Kondo scattering in δ-doped LaTiO₃/SrTiO₃ interfaces: Renormalization by spin-orbit interactions

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We present a study of δ doping at the LaTiO₃/SrTiO₃ interface with isostructural antiferromagnetic perovskite LaCrO₃ that dramatically alters the properties of the two-dimensional electron gas at the interface. The effects include a reduction in sheet-carrier density, prominence of the low-temperature resistivity minimum, 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 fields, respectively, and the field and temperature dependencies of MR suggest Kondo scattering by localized Ti³⁺ moments renormalized by spin-orbit interaction at T < 10 K, with the increased δ-layer thickness. Electron-energy-loss spectroscopy and density functional calculations provide convincing evidence of blocking of electron transfer from LTO to STO by the δ layer.

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The phenomenon of the formation of a two-dimensional electron gas (2DEG) at the interface of epitaxially grown LaTiO₃ (LTO) or LaAlO₃ (LAO) on TiO₂-terminated SrTiO₃ (STO) [1–3] has attracted much attention in recent years [4–9]. It is generally agreed that the gas is formed by the transfer of electrons from the polar layer of LAO or LTO to the top TiO₂ layer of STO. Since the carrier concentrations n₀ are large (∼3 × 10¹⁴/cm²) and some of the Ti³⁺ ions at the interface may also get converted to Ti⁴⁺ with S = 1/2 localized spin, the electron dynamics is likely to be controlled by weak electron-electron (e-e) scattering and magnetic scattering in addition to the effects of weak static disorder. Moreover, as the interface breaks inversion symmetry, there is a possibility of Rashba spin-orbit scattering [10] emanating from the interface electric field. Some of these issues have been addressed by measuring the magnetoresistance (MR) of 2DEG formed at LAO/STO [11–13] and electrolyte-gated STO [14]. However, no consensus has emerged on the origin of a strong positive MR Rashba spin-orbit scattering [10] emanating from the interface.

In order to address the mechanism of 2DEG formation at the LTO/STO interface and to identify the dominating scattering processes that control the nature of MR in this system, we have used the approach of δ doping of the interface. The doped structure consists of LTO(m unit cell (uc))/LCO(δ uc)/TiO₂ terminated STO. LaCrO₃ (LCO)/STO alone does not form a 2D gas. The LCO film remains an antiferromagnetic insulator with a Cr site spin of ½ and T_N = 298 K. This is interesting because Cr follows vanadium in the 3d transition series and the LaV₀₅/SrTiO₃ interface is conducting [15]. However, when LCO is inserted as a δ layer, the 2DEG nature of LTO/STO is retained for smaller values of δ (<3), but with increasing δ, a significant blocking of carriers by LCO makes the interface insulating. The temperature, magnetic field, and angular dependence of MR in δ = 0 indicate a dominant Kondo-type s-d scattering for the H₁ field. However, the Kondo’s characteristic negative MR is superseded by positive MR resulting, presumably, from the enhanced forward scattering of diffusive electrons by the spin-orbit (S-O) interaction in the T ≤ 10 K regime. For H₂, the classical positive MR quadratic in the field is seen at T > 10 K. 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 pulsed laser ablation on STO, as described in our earlier works [3,16]. We have deposited three sets of films. In the first set 0, 0.5, 3, 5, and 10 uc of LCO were grown on STO, followed by a 20-uc-thick LTO film. In the second set the δ is 5 uc, and the LTO was varied from 4 to 24 uc. In the last set, the LTO is 16 uc, while LCO was reduced from 5 to 0 uc in steps of 1 uc. The atomic and chemical states of the interface have been studied using x-ray reflectivity and cross-sectional scanning transmission electron microscopy (STEM) in conjunction with electron-energy-loss spectroscopy (EELS). In addition, density functional theory (DFT) calculations have been performed to analyze the charge-density profile of the interface. Electron transport measurements have been performed in a 14-T system (Quantum Design PPMS) fitted with a sample rotator which allowed measurement of angular MR.

Figure 1 shows a sketch of various atomic planes of the heterostructure along with high-angle angular-dark-field (HAADF) images taken from STEM. The atomically sharp interfaces and uniformly distributed 3-uc LCO between LTO and STO are clearly seen with the bright background contrast due to the high atomic number Z in the LCO unit cell. The peak intensity marked by the red arrows in Fig. 1(d), which is higher than the average Sr peak in STO, indicates diffusion of La/Cr into STO, limited to 1 to 2 uc. A 2D elemental map based on the EELS spectrum image shown in Fig. S1 of the Supplemental Material [17] also confirms the coherent and atomic sharp interfaces. An EELS image with the Ti L₂,₃, O K, and Cr L₂,₃
The overlaid red lines are the results from the multiple linear least-squares fitting, the spectrum with the weighted linear correction of the $\delta$-doped interface. This plot also shows the Cr $L_3/L_2$ intensity ratio across the interface (brown inverted triangles). (c) and (d) HAADF image showing interfaces between LTO, LCO, and STO with 3-uc LCO (bright atom columns). An intensity line profile (yellow) from the column marked by the white square in (c) is extended into the STO surface from the LTO layers to suppress the polarization catastrophe. The insertion of a few unit cells of LCO leads to truncation of the divergence of the MR data, a key observation of Fig. 2(b) is the upturn at 7 K is seen for $\delta = 0$. As the $\delta$ layer becomes thicker, the minimum $T_m$ shifts towards higher temperature, and the upturn becomes more prominent. Figure 2(a) shows the sheet resistance $R_{\square}$ as a function of temperature $T$ for LTO(20 uc)/LCO/STO of $\delta = 0$ and 10 uc. We see a metallic behavior upon decreasing $T$ from 300 K. On cooling below $\approx \! 20 K$, a resistance minimum followed by a slight upturn and then saturation of $R_{\square}$ at $T \leq 7K$ is seen for $\delta = 0$. As the $\delta$ layer becomes thicker, the minimum $T_m$ shifts towards higher temperature, and the upturn becomes more prominent. This trend in $R_{\square}$ was seen in all samples of $\delta = 0.5, 3, 5$, and 10 uc. The inset of Fig. 2(a) shows $R_{\square}$ and $n_{\square}$ at 300 K as a function of $\delta$-layer thickness. While $R_{\square}$ increases progressively, $n_{\square}$ decreases with the increase in the $\delta$ layers. For $\delta = 0$, $n_{\square}$ 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 the 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 $n_{\square}$, by a factor of 50 and 280 for $\delta = 3$ uc and $\delta = 5$ uc, respectively, at 300 K. These observations are consistent with STEM results, which suggest conversion of Cr$^{3+}$ to Cr$^{2+}$ in the LCO layers, and the results of the DFT calculations.

Figure 2(b) is a plot of $R_{\square}(T)/R_{\square}(2 K)$ of $\delta = 0.5$, 2, and 5 uc to emphasize the minimum in $R_{\square}(T)$ at $T_m$. Below $T_m$ the resistance follows a $\ln T$ dependence, but this divergence is cut off on further decreasing the temperature. This saturating tendency of $R_{\square}$ is prominent in $\delta = 0$. The simplest interpretation for the $\ln T$ rise can be given in terms of weak localization (WL) in 2D where a constructive interference between partial waves of diffusive electrons can lead to enhanced 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 [20,21]. Since weak localization is an orbital effect, it has a distinct dependence on the angle between $H$ and the plane of the film. $H_{\perp}$ quenches quantum backscattering because of the Aharonov-Bohm phase acquired by the partial waves. A similar dependence of $R_{\square}$ in zero field also results from the $e$-$e$ interaction in 2D [22,23]. The distinction between the two can be made by measuring the MR, which in the latter case is positive and mostly isotropic. However, when we dwell upon the MR data, a key observation of Fig. 2(b) is the truncation of the divergence of $R_{\square}$ at $T \approx T_m$. Such an effect can arise due to a phenomenon closely associated with WL in...
the presence of the S-O interaction. The dephasing of the spin degree of freedom by S-O in diffusive trajectories can suppress the quantum backscattering and thereby truncate the lnT growth of \( R_{\text{C}} \) at low temperatures. This weak antilocalization (WAL) [20] becomes prominent at \( T \ll T_m \) as the S-O gains strength at lower temperatures.

Here it is pertinent to introduce one more scattering phenomenon which can lead to a minimum followed by saturation of \( R_{\text{C}} \) in disordered metallic films. This is the Kondo scattering of conduction electrons of spin \( \vec{S}_c \) by a localized magnetic impurity in a system of spin \( \vec{S}_m \). The interaction between the two moments is given by the Hamiltonian

\[
H_{\text{ex}} = J \cdot \vec{S}_c \cdot \vec{S}_m,
\]

where \( J \) is positive, and hence a stable configuration demands antiparallel arrangement of \( \vec{S}_c \) and \( \vec{S}_m \). The Kondo interaction leads to a resistivity \( \Delta \rho_k = -B \ln T \), where \( B \) is a positive constant and a function of \( J, N(E_F) \) (the density of states at the Fermi level), and other properties of the electron gas. However, \( \Delta \rho_k \) cannot increase without a bound [24]. Eventually, the divergence of \( \Delta \rho_k \) is cut off, and it becomes constant below a temperature of the order of the Kondo temperature, \( T_K = T_r \exp(\frac{1}{k_B T}) \). This unitary limit is, however, not reached in metal films [25–27]. An \( H \) field suppresses Kondo scattering, thereby leading to a negative isotropic MR. Recently, a Kondo mechanism has been proposed for \( R_{\text{C}}(T, H) \) of a 2DEG formed on the surface of STO by electrostatic gating [14]. It has been argued that highly localized \( 3d^1 \) electrons of some Ti\(^{3+} \) ions (spin 1/2) are the source of Kondo scattering. The idea of magnetic scattering is supported by the recent observation of ferromagnetism at the LAO/STO interface [7].

In Fig. 3 we show \( R_{\text{C}}(T) \) at different \( H_\perp \) for \( \delta = 0, 0.5, 3, \) and 5 uc. \( H_\perp \) shifts the resistivity minimum to higher \( T \) (see insets), and a dramatic positive MR is evident which is inconsistent with the WL but agrees broadly with the e-e scattering scenario. In the latter case the magnetococonductance increases as \( -\frac{e^2}{h} \frac{F_\sigma}{a} (0.084)(\frac{4\pi a H}{k_B T})^2 \) for \( \frac{4\pi a H}{k_B T} \ll 1 \), where \( F_\sigma \)

![FIG. 3. (Color online) (a)–(d) \( R_{\text{C}}(T) \) of LTO(20 uc)/LCO(\( \delta \) uc)/STO films as a function of lnT for different \( H_\perp \). The inset shows \( \delta T_m \) vs \( H_\perp \), where \( \delta T_m = T_m(H) - T_m(0) \). All the samples show positive MR down to 2 K.](image_url)

![FIG. 4. (Color online) (a)–(c) MR of \( \delta = 0, 0.5, \) and 3 uc, respectively. The inset in (a) shows a Kohler plot for \( \delta = 0 \) uc, while the inset in (c) reveals the WAL effect after subtracting high-field \( H^2 \) data. The solid curves in the inset in (c) are the fit to the Eq. (1). (d)–(f) MR of the same set of samples. A negative MR for all three temperatures is seen for \( \delta = 0 \), but \( \delta = 0.5 \) and 3 uc show positive MR at lower field at 2 K and a crossover from positive to negative MR at higher field. In (e) and (f) the black solid line for 10 K MR is the fit using the Kondo model [Eq. (2)], and at 2 K it is fitted using Kondo + WAL in the range \(-5 \leq H \leq 5 \) T.](image_url)
respectively. The inset of Fig. 4(c) shows the fits of Eq. (1) to MR nature of the metallic state in these interfaces. This MR anisotropy also supports the Kondo mechanism. To establish this idea further, we fit the MR of $\delta = 0.5$ and 3 uc films. The angular variation $\sim 0.1$ and 2.5 T, respectively [11,31,32]. This in-plane positive $MR_0$ diminishes above $\sim 5$ K.

The negative $MR_1$ supports the Kondo mechanism. To establish this idea further, we fit the $MR_1$ of $\delta = 0, 0.5$, and 3 uc at 10 K to a simple Kondo model [14],

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

where $R_0$ is the residual resistance, $R_K (H_1/H_1)$ is a function of the zero-temperature MR of Kondo impurity, which is related to magnetization and can be calculated using the Bethe-ansatz technique [17], and $H_1$ is an $H$-field scale related to $T_K$ and the $g$ factor of the impurity spin [33]. The $MR_1$ at 2 K for $\delta = 0$ uc also fits to the Kondo model [Eq. (2)]. We note that the negative $MR_1$ at 10 T [Figs. 4(e) and 4(f)] increases with $\delta$-thickness layer and thus bears an inverse relation to $n_{d}$ [see Fig. 2(a)]. In Kondo’s theory $R_K(T=0,H=0) \propto n_{d}^{-1} N(E_F)\sim 1$ [34]. The data shown in Figs. 4(e) and 4(f) is consistent with this picture.

The positive $MR_2$ at 2 K for $\delta \neq 0$ at fields below the critical value appears to be the contribution of the WAL. To fit the 2 K data we add the WAL and Kondo terms [Eqs. (1) and (2)]. As the WAL effect is insignificant at higher fields, we fit the 2 K data in the range $-5$ T $\leq H$ $\leq 5$ T. The black line in Figs. 4(e) and 4(f) for the 2 K data is this fit [17]. The quality of the fit strongly suggests that the WAL effect overrides the Kondo scattering at $T < 10$ K.

The MR for $\delta = 0, 0.5$ and 3 uc for different orientations $\theta$ of $H$ with respect to the sample normal has been measured (see Fig. S6 in the Supplemental Material). As we tilt $H$ towards the sample plane, a crossover from positive MR to negative MR is observed. This change in sign at 10 T happens at $80^\circ$, $70^\circ$ and $50^\circ$ for $\delta = 0, 0.5$, and 3 uc, respectively. The angular variation of $MR_2$ is of the type $R(\theta,T) = R(T) \cos^2(\theta) + R_0(T)$, 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, respectively.

In summary, we have established a strong suppression of $n_{d}$ in a 2DEG at the LTO/STO interface by inserting a $\delta$-thick layer of an isostructural perovskite LCO. Our spectroscopic measurements suggest that Cr ions at the interface act as traps and absorb the electron donated by the LTO. The saturation tendency of resistance at $T \leq 10$ K and the $InT$ dependence between 10 K and $T_m$ are consistent with the Kondo scattering of electrons by localized spins. The origin of the latter can be attributed to electrons in the Ti $d^1$ configuration which are presumably, in Ti$_x$ orbitals, forming heavy polarons with spin $S = 1/2$ while the conduction takes place in the extended band of the Ti$_{yz/zx}$ motif [14,35–37]. Such a Ti$^{3+}$ site will presumably have zero spin due to complete delocalization of the 3$d^1$ electron. We also argue that the interfacial Cr$^{3+}$ ions ($S = 3/2$) may also contribute to $s$-$d$ scattering. However, some of the Cr$^{3+}$ ions are converted into Cr$^{2+}$, as indicated by our EELS measurements and also suggested by the depletion of 2DEG carrier density on $\delta$ doping, the site spin of Cr$^{3+}$ would deviate from $S = 3/2$ and affect the antiferromagnetic arrangement. The emergence of a cusp in the positive MR for $H_L$ in $\delta$-doped samples at $T < 10$ K is in agreement with the prediction of 2D WAL theory, as shown by the large value of $L_{ef}$. The 2D WAL also couples with the Kondo MR response of the sample at $T < 10$ K and $H_L \leq 3$ T. An important finding of this work is the enhanced S-O interaction in the presence of the $\delta$ layer. In the Rashba scenario, how the $\delta$ layer enhances the local electric field at the interface remains to be seen.

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