Delta Doping of Ferromagnetism in Antiferromagnetic Manganite Superlattices

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We directly demonstrate the length scale over which charge spreads from a single atomic dopant layer in a manganite superlattice. These delta-doped carriers are inserted using a digital synthesis technique to create a dimensionally confined region of metallic ferromagnetism in an antiferromagnetic (AF) manganite host, without introducing any explicit disorder due to dopants or frustration of spins. Theoretical consideration of these additional carriers show that they cause a local enhancement of ferromagnetic (F) double-exchange with respect to AF superexchange, resulting in local canting of the AF spins. This leads to a highly modulated magnetization, as measured by polarized neutron reflectometry. The spatial modulation of the canting is related to the spreading of charge from the doped layer, and establishes a fundamental length scale for charge transfer, transformation of orbital occupancy and magnetic order in these manganites. Furthermore, we confirm the existence of the canted, AF state as was predicted by de Gennes in 1960, but had remained elusive.

In semiconductors, delta-doping strategies have been used to create very high mobility two dimensional electron gases (2-DEGs) that have led to a number of fundamental discoveries, including the quantum Hall effects. In the correlated complex oxides, similar doping strategies may be used to create two-dimensional analogs of collective phases such as superconductivity. In this work we use delta doping to tailor the magnetic exchange interactions. In semiconductors, the long-range Coulomb interactions are screened over several nanometers or more. In contrast, the Thomas-Fermi screening length in many complex oxides is much shorter (< 1 nm), and the exchange interactions that we aim to tailor operate between nearest-neighbors. This requires that the delta-dopants be placed with single atomic layer precision. Using La$_{1-x}$Sr$_x$MnO$_3$ as the host material with its composition tuned to the AF side of the F/AF phase boundary ($x \sim 0.5$), we have devised a delta-doping strategy for locally tailoring the strength of the F double-exchange interactions relative to AF superexchange, without introducing a random disorder potential due to dopants or the frustration inherent to some AF/F interfaces. This approach is unique to the correlated manganites and cannot be realized in conventional semiconductors or metals.

In the seminal work of de Gennes, it was recognized that when mobile carriers are added to an insulating, AF parent compound of a manganite, the carriers near the bottom of the conduction band want to delocalize via the double-exchange mechanism. This favors F align-
ment and charge itinerancy and competes with AF superexchange between the core spins of the parent compound. Starting with an AF insulating state, doping with carriers leads to a canting of the spins away from purely AF alignment, allowing the electrons to become more itinerant and take advantage of the gains in double-exchange energy. In real materials, the picture is complicated, as coupling of charge carriers to the lattice (Jahn-Teller (JT) effects), on-site Coulomb repulsions (Mott-Hubbard effects) and charge/orbital ordering instabilities all favor localizing the charge carriers and compete with double-exchange. As a result, the transition between an AF insulator such as LaMnO$_3$ to an F metal such as La$_{1-x}$Sr$_x$MnO$_3$ for $x \sim 0.2$ takes place through a canted AF insulator and what is believed to be a mixed phase for intermediate values of $x$.

The story is quite different if one starts with La$_{1-x}$Sr$_x$MnO$_3$ for $x > 0.5$, which contains the AF metallic state investigated in this study. The $e_g$ electrons in this material can go into one of two partially filled bands made of degenerate $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals. For $0.5 < x < 0.7$ the $e_g$ degeneracy is removed by the formation of a highly anisotropic $A$-type AF order (planes of F spins that are mutually AF), with the electrons mainly occupying the $d_{x^2-y^2}$ orbital states. The transport in this state is nearly metallic in-plane due to double exchange. However, the out-of-plane resistivity is orders of magnitude higher and insulating since the $d_{3z^2-r^2}$ states are unoccupied, and AF superexchange dominates in this direction. Upon doping this 2-dimensional AF metal with electrons toward the $x < 0.5$ region, the $d_{3z^2-r^2}$ orbitals begin to be occupied, double exchange begins to act in the out-of-plane direction, and the material transforms into a 3-dimensional F metal. We show in this work that by locally varying the doping level in an AF manganite SL, we locally enhance the double exchange and thereby the degree of spin canting, resulting in a highly modulated magnetization. Our theoretical investigation shows that a JT distortion is instrumental in stabilizing this canted spin structure lying in the midst of the crossover from a 2D antiferromagnet to a 3D ferromagnet near $x = 0.5$.

We synthesized cation-ordered analogs of La$_{0.5}$Sr$_{0.5}$MnO$_3$ having $A$-type AF order, by alternating single unit cell layers of LaMnO$_3$ (LMO) and SrMnO$_3$ (SMO) with atomic layer precision using ozone-assisted molecular beam epitaxy. Neutron diffraction experiments on these (LaMnO$_3$)$_1$/(SrMnO$_3$)$_1$ superlattices confirmed the $A$-type AF phase, and magnetometry measurements using a superconducting quantum interference device (SQUID) showed a net moment near zero at low field. Here, we present the slightly La-rich compositions
$x = 0.44$ and 0.47, which are electron-doped. The $x = 0.44$ SL was made by alternating unit cell layers of LaMnO$_3$ and SrMnO$_3$ and inserting an additional LaMnO$_3$ layer for every four LaMnO$_3$/SrMnO$_3$ bilayers. This sequence was repeated 9 times (9 supercells), to form the superlattice [(SMO1/LMO1)x4,LMO1]x9 shown schematically in Fig. 1. A La$_{0.56}$Sr$_{0.44}$MnO$_3$ alloy film with a thickness of 81 uc was made for direct comparison. The $x = 0.47$ SL was made by inserting an extra LaMnO$_3$ layer for every 9 LaMnO$_3$/SrMnO$_3$ bilayers, repeated 4 times: [(SMO1/LMO1)x4,LMO1,(SMO1/LMO1)x5]x4. By periodically inserting the extra LaMnO$_3$ unit cell layer, we have implemented delta doping of the MnO$_2$ planes in the vicinity of the inserted LaMnO$_3$ unit cell. Our investigation of these SLs by neutron scattering techniques was aimed at determining the influence of these delta-doped charges on the $A$-type spin structure.

Structural characterization of the SLs by x-ray reflectivity (XRR) and x-ray diffraction (XRD) is shown Fig. 1. The Bragg peaks in the XRR spectra verify the 9 unit cell-thick supercell in the $x = 0.44$ SL, and the 19 unit cell-thick supercell in the $x = 0.47$ SL. By fitting these spectra using the Parratt formalism, we extracted the interface and surface roughnesses and layer thicknesses, listed in Fig. 1. Ideally, because the layers are just a single unit cell in thickness, the XRR analysis should give the unit-cell thickness for the SrMnO$_3$ and LaMnO$_3$ layers, and the $(0 0 2)$ peak of the SL in the XRD pattern gives the average $c$-axis parameter ($c$). For the $x = 0.44$ SL, the SrMnO$_3$ and LaMnO$_3$ layer thicknesses were in agreement with previous studies. For the $x = 0.47$ SL, the SrMnO$_3$ thickness was less than 1 uc. This is likely due to a Sr deficiency (actual $x$ in the range 0.46–0.47), in agreement with the observed downward drift of the Sr deposition rate during growth of this sample. The $c$ value for the $x = 0.47$ SL is intermediate between the $c$ values measured for our $x = 0.44$ and 0.50 SLs (see Fig. 2c).

It is known from the La$_{1-x}$Sr$_x$MnO$_3$ phase diagram that the $x = 0.44$ and 0.47 compositions are ferromagnetic, and indeed these SLs and the alloy do have a net moment ($M$) in an applied magnetic field ($H$), as shown in $M(H)$ loops in Fig. 2a,b. Note that the moment at the maximum field (7 Tesla) is less than the expected value of $(4 - x)\mu_B$ for complete F alignment of all Mn$^{3+/4+}$ spins, which suggests canting of spins away from the applied field direction. Metal-like behavior is shown by the 4-terminal, in-plane resistivity measurements in Fig. 2e. For reference, our $x = 0.50$ SL has a smaller moment and larger resistivity, as expected for this composition.
FIG. 1: Structure of the LaMnO$_3$/SrMnO$_3$ superlattices. a, Schematic of the SL structure. b, X-ray reflectivity spectra of the $x = 0.44$ and 0.47 SLs and fit (solid lines) using Parratt’s dynamical formalism. The inset shows the (0 0 2) x-ray diffraction peaks of the SLs and STO substrate. c, Table of the XRD and XRR analysis of the SLs. All parameters are given in nm (except for % error). The average c-axis parameter was determined from the (0 0 2) diffraction peaks. Roughness and thickness parameters were found from the XRR fit. The error is defined as the percent difference between the total thickness values found from the XRR fit and from the XRD measurement.

Using our digital synthesis technique, the majority of these SLs consists of LaMnO$_3$/SrMnO$_3$ bilayers having $x = 0.50$ composition which has A-type AF order. We performed neutron diffraction measurements to directly probe the A-type spin structure in the $x = 0.44$ SL and alloy. The A-type order is manifested by a structurally-forbidden (0 0 1 2) Bragg peak, shown in Fig. 3a, signifying a spin alignment with a periodicity of 2$c$ normal to the film plane. From the full width at half-maximum of the peak, a magnetic coherence length of $\sim$28.5 nm was determined, nearly the entire film thickness (30.9 nm). The coexistence of both a (0 0 1 2) neutron diffraction peak, signifying AF order, and a net moment in the sample (from $M(H)$ data) suggests a canted AF structure, in which the spins in a single plane are ferromagnetically aligned and the spins on adjacent planes are canted at a relative angle $\theta_z < 180$ degrees, where $\theta_z/2$ is the angle between each spin and the applied magnetic field direction (see inset of Fig. 3b). Notably, there is no measurable change in peak intensity with field, when measured from zero field up to 675 mT (same field used in PNR measurements), shown in the inset of Fig. 3a. Taking into account the noise in the data, we estimate that the canting angle $\theta_z$ does not decrease by more than 12 degrees.
FIG. 2: Magnetic properties and resistivity of the superlattices. a, $M(H)$ of the $x = 0.44$ SL and alloy at 5 K and the $x = 0.47$ SL at 10 K, measured with a SQUID magnetometer. b, $M(H)$ at 120 K, measured out to the field applied for the PNR measurement. The insets of a and b are zoomed-in views of the coercive field regions. c, The average c-axis parameter of the SLs as a function of $x$. d, $M(T)$ of the $x = 0.44$, 0.47 and 0.50 SLs measured with $H = 20$ mT while increasing $T$ after zero-field cooling (closed symbols) and cooling in 20 mT (open symbols). e, Resistivity ($\rho$) versus $T$ measured while increasing $T$ in zero field (closed symbols) and in 7 tesla (open symbols). The $\rho$ of the $x = 0.44$ SL is 0.07 m$\Omega$-cm at 5 K. f, Resistivity of the SLs as a function of $x$, with and without 7 T field.

in this field range. Therefore, applying a field causes alignment of domains all having the canted $A$-type structure while the canting angle may change by only a small amount. This is consistent with the M(H) loops in Fig. 2 as well. The temperature ($T$) dependence of the peak intensity in Fig. 3b indicates that the $A$-type order in the SL disappears at $\sim 260$ K, while the $M(H)$ loop measured in the SQUID indicates that a net moment persists out to 305 K. This suggests that the superexchange interaction between adjacent MnO$_2$ planes dies
FIG. 3: *A*-type antiferromagnetic structure shown by neutron scattering. *a*, The structurally-forbidden (0 0 \( \frac{1}{2} \)) neutron diffraction peak for the \( x = 0.44 \) SL at the indicated temperatures. The lines are a guide to the eye. The field dependence of the peak is shown in the inset, measured with increasing field after cooling in zero field to 120 K. *b*, Temperature dependence of the integrated intensity of the diffraction peak for the \( x = 0.44 \) SL and alloy, measured while increasing \( T \) in zero field, after cooling in zero field. The inset is a schematic of the canted, *A*-type order. *c*, Diffraction with polarized neutrons and polarization analysis, measured at \( T = 120 \) K in a 820 mT field. Peaks in the spin-flip intensities at high \( q \) directly confirm the canted, modulated spin structure. The inset shows the non-spin flip intensities.

out at \( \sim 260 \) K, at which point all spins are aligned ferromagnetically with the field, out to 305 K.

To determine the depth-dependent magnetization profile, we performed PNR measurements. Specular PNR is a powerful technique for determining the magnetization and structure of thin film multilayers as functions of sample depth along the surface normal and detects only the component of magnetization in the plane of the film. The non-spin-flip reflectivities, \( R^{++} \) and \( R^{--} \) shown in Fig. 4a for the \( x = 0.44 \) SL, are predominately sensitive to the component of magnetization parallel to the applied field direction. Because the nuclear scattering length densities of SrMnO\(_3\) and LaMnO\(_3\) are nearly identical (3.65 \( \times 10^{-6} \) \( \text{Å}^{-2} \) and 3.64 \( \times 10^{-6} \) \( \text{Å}^{-2} \), respectively), only magnetic variations in the layer profile are detectable. The key feature of interest here is the Bragg peak at \( q = 0.18 \) \( \text{Å}^{-1} \), indicating that the magnetization is in fact *modulated* with a periodicity that closely matches the supercell periodicity of the SL.
FIG. 4: Polarized neutron reflectometry showing the magnetic depth profile. a, PNR for the $x = 0.44$ SL at $T = 120$ K and with $H = 675$ mT applied in the plane of the film, has a Bragg peak signifying that the magnetization is modulated. The solid lines are the fit to the data. The inset shows the PNR of the $x = 0.44$ alloy film having no Bragg peak. b, Two possible magnetic profiles as a function of film depth from the fit to the PNR spectra of the $x = 0.44$ SL. The location of the LMO (pink) and SMO (green) layers in the SL and the STO substrate (gray) are also shown. The high moment peaks in the depth profile coincide with the double-LMO layers. c, PNR for the $x = 0.47$ SL with $H = 815$ mT and $T = 120$ K, has 2 Bragg peaks due to the longer period of the magnetic modulation. The inset shows the same reflectivity data multiplied by $q^4$. d, The magnetic depth profile from the best fit to the PNR spectra of the $x = 0.47$ SL.

To fit the PNR data with the co_refine routine, a model consisting of 9 supercells was used, where each supercell consisted of a high moment sublayer and a low moment sublayer. The sublayer thicknesses, magnetic roughnesses and magnetic scattering length densities (a quantity directly proportional to the magnetization) of the seven interior supercells were fit while constrained to be identical, whereas the topmost and bottommost supercells could vary independently. For this data and model, there are several sets of possible fit parameters that yield the same lowest $\chi^2$ value to within 1%. Two such profiles are shown in Fig. 4b.
Even though highest (lowest) moment in the modulation period, $M_{\text{max}}$ ($M_{\text{min}}$) can each vary by as much as 0.25 $\mu_B$, we can conclude with certainty across all sets of fit parameters that 1) the period of the magnetic modulation matches the structural supercell to within 0.1 nm; 2) the high moment sublayer contains the extra LMO layer and 3) the magnitude of the modulation is quite large, with $M_{\text{max}}/M_{\text{min}} = 3 \pm 0.3$.

The $x = 0.47$ SL has a thicker supercell with one extra LaMnO$_3$ layer for every 19 uc, such that two Bragg peaks are detectable, as shown in the PNR spectra in Fig. 4c. With now two Bragg peaks and thus more information on the magnetic modulation compared to the $x = 0.44$ SL data set, the fitting routine produces a single set of best fit parameters at the lowest $\chi^2$ for the $x = 0.47$ SL. A model similar to the one previously described, containing alternating high moment and low moment sublayers, was used to fit this data. The moment is again highly modulated, alternating between a high moment region across 6 uc (the full-width half-maximum of the peaks in Fig. 4d) containing the extra LaMnO$_3$ unit cell and having a maximum moment $M_{\text{max}} = 2.2\mu_B$, and a low moment region spanning 13 uc having a minimum moment $M_{\text{min}} = 0.7\mu_B$. The gradual transition between $M_{\text{max}}$ and $M_{\text{min}}$ occurs over 4 uc, and as we shall show, this occurs by varying the canting angle. Using $M_{\text{tot}} = (4 - x)\mu_B$ as the magnitude of the moment of a Mn$^{3+/4+}$ spin and applying a $M_{\text{tot}} = M\cos(\theta_z/2)$ relation, a modulation between a net moment of $M_{\text{max}} = 2.2\mu_B$ and $M_{\text{min}} = 0.7\mu_B$ corresponds to a modulation of canting angle between $\theta_z = 103$ and 157 degrees, respectively. These fit parameters also work for the $x = 0.44$ SL, where the high moment region extends across 6 uc with $M_{\text{max}} = 2.2\mu_B$ and the low moment region extends across 3 uc with $M_{\text{min}} = 0.7\mu_B$, as shown in Fig. 4b (black line). In comparison, the PNR measurement of the $x = 0.44$ alloy film (inset of Fig. 4a) shows a net moment without any modulation (no Bragg peak). Thus, the spin canting in the alloy is uniform, and the modulated magnetization in the $x = 0.44$ and 0.47 SLs only occurs due to the delta-doping method employed in the synthesis.

To investigate this canted spin structure even further, we carried out diffraction measurements with polarized neutrons and polarization analysis at higher $q$ in the range of the AF peak for the $x = 0.44$ SL, as shown in Fig. 3c. The peak in spin-flip intensities, $I^{+-}$ and $I^{-+}$, at $q = 0.82$ Å$^{-1}$ results from the layers of canted AF spins with each sublattice having a component of magnetization pointing perpendicular to the applied field direction, with a period of 2$c$, as shown schematically in the inset of Fig. 3b. Moreover, the superlattice
FIG. 5: Schematic of the canted, modulated spin structure. Four supercells (9 uc each) in the interior of the \( x = 0.44 \) SL are shown here. Pink and green arrows represent the F spin alignment within the MnO_2 planes of the LMO and SMO unit-cell layers, respectively. The dotted blue lines are the projection of the spins onto the \( yz \)-plane and signify the magnetic potential measured by neutron diffraction. The dotted purple lines are the projection of the spins onto the \( xz \)-plane and signify the magnetic potential measured by PNR. The dotted red lines are the projection of the spins onto the \( xy \)-plane, showing the canting angles corresponding to \( M_{\text{min}} \) and \( M_{\text{max}} \), \( \theta_z = 157 \) and 103 degrees respectively, and an intermediate canting angle. The black lines (connecting the spins on each side of \( \theta_z = 0 \)) aid the eye in identifying the spin modulation.

Peak at \( q = 0.64 \) Å\(^{-1} \) signifies that the canted spin structure is modulated with a period of 9 uc, consistent with the supercell period and the periodicity of the F component revealed by the low \( q \) PNR measurements. These peaks in the spin-flip intensities directly confirm the canted, modulated spin structure. Fig. 5 shows the canted, modulated spins structure as deduced by the PNR and diffraction measurements.

In order to explore theoretically this canted spin state, we consider the standard two-orbital model for manganites\(^{15} \) with the Hamiltonian,

\[
H = H_{DE} + H_{SE} + H_{JT}.
\]
FIG. 6: Model of the doping dependence of the exchange interactions and canting angle. a, The effective F exchange constant arising from the double-exchange interaction, shown here for a fixed Jahn-Teller distortion and a ferromagnetic spin state for all $x$. The presence of a JT distortion leads to a difference in orbital occupancy, which in turn leads to anisotropic exchange parameters. A typical value of the AF coupling, $J_{S} = 0.14t$, is shown as a dashed line. b, Doping dependence of the canting angle $\theta_z$ for various values of $J_{S}$. The canting angle is obtained by minimizing the total energy at a given $x$, where both the Jahn-Teller distortion and the canting angle are allowed to vary.

The microscopic details and the precise nature of the terms in Eq. (1) are discussed in the Methods section. Here we simply describe the qualitative effects contained in the various terms of the Hamiltonian. The double-exchange part $H_{DE}$, which arises from a combination of kinetic energy and strong Hund’s rule coupling, favors the F state. The superexchange term $H_{SE}$ is the Heisenberg interaction between $t_{2g}$-spins favoring AF coupling. The Jahn-Teller term $H_{JT}$ represents the coupling of the $e_g$ electrons to the lattice distortions.

Before understanding the canted magnetic states, it is essential to understand the stability of $A$-type AF order near $x = 0.5$ in manganites. It is an outcome of a competition between the ferromagnetic $H_{DE} = J_{F} \sum \cos(\theta_{ij}/2)$ and the antiferromagnetic $H_{SE} = J_{S} \sum \cos(\theta_{ij})$ terms, where $\theta_{ij}$ denotes the relative angle between spins $S_i$ and $S_j$, and the summation is over all nearest neighbors. $A$-type order requires the F term to dominate in the $xy$ plane and the AF term to be stronger along the $z$-axis. We show in Fig. 6a that the presence of a uniform JT distortion can favor the occupation of $d_{x^2-y^2}$ orbitals, which then leads to a strong F interaction in the $xy$ plane, and a much weaker one along the $z$-axis ($J_{F} \sim x_z t_z$, $J_{S} \sim 0.14t$).
where \( x_z \) is the \( d_{3z^2-r^2} \) orbital occupancy and \( t_z \) is the hopping integral in the \( z \) direction. If the superexchange coupling \( J_S \) (shown as dashed line in Fig. 6a) is much stronger than \( J_F^z \) then the \( A \)-type AF state becomes the ground state. Upon reducing \( x \) so that filling of the \( e_g \) band continues, the doped electrons begin to fill the higher \( e_g \) states (the \( d_{3z^2-r^2} \) states), so that \( J_F^z \) increases and competes with \( J_S \) while the in-plane order remains unaffected, as shown in Fig. 6a. Such a competition between F and AF interactions along the \( z \)-axis can lead to canted spin states. From a simple energy minimization \( dE/d\theta_z = 0 \) for \( E = -J_F^z \cos(\theta_z/2) + J_S \cos(\theta_z) \), one finds that the canting angle \( \theta_z = 2 \arccos(J_F^z/4J_S) \) if \( J_F^z < 4J_S \), and is \( \theta_z = 0 \) otherwise. Note that within this simple scenario one needs \( J_S = \infty \) to obtain \( \theta_z = \pi \). In reality there is a feedback effect of the spin states on the orbital occupancies and therefore the variation of \( \theta_z \) can be very different.

In order to test this explicitly, we minimize the total energy of the Hamiltonian for variational parameters \( \theta_z \) and JT distortions and hence allowing for this feedback effect in the following manner. At a fixed \( x \), Jahn-Teller distortions lead to a reduction in electronic energy but there is also an elastic cost associated with making these distortions (see Methods section). The optimum value of the distortion is selected due to the above competition. This generates an \( x \) dependence on the magnitude of the distortions and therefore an additional \( x \) dependence on the values of \( J_F^z \). The resulting optimum angle \( \theta_z \) is plotted in Fig. 6b for a few values of \( J_S \). One finds that the canting angle changes rapidly from \( \pi \) to 0 upon reducing \( x \) below 0.5. Therefore, even a small variation in the doping level can lead to significant changes in canting angle and thus the net moment. The large modulation in moment as a function of depth in these delta-doped SLs is essentially a realization of this scenario. Attempts to realize the canted AF state near \( x = 0 \) as proposed by de Gennes and near \( x = 0.5 \) have typically been obscured by phase segregation into F and AF domains, which is avoided in our digital synthesis approach of charge doping without disorder.

The abruptness of the change in canting angle below \( x = 0.5 \) is mirrored in the abrupt change of slope in the variation of the \( c \)-axis parameter and resistivity of the SLs with \( x \), shown in Figs. 2c and f respectively. The \( c \)-axis swells as the \( d_{3z^2-r^2} \) states begin to be occupied upon reducing \( x \) below 0.5. Accompanying this increased occupancy is the strengthening of the double-exchange interaction along the \( z \)-axis, \( J_F^z \). This leads to the sharp decrease in resistivity observed below \( x = 0.5 \). As demonstrated here, these SLs provide a model system for observing the strong correlations between spin, charge, orbital
and lattice degrees of freedom in the manganites and tuning the properties at the F/AF phase boundary.

Because the $A$-type AF state arises due to occupancy of the in-plane $d_{x^2-y^2}$ orbitals and the F state is characterized by a mixing of $d_{x^2-y^2}/d_{3z^2-r^2}$ orbitals, an orbital superlattice is expected to accompany this modulated spin state. An orbital superlattice, or the periodic alternation between these two orbital states, has been observed in a resonant x-ray scattering study by Kiyama et al of F/AF superlattices with $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ as the ferromagnet and $\text{La}_{0.45}\text{Sr}_{0.55}\text{MnO}_3$ as the $A$-type antiferromagnet. In the latter study, their SLs had abrupt interfaces between alloy films having two distinct compositions and orbital ground states, where spin frustration and cation intermixing may occur. Whereas, in our study we have employed delta doping to exploit the competing double-exchange and superexchange interactions and tailor the magnetic structure. Localized regions of enhanced F exchange were created in an otherwise AF structure, where the transition between the high moment region and the low moment region does not occur abruptly, but rather via a continuous variation of canting angle that is governed by the spreading of charge near the delta-doped layer. Furthermore, the PNR technique enables us to determine a length scale of 6 uc for the region of enhanced moment that is induced by the delta-doped layer. The result that the SL magnetization is highly modulated is evidence that the doped charges are not completely delocalized over the entire SL. Charge spreading out to 3 uc from both sides of the delta-doped layer is consistent with previous theoretical and experimental works that had inferred a length scale for charge spreading via more indirect means.\footnote{18,19} We believe this to signify a fundamental length scale for the spreading of charge normal to the layers.

I. METHODS

Structure: The SLs were synthesized by molecular beam epitaxy on TiO$_2$-terminated SrTiO$_3$ substrates, using pure ozone as the oxidizing agent. The LMO (SMO) layers were deposited by co-evaporation of La and Mn (Sr and Mn) in ozone. The alloy $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ films were deposited by co-evaporation of La, Sr and Mn in ozone. Details of the synthesis are described elsewhere.$^9$ The \% error for the $x = 0.47$ SL given in Fig. 1 is the difference between the total thickness values found from the XRD measurement ($c \times$ total number of unit cells = 0.3809 nm x 76 uc = 28.950 nm) and the XRR fit (0.358 nm x 36 uc of SMO+...
0.395 nm x 40 uc of LMO = 28.680 nm). The % error for the $x = 0.44$ SL was calculated in the same manner.

*Neutron scattering:* Neutron diffraction measurements were carried out using the HB-1A triple-axis spectrometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory and the BT9 triple-axis spectrometer at the NIST Center for Neutron Research (NCNR). PNR measurements and the diffraction measurement with polarized neutrons and polarization analysis were carried out on the NG1 reflectometer at the NCNR. The PNR data were corrected for instrument background, polarizing element efficiencies and beam footprint. The measurements were carried out at 120 K in order to avoid the loss of specularly reflected intensity caused by the buckling of the SrTiO$_3$ substrate at its cubic-to-tetragonal structural phase transition below 105 K. This is believed to be the cause of the reduced intensity in the temperature dependent diffraction measurements below 100 K (Fig. 3b).

The spin-flip reflectivities in the PNR measurement for $q < 0.2$ Å$^{-1}$ in the high field condition were very low, near the background intensity, as expected because the canting of the spins by an equal amount on either side of the field direction cancels within the coherence length of the neutron in the low $q$ range. A spin-flip signal was measured in the $x = 0.44$ SL when the sample was cooled in zero field and measured at 0.55 mT. Since we know from the neutron diffraction measurement that the $A$-type spin structure persists at zero field (Fig. 3), measurement of a spin-flip signal is consistent with randomly-oriented, canted domains at zero field. To investigate further the in-plane domain structure, we measured specular as well as off-specular reflectivities with unpolarized neutrons using the AND/R reflectometer with a position sensitive detector at the NCNR. By comparing the off-specular reflectivities in the zero field cooled state and high field (675 mT) state, we were able to extract a domain size of $\sim 4\mu$m.

*Magnetometry:* To determine the moment of the SL from the SQUID magnetometry data, the diamagnetic signal of the SrTiO$_3$ substrate was subtracted from the measured magnetization signal. The volume-normalized diamagnetic signal of the STO substrate used in the subtraction was obtained from the measurement of a reference STO substrate. To compare the PNR data and the SQUID magnetometry data, we integrated the area under the magnetic depth profile to obtain the total moment of the SL ($M_{PNR}$) and compared it to the SL moment measured by the SQUID magnetometer ($M_{SQUID}$) at the corresponding applied field. For the $x = 0.44$ SL, $M_{PNR} = 250$ emu/cm$^3$ and $M_{SQUID} = 225$ emu/cm$^3$. 

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a small discrepancy of 10%. For the $x = 0.47$ SL, $M_{PNR} = 174$ emu/cm$^3$ and $M_{SQUID} = 118$ emu/cm$^3$, a discrepancy of 32%. The source of this sizable discrepancy is unknown. However, the low moment sublayer of the $x = 0.47$ SL, which has a composition closer to $x = 0.50$, has a moment $M_{\text{min}} = 108$ emu/cm$^3 = 0.7\mu_B$, as determined in the magnetic depth profile, which matches exactly to $M_{SQUID} = 108$ emu/cm$^3$ for our $x = 0.50$ SL in the same applied field.

Microscopic model: The microscopic model Hamiltonian$^{15}$ discussed qualitatively in the main text is given by,

$$H = - \sum_{\langle ij \rangle, \alpha\beta} \left( t_{ij}^{\alpha\beta} c_{i\alpha}^\dagger c_{j\beta} + H.c. \right) + J_S \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + \lambda \sum_i (Q_i \tau_{i,x} + Q_i \tau_{i,z}) + 1/2 \sum_i |Q_i|^2.$$

Comparing with Eq. (1), the first term corresponds to $H_{DE}$, the second to $H_{SE}$, and last two terms belong to $H_{JT}$. Operator $c_{i\alpha}^\dagger (c_{i\alpha})$ creates (annihilates) an electron in orbital $\alpha \ (= d_{x^2-y^2} \text{ or } d_{3z^2-r^2})$ with the spin pinned along the direction of the core spin $\mathbf{S}_i$ due to strong Hund’s rule coupling. $Q_x$ and $Q_z$ are the two modes for the JT distortions which couple to the components of the orbital pseudospin $\tau_{i,x}$ and $\tau_{i,z}$. $J_S$ is the AF superexchange interaction between the core spins, and the last term is the elastic cost for lattice distortions. As a consequence of double-exchange, the hopping integrals are renormalized by a factor that depends on the angle between neighboring core spins: $t_{ij}^{\alpha\beta} = \cos(\theta_{ij}/2)t^{\alpha\beta}$. The bare hopping integrals $t^{\alpha\beta}$ are given by the Slater-Koster integrals$^{20}$ as follows: $t_{11}^{x} = t_{11}^{y} = t$, $t_{12}^{x} = t_{21}^{x} = -t^{21}$, $t_{12}^{y} = t_{21}^{y} = -t^{21} = -t/\sqrt{3}$, $t_{11}^{z} = t_{21}^{z} = t_{22}^{z} = 0$, $t_{12}^{z} = 4t/3$, where 1 and 2 represent the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals, respectively.

Variational scheme: The aim is to study the competition between the $A$-type AF and F states, and to explore the possibility of an intermediate state with a finite canting of the F planes. Therefore, we assume the planes to be F and introduce a variational parameter $\theta_z$ which connects continuously the F ($\theta_z = 0$) state to the $A$-type AF state ($\theta_z = \pi$). The $A$-type AF state near $x = 0.5$ in the manganites is known to accompany a ferro-orbital order, which corresponds to a $Q_z$-type JT distortion$^{21}$ with a uniform magnitude $Q$. With these assumptions it is possible to rewrite the Hamiltonian as a 2x2 matrix in momentum space, which can easily be diagonalized for variational parameters $\theta_z$, $Q$ and $\theta_o$, where $\theta_o$ determines the local mixing of the two $e_g$ orbitals. The Hamiltonian in $k$-space becomes,

$$H_{11} = \epsilon_{11}(k) + \lambda Q \cos(\theta_o)$$

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\[ H_{12} = \epsilon_{12}(k) + \lambda Q \sin(\theta_o) = H_{21} \]

\[ H_{22} = \epsilon_{22}(k) - \lambda Q \cos(\theta_o), \]

with \( \epsilon_{\alpha\beta} = -2(t_{x}^{\alpha\beta} \cos(k_x) + t_{y}^{\alpha\beta} \cos(k_y) + t_{z}^{\alpha\beta} \cos(\theta_z/2)\cos(k_z)) \).

Note that the ferro-orbital metal phase is consistent with the Monte-Carlo simulations based on the above Hamiltonian, therefore the above assumptions are justified. Moreover within the variational search we find that \( \theta_o = \pi \), which corresponds to a preference for the \( d_{x^2-y^2} \) state. The minimum energy solutions within this variational search are shown in the Fig.6b. The origin of the canted spin states lies in the asymmetric F exchange emerging from the double-exchange interactions. One can explicitly calculate the F exchange parameters as, \( J_{FM}^{\mu} = \sum_{\alpha\beta} t_{i,i+\mu}^{\alpha\beta} \langle c_{i,\alpha}^{\dagger} c_{i,\beta} + H.c. \rangle \), where \( i_{\mu} \) is the neighbor of site \( i \) along direction \( \mu \) (x, y or z). The angular brackets denote the quantum expectation value in the ground state of the enclosed operator. From these calculations we find that even for a weak JT distortion the F exchange along x and y directions is much stronger than that along z, thereby justifying our assumption of F planes in the variational calculations.

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This is not surprising, considering that $\bar{m} \cdot \bar{H}$ for spin $\frac{3}{2}$ Mn for $\mu_0 H = 675 \text{ mT}$ is \(\sim 60 \mu \text{eV} \ll J_{SE} \sim 3.5 \text{ meV} \).