Spin-orbit interaction renormalized Kondo scattering in δ-doped LaTiO$_3$/SrTiO$_3$ interfaces

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The breaking of inversion symmetry combined with polar discontinuity and the presence of strong electronic correlations due to partially filled 3d electronic shell of Ti ions at the LaAlO$_3$/SrTiO$_3$ (LAO/STO) and LaTiO$_3$/SrTiO$_3$ (LTO/STO) interfaces conspire to produce exotic electronic phases. These include macroscopic superconducting and ferromagnetic orders and electronic transport renormalized by strong spin-orbit (S-O) interaction originating to the built-in electrostatic fields at the interface and scattering by localized moments. An important ingredient in this exotic soup of causes and effects is also the quantum paraelectric nature of STO. In order to separate out the contributions of these phenomena from electronic behavior of oxide interfaces, new approaches need to be developed. Here, we present a study of delta doping at LTO/STO interface with iso-structural perovskite of LaCrO$_3$ (LCO) that dramatically alters the properties of the two dimensional electron gas (2DEG) at the interface. The effects include a reduction in sheet-carrier density, prominence of the low temperature resistivity minimum in LAO/STO and LTO/STO 2DEG, enhancement of weak antilocalization below 10 K and observation of a strong anisotropic magnetoresistance (MR). The positive and negative MR for out-of-plane and in-plane field respectively and the field and temperature dependencies of MR suggest Kondo scattering by localized Ti$^{3+}$ moments renormalized by S-O at $T < 10$ K, with the increase of Cr$^{3+}$ concentration at the interface.

The phenomenon of the formation of a 2-dimensional electron gas (2-DEG) at the interface of epitaxially grown LaTiO$_3$ (LTO) or LaAlO$_3$ (LAO) on TiO$_2$ terminated (100) SrTiO$_3$ (STO) has attracted much attention owing to the observations of magnetism, superconductivity and fractional quantum Hall effect in the 2-DEG. So far, one of the accepted mechanisms for the formation of the 2D electron gas in these structures is the transfer of electron from the polar layer of LAO or LTO to the top TiO$_2$ layer of STO. Such a transfer pushes the conduction band edge of STO below the Fermi level, and the charge carriers are confined in a triangular potential well at the interface with a free electron like dynamics in the plane of the interface and quantization perpendicular to it. Since the carrier concentrations are large ($\sim 3 \times 10^{14}$ cm$^{-2}$), and some of the Ti$^{4+}$ ions at the interface may also get converted to Ti$^{3+}$ with $S = \frac{1}{2}$ localized spins, the electron dynamics is likely to be subjected to weak electron-electron scattering and magnetic scattering in addition to the scattering by a weak static disorder. Moreover, as the interface breaks inversion symmetry, there is also a possibility of Rashba spin-orbit scattering emanating from the interface electric field. Some of these issues have been addressed by measuring the low temperature magnetoresistance (MR) of 2DEG formed at LAO/STO and electrolyte gated STO, but no consensus has emerged on the origin of a strong positive MR observed in the geometry where the external magnetic field is perpendicular to the plane of the film ($H_{\perp}$), a change in the sign of the MR when the field is brought in the plane ($H_{\parallel}$), a characteristic minimum in $R(T)$ below $\sim 100$ K followed by a log$T$ behavior below the minimum, and finally, saturation of $R(T)$ at still lower temperatures.

In order to address some of the puzzles related to the mechanism of 2DEG formation at LTO/STO interface, and to identify the dominant scattering processes that control the nature of MR in this system, we have used a novel approach of delta ($\delta$) doping of the interface. The doped structure consists of LTO(m unit cell(uc))/LaCrO$_3$($\delta$ uc)/TiO$_2$ terminated STO, where $m = 20$ and the $\delta$ varies from a fraction to 10 uc. The LaCrO$_3$(LCO)/STO structure alone does not form a 2D gas. In this case the LCO film remains an antiferromagnetic insulator with Cr site spin of $S = \frac{3}{2}$. This is interesting in itself because Cr follows vanadium in the 3d transition series and LaVO$_3$/STO interface is conducting. However, when LCO is inserted as a $\delta$ layer, the 2DEG nature of LTO/STO is retained for smaller values of $\delta$ ($< 3$), but with the increasing $\delta$, a significant blocking of carriers by LCO drives the interface insulating. The temperature, magnetic field and angular dependence of MR in $\delta = 0$ sample indicates a dominant Kondo-type s-d scattering for in-plane field. However, the characteristics negative MR of Kondo is superceded by positive MR resulting presumably from the enhanced forward scattering of diffusive electrons by the S-O interaction in the $T \leq 10$ K regime.
negative MR quadratic in-field is seen at $T > 10$ K due to the enhanced elastic scattering of electrons while going into the cyclotron orbit. It is interesting to note that the Rashba coupling at the interface of LTO/STO can be modulated by insertion of LCO layers.

The films are deposited using a KrF excimer laser based Pulsed Laser Deposition (PLD) technique on TiO$_2$ terminated STO (100) single crystal substrates as described on our earlier work [16]. The laser was fired at a repetition rate of 1 Hz and fluence of 1.2 J/cm$^2$ onto the surface of well-sintered polycrystalline targets of LTO and LCO which led to a growth rate of $\approx 0.1$ /s. Like LTO, LCO is also an orthorhombic perovskite in bulk with lattice parameter $a = 5.513$, $b = 5.476$ and $c = 7.759$, but its pseudocubic lattice parameter of 3.885 gives excellent lattice matching on STO (100). This compound is an antiferromagnetic insulator with the Neel temperature of $\sim 298$ K. Just before the commencement of deposition, substrates were annealed at 800 °C for 1 hour in 7.4x$10^{-2}$ mbar oxygen pressure to remove any surface defects. The growth was carried out at the same temperature in 10$^{-3}$ mbar oxygen. The atomic and chemical states of the interface has been studied extensively using x-ray reflectivity and cross sectional electron microscopy in conjunction with electron energy loss spectroscopy (EELS). We have carried out Density Functional Theory (DFT) calculations for charge density analysis of LTO/LCO/STO heterostructures. For measurement of electron transport in four probe and van-der pauw geometries, Ag/Cr electrodes were deposited by thermal evaporation through a shadow mask. Initial screening of electron transport was done in a 4.2 K dry cryostat, where as for detailed measurements of longitudinal and Hall resistivity and MR we have used a commercial 14 tesla (T) wet helium system (Quantum Design Physical Property Measurement System) fitted with a precision sample rotator which allowed measurement of angular MR. We have deposited three sets of films. In first set 0, 0.5, 3, 5 and 10 uc of LCO were deposited first on (100) STO followed by 20 uc thick LTO film. In the second set while keeping the LTO thickness fixed at 5 uc, the LTO thickness was varied from 4 to 24 uc in a step of 4 uc. We observed that a metallic conduction occurs only when the LTO layer thickness reaches to 16 uc and beyond. In the third set, while keeping LTO of 16 uc, LCO thickness is reduced from 5 to 0 uc in steps of 1 uc to investigate how the conductivity and carrier density change with the $\delta$-layer thickness.

Fig. 1(a) shows a sketch of various atomic planes along [001] direction of the heterostructure. We first describe the atomic and chemical structure of the interfaces as probed with high resolution scanning transmission electron microscopy (STEM). Fig. 1(c, d) shows high angle angular dark field (HAADF) image taken from STEM, showing sharp and coherent interface between LTO, LCO and STO. The atomically sharp interfaces and uniformly distributed 3 uc LCO (each centered with the Cr-atoms) between LTO and STO is clearly seen with bright background contrast due to the high atomic number Z in the LCO unit-cell. The higher peak intensity marked by the red arrows in Fig. 1(d) than the average Sr peak in STO indicate the diffusion of La/Cr into STO. However, the diffusion length is limited to one to two uc. A two dimensional elemental map based on EELS spectrum image shown in Fig. S1 (see supplementary materials) also confirms the coherent and atomic sharp interfaces. An EELS spectra image with the Ti L$_{2,3}$, O K and Cr L$_{2,3}$ edges from the vertical scan line in (c) but extended into STO (three-times more than the area shown in (c)), is depicted in Fig. (e). Dual EELS was used to simultaneously acquire the core-loss and zero-loss regimes for energy alignment and for detecting possible chemical shift. EELS spectra (open dots) as a function of atomic position (Fig. 1(c)) are plotted in Fig. 1(f). Each spectrum is averaged vertically over 15 spectra with the center at the Ti or Cr atoms to improve the signal/noise ratio. The overlaid red lines are results from the multiple linear least square (MLLS) fitting which fit the spectrum with weighted linear combination of Ti$^{3+}$ and Ti$^{4+}$ reference spectra (acquired from LTO side and STO side away from the interface). Four distinct peaks representing $e_g$ and $t_{2g}$ electron orbital of Ti - L$_2$ and L$_3$ energy level is clearly visible on the STO side and they became broader with peak separation of $e_g$ and $t_{2g}$ less pronounced at the interface and into the LTO side, indicating an increase of the Ti$^{3+}$ state. Composition mapping revealed a constant distribution of oxygen content across the region and complementary increase and decrease in Cr and Ti, respectively, in the LCO layer with a 1-2 uc diffusion length, based on the FWHM measurements of the elemental intensities (Fig. 1(g)). The peak position of Cr L$_3$ edge was fitted using a combined Gaussian and Lorentz function. The refined Cr L$_3$ peak positions are 578.0, 577.9 and 577.9 eV from top to bottom, respectively, less than the value (578.71 eV) of LCO reported by Daulton et. al. [13], implying possible reduced Cr valence (Cr may gain electrons rather than donate electrons in the film). The percentage of Ti$^{3+}$ over the sum of Ti$^{3+}$ and Ti$^{4+}$ (denoted as Ti$^{3+}$)/Ti percentage) cross the interface (Fig. 1(g)) suggests the significant charge transfer from LTO to STO near the interface. To confirm these findings, we conducted density functional theory (DFT) calculations by constructing a supercell with 3 uc LTO on the left, $\delta$ uc LCO in the middle and 3 uc STO on the right, denoted as (LaTiO$_3$)$_3$(LaCrO$_3$)$_\delta$SrTiO$_3$ (for details see supplementary materials). The orbital projected charges are analyzed by Löwdin scheme, and charge of Ti and Cr d orbitals in supercell are compared with those in their bulk counterpart, LaTiO$_3$, LaCrO$_3$ and SrTiO$_3$. The calculations show significant charge transfer from LTO to STO (Fig. 1b), is consistent with the EELS measurements. However, the amount of charges received
FIG. 1: Atomic and chemical structure of LTO/LCO/STO interface probed with High resolution electron microscopy and electron energy loss spectroscopy measurements. a, A sketch of various elemental oxides planes along [001] direction of the δ-doped interface. b, Charge transfer of (LaTiO\textsubscript{3})\textsubscript{3}(LaCrO\textsubscript{3})\textsubscript{δ}(SrTiO\textsubscript{3})\textsubscript{3}. The positive value means the gain of charge while the negative value means the lost of charge. The left, middle and right regions are 3 unit cells (uc) of LaTiO\textsubscript{3} (LTO), δ uc of LaCrO\textsubscript{3} (LCO) and 3 uc of SrTiO\textsubscript{3} (STO), respectively. c,d, High angle annular dark field (HAADF) image showing two sharp and coherent interfaces between LTO, LCO and STO with 3 uc LCO (bright atom columns) uniformly distributed between LTO and STO. An intensity line-profile (yellow) from the column marked by the blue dark line is included in (d). The red arrows indicates the possible diffusion of La/Cr into STO. e, EELS spectrum image from vertical scan line in (c), showing Ti L\textsubscript{2,3}, O K and Cr L\textsubscript{2,3} edges. The core-loss and zero loss spectra were acquired simultaneously to detect chemical shift. The dispersion and scan step were set to be 0.1 eV/chanel and 0.0245 nm. (f) a series of Ti L\textsubscript{2,3} edges (black circles) across two interfaces from the spectrum image (e) acquired from the line scan partially shown in (c). Each spectrum is averaged vertically over 15 spectra with center at the Ti or Cr atom. The purple lines are from the multiple linear least-square fitting with Ti\textsuperscript{3+} and Ti\textsuperscript{4+} reference spectra (acquired from the LTO side and STO side away from the interface), indicating the change of e\textsubscript{g} and t\textsubscript{2g} intensities. (g) Relative atomic composition of O, Ti and Cr derived from EELS measurement, as well as Ti\textsuperscript{3+}/Ti percentage as a function of probe position.

by the STO reduces with the increase of δ. Interestingly, Cr in LCO also receives electrons, confirming its reduced valence state suggested by EELS measurements.

Fig. 2(a) shows the sheet resistance (R\textsubscript{□}) as a function of temperature for LTO(20 uc)/LCO(δ uc)/STO samples of δ = 0 and 10. We see a metallic behavior upon lowering the temperature from 300 K. On further cooling below ≈ 20 K for the δ = 0 sample, a resistance minimum followed by a slight upturn of resistance and then saturation at T ≤ 7 K is seen. As the δ-layer thickness is increased, the low temperature resistance minimum (T\textsubscript{M}) shifts towards higher temperatures and the upturn becomes more prominent. This trend of R\textsubscript{□} has been seen in all samples of δ = 0.5, 3, 5 and 10 uc. Inset of Fig. 2(a) shows the room temperature sheet resistance and sheet carrier density as a function of δ-layer thickness for LTO(16 uc)/LCO(δ uc)/STO samples with δ = 0, 1, 2, 3, 4, 5 uc. The room temperature R\textsubscript{□} increases progressively with δ-layer thickness. For example, the R\textsubscript{□} of a sample with δ = 5 uc is 100 times larger than the R\textsubscript{□} of
Note that all these samples display a minimum in $R_m$ and the $T_m$ in fact by a factor of 50 and 280 for few unit cells of LCO leads to a dramatic decrease in $n_\square$ and thereby suppress the polarization catastrophe. The insertion of an extra layer is transferred to STO surface from the LTO layers to increase the $\delta$-doping is consistent with electron-magnetic field interaction effects in 2D.\cite{20, 21} The distinction between the two can be made by measuring the MR, which in the latter case is positive and mostly isotropic. However, before we dwell upon the MR data, a key observation of Fig. 2(b) is the truncation of divergence of $R_\square$ at $T \ll T_m$. Such an effect can arise due to a phenomenon closely associated with weak localization in the presence of strong spin-orbit (S-O) interaction in the system. The dephasing of the spin degree of freedom by S-O in diffusive trajectories can suppress the quantum backscattering process and thereby truncate the lnT growth of $R_\square$ at low temperatures. This phenomenon is known as weak antilocalization (WAL)\cite{18}, and can become prominent at $T \ll T_m$ as the S-O gains strength at lower temperatures. The WAL has it’s own magnetic field dependence which counteracts the MR due to WL.

Here it is also pertinent to address one more scattering phenomenon which can lead to a minimum followed by a saturation of $R_\square$ in disordered metallic films. This effect is related to the Kondo scattering of conduction electrons of spin $\frac{1}{2}$ by localized magnetic impurity in the system of spin $\frac{3}{2}$. The interaction between the two moments is given by the hamiltonian, $H_{ex} = J S_i^z S_{i'}^z$, where $J$ is positive and hence a stable configuration demands anti parallel arrangement of $\vec{S}_i$ and $\vec{S}_{i'}$. At higher temperature, Kondo interaction leads to a contribution to resistivity which goes as $\Delta \rho_k = -B \log T$, here $B$ is a positive con-

\[ \Delta R_\square(T) = -K(p/2) \ln[T/T_0] \]  

where $K$ is a constant involving $e$ and $h$; $p$ is an index related to Thouless length and $T_0$ is a characteristic temperature. A similar dependence of resistance with temperature in zero external magnetic field is also predicted by electron-electron interaction effects in 2D.\cite{20, 21} The distinction between the two can be made by measuring the MR, which in the latter case is positive and mostly isotropic. However, before we dwell upon the MR data, a key observation of Fig. 2(b) is the truncation of divergence of $R_\square$ at $T \ll T_m$. Such an effect can arise due to a phenomenon closely associated with weak localization in the presence of strong spin-orbit (S-O) interaction in the system. The dephasing of the spin degree of freedom by S-O in diffusive trajectories can suppress the quantum backscattering process and thereby truncate the lnT growth of $R_\square$ at low temperatures. This phenomenon is known as weak antilocalization (WAL)\cite{18}, and can become prominent at $T \ll T_m$ as the S-O gains strength at lower temperatures. The WAL has it’s own magnetic field dependence which counteracts the MR due to WL.

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FIG. 2: Sheet resistance ($R_\square(T)$) of $\delta$-doped LTO/STO interface. a, Temperature dependence of sheet resistance of LTO(20 uc)/LCO($\delta$ uc)/STO heterostructure; where $\delta = 0, 10$ uc. The heterostructure is schematically included. The variation of room temperature sheet resistance and sheet carrier density with doping, in LTO(16 uc)/LCO($\delta$ uc)/STO heterostructures; where $\delta = 0, 1, 2, 3, 4$ and 5 uc is shown in the inset of the Fig. b, Temperature dependence of resistance normalized by $R_\square(2K)$ of $\delta = 0, 0.5$ and 5 uc samples. The solid line in $\delta = 5$ uc graph is the lnT fit in the temperature range 9 K to 21 K. 

the $\delta = 0$ sample. The sheet carrier density ($n_\square$) at ambient temperature decreases with increase of the $\delta$ layer thickness. For $\delta = 0$ sample, the $n_\square$ at 300 K is $\approx 3 \times 10^{14}$ cm$^{-2}$, which is very close to the areal charge density ($3.2 \times 10^{14}$ cm$^{-2}$) expected if half an electron per unit cell is transferred to STO surface from the LTO layers to suppress the polarization catastrophe. The insertion of a few unit cells of LCO leads to a dramatic decrease in $n_\square$, in fact by a factor of 50 and 280 for $\delta = 3$ and $\delta = 5$ uc samples respectively at room temperature. The observed drop in $n_\square$ with $\delta$-doping is consistent with electron microscopy results, which show conversion of Cr$^{3+}$ to Cr$^{2+}$ in the LCO layers. This is also in agreement with the DFT calculations.

Fig. 2(b) shows the $R(T)/R(2K)$ of three samples $\delta = 0, 0.5$, and 5 uc plotted as a function of temperature. We note that all these samples display a minimum in $R_\square(T)$ and the $T_m$ moves to higher temperatures with the increasing $\delta$. Below $T_m$ the resistance follows a lnT dependence, but this divergence is cutoff at still lower temperatures and the growth of $R_\square$ flattens off as $T$ goes to zero. This saturating tendency of $R_\square$ is prominent in the $\delta = 0$ sample. While various quantum effects contribute to low temperature electronic transport in 2-dimension (2D) metallic films\cite{18, 19}, the simplest interpretation for the lnT rise can be given in terms of the weak localization (WL) theory in 2D where a constructive interference between partial waves of diffusive electronic motion can lead to enhance backscattering and hence an increase in resistance, which continues to grow at lower temperatures as the dephasing inelastic scattering is reduced due to phonon freeze out. Since weak localization is an orbital effect, it has a distinct dependence on the angle between the magnetic field and the plane of the film. Magnetic field quenches quantum backscattering because of the Aharonov-Bohm phase acquired by the partial waves. The temperature dependence of sheet resistance in 2D due to WL is given as;

\[ \Delta R_\square(T) = -K \frac{p/2}{2} \ln\frac{T}{T_0} \]
stant and a function of $J$, $N(E_F)$ and other properties of the electron gas. This contribution to electron back scattering first calculated by Jun Kondo \cite{22} in a perturbative approach, is a topic of keen interest today in isolated large spin systems. However, $\Delta \rho_0$ can not increase without a bound because there is an upper limit up to which a single impurity spin can scatter. Eventually, the divergence of $\Delta \rho_0$ is cutoff and $\Delta \rho_0$ becomes constant below a temperature of the order of Kondo temperature, $T_K = T_F \exp(-1/(J N))$, where $T_F$ is the Fermi temperature and $N(E_F)$ the DOS at $E_F$. This effect amounts to the formation of bound singlets of $\vec{S}_i$ and $\vec{S}_c$, and the backscattering of conduction electron is truncated. High magnetic field has the tendency to suppress Kondo scattering and this leads to a negative isotropic MR. Recently, Kondo mechanism has been proposed for the resistivity and MR of a 2D electron gas formed on the surface of STO by electrostatic gating.\cite{14} It has been argued that uncompensated Ti$^{3+}$ (spin 1/2) ions are the source of Kondo scattering. A further support to the idea of magnetic scattering comes from the recent observation of ferromagnetism at LAO/STO interface.\cite{2} A Kondo type behavior has been seen earlier in strongly magnetic metallic glasses such as FePdSi.\cite{23} A pertinent question related to Kondo in the present situation is the dimensionality of the sample. The Kondo cloud in this case will be a disk rather than a sphere.

Having enumerated the likely mechanisms for a minimum in resistivity followed by lnT growth at still lower temperatures, we now present a detailed study of magnetic field dependence of resistivity of LTO/δ-LCO/STO heterostructures. In Fig. 3 we show $R_{\perp}(T)$ at various value of magnetic field applied perpendicular to the plane of the film for undoped and $\delta = 0.5$ and 5 uc doped samples. In all three cases a dramatic positive MR is evident which is inconsistent with the prediction of WL theory but agrees broadly with the e-e scattering scenario. In the latter case the magnetoconductance goes as $\sim - \frac{e^2}{\hbar} \frac{F_m}{2\pi^2} (0.084) \times \left( \frac{g \mu_B H}{k_B T} \right)^2$ for $\frac{g \mu_B H}{k_B T} \ll 1$, where $F_m$ has the upper bound of 4/3. Clearly a positive MR is expected which goes as $H^2$. At high field a ln(H) dependence of MR has been predicted. In the inset of Fig. 3 we show the magnetic field dependence of $\delta T_m$, where $\delta T_m = T_m(H) - T_m(0)$, the shift in temperature where the resistance minimum occurs. The latter moves to higher temperature on increasing the out-of-plane field. In Fig. 3(d) we also show the slope of $R_{\perp}$ vs lnT plotted as a function of magnetic field for $\delta = 0, 0.5, 5$ uc doped samples. The fitting has been done over a narrow temperature range below $T_m$. The slope remains insensitive to field within the margin of error.

We probe the MR further as a function of magnetic field since it gives a better insight of the mechanisms of weak scattering in disordered low dimensional metals. The MR is defined as $\frac{\Delta R}{R_0} = \frac{R(H) - R(H=0)}{R(H=0)}$, where $R(H)$ is the resistance in a magnetic field $H$. The out-of-plane MR ($MR^\perp$) of undoped sample is shown in Fig. 4(a). A Positive (≈14%) $MR^\perp$ is observed at 2 K when the magnetic field is increased to 10 T. The out-of-plane MR for undoped sample shows a quadratic field dependence, which, at first glance can be attributed to the e-e scattering as well as the classical defect scattering resulting from enhanced transit path of electron due to their cyclotron motion.\cite{24} In the former case the upper bound for $H$ to see $H^2$ dependence at 4.2 K is $\approx 3.16$ T and the slope of $MR$ vs $H^2$ curve is $\approx 0.714 \times 10^{-7} /T^2$ (calculated from the expression of magnetoconductance of e-e scattering). However the measured slope from $MR$ vs $H^2$ curve of undoped sample is $1.69 \times 10^{-3} /T^2$, which suggests that the e-e interaction effect is not solely responsible for the large out-of-plane MR in these heterostructures. A sizable contribution to MR can also come from the classical orbital effect that follows the Kohler’s rule: $\frac{\Delta R}{R_0} \propto a (\frac{\mu_B H}{k_B T})^{2}$. The inset of Fig. 4(a) shows Kohler’s plot for undoped samples which follows linearity as expected. From this $MR^\perp$ data we calculated the mobility of carriers at 2 K and 100 K, which is 403 and 86 cm$^2$V$^{-1}$S$^{-1}$ respectively. The quadratic like behavior of ordinary MR has been also observed in LAO/STO film grown under different oxygen
dependence seen at $H_{\parallel} \gtrsim \text{contribution of this new process by extrapolating the } H_{\parallel}^2$

the presence of an additional scattering mechanism which

dependence and a cusp appear near $H = 0$. This indicates

the MR at lower fields deviates from its quadratic field
to 9% and 4% respectively. Here we also notice that

subtracting the extrapolated value from the measured

data is the theoretical fit using Kondo model (equation (3))

sample shows negative inplane MR for all three temperatures

higher magnetic field. In (a) shows Kohler plot of $\delta = 0$ uc sample and this critical field decreases

very little with the increasing $\delta$-layer thickness (3.2 T for 3 uc). In our LTO/LCO/STO samples this maxima is

observed at a much higher field than seen previously in

2D disordered metal films where the crossover field was

$\sim 0.1 \text{ T in Bi films}[27]$ and $\sim 2.5 \text{ T in Au films}[28]$. The inplane positive MR decreases with increasing temperature and diminishes above $\sim 5 \text{ K}$. Moreover, it is not seen in the undoped LTO/STO films.

More interesting in-plane MR has been observed at 2 K for $\delta = 0.5$ and 3 uc doped samples shown in Fig. 4(c) and (f) respectively. Here, the MR can be divided in two regions, a positively sloped MR at lower magnetic field and a negatively sloped MR at the higher magnetic field, resulting in a local MR maximum, which is seen at 3.6 T for $\delta = 0.5$ uc sample and this critical field decreases very little with the increasing $\delta$-layer thickness (3.2 T for 3 uc). In our LTO/LCO/STO samples this maxima is observed at a much higher field than seen previously in 2D disordered metal films where the crossover field was $\sim 0.1 \text{ T in Bi films}[27]$ and $\sim 2.5 \text{ T in Au films}[28]$. The inplane positive MR decreases with increasing temperature and diminishes above $\sim 5 \text{ K}$. Moreover, it is not seen in the undoped LTO/STO films.

The negative MR in parallel field can appear due to two reasons. One is due to WL and other from Kondo scattering. We have already ruled out WL as it is not consistent with the positive MR seen in the $H_{\parallel}$ geometry. To establish the Kondo effect, we fit the in-plane MR of $\delta = 0.5$ uc sample at 10 K to a simple Kondo model [14]

$$R^{\text{model}} (H_{\parallel}) = R_0 + R_K (H_{\parallel}/H_1)$$

where $R_0$ is the residual resistance due to static disorder, $R_K (H_{\parallel}/H_1)$ is a universal function for zero temperature magnetoresistivity of Kondo impurity, which is related to magnetization and can be calculated using Bethe-ansatz.

where $\Delta R_{\parallel}(H) = R_{\parallel}(H) - R_{\parallel}(0)$, $\Psi(x)$ is the digamma function, the characteristics magnetic field

$$H_{\varphi} = \frac{\hbar}{4eL_{\varphi}^2}, \text{ phase coherence length } L_{\varphi} = \sqrt{D\tau_{\varphi}},$$

$D$ is diffusion constant and $\tau_{\varphi}$ phase coherence time. Inset of Fig. 4(c) shows the fitting of equation (2) to the MR data of $\delta = 0.5$ and 3 uc samples. From this extracted values of $L_{\varphi}$ are $\approx 33 \text{ nm}$ and $46 \text{ nm}$ for $\delta = 0.5$ and 3 uc samples respectively, which are larger than the thickness of the films. However, these numbers are reasonable considering the fact that the scattering is taking place in the plane of the film.

Fig. 4(d-f) shows in-plane MR (field is parallel to film surface but perpendicular to the direction of current) of $\delta = 0, 0.5$ and 3 uc LTO/LCO/STO heterostructures. This geometry of measurement allows separation of the orbital contribution to MR. Interestingly, undoped sample shows negative inplane MR at temperature $T < 50 \text{ K}$. The suppression of classical positive MR, in this case, can be explained as the thickness of interfacial metallic layer is within one carrier mean free path. This MR anisotropy also supports the 2D nature of the metallic state in these interfaces.

FIG. 4: Positive and negative MR of $\delta$-doped
LTO/STO interface in out-of-plane and in-plane geometries respectively. a-c, Show out-of-plane MR of $\delta = 0, 0.5$ and 3 uc samples respectively. All the samples show positive out-of-plane MR. Inset of (a) shows Kohler plot of $\delta = 0$ uc sample. Inset of (c) show the WAL effect after subtracting high field $H_{\parallel}^2$ fitting data. The solid curve in the inset of (c) are the theoretical prediction of equation (2). d-f, show in-plane MR for the same set of samples. $\delta = 0$ uc sample shows negative inplane MR for all three temperatures but the $\delta = 0.5$ and 3 uc samples show positive MR at lower field at 2 K and a crossover from positive to negative MR at higher magnetic field. In (e) the black solid line at 10 K MR data is the theoretical fit using Kondo model (equation (3)) and at 2 K it’s fitted using Kondo + WAL in the range $-5 \text{T} \leq H \leq 5 \text{T}$.

pressure.\[12\][13].

Fig. 4(b) and (c) show that the out-of-plane MR at $2 \text{ K and } 10 \text{ T for } \delta = 0.5$ and 3 uc samples decreases to 9% and 4% respectively. Here we also notice that the MR at lower fields deviates from it’s quadratic field dependence and a cusp appear near $H = \text{0}$. This indicates the presence of an additional scattering mechanism which becomes operational below $\approx 10 \text{ K}$. We separate out the contribution of this new process by extrapolating the $H_{\parallel}^2$ dependence seen at $H \geq 6 \text{ T}$ to lower fields and then subtracting the extrapolated value from the measured $R_{\parallel}(H)$ data. This result is shown in the inset of Fig. 4(c) for $\delta = 0.5$ and 3 uc samples. We attribute this distinct additional contribution to MR at $T \leq 10 \text{ K}$ to spin-orbit scattering, which in the 2D limit for perpendicular field

$$\Delta R_{\parallel}(H) = -\frac{e^2}{2\pi^2\hbar} [\Psi \left(\frac{1}{2} + \frac{H_{\parallel}}{H_{\varphi}}\right) - \ln \frac{H_{\parallel}}{H_{\varphi}}]$$

(2)
technique (please see supplementary materials), and \( H_1 \) is a magnetic field scale related to Kondo temperature and \( g \)-factor of impurity spin.\[^{29}\] We have taken the form of \( R_K(H_1/H_1) \) from Ref. 14 and have chosen \( H_1 = 25 T, 28.5 T \) and \( 22 T \) for \( \delta = 0, 0.5 \) and 3 uc sample respectively to fit the data. The black solid line in Fig. 4(d)-(f) for the 10 K data is the Kondo fit. The in-plane MR at 2 K of \( \delta = 0 \) uc sample also fits to the Kondo model (equation 3) taking \( H_1 = 23 T \). The excellent agreement between experimental data and the theoretical model strengthens our explanation. We note that the negative in-plane MR at 10 T (Fig. 4(e, f)) increases with \( \delta \)-layer thickness and thus bears an inverse relation with \( \delta \) (see Fig. 2(a)). The dependence of low temperature Kondo resistivity on the Fermi energy while the magnetic impurity concentration is held fixed, is expected to be given by \( R_K(T = 0, H = 0) \propto n_{\text{e}}^{-1}v_{0}^{-1} \), where \( n_{\text{e}} \) and \( v_{0} \) are the conduction electron density and density of states at the Fermi level.\[^{30}\] The data shown in Fig. 4(e, f) are consistent with this picture.

The positive MR at 2 K in fields below a critical value appears to be the contribution of the WAL effect. To fit the 2 K data we add the WAL term (equation (2)) to the Kondo contribution. As the WAL effect is insignificant at higher magnetic fields, we fit the 2 K data in the range \(-5 \leqslant H \leqslant 5 \) T. The black solid line in Fig. 4(e) and (f) for the 2 K data is the fit using Kondo + WAL. The details of this fitting is discussed in supplementary section. The quality of fit strongly suggests that the WAL effect rides over the Kondo scattering contribution to resistivity and MR at \( T < 10 \) K.

The magnetoimpedance \( R(H) - R(H = 0) \) of the \( \delta = 0, 0.5 \) and 3 uc samples for different orientation (\( \theta \)) of the magnetic field with respect to sample normal is shown in Fig. 5 (a-c). At \( \theta = 90^\circ \), \( \vec{H} \) is in the film plane but perpendicular to the direction of current. For \( \vec{H} \parallel \delta \) configuration (\( \theta = 0 \)), all the samples shows positive MR. As we tilt the magnetic field towards sample plane, a crossover from positive MR to negative MR is observed. This change of sign at 10 T happens at \( 80^\circ, 70^\circ \) and \( 50^\circ \) for \( \delta = 0, 0.5 \) and 3 uc doped samples respectively. A similar crossover from positive out of plane MR to negative in plane MR has been observed in LAO/STO\[^{31}\] and electrolyte gated STO\[^{14}\].

In the inset of Fig. 5(a-c) the resistance at 2 K as a function of angle \( \theta \) of the 10 T field is shown. The resistance minimum is observed when the magnetic field is in the plane of the surface. The black line in inset of Fig. 5(a-c) is a fit using \( R(\theta, T) = r(T) \cos^2(\theta) + R_0(T) \), where \( r(T = 2 K) = 33, 36, 44 \) \( \Omega \) and \( R_0(T = 2 K) = 233, 466, 906 \) \( \Omega \) for \( \delta = 0, 0.5, 3 \) uc samples respectively. The origin of two-fold oscillation in anisotropic magnetoimpedance can be from the Lorentz scattering of the charge carriers, which follows the \( \cos^2\theta \) dependence. This also suggests the 2-D nature of the electron confinement at the interface.

In summary, We have established a strong modulation of carrier density in 2-DEG at LTO/STO interface by inserting \( \delta \)-thick layer of an iso-structural perovskite LaCrO\(_3\). The sheet carrier density of the 2DEG decreases linearly with the increase of the \( \delta \)-layer thickness. Our spectroscopic measurements clearly show that Cr ions at the interface act as traps and absorb electron donated by the LaTiO\(_3\). While the low temperature resistance minimum followed by a \( \ln T \) increase of \( R_{\square} \) below the minimum suggest e-e interaction and/or WL effects as the mechanism for \( R_{\square}(T) \), the positive out-of-plane MR is inconsistent with the WL theory. The MR due to e-e interaction should be isotropic and positive. However, the observed negative in-plane MR is not consistent with
the e-e picture. The saturation tendency of resistance at $T \leq 10$ K can result due to WAL. The lnT dependence followed by saturation of $R(T)$ at the lowest temperature are also consistent with the Kondo type scattering of electron by localized spins. The origin of the latter can be attributed to localized electrons in Ti d orbitals forming heavy polarons, while the conduction takes place in extended band of Ti $e_y$ orbitals. We also argue that the interfacial Cr$^{3+}$ ions (S = 3/2) may also contribute to s-d scattering. The emergence of a cusp in the positive MR for $H_{||}$ in $\delta$-doped samples at $T < 10$ K is in agreement with the prediction of 2D-WAL theory as evidence by the large value of $L_\phi$. The 2D-WAL also couples with Kondo MR response of the sample at $T < 10$ K and field ($H_{||}$) $\leq 3$ T. At higher values of T and $H_{||}$, the negative MR is consistent with Kondo picture. Our angle dependent measurement also highlight the crossover from positive out-of-plane MR to negative in-plane MR. An important finding of this work is the enhanced spin-orbit interaction in the presence of $\delta$-layer. In the Rashba scenario, it needs to be seen how the $\delta$-layer enhances local electric field due to breakdown of inversion symmetry.

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[1] Ohtomo, A., Muller, D. A., Grazul, J. L. & Hwang, H. Y. Artificial charge-modulation in atomic-scale perovskite titanate superlattices. *Nature (London)* 419, 378-380 (2002).

[2] Shibuya, K., Ohnishi, T., Kawasaki, M., Koimura, H. & Lippmaa, M. Metallic LaTiO$_3$/SrTiO$_3$ films on the SrTiO$_3$ (100) surface. *Jpn. J. Appl. Phys.* 43, L1178-L1180 (2004)

[3] Ohtomo, A. & Hwang, H. Y. A high-mobility electron gas at the LaAlO$_3$/SrTiO$_3$ heterointerface. *Nature (London)* 427, 423-426 (2004).

[4] Siemons, W. et. al. Origin of charge density of LaAlO$_3$ and SrTiO$_3$ heterointerface: possibility of Intrinsic doping. *Phys. Rev. Lett.* 98, 196802 (2007).

[5] Dikin, D. A. et. al. Coexistence of conductivity and ferromagnetism in two dimensions. *Phys. Rev. Lett.* 107, 056802 (2011).

[6] Li, L., Richter, C., Mannhart, J. & Ashoori, R. C. Coexistence of magnetic order and two-dimensional superconductivity at LaAlO$_3$/SrTiO$_3$ interface. *Nat. Phys.* 7, 762-766 (2011).

[7] Brinkman, A. et. al. Magnetic effects at the interface between non-magnetic oxides. *Nat. Mater.* 6, 493-469 (2007).

[8] Herranz, G. et. al. High mobility in LaTiO$_3$/SrTiO$_3$ heterostructure: origin, dimensionality and perspectives. *Phys. Rev. Lett.* 98, 216803 (2007).

[9] Thiel, S., Hammerl, G., Schmelch, A., Schneider, C. W., & Mannhart, J. Tunable quasi-to-dimensional electron gases in oxides heterostructures. *Science* 313, 1942-1945 (2006).

[10] Biscaras, J. et. al. Two-dimensional superconductivity at a mott-insulator/band-insulator interface: LaTiO$_3$/SrTiO$_3$. *Nat. Commun.* 1, 89 (2010).

[11] Caviglia, A. D. et. al. Tunable Rashba spin-orbit interaction at oxide interface. *Phys. Rev. Lett.* 104, 126803 (2010).

[12] Wang, F. J., Chopdekar, R. V. & Suzuky, Y. Disorder and localization at the LaTiO$_3$/SrTiO$_3$ heterointerface. *Phys. Rev. B* 82, 165413 (2010).

[13] Wang, X. et. al. Magnetoresistance of the two-dimensional and three-dimensional electron gas in LaAlO$_3$/SrTiO$_3$ heterostructures: Influence of magnetic ordering, interface scattering and dimensionality. *Phys. Rev. B* 84, 075312 (2011).

[14] Lee, M., Williams, J. R., Zhang, S., Frisbie, C. D. & Gordon, D. G. Electrolyte gate-controlled Kondo effect in SrTiO$_3$. *Phys. Rev. Lett.* 107, 256601 (2011).

[15] Hotta, Y., Susaki, T. & Hwang, H.Y. Polar discontinuity doping of the LaVO$_3$/SrTiO$_3$ interface. *Phys. Rev. Lett.* 99, 236805 (2007).

[16] Rastogi, A., Kushwaha, A. K., Shiyani, T., Gangawar, A. & Budhani, R. C. Electrically tunable optical switching of a mott insulator - band insulator interface. *Adv. Mater.* 22, 4448-4451 (2010).

[17] Daulton, T. L. & Little, B. J. Determination of chromium valence over the range Cr(0)-Cr(VI) by electron energy loss spectroscopy. *Ultramicroscopy* 106, 561-573 (2006).

[18] Bergmann, G. Weak localization in thin films: a time-of-flight experiment with conduction electrons. *Physics Reports* 107, 1-58 (1984).

[19] Lee, P. A. & Ramakrishnana, T. V. Disordered electronic systems. *Rev. Mod. Phys.* 57, 287-337 (1985).

[20] Chiu, S.-P. & Lin, J.-J. Weak antilocalization in topological insulator Bi$_2$Te$_3$ nanofilms. *Phys. Rev. B* 87, 035122 (2013).

[21] Liu, M. et. al. Electron interaction-driven insulating ground state in Be$_2$Se$_3$ topological insulators in the two-dimensional limit. *Phys. Rev. B* 83, 165440 (2011).

[22] Kondo, J. Resistance minimum in dilute magnetic alloys. *Prog. Theor. Phys.* 32, 37-49 (1964).

[23] Hasegawa, R. & Tsuei, C. C. Kondo effect in amorphous Fe-Pd-Si and Co-Pd-Si alloys. *Phys. Rev. B* 28, 216803 (2010).

[24] Tuft, O. N. & Stelzer, E. L. Magnetoresistance in two-dimensional random system. *Prog. Theor. Phys.* 63, 707-710 (1980).

[25] Grbic, B. et. al. Strong spin-orbit interactions...
and weak antilocalization in carbon-doped p-type GaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As heterostructures. *Phys. Rev. B* **77**, 125312 (2008).

[27] Komnik, Y. F., Andrievskii, V. V. & Berkutov, I. B. Manifestation of the spin-orbit interaction in bismuth films in a parallel magnetic field. *Low Temp. Phys.* **33**, 79 (2007).

[28] Kawaguti, T. & Fujimori, Y. Magnetoresistance and inelastic scattering time in thin films of silver and gold in weakly localized regime. *J. Phys. Soc. Jpn.* **52**, 722-725 (1983).

[29] Andrei, N., Furuya K. & Lowenstein, J. Solution of Kondo problem. *Rev. Mod. Phys.* **55**, 331-402 (1983).

[30] Costi, T. A. Kondo effect in a magnetic field and the magnetoresistivity of Kondo alloys. *Phys. Rev. Lett.* **85**, 1504-1507 (2000).

[31] Shalom, M. B. et. al. Anisotropic magnetoresistance at the SrTiO\textsubscript{3}/LaAlO\textsubscript{3} interface. *Phys. Rev. B* **80**, 140403 (2009).

[32] Nanda, B. R. K. & Satpathy, S. Electronic phases and phase separation in the Hubbard-Holstein model of a polar interface. *Phys. Rev. B* **83**, 195114 (2011).