.33}$MnO$_3$ thin-films using variable temperature x-ray diffraction (XRD) would be useful in confirming the presence of the hypothesized structural transition. These results add to our understanding of the fundamental magnetostructural properties of the heteropitaxial material systems that are expected to play a key role in the development of future oxide-based nanodevice technologies.

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