

# Nanoscale modulation of the density of states at the conducting interface between $\text{LaAlO}_3$ and $\text{SrTiO}_3$ band insulators

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**Abstract** – The appearance of high-mobility electrons at the  $\text{LaAlO}_3/\text{SrTiO}_3$  interface has raised strong interest in the material science community and a lively debate on the origin of the phenomenon. A possible explanation is an electronic reconstruction, realizing a transfer of electrons to  $\text{SrTiO}_3$  at the interface, thereby avoiding the build-up of excessive Coulomb energy as described by the “polarization catastrophe” associated with the alternating polar layers of the  $\text{LaAlO}_3$  film. Theoretical models predict that electrons are transferred into titanium  $3d_{xy}$  interface states and, in the presence of strong correlations, generate a charge and orbital order. Here we provide experimental evidence that at room temperature the local density of states of the  $\text{LaAlO}_3/\text{SrTiO}_3$  conducting interface is modulated at the nanoscale in a short-range quasi-periodic pattern, which is consistent with the appearance of an orbital (short-range) order. This result, together with the splitting of the 3d states, confirms that an electronic reconstruction drives the functional properties of the  $\text{LaAlO}_3/\text{SrTiO}_3$  oxide interface. The short-range superstructure does not fully agree with the theoretical predictions. Thus, further experimental and theoretical investigations are required to understand the electronic properties of the 2D electron system realised at the  $\text{LaAlO}_3/\text{SrTiO}_3$  interface.

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**Introduction.** – Atomically controlled interfaces exhibit exotic phenomena, such as two-dimensional conductivity that can be induced by combining insulating materials [1–4]. These discoveries generated new paradigms and challenges in condensed-matter physics and require non-conventional approaches for their understanding. One of these is based on the possible stabilization of complex surfaces and interfaces by an electronic reconstruction mechanism, which differs substantially from the well-known classical atomic reconstruction. The electronic reconstruction idea was originally introduced in the case of  $\text{K}_3\text{C}_{60}$  surfaces [5], but recently it has been considered to play a key role in the physics of oxides interfaces [2,3]. The most studied example is the

interface between  $\text{LaAlO}_3$  (LAO) and  $\text{SrTiO}_3$  (STO) band insulators realized by the deposition of epitaxial LAO(001) films on  $\text{TiO}_2$ -terminated STO(001) single crystals. It is widely accepted that the characteristics of this system are strongly influenced by the polar nature of the LAO atomic layers, which introduces an instability associated to the divergence of the electrostatic potential. In their seminal work [2], Ohtomo and Hwang suggested that the appearance of conductivity at the LAO/STO is effectively an electronic stabilization to avoid a “polarization catastrophe” by a transfer of electrons to the STO conduction band at the interface. However, in spite of the recent theoretical and experimental efforts to understand the origin of this phenomenon, no consensus on the role of defects in the mechanism has been achieved yet. In particular cation intermixing and oxygen vacancies, which

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are known to dope pure bulk STO, have been suggested to generate the mobile electron system [6,7].

From a theoretical point of view, a pure electronic reconstruction of the LAO/STO interface is sufficient to stabilize the system [8]. In particular, in order to eliminate the divergence of the electrostatic potential, a fraction of titanium ions have to change their valence from  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ . Unfortunately, the appearance of  $\text{Ti}^{3+}$  is not a sufficient proof of the electronic reconstruction mechanism, since defects in STO, acting as dopants, are also known to induce partially occupied 3d titanium states. However, theoretical calculations foresee other distinctive electronic properties of LAO/STO compared to simple doped STO. As in the case of other transition metal oxide interfaces [9–11], the appearance of confined 3d electrons makes the system susceptible to correlation effects, possible accompanied by a charge and orbital ordering [8,12,13]. In particular, local density approximation (LDA) plus on-site potential ( $U$ ) calculations on the LAO/STO system predicted that strong correlations could stabilize an order superstructures consisting of a ferro-distorted  $2 \times 2$  checkerboard pattern of filled  $3d_{xy}$  states [8,12]. While the importance of electronic correlations was demonstrated in a recent low-temperature scanning tunnelling spectroscopy study [14], up to now the appearance of an orbital and charge order has not been validated by experiments. In order to accomplish this difficult task, complex measurements able to explore the electronic properties of a buried interface with orbital selectivity and nanometer resolution are required. Here we present combined X-ray absorption spectroscopy (XAS) and scanning tunnelling microscopy/spectroscopy (STM/STS) experiments on conducting LAO/STO bilayers which reveal that the density of states of the interface is modulated with a short-range quasi-periodic pattern, which is consistent with an orbital (short-range) order. This result gives strong constraints to the mechanisms responsible for the realization of a metallic interface between LAO and STO band insulators. However, there is not a complete agreement between the experimental data and theory, which thus requires further experimental and theoretical investigation.

**XAS results.** – The experiments were carried out on interfaces realized by depositing  $\text{LaAlO}_3(001)$  films on  $\text{TiO}_2$ -terminated  $\text{SrTiO}_3(001)$  single crystals by pulsed-laser deposition [15]. The samples were grown in a background oxygen pressure of  $8 \times 10^{-5}$  mbar at  $780^\circ\text{C}$  followed by an *in situ* oxygen annealing step to fill oxygen vacancies.

X-ray absorption spectroscopy measurements were performed at the ID08 beam-line of the European Synchrotron Radiation Facility (ESRF). XAS spectra provide information on the unoccupied electronic states of a given material with chemical and orbital selectivity, as probed by the X-ray excited electrons. Recently, we found by XAS that the degeneracy of the 3d Ti levels is removed

when the LAO film is at least four unit cells thick and the interface is therefore conducting [16]. In particular, the  $3d_{xy}$  and  $3d_{x^2-y^2}$  states are pushed by 60 meV and 100 meV, respectively, below the out-of-plane  $3d_{xz}$ ,  $3d_{yz}$  and  $3d_{z^2}$  states. Interestingly, this orbital reconstruction is due to the splitting of the 3d levels of the majority of Ti ions that retain their nominal 4+ valence. Based on XAS measurements, an upper limit for the percentage of  $\text{Ti}^{3+}$  was estimated to be 10%, which is consistent with hard X-ray photoemission experiments on well-oxidized LAO/STO samples [17] and on transport data.

Here we show that the removal of the 3d degeneracy and the consequent anisotropy in the electronic states is also reflected in the relative contributions of the in-plane and out-of-plane orbitals to the conduction band of the interface. This behaviour was determined from oxygen  $K$ -edge XAS spectra measured with the interface sensitive total electron yield (TEY) method as function of the linear polarization of the photons (fig. 1). In this X-ray absorption process, 1s core electrons belonging to the oxygen ions are excited to the 2p states. Since the oxygen 2p states are nominally filled in both LAO and STO, a  $1s \rightarrow 2p$  transition occurs only due to the hybridization of the 2p states with the d-orbitals of the cations in the system. Because of this hybridization, the peak A of fig. 1a at 531 eV is related to the conduction band, located in STO just above the Fermi level, and is composed of Ti  $3d_{t_{2g}}$  ( $3d_{xy}$ ,  $3d_{xz}$ ,  $3d_{yz}$ ) orbitals hybridized with oxygen 2p states [18]. By using the TEY method of detection and grazing incidence conditions, a major contribution to XAS spectra in the 529–533 eV region comes from the  $\text{TiO}_2$  interface layer. While no polarization dependence is observed for an STO single crystal, the absorption line of conducting LAO/STO samples shifts by about 50 meV toward the Fermi level when the photon polarization is parallel to the  $xy$ -plane (fig. 1b)<sup>1</sup>. In the  $xy$ -polarized spectra the peak A represents the contribution to the conduction band of in-plane titanium  $3d_{xy}$  hybridized with oxygen  $2p_{x,y}$  states. Its shift towards the Fermi energy shows that at room temperature the conduction band of the LAO/STO interface is split and that the  $3d_{xy}$  Ti + O  $2p_{x,y}$  band is the lowest in energy. The splitting of the conduction band occurs for conducting samples, characterized by a number of LAO layers of at least 4 unit cells (uc), confirming that the orbital reconstruction and the appearance of 2D-electrons with a partial 3d character are simultaneous phenomena [16,19].

**STM/STS results.** – Fingerprints of the nature of the orbital reconstruction are obtained by measuring the local density of states (LDOS) of conducting LAO/STO

<sup>1</sup>The experimental shift is estimated as the separation between the absorption lines close to the peak A (estimated at the pre-peak energy positions corresponding to 90% of the maximum). The experimental error on this value, determined by repeated measurements, is of the order of the statistical error obtained from a Lorentzian fit, *i.e.* about 10 meV. Therefore the measured shift is above the statistical error.

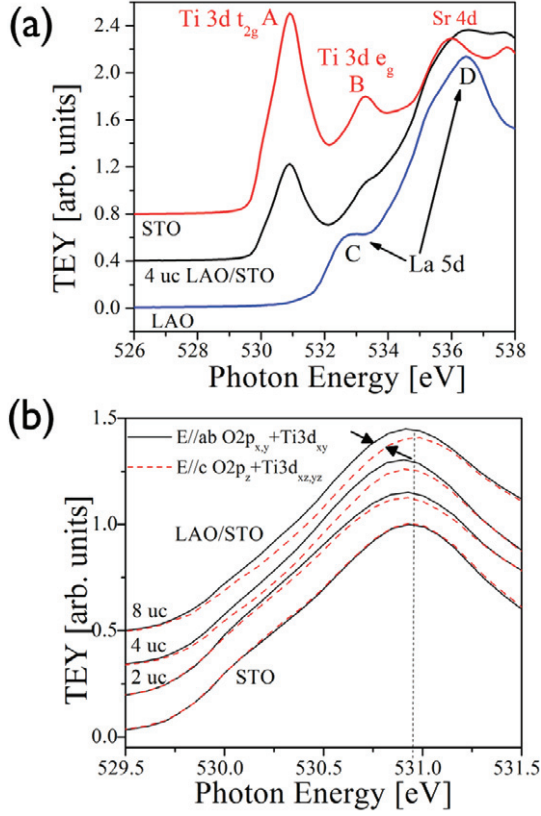


Fig. 1: (Color online) (a) Comparison between oxygen XAS spectra of  $\text{SrTiO}_3$  (upper curve, red line),  $\text{LaAlO}_3$  (bottom curve, blue line) single crystals and of a 4 uc LAO/STO conducting interface (middle curve, black line) measured at 300 K. Peaks A and B correspond to  $\text{O}2\text{p}$  states hybridized with the  $t_{2g}$  and  $e_g$   $\text{Ti}3\text{d}$  states, respectively, while peaks C and D in the LAO spectra correspond to  $\text{La}5\text{d}$  states hybridized with  $\text{O}2\text{p}$ ; (b)  $K$ -edge oxygen spectra around the peak A, relative to the two polarizations (continuous black lines  $E//ab$ , dashed red lines  $E//c$ ) for  $\text{TiO}_2$ -terminated STO (lower curves) and LAO/STO conducting interfaces with LAO thickness from 2 to 8 uc (upper curves). The data, normalized to the intensity of the peak A taken with  $E//ab$  polarization, are displaced by a constant offset for clarity. The arrows in (b) indicate the energy shift of the absorption lines using two different polarizations of the photons in the case of conducting 8 uc LAO/STO (see footnote <sup>1</sup>).

interfaces by STM/STS. STM data were collected on LAO/STO films characterized by a thickness of 4 uc. This is the minimum thickness required for the realization of a metallic interface allowing at the same time STM-tunnelling of electrons into the interface states. Below the threshold of 4 uc the system is indeed insulating and tunnelling is not possible [15]. STM and atomic force microscopy (AFM) measurements have been performed in dark conditions at room temperature and in ultra-high vacuum ( $p < 10^{-10}$  torr) using a commercial VT-AFM Omicron system able to operate in both STM and AFM modes. In the STM mode, the bias voltage is applied to an Ir tip, while the sample is grounded through a

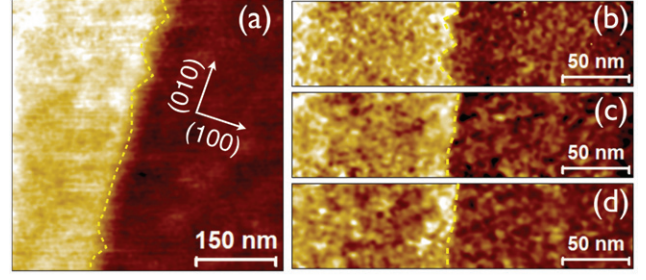


Fig. 2: (Color online) (a) Contact AFM topography of the LAO surface ( $256 \times 256 \text{ nm}^2$ ,  $z$ -scale from 0 to 0.6 nm), showing smooth terraces (rms roughness 0.1 nm); locally the step edge is faceted along the (110) and (1-10) directions of the STO substrate; (b)–(d) constant current mode (tunnelling current of 0.75 pA) STM topographies acquired simultaneously in the same region at different bias voltages: (b)  $V_{bias} = +3.5 \text{ V}$  ( $z$ -range = 0 to 0.7 nm, rms roughness on a single terrace = 0.1 nm), (c) +2.0 V ( $z$ -range = 0 to 1.1 nm, rms roughness on a single terrace = 0.2 nm) and (d) +1.1 V ( $z$ -range = 0 to 1.3 nm, rms roughness on a single terrace = 0.3 nm).

metal electrode directly deposited onto the interface. For all measurements presented,  $V_{bias}$  is, however, referred as the sample to tip bias voltage. To investigate the role of adsorbates at the surface we have performed several experiments. In particular we studied as-grown samples after different periods of exposure to UHV conditions (one hour, one week, months), and measured the same samples before and after successive cleaning in ethanol (99.9%), and/or isopropanol (99.9%), which yielded identical results. The experimental results proved to be extremely reproducible and independent of possible surface contaminations.

Separating the surface and interface contribution in a tunnelling experiment from a buried interface is intrinsically difficult. This problem has been overcome by selecting the bias voltage respect the conduction band minimum (CBM) of  $\text{LaAlO}_3$  and by working with tunnelling currents in picoampere and sub-picoampere regimes. The latter condition is necessary to maintain true tunnelling conditions with the tip not in contact with the LAO surface, which is essential to obtain reproducible topographic and spectroscopic measurements at room temperature. Selective tunnelling using this method was successfully employed, for example, for  $\text{MgO}/\text{Ag}$  heterostructures, to image the insulating  $\text{MgO}$  surface or the interface [20].

From the oxygen-edge XAS data shown in fig. 1a we know that the conduction band minimum (CBM) of LAO is at an energy  $E^{CBM}(\text{LAO}) \sim +2.2\text{--}2.5 \text{ eV}$  above the CBM of the STO. Therefore, by working with  $eV_{bias}$  above or below  $E^{CBM}(\text{LAO})$ , STM/STS is sensitive to the surface or to the interface of the LAO/STO bilayers, respectively. This is demonstrated in figs. 2a–d. The surface morphology of 4 uc LAO(001) film measured by contact AFM, shows well-ordered surfaces, characterized by terraces and regular step edges (fig. 2a). *In situ*

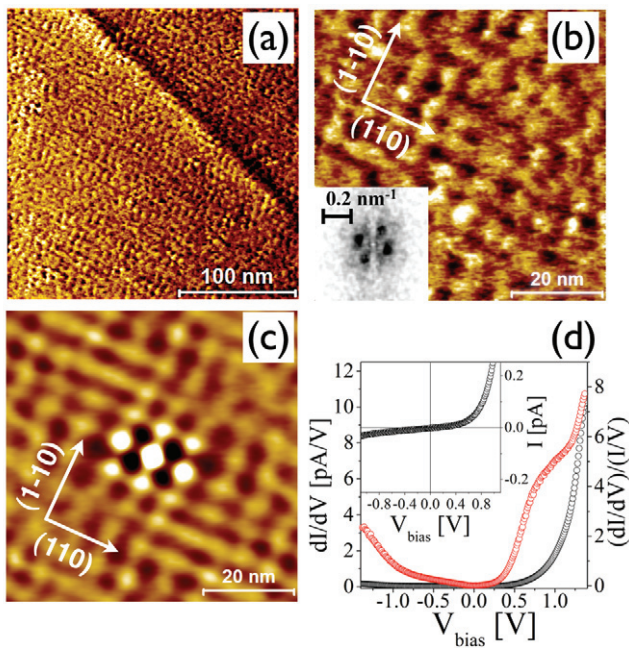


Fig. 3: (Color online) (a) STM image taken at  $V_{bias} = +0.9$  V and tunnelling current  $I_t = 0.25$  pA on an  $250 \times 250$  nm<sup>2</sup> area ( $1000 \times 1000$  pixel<sup>2</sup>) of the LAO/STO interface showing the presence of an ordered superstructure on top of well-ordered terraces; (b) middle of the upper terrace at enhanced magnification, its 2D FFT (in the left bottom part of (b)) and (c) autocorrelation image enhancing the superstructure in the real space; (d)  $I$ - $V$  (in the inset),  $dI/dV$  (black closed squares, left axis) and  $LDOS \propto (dI/dV)/(I/V)$  (red open circles, right axis) spectroscopy data of the interface obtained by averaging 4096 spectra acquired on an area of  $64 \times 64$  nm<sup>2</sup>.

reflection high-energy electron diffraction (RHEED) established that LAO grows mainly in a layer-by-layer mode. However, some lateral growth due to the diffusion of the adatoms cannot be avoided. Therefore, the surface morphology is expected to be locally different from the morphology of the STO substrate, and thus also different from the interface. Indeed, the AFM shows that a part of the step-edge is faceted along the (110) or (1-10) directions. These facets observed by AFM (fig. 2a) appear also in constant current STM images acquired with a  $V_{bias} > +2.5$  V; strikingly for  $V_{bias} < +2.5$  V, the facets disappear, the step-edge is slightly advanced and a larger vertical corrugation is observed (figs. 2c,d). Indeed, tunnelling electrons from the tip having energies below +2.5 eV do not find available states at the LAO and will tunnel directly into the interface. By changing the bias voltage it is therefore possible to image the LAO surface or the LAO/STO interface, tuning the relative weights of the contributions to the tunnel current.

Intriguingly, STM images of the interface with nanometer spatial resolution, taken with a  $V_{bias}$  of +0.9 V, show the presence of a periodic pattern on top of the well-ordered terraces (figs. 3a-c). The 2D Fourier transform in the inset of fig. 3b, as well as the autocorrelation image

of fig. 3c, confirm that this pattern corresponds to a short-range-ordered superstructure. The superstructure consists of 3 nm wide spots that are quasi-periodically arranged along [110] and [1-10] directions, forming a  $6 \times 8$  nm<sup>2</sup> period that comprises several in-plane STO unit cells. The vertical modulation of the superstructure is of the order of 0.4–0.6 nm peak-to-peak, which explains why STM topography images of the interface show a roughness that is larger compared to the LAO surface. The quasi-periodic pattern was reproducibly observed on several area of the same interface and in different conducting 4 uc LAO/STO samples.

At first glance, this superstructure might be attributed to a real structural periodic corrugation of the interface. High-resolution electron microscopy reports [21,22], showed that the  $n$ -type TiO<sub>2</sub>/LaO interface indeed exhibits a larger roughness than the  $p$ -type SrO/AlO<sub>2</sub> interface. This result was attributed to cation intermixing occurring at TiO<sub>2</sub>/LaO interface that, together with the “electronic reconstruction”, was considered a necessary mechanism to eliminate the polar discontinuity. Cation intermixing and structural distortions are probably present with some degrees at these interfaces, but the height modulation observed by STM in figs. 3a,b far exceeds the values that can realistically be expected from structural distortions alone. Additionally, the presence of a quasi-periodic two-dimensional superstructure is hardly explained by disorder. Thus, the data suggest that the superstructure is caused by a combination of structural/atomic and electronic reconstructions.

To analyze the electronic contribution to the superstructure,  $I$ - $V$  and conductance spectroscopy maps were measured. Specific features characterize the electronic properties of the interface, as determined from  $I$ - $V$  and normalized  $(dI/dV)/(I/V)$  spectra, the latter of which is a measure of the LDOS [23]. As shown in fig. 3d, there is no clear evidence of a gap between occupied (negative  $V_{bias}$ ) and unoccupied (positive  $V_{bias}$ ) states, which is consistent with a metallic behaviour, but the tunnel conductance and the density of states at the Fermi level are very small. Additionally, on a scale of hundreds of nanometers, the spectroscopic maps appear to be relatively homogeneous, but at higher resolution they are clearly not. In particular, simultaneous topography and conductance maps on a  $32 \times 32$  nm<sup>2</sup> area (figs. 4a,b) show the same periodic pattern detected on a twice larger lateral scale in fig. 3b, as well as a close relationship between the STM topographic image (fig. 4a) and the purely electronic spectroscopy image at +0.4 V (fig. 4b). Below +0.3 V (around the Fermi level and for occupied states, not shown) the spectroscopic maps still show the signatures of a modulated density of states, but the signal-to-noise ratio becomes too small to firmly establish a correlation between topography and spectroscopy at the Fermi level. Thus, to further highlight the spectroscopic changes associated with the superstructure, we applied a  $K$ -means algorithm [24] to classify the typologies of LDOS spectra

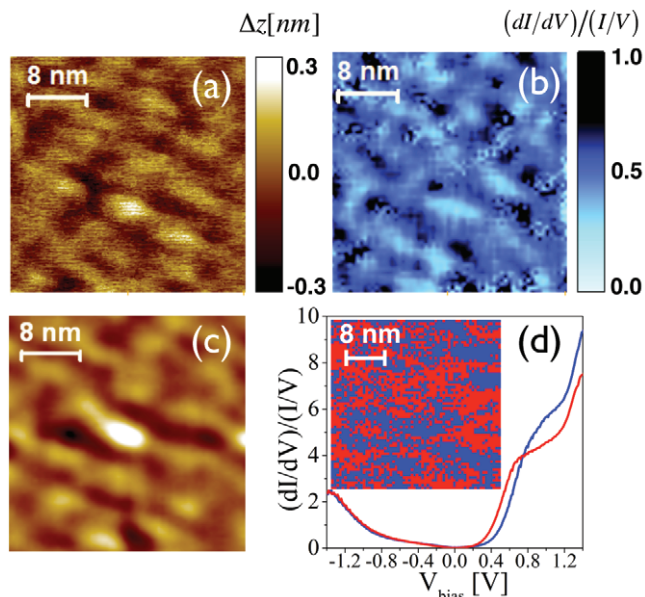


Fig. 4: (Color online) (a) STM topographic image of a  $32 \times 32 \text{ nm}^2$  area ( $V_{bias} = +0.9 \text{ V}$ ,  $I_t = 0.75 \text{ pA}$ ,  $256 \times 256 \text{ pixels}^2$ ) and (b) simultaneous LDOS  $\propto (dI/dV)/(I/V)$  map at  $+0.4 \text{ V}$  ( $64 \times 64 \text{ pixels}^2$ ). To reduce the noise the data have been averaged over an energy window of  $50 \text{ meV}$  (corresponding to an average of 5 spectroscopic maps around  $+0.4 \text{ V}$ ). (c) Cross-correlation image between spectroscopic and topographic images showing a peak in the center, which demonstrates the close relationship between the two images, and a pattern resembling the nanoscale modulation present in the two images. (d) Results of the  $K$ -means classification on the LDOS *vs.*  $V$  data: the  $(dI/dV)/(I/V)$  *vs.*  $V$  red and blue spectra correspond to regions having higher and lower conductance below  $V_{bias} = +0.6 \text{ V}$ , respectively; the inset shows the  $K$ -means classification map with a color coding assignment consistent with the plotted LDOS.

and to determine the main spectroscopic changes associated to the superstructure. Using this algorithm, we assumed for clarity the presence of only two separate classes on the spectroscopy map. Thus, in the class-image shown in the inset of fig. 4c, each pixel corresponds to one of the two characteristic  $(dI/dV)/(I/V)$  *vs.*  $V$  spectra (red or blue lines in fig. 4c) representing one of the two classes. We notice a close correspondence among the spectroscopy class-image (inset of fig. 4c), the STM image (fig. 4a), and the LDOS map measured at  $V_{bias} = +0.4 \text{ V}$  (fig. 4b). The main differences between the two-class spectra are more evident above  $V_{bias} = +0.3 \text{ V}$ , and in particular between  $+0.6 \text{ V}$  and  $+0.8 \text{ V}$ , where the LDOS exhibits a bump which is close in position to features reported at low temperatures by STS in [14]. LDA, LDA +  $U$  calculations and the oxygen edge XAS data show that between  $+0$  and  $+1.5 \text{ eV}$  the main contribution to the density of states comes from  $t_{2g}$  3d orbitals of the  $\text{TiO}_2$  layer at the interface [8,14]<sup>2</sup>. Therefore, fig. 4c

<sup>2</sup>While also the LAO surface is expected to contribute to the LDOS below  $+0.5 \text{ eV}$ , we did not have signatures from our data of

shows that the most evident spectroscopic changes characterizing the superstructure consist in an energy shift of the  $t_{2g}$  3d-states. From the XAS spectroscopy of fig. 1b, we know that the degeneracy of the 3d  $t_{2g}$  states is removed and that the  $3d_{xy}$  orbitals shift to lower energy toward the Fermi level. The STS data also show that the 3d  $t_{2g}$  LDOS is modulated. These results are explained by the occurrence of a spatially ordered orbital reconstruction that characterizes the electronic properties of the conducting LAO/STO system. In particular, the interface appears to be composed of regions in which the  $3d_{xy}$  states are gradually shifted toward the Fermi level, eventually crossing it, and other regions where this does not happen. These two regions are arranged with a short-range order with a period of 6 and 8 nm along the  $[110]$  and  $[1-10]$  directions.

**Discussion.** – The orbital short-range order found by STM differs in some respects from the predicted one. We underline that in the extreme conditions of the experiment and in particular because of the large barrier thickness (vacuum +  $1.5 \text{ nm}$  of LAO), the spatial resolution is not sufficient to detect a  $2 \times 2$  pattern (period of  $0.78 \times 0.78 \text{ nm}^2$ ), which is the one predicted in [8,12]. However, a  $2 \times 2$  checkerboard pattern of filled  $3d_{xy}$  states requires 50% of  $\text{Ti}^{3+}$  at the interface, which is well above the experimental values of 5% of  $\text{Ti}^{3+}$  obtained from hard photoemission [17] and from transport data. Therefore it is not surprising that the superstructure observed by STM has a different period, and in particular a larger period than the one predicted by LDA +  $U$  calculations. However, a charge order state is in general a characteristic of an insulator or of a bad metal. Therefore, an important question raised by our results is the consistency between the good metallic properties of the LAO/STO interface and the measured STM/STS local density of states. Theoretically, the charge order state is effectively suppressed if ionic relaxation is taken into account within a generalized gradient approximation (GGA), which does not include on-site correlations [12]. In this case it is also predicted that at the interface an orbital  $3d_{xy}$  order survives but electrons are no more localized and are also partially transferred to the other  $\text{TiO}_2$  layers. In particular, the  $t_{2g}$  states of the interface layer should cross the Fermi level, which seems not to be the case. We notice that by STM we are definitively measuring the LDOS of the topmost  $\text{TiO}_2$  layer. Therefore our data, which show that at the interface the LDOS is suppressed around the Fermi level and that it is spatially modulated, does not fully support the GGA calculations. The experimental data and theory can be at least qualitatively explained by taking into account that

the presence of these states. Indeed, from an experimental point of view, this states would be characterized by a very favorable tunnelling probability, since electrons should not cross the LAO layer to contribute to the tunnelling current. It is very likely that surface reconstruction could effectively suppress these surface states.

the presence of electronic correlations, confirmed by the experiments [14], could effectively lead to a suppression of the LDOS around the Fermi level. Additionally, we notice that the interface is certainly affected by some amount of structural and/or chemical disorder, therefore it is likely that 3d electrons in this layer have a larger tendency toward localization [25]. The system can behave as a good metal due to the electrons transferred into the TiO<sub>2</sub> layers below the interface and at the same time exhibiting an orbital and possibly charge order. Thus the appearance of a short-range order and the removal of the 3d degeneracy are a manifestation of the electronic reconstruction of the interface that stabilizes the system. Another point to be considered is the discrepancy between the experimental value of the energy splitting between the 3d<sub>xy</sub> and the 3d<sub>xz,yz</sub> states (of order 50 meV) and the one predicted for the Ti<sup>3+</sup> sites (of order eV). According to prediction, the 3d<sub>xy</sub> states should in part cross the Fermi level, giving rise to partially occupied states. From the STS data, we did not find a clear signature of 3d<sub>xy</sub> feature between -1.0 eV and the Fermi level, but this could be attributed also to the limited spatial resolution that can be achieved by STM in the present experimental configuration. Even by STS it quite difficult to detect the characteristic local electronic features, foreseen by theory, associated with the small fraction of Ti<sup>3+</sup> sites (below 10%). Further experimental and theoretical investigations are thus required to better understand the microscopic picture emerging from these experimental data.

**Conclusions.** – In conclusion, by combining XAS and STM/STS techniques we have found evidence for an orbital order at the conducting interface between LaAlO<sub>3</sub> and SrTiO<sub>3</sub>. The appearance of this kind of “electronic reconstruction” between band insulating oxides indicates that such ordering phenomena may also be associated with the reconstruction of other oxide interfaces and surfaces, thereby affecting their basic electronic properties as well as their functional behaviour.

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