

Structural and Electronic Reconstructions at the LaAlO₃/SrTiO₃ Interface

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The physics of transition metal oxide heterostructures is a subject of great interest due to the observations of new interface electronic and magnetic states.^[1] The two-dimensional electron gas (2DEG) discovered at the interface between insulating LaAlO₃ (LAO) thin films and bulk SrTiO₃ (STO) crystals stands as a model and has boosted the great expectations placed in oxide electronics.^[2,3] Recently, it has been found that also the (001) SrTiO₃ surfaces, obtained by cleaving SrTiO₃ in ultra-high vacuum (UHV)^[4,5] or by annealing in reducing conditions,^[6] exhibit two-dimensional electronic states, independent of the bulk doping. From these studies it emerges that, despite possible different doping mechanisms, a similar band splitting characterizes the electronic properties of vacuum/STO and LAO/STO^[7] interfaces.

As matter of fact, while electron doping is believed to occur by creation of oxygen vacancies in STO surfaces,^[5,6,8] in the case of LAO/STO interfaces the primary origin of the charge carriers is attributed to an electrostatic instability of the system. In particular, a scenario of electronic reconstruction has been proposed,^[9,10] where a Zener breakdown takes place above a LAO thickness of 3 unit cells (uc), as experimentally observed.^[11,12] According to this picture, once the electron transfer occurs, carriers spontaneously occupy bands composed by Ti-3d orbitals, starting with d_{xy}-symmetry bands located within the first adjacent SrTiO₃ layers.^[13] Moreover, according to DFT calculation

on LAO/STO bilayers,^[14] the distribution of electrons accumulated within the first STO layers gives rise to an electric field, which in turn induces a rumpling of the SrO and TiO₂ interface atomic planes within the same region hosting the 2DEG.

Thus, a polar instability scenario predicts for LAO/STO heterostructures structural and electronic modifications of the first SrTiO₃ unit cells occurring simultaneously with the appearance of a 2D-metal. However, not all the experimental results are fully consistent with this picture. For example, second harmonic generation experiments suggested that polar distortions in STO appear below the LAO threshold thickness of 4-uc, i.e., before the realization of 2D electron system.^[15] More recently, a rumpling of the STO interface layers was observed also in p-type LAO/STO insulating interfaces, as shown by grazing incidence X-ray diffraction (GIXD).^[16]

To clarify these issues, we have used a combination of advanced X-ray synchrotron-based spectroscopic and structural measurements to study the evolution of the electronic properties and ionic positions at LAO/STO interfaces as a function of the LAO thickness (**Figure 1**). We find that an orbital reconstruction occurs also in insulating 2-uc LAO/STO, before the appearance of the metallic state. Partial or complete inversion of the 3d-t_{2g} energy levels in insulating samples is correlated to partial or complete coverage of the STO surface by an ordered polar layer. We also find that a rumpling of the TiO₂ and SrO atomic planes accompanies a band splitting already in 2-uc LAO/STO, indicating that structural distortions appear in STO before the insulating to metal transition. These results suggest that the orbital reconstruction is due to the combination of interface symmetry breaking and of the transfer of localized electrons to interface states before the realization of a mobile 2DEG.

Following the method used in ref. [7], we have performed X-ray absorption spectroscopy (XAS) measurements at the Ti L_{2,3} edges of several STO based heterostructures prepared in Augsburg (set-A)^[10] and in Geneva (set-B).^[17] By using XAS, we probed the density of states of the unoccupied Ti 3d orbitals with a given symmetry selected by the direction of the linear polarization of the photons, i.e., parallel (I_{ab} XAS spectra) and perpendicular (I_c XAS spectra) to the interface. The X-ray linear dichroism (XLD), i.e., the difference between absorption spectra acquired with the two polarizations [XLD = (I_c - I_{ab})/I_{ave} (L₃ peak)], is then very sensitive to the energy splitting of unoccupied 3d states,^[7] which can be precisely determined by fitting the data by multiplet atomic model calculations with point charge crystal field.^[18] In **Figure 1b** we show XLD data acquired at room temperature on a number of STO based heterostructures. The linear dichroism of a non-cleaved, just etched and oxygen annealed, TiO₂ terminated STO surface

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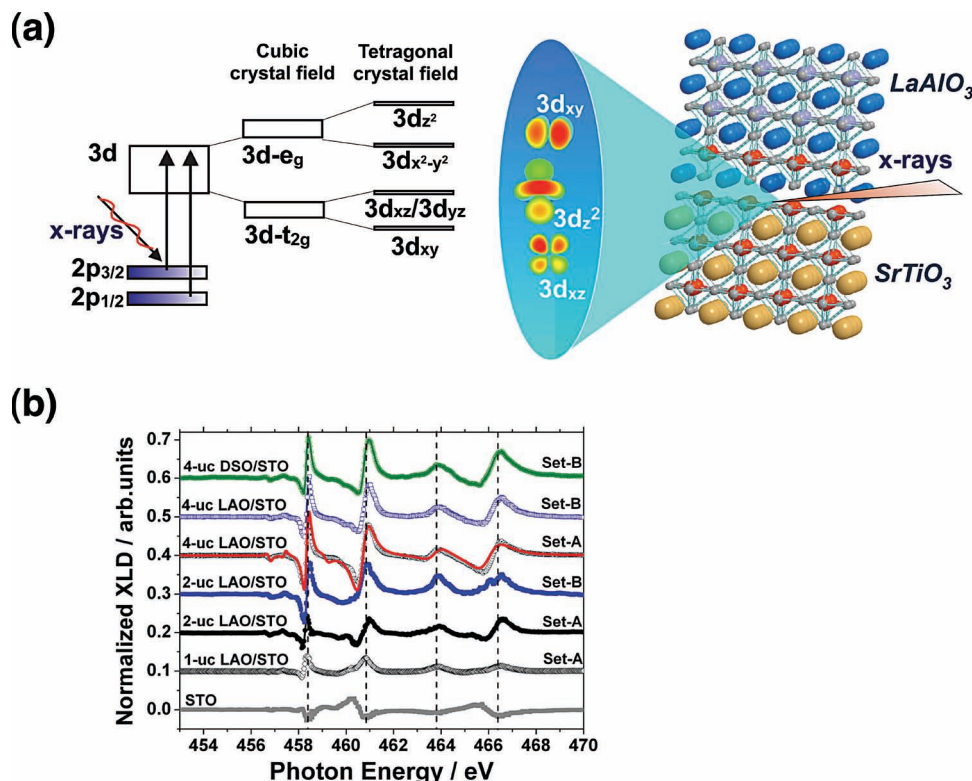


Figure 1. a) Conceptual schematic of the X-ray experiments performed on LAO/STO interface; b) X-ray linear dichroism spectra at the Ti $L_{2,3}$ edge, normalized to the maximum of the L_3 XAS intensity, of different SrTiO_3 interfaces [XLD = $(I_{\text{c}} - I_{\text{ab}}) / I_{\text{ave}}(L_3 \text{ peak})$]: TiO_2 terminated, etched and annealed SrTiO_3 (gray circles), 1uc, 2uc and 4uc Augsburg (set-A) LAO/STO samples (black diamond, closed and open circles respectively) and 2uc, 4uc Geneva (set-B) LAO/STO samples (closed and open blue squares). Data from a 4uc $\text{DyScO}_3/\text{SrTiO}_3$ (DSO/STO) bilayer are also shown for comparison (dark green circles). The red line shows the results of the calculation, which reproduces the data on 4uc Augsburg sample (see text). Dashed lines are guides for eyes.

is small but different from zero.^[7] We note that this bare STO surface is insulating, i.e., it does not show any 2DEG. From a fitting of the XLD spectra performed in D4h symmetry (tetragonal), we find that the $3d_{xz}/3d_{yz}$ t_{2g} orbitals are 25 meV below the $3d_{xy}$ ones and the $3d_{z^2}$ e_g level is 40 meV below the $3d_{x^2-y^2}$. This splitting is opposite to the LAO/STO case (see below) and to the one found in the case of cleaved STO surfaces in ref. [4], which exhibit a 2DEG. Indeed, by depositing only one nominal LAO unit cell the linear dichroism changes sign, showing that already at this thickness the degeneracy of the 3d states is partially modified. The XLD signal increases with the LAO thickness until the insulator-metal transition, i.e., at 4-uc, and then remains approximately constant. The shape of the XLD spectra is quite sensitive to the titanium valence and to the actual splitting of the levels. In conducting LAO/STO it is reproduced quantitatively (Figure 1b) by assuming a full inversion of the degeneracy of the Ti^{4+} ions in the first 6 STO unit cells.^[19] We find, in particular, that the $3d_{xy}$ unoccupied states are now 50 meV below the $3d_{xz}/3d_{yz}$ states. The contribution to the XLD signal from Ti^{3+} ions in a $3d^1$ configuration is below the detection limit, showing that also after the appearance of the 2DEG the dichroism is fully accounted by the majority of titanium ions characterized by nominal $3d^0$ configuration.^[20]

Interestingly, the spectral features do not change substantially as function of the LAO thickness, but the amplitude of dichroic signal does, showing that 4-uc and 2-uc LAO/STO interfaces have different fractions of titanium sites characterized by an inversion of the 3d energy levels.

While the XLD spectra of metallic LAO/STO bilayers belonging to the two sets of samples are very similar, striking differences are observed when the LAO thickness is below 4-uc, i.e., in insulating samples. Indeed, in 2-uc set-B films we find that the XLD amplitude is only slightly smaller than observed in 4-uc LAO/STO, suggesting that here the splitting of the Ti-3d states involves a comparable number of titanium sites. Consequently the data show that the orbital reconstruction takes place before the appearance of a mobile electron system.

To better understand these results, we studied other insulating titanate interfaces. The linear dichroism of an insulating interface composed by a 4-uc DyScO_3 film (which is also polar) and TiO_2 terminated SrTiO_3 , is similar to that one of LAO/STO conducting samples (Figure 1b), confirming that the orbital reconstruction is not correlated only to the appearance of a 2D metal, i.e., to the transfer of mobile charges at the interface, although we cannot exclude a partial doping induced by the synchrotron light itself. However, photo-doping effects are unable to induce a similar reconstruction in bare insulating

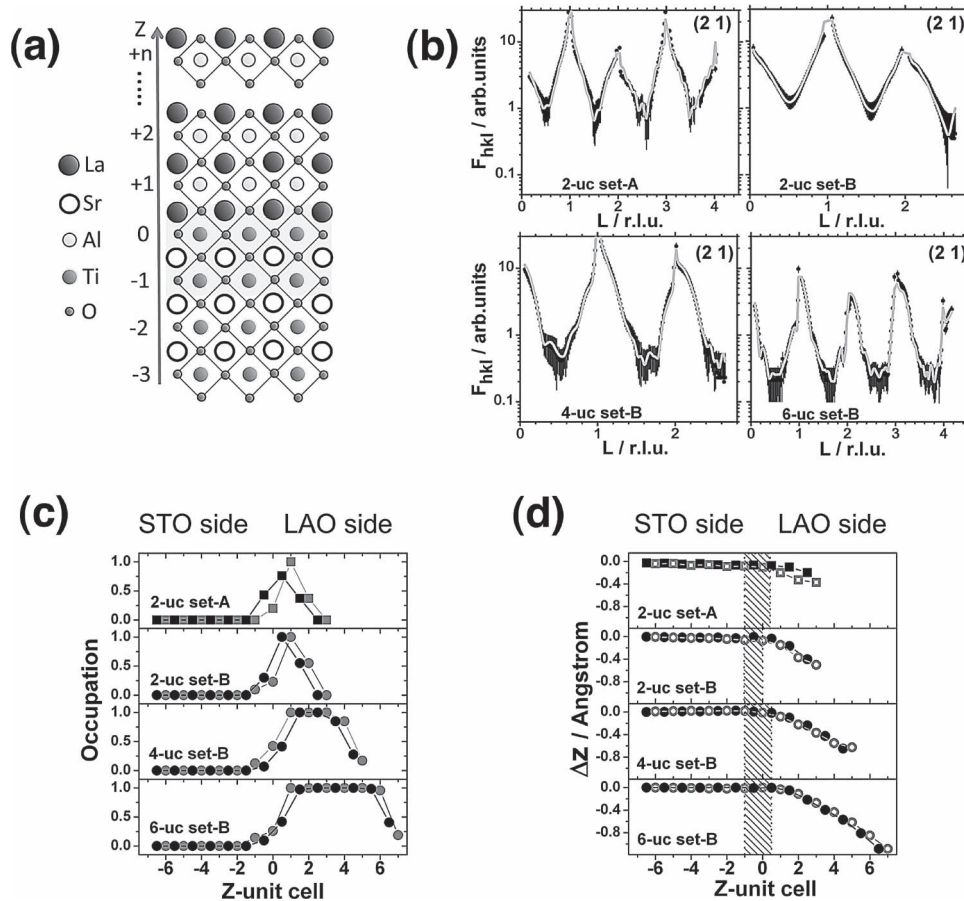


Figure 2. (a) Model structure used for GXID. In the shaded area cation intermixing is allowed in the model; (b) (2 1) CTR's (black closed circles and error bars) and correspondent fit (light gray line) for the three LAO thicknesses considered as indicated in the figures; c) Al (gray symbols) and La (black symbols) occupancies of 2uc set-A (open squares) and 2uc, 4uc and 6uc set-B samples (closed circles); (d) Displacements from ideal STO positions of A-site (gray open symbols) and B-site (black closed symbols) of LAO/STO samples as indicated in the text. Large displacements on the LAO side ($Z > 0$) increasing with Z are related to an LAO c -axis shorter than STO. The shaded areas in the figure are the regions where intermixing is found from the refinement.

STO surfaces, and in LAO/STO the dichroic signal is clearly dependent on the nominal LAO thickness.

An orbital reconstruction taking place before the effective realization of a metallic state needs a thoughtful comparison between the properties of insulating and conducting LAO/STO samples. To this end we used grazing incidence X-ray diffraction at room temperature, to get a complete structural refinement of 2-uc, 4-uc and 6-uc LAO/STO bilayers, and compared the results obtained from the two sample sets. The structural refinement was performed by fitting simultaneously, for each sample, several non-equivalent crystal truncation rods (CTR's),^[21,22] i.e., the profile along l of the structure factor F_{hkl} (Figure 2).

The first outcome of the refinement is that the topmost layers of all the LAO/STO heterostructures investigated are incomplete. This agrees with atomic force microscopy (AFM) measurements.^[23] However, the termination of the films is AlO_2 , in line with the expected growth sequence imposed by the TiO_2 termination of the STO substrate.

A second result concerns the actual composition of each layer. Figure 2c shows the atomic occupancies as a function of

the Z out-of-plane coordinate for samples with LAO thicknesses of 2, 4 and 6 unit cells. We find that a film with a LAO nominal thickness of 2-uc (set-B), estimated by counting the RHEED oscillations, is composed of an incomplete upper LAO unit cell, a complete inner unit cell at the interface (second level), and finally a fraction of AlO_2 (30%) and LaO (20%) atomic planes replacing TiO_2 and SrO , respectively, in the first STO unit cell. Moreover, we find that the overall composition of the films is La deficient with a ratio of $\text{La}/\text{Al} = 0.9(0)$. As a function of the LAO thickness, we can notice that conducting 4-6 uc LAO/STO samples are characterized by a more pronounced mixing of LaO/SrO and $\text{AlO}_2/\text{TiO}_2$ planes (Figure 2c). However, the ratio between La and Al does not change substantially as function of the thickness. Both sets of conducting samples are characterized by similar properties and in particular by a similar lanthanum deficiency, and similar cation stoichiometry in the first layers at the interface.^[14]

On the other hand, the structural refinement shows differences between insulating 2-uc LAO/STO films belonging to the two sample sets, which can be traced back to the differences in the amplitudes of the linear dichroism shown in Figure 1.

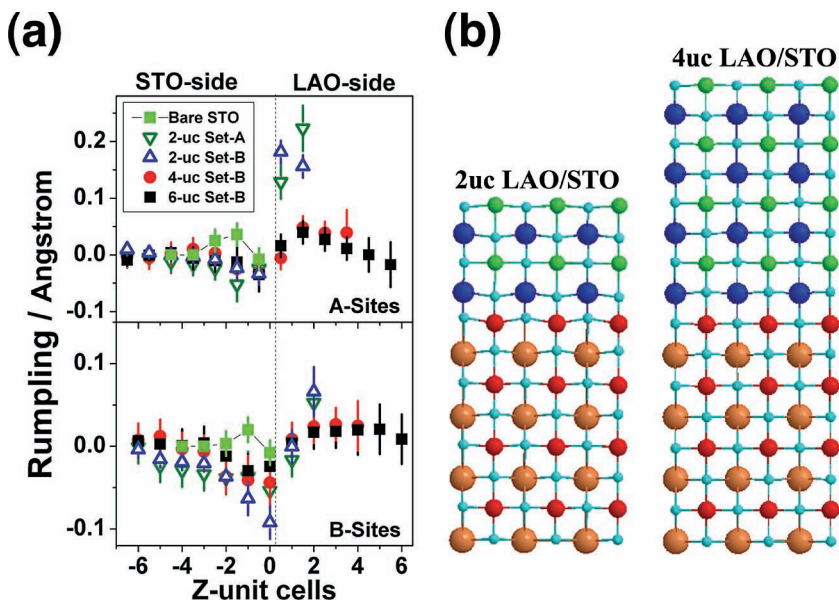


Figure 3. (a) Results of the structural refinement on LAO/STO samples, showing the rumpling of the AO (A-sites, upper panel) and BO_2 (B-sites, bottom panel) planes; closed green squares are for a bare STO surface, open symbols are for the 2-uc set-A (green, down triangles) and 2-uc set-B (blue, up triangles) samples, while closed symbols are for 4-uc (red circles) and 6-uc (black squares) set-B samples. (b) LAO/STO structures of 2-uc and 4-uc samples (set-B) as result of the structural refinement. Blue and green spheres are La and Al ions, while red and orange spheres are Ti and Sr ions. Oxygen ions are the small cyan spheres.

In particular, the coverage of the STO surface in 2-uc sample from set-A is only partial (Figure 2c), i.e., in spite of the same nominal thickness, the effective number of LAO unit cells in the two sample sets is different. These variations are interestingly correlated to the electronic properties, i.e., in particular larger amplitudes of the XLD signal are associated to higher effective LAO thickness. Only in 2-uc LAO/STO from set-B a complete LAO unit cell faces an almost completely TiO_2 terminated surface, while in 2-uc LAO/STO from set-A even the first LaAlO_3 unit cell is incomplete. By increasing the nominal thickness, a complete LaAlO_3 layer is formed also in LAO/STO films belonging to the sample set-A, and the amplitude of the XLD signal increases and saturates. Thus we find that a full removal of the degeneracy, which is correlated to the amplitude of the XLD, is achieved when at least a complete LAO unit cell is deposited on top of the STO crystal.

The last important outcome of the GXID experiment concerns the displacements of the ions along the interface normal (Figure 2d), and in particular the rumpling of AO and BO_2 planes ($A = \text{La, Sr}$ and $B = \text{Al, Ti}$) (Figure 3a). On the LAO side, we found that the evolution of the atomic displacements and of the c-axis, as a function of the layer thickness, is in good agreement with the experimental data presented in ref. [12,14]. In particular our experiment confirms that insulating interfaces, below 4-uc, are characterized by a large rumpling of the LaO and AlO_2 layers [Figure 3] and by an expansion of the LAO unit cell (up to 3.82 \AA in agreement with ref. [12]). The rumpling is strongly reduced in compensated, i.e., conducting, LAO/STO interfaces.

However, interesting surprises arise when examining the interface STO layers as function of the LAO thickness. First,

we found that at any thickness the cation displacements in STO are relatively small. This result agrees with previous measurements on set-A,^[14] but disagrees with report on conducting samples deposited by PLD without post-annealing in oxygen.^[24] On the other hand, while DFT calculations suggested negligible displacements of the oxygen ions within the STO layers of insulating interfaces, here we find a different behavior. As shown in Figure 3, 2-uc LAO/STO films show a measurable rumpling of the STO planes, larger in the case of samples from Set-B, that gradually reduces to zero into the bulk. This rumpling is due mainly to the displacement of the oxygen ions towards the interface, while the cations remain close to the ideal positions or slightly move towards the bulk. In thicker films, i.e., for 4-uc and 6-uc LAO/STO, contrary to the expectation of DFT calculations,^[14] the rumpling of the STO planes does not increase. From the data it can be argued that a residual rumpling of the planes remains also at the interface of conducting LAO/STO, but it is reduced compared to 2-uc samples (see Figure 3). Note that in the case of the bare TiO_2 terminated STO surface (Figure 3, green square symbols), the rumpling is exactly opposite to the

one observed in LAO/STO samples. Thus a rumpling of the STO layers develops as soon as few LAO layers are deposited on STO, and it already appears in insulating 2-uc LAO/STO before the formation of the 2DEG, and not after. This result has been subsequently confirmed on another nominal 2-uc LAO/STO from sample set-B. Consequently, the structural refinement shows that insulating 2-uc LAO/STO samples are characterized by polar distortions within the STO layers and within the LAO, while these distortions, in particular those concerning the LAO film, reduces in conducting samples.

Discussion In the “polarization catastrophe” picture, the 2DEG is related to the polar discontinuity between the LAO film and the STO substrate. Without any external charge, i.e., below 4-uc, the built-in electric field can be partially compensated only by the finite ionic polarizability of LAO through out-of-plane outward (toward the surface) displacements of La and Al cations and inward (toward the interface) displacements of oxygen ions in LAO. The distortions reduce considerably when the interface becomes conducting. These structural effects are qualitatively reproduced also in DFT calculations,^[14,25] even if from the experimental results it emerges that the rumpling reduction is more abrupt than the one predicted by DFT.^[14] In particular, the evolution of the structural distortions in LaAlO_3 seems directly correlated to the abrupt changes in the electrostatic boundary conditions occurring after the creation of a metal at the interface.^[26,27]

However, the most interesting, yet unexpected, outcome of the structural data is that the atomic layers within the STO unit cells close to the interface are corrugated even at a LAO thickness below the threshold necessary for the appearance of the

2DEG. These experimental results disagree with the expectation of DFT calculations,^[14] suggesting that the origin of the distortions has to be found elsewhere.

First we explore any explanation involving a possible role of oxygen vacancies. DFT calculations in the presence of oxygen vacancies were used recently to explain the large cation displacements observed in metallic SrRuO₃/La_{1-x}Sr_xMnO₃ superlattices.^[28] To verify this possibility, we have analyzed the effect of oxygen vacancies in the structural refinements of the GXID data [Figure S1 in the supporting information]. For all the samples investigated, independent on the sample set and on the LAO thickness, the fit converged to solutions compatible with an oxygen-vacancy percentage around 2% in the first two STO layers (and in the LAO film). The displacements of the ions were only slightly modified by the introduction in the model of oxygen vacancies. In particular, the rumpling of the STO planes in our LAO/STO bilayers was mostly unchanged within the error bar [Figure S1] and, as before, the oxygen ions displace towards the interface, while the cations remain quite close to the ideal bulk positions. Thus, our distortions, not related to a cation movement, are qualitatively different from the ones expected in the case of oxygen vacancies reported.^[28]

Thus, we propose that the distortions observed in LAO/STO samples annealed in oxygen (shown here) are due to an intrinsic surface instability of STO (100) surfaces, which give rise to a polar response of the STO interface layers and eventually to a transfer of localized charges also below the critical thickness. Indeed, STO surfaces have tendencies towards complex reconstructions and polar distortions^[29] also in heterostructures, as recently observed in Si/STO interfaces.^[30] This fact is naturally correlated to the signatures of orbital reconstruction, i.e., full removal of the degeneracy of the 3d Ti states, taking place at a LAO thickness smaller than 4-uc.

These experimental results are in line with the ab-initio calculation study presented in ref. [13]. Indeed, it has been shown that the main driving force for the orbital reconstruction is the breaking of the inversion symmetry at the interface, combined with the strong localized nature of the d-orbitals.^[13] In presence of an infinite barrier at the (001) surface of a truncated STO crystal, the titanium 3d bands split and the electrons in the system tend to confine spontaneously in 2D. Consequently, a necessary condition for the orbital reconstruction at the LAO/STO is a full breaking of the symmetry at the interface, which on the other hand takes place hence a full LAO layer is deposited on SrTiO₃. However, the transfer of mobile electrons at the interface is a second step process, i.e., it is not by itself the cause of the orbital reconstruction. The characteristic band splitting discovered at the cleaved STO surfaces^[4,5] is, in our opinion, due to the same phenomenon, which can explain some of the similarities between the 2DEG formed at the LAO/STO interface and at the STO surface.

These kinds of phenomena may occur in many other perovskite oxides, which is promising in view of the discovery of novel functional interfaces. However, our work shows that the extraordinary physics originating in LAO/STO is strongly related to the electronic as well as structural surfaces instabilities of each layer composing the heterostructures, which demonstrates that further progresses in surface/interface science of transition metal oxides, well-established in the case of

semiconductors, are necessary to exploit the full potential of this class of materials.

Experimental Section

The LAO/STO thin films studied here were prepared by pulsed laser deposition at the University of Augsburg (set-A) and at the University of Geneva (set-B). All samples were annealed in oxygen after the deposition. The nominal number of LAO unit cells was determined by monitoring the RHEED (reflection high energy electron diffraction) oscillations during the growth and by stopping the deposition at the maximum of the specular diffracted intensity.

X-ray absorption spectroscopy and X-ray linear dichroism (XLD) measurements were performed at the ID08 beam-line of European Synchrotron Radiation Facility (ESRF) at room temperature (and at 10 K with similar results), in total electron yield detection mode. Grazing incidence X-ray diffraction (GXID) experiments at room temperature were performed in UHV at the ID03 and BM25 ESRF beam-lines. The XLD amplitude have been normalized to the maximum of the L₃ edge to get a meaningful comparison between spectra acquired in different conditions and characterized by different thicknesses. Multiplet atomic model calculations with point charge crystal field were performed in D4h symmetry (tetragonal symmetry) and included spin-orbit coupling in the ground state as-well-as in the final 3d states. The structural refinement was performed by simultaneously fitting 15 non-equivalent crystal truncations rods (CTRs). The same unreconstructed 1 × 1 structural model (P4mm symmetry), which includes a bulk STO unit and a surface composed by 6 STO uc and a number of n LAO uc (with n = 2, 4 and 6), was used for each sample. The refinement was performed using a modified version of the R_{OD} software program.^[21] The reduced $\chi^2 = \frac{1}{N-P} \sum_i \left(\frac{(F_i^{Th})^2 - (F_i^{Exp})^2}{\sigma_i} \right)^2$ of the refined models were 0.55, 0.64 and 1.0 for the 2uc, 4-uc and 6-uc samples.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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