Titanium $d_{xy}$ ferromagnetism at the LaAlO$_3$/SrTiO$_3$ interface

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**S1. Probing for magnetic impurities:** As discussed in the manuscript, we explored the possible presence of magnetic impurities in the samples. In general, ferromagnetic 3$d$-transition metals (i.e., Cr, Mn, Fe, Co, and Ni) are the most likely candidates. For this purpose, we employed XAS measurements (an element specific technique). The scanned energy range is from 560 eV to 890 eV; the presence of magnetic impurities in a sample can be detected via characteristic $2p \rightarrow 3d$ dipole transitions. The sample shown here is LAO(3.3 UC)/STO, also used in the XMCD measurement in the manuscript. Figure S1 shows the XAS spectra at Cr, Mn, Fe, Co, and Ni $L_{2,3}$-edges. Note that the signals (upper panel in the figure) via total electron yield (TEY) were normalized by $I_0$ signals (lower panel in the figure). No spectral features are observed at each $L_{2,3}$ edges, except in the case of Ni where it shows a dip near the energy positions corresponding to Ni absorption edges. If such behavior is due to the sample, the spectral feature should be rather a peak; we confirmed that the dip is due to variation of $I_0$. These measurements exclude that the presence of 3$d$ magnetic impurities in the probing volume of our sample within the detection limit ($\sim 10^{12}$ atoms/cm$^2$) of our experiment.

**S2. Estimating the magnitude of the interfacial Ti moment:** In a thin LAO/STO heterostructure, the Ti $L$-edge absorption signal comes from both the interfacial Ti ions and those Ti extending into the STO substrate. Here, we estimate the Ti magnetic moment assuming all the magnetic Ti ions are located in the first unit cell ($\sim 0.4$ nm) of interfacial STO. To do this, we first consider the total electron escape profile which is described as [S1]: $I(x) = I_0 \exp(-x/x_0)$. Here $x_0$ is the escape depth of secondary electrons in the material. For 3$d$ metals, $x_0$ is measured to be around 2.5 nm. In some previous reports [S2, S3], $\sim 5$ nm was used for perovskite
transition metal oxides. We used an escape depth $x_0 = 4$ nm, measured in another experimental study of the same LAO/STO system [S4].

Based on this parameter, the ratio between the TEY, $I(x)$, to the total excited electron intensity ($I_t$) is shown in Figure S2. If we choose 10% as a cutoff for the TEY signal, then the Ti TEY measurement would be sensitive to a ~7.8 nm interfacial region of the entire STO substrate, in addition to the 1.2 nm of the LAO that is above the STO layer (i.e., a total probing depth of ~10 nm; this can be crosschecked using the Ti $L$-edge spectra as a function of LAO-thickness). Thus, based on this first order estimation, the contribution to the measured Ti XMCD should be primarily coming from a 7.8 nm layer in the STO below the LAO.

To estimate the magnetic moment of this 7.8 nm layer, the detailed information about the profile of the magnetic moment is needed. Using the sum rule, the magnetic moment has been estimated to be about $0.01 \mu_B/Ti$. However, estimating the exact value of the moment entails a large error since the exact electron number of the Ti valence state is not known. Nevertheless, to give an approximate description, a profile with exponential decay is assumed:

$$m(x) = m_0 \exp[-(x - 1.2)/x']; \ 1.2 \text{ nm} \leq x \leq 10 \text{ nm}, \text{ with } x' \text{ chosen as } 0.4 \text{ nm, the single unit cell thickness of STO just at the interface. Then the TEY intensity from the Ti } L\text{-edge could be estimated as: } I_1 = I_t \left( \int_{1.2}^{10} \exp[-(x - 1.2)/4]dx \right).$$

The TEY intensity coming from the ferromagnetically polarized Ti could be estimated as:

$$I_2 = I_t \left( \int_{1.2}^{10} \exp[-(x - 1.2)/4] \exp[-(x - 1.2)/0.4]dx \right).$$
Then, \( I_1/I_2 = 3.5582/0.3648 = 9.7538 \). Therefore, the magnetic moment at the interface can be estimated to be \( 0.0975 \mu_B/Ti \) \((9.7538 \times 0.01 \mu_B/Ti)\). We note that this estimate will change with the value of \( x' \).

**S3. Thickness dependent XAS at the Ti L\(_2\)-edge:** In the manuscript, we examined in detail the XAS features around the Ti L\(_3\)-edge, using a 2-dimensional map (LAO-thickness vs. photon energy). Here, we show that the spectral features at the Ti L\(_2\)-edge are similar (Fig. S3). With different thicknesses of LAO, a change in photon energy of the \( e_g \) level is negligible. In contrast, the \( t_{2g} \) level shows an energy shift with increasing LAO thickness, for which the interfacial Ti is relatively enhanced. The \( t_{2g} \) level moves to a lower photon energy, by an amount estimated to be about 40 meV. From these findings, we confirm similar spectral features at both \( L_{2,3}\)-edges with the same corresponding implications as discussed in the main text.

**S4. Polarization dependence of XAS at the Ti L\(_{2,3}\)-edges:** To determine the distortion of the TiO\(_6\) octahedron in STO, we performed polarization-dependent Ti L\(_{2,3}\) XAS measurements as shown in Fig. S4. The polarization directions of the linearly polarized x-rays (98% polarized) are tuned by rotating the x-ray incident angle, with 90\(^{\circ}\) and 30\(^{\circ}\) incident corresponding to complete in-plane (\( E_{ab}: E//a \) or \( E//b \)) and out-of-plane (\( E_{c}: E//c \)) polarized components, respectively (see the inset of the figure). Generally, any anisotropic orbital distribution can be estimated by the asymmetric x-ray linear dichroism (XLD) intensity [S5]. At both Ti \( L_{2,3}\)-edges, we found strong polarization effects, showing features corresponding to both \( t_{2g} \) and \( e_g \) orbitals, which implies an electronic (orbital) anisotropy in the TiO\(_6\) octahedron.
The overall shape of these polarization-dependent XAS spectra is similar with Salluzzo et al.’s previous XLD measurements [S6]. However, the dichroic spectrum of Fig S4 is not completely identical to the previous work: here the integrated XLD is slightly positive, because at each peak the positive part of the derivative-like shape is much stronger than the negative one, whereas in the reference the integral is very close to zero. A nonzero XLD integral indicates the presence of Ti$^{3+}$ state, which is totally consistent with the detection of Ti local magnetic moments. Moreover, to quantify this distortion, we fit the XLD spectra, using the cluster model calculations. The estimated results are summarized in the manuscript in Fig. 3.

**LIST OF REFERENCES**


FIGURE CAPTIONS

Figure S1| XAS spectra of the LAO(3.3 UC)/STO heterostructure. Spectra (upper panel) are normalized by the $I_0$ signal (lower panel). Both $I_0$ and the sample signals were acquired by recording the total electron yield (TEY).

Figure S2| TEY intensity profile for the LAO(3.3 UC)/STO heterostructure.

Figure S3| 2-dimensional map of the XAS spectra around the Ti $L_2$-region (left panel). The white dashed lines indicates the energy position of the thinnest structure, LAO(1 UC)/STO. The enlarged $t_{2g}$ level is shown in the right panel. The black dashed line indicates the energy position of the $t_{2g}$ level.

Figure S4| Polarization dependent XAS spectrum and XLD at the Ti $L_{2,3}$-edges. The inset shows a schematic picture of the experimental configuration.
Figure S1: Lee et al.
Figure S2: Lee et al.

Figure S3: Lee et al.
Figure S4: Lee et al.