Orbital Reconstruction and the Two-Dimensional Electron Gas at the $\mathrm{LaAlO_3/SrTiO_3}$ Interface

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In 2004, Ohtomo and Hwang discovered that an electron gas is created at the interface between insulating $\mathrm{LaAlO_3}$ and $\mathrm{SrTiO_3}$ compounds. Here we show that the generation of a conducting electron gas is related to an orbital reconstruction occurring at the $\mathrm{LaAlO_3/SrTiO_3}$ interface. Our results are based on extensive investigations of the electronic properties and of the orbital structure of the interface using x-ray absorption spectroscopy. In particular, we find that the degeneracy of the Ti $3d$ states is fully removed and that the Ti $3d_{xy}$ levels become the first available states for conducting electrons.

Interfaces between transition metal oxides can exhibit electronic properties that are absent in the individual layers. A prominent example is the electronic conduction at the $\mathrm{TiO_2/LaO}$ n-type interfaces in $\mathrm{LaAlO_3/SrTiO_3}$ (LAO/STO) [1–4], $\mathrm{LaTiO_3/SrTiO_3}$ [5], and $\mathrm{LaVO_3/SrTiO_3}$ (LVO/STO) [6] bilayers composed by excellent insulators. These heterostructures are believed to avoid electronic instabilities at their interfaces by an electronic reconstruction mechanism that is expected to occur in addition to the classical structural reconstructions. Consequently, the properties of transition metal oxide interfaces are thought to be sensitively controlled by polar discontinuities, band bending, epitaxial strain, and related phenomena [7].

The LVO/STO and LAO/STO bilayers only generate a conducting interface if the thicknesses of the LVO and LAO films reach a critical value, which are 5 [2] and 4 unit cells (uc) [8], respectively. This behavior is consistent with the polarization catastrophe mechanism, which attributes the induction of mobile charges at the interface to the large electrostatic energy of thick LVO or LAO layers [1,9]. Various sources of instabilities could simultaneously drive the introduction of lattice distortions and of chemical defects close to the interface, like cation substitution and oxygen vacancies, possibly creating conducting $\mathrm{La_{1-x}Sr_xTiO_3}$ or oxygen-deficient $\mathrm{SrTiO_3}$ layers [10]. Therefore, modifications of structural, chemical, and electronic properties of the $\mathrm{LaAlO_3}$ and $\mathrm{SrTiO_3}$ films may be induced, raising the questions whether the formation of an electron gas at the LAO/STO interface is simply a result of off stoichiometry, whether it is related to the induction of charge carriers, or whether it is associated with further changes of the electronic or lattice structure of the oxide layers.

To resolve these problems, we have applied x-ray absorption spectroscopy (XAS) as a probe of the interface electronic states of the LAO/STO system with chemical and orbital sensitivity. This technique has recently been used with great success to shed light on the interface electronic states in manganite or cuprate bilayers [11].

The XAS measurements have been performed at the ID08 beam line of the European Synchrotron Radiation Facility. XAS spectra were collected at the Ti $L_{2,3}$ absorption edge of n-doped interfaces in LAO/STO heterostructures grown by pulsed laser deposition. The spectra were measured as a function of the thicknesses of the LAO films. The analyzed samples were grown at the University of Augsburg at an oxygen pressure of 8×10^{-5} mbar and at the University of Twente at an oxygen pressure of 2×10^{-3} mbar. The former show low temperature superconductivity [2], and for the latter magnetic effects were reported [3,5]. The LAO/STO films grown in Augsburg were deposited at 780 °C with a laser fluence of 1.0 Joule/cm² and were oxygenated *in situ* at an oxygen pressure of ∼0.5 bar. The Twente samples were deposited at 850 °C using a laser fluence of 1.3 Joule/cm² and were cooled down at the deposition pressure of 2×10^{-3} mbar. By using scanning probe microscopy, these procedures have been demonstrated to create a conductive layer only at the interface [12].

In x-ray absorption, photons excite core electrons to the unoccupied states of the solid. In $\mathrm{SrTiO_3}$, the first available unoccupied states are the empty $3d$ levels of the $\mathrm{Ti^{4+}}$ ions [Fig. 1(a)]. All features of the measured $L_{2,3}$ Ti-edge spectra agree with the results of atomic multiplet calculations, performed using the MISSING scientific package [13] [Fig. 1(b)]. The first two main spectral peaks a_1 and b_1 are attributed to Ti $2p_{3/2} \rightarrow 3d$ transitions and have a contri-
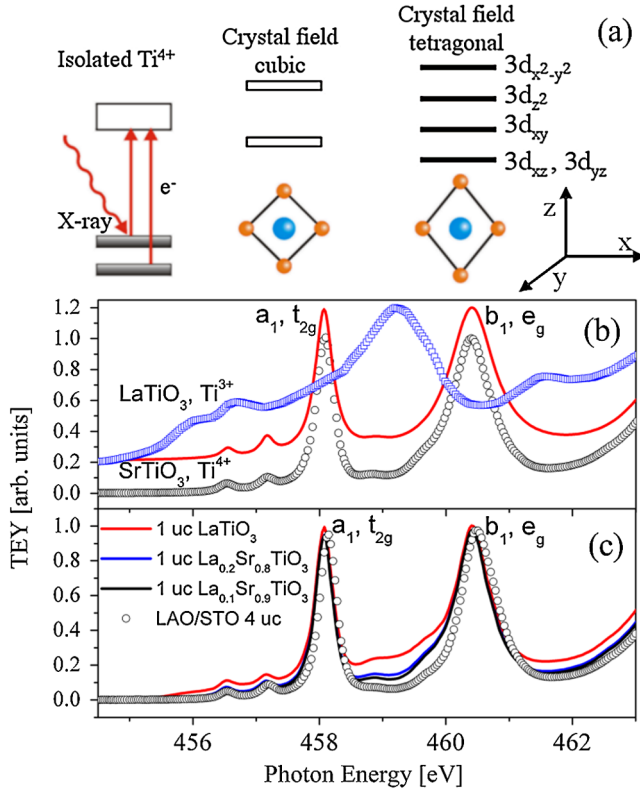
FIG. 1 (color online). (a) A sketch of the XAS process for $2p \rightarrow 3d$ transitions. The available, empty $3d$ Ti^{4+} states are depicted for cubic (middle) and tetragonal (right) crystal fields. (b) Total electron yield XAS spectra (normalized to the peak a_1), acquired with $E \parallel ab$ (I_{ab}) on a TiO_2-terminated $SrTiO_3$ single crystal (black circles). The blue circles show reference XAS spectra taken on a $LaTiO_3$ single crystal, and the red continuous line is the result of the atomic multiplet simulation for STO [13]. (c) Experimental total electron yield XAS spectrum of a conducting 4 uc LAO/STO interface (black circles) compared to calculated XAS spectra (continuous lines) of STO covered by one monolayer of $La_xSr_{1-x}TiO_{3-d}$ with $x = 1$ (red line), $x = 0.2$ (blue line), and $x = 0.1$ (black line).

bution from t_{2g} (d_{xz}, d_{yz}, and d_{xy}) and e_g (d_{z^2} and $d_{x^2-y^2}$) levels, respectively. Here the z direction refers to the surface normal. The XAS spectra are strongly sensitive to the valence of the Ti ions [14]. Indeed, data taken on $LaTiO_3$, which comprises Ti^{3+} only, differ considerably from those taken on STO [Fig. 1(b)]. Moreover, the XAS process is strongly influenced by the splitting of the $3d$ levels and therefore provides information on the crystal field. By using linearly polarized light, it is possible to select an in-plane (d_{xy} and $d_{x^2-y^2}$) or an out-of-plane (d_{xz}, d_{yz}, and d_{z^2}) orbital as the final state, corresponding to XAS spectra with in-plane (I_{ab}) and out-of-plane polarizations (I_c), respectively. The linear dichroism, obtained by subtracting I_c from I_{ab} XAS data, is particularly sensitive to any distortion of the TiO_6 octahedra and therefore provides valuable information on the eventual presence of orbital reconstructions.

Fluorescence yield (FY) XAS spectra of LAO/STO interfaces, composed of 2, 4, 8, and 12 uc LAO layers, of insulating and of conducting, Nb-doped (1% at.), STO crystals are very similar. Moreover, as a function of the polarization, the data do not show any appreciable difference. The total electron yield (TEY) XAS spectra, acquired simultaneously with the FY XAS spectra, however, vary among the samples and depend significantly on the polarization. The differences between FY and TEY data are related to the different sampling depths of the two techniques. For the soft x-ray energies used (<500 eV), the sampling depth in the FY mode is several tens of nanometers, while in the TEY mode it is between 1.5 and 3.0 nm [15]. Thus, the TEY mode is mainly probing the STO interface layers. The differences of the two data sets therefore provide clear evidence that the electronic states at the interfaces of the LAO/STO bilayer differ from the bulk states.

The measurements reveal that the interface electronic states cannot be explained by the possible formation of a $La_xSr_{1-x}TiO_{3-d}$ solid solution. Figure 1(c) compares data measured at a conducting LAO/STO sample (4 uc) with calculated spectra of a hypothetical interface layer of $La_xSr_{1-x}TiO_{3-d}$. The latter are obtained by appropriately combining the measured TEY of $LaTiO_3$ and $SrTiO_3$ crystals. Figure 1(c) reveals that complete $LaTiO_3$ or $La_xSr_{1-x}TiO_{3-d}$ layers ($x > 0.1$) are unable to match the experimental results, in agreement with previous electron energy loss spectroscopy measurements [2]. Moreover, this result suggests that the carriers are not transferred to localized $3d$ Ti^{3+} states, as expected in the simple ionic polar catastrophe picture, but are delocalized as in a metal, possibly forming states with some degree of covalency.

TEY XAS spectra and the linear dichroism (LD) of LAO/STO heterostructures [Fig. 2(a)] provide key information on the electronic properties of the interface. A marked change in the LD data is found as a function of the number of LAO layers. In a perfectly symmetric Ti^{4+} system, as in cubic STO without distorted TiO_6 octahedra, the dichroism needs to disappear. A deviation from the cubic symmetry, for example, by a tetragonal distortion, produces a dichroism and causes an energy splitting of the t_{2g} and e_g states. Remarkably, STO and metallic Nb-doped STO reference samples show a dichroism opposite to the one of the LAO/STO interface [Fig. 2(a)]. In the case of STO and Nb-doped STO, the experimental results are well reproduced by a positive energy splitting of about 20 meV between the d_{xy} and the (d_{xz}, d_{yz}) orbitals and of 40 meV between the $d_{x^2-y^2}$ and d_{z^2} states, corresponding to an elongation of the TiO_6 octahedra along the surface normal [16]. After depositing a few unit cells of $LaAlO_3$ on such a surface, however, the LD changes sign, and, quite remarkably, it becomes much more pronounced when the LAO thickness exceeds the critical value of $d \geq 4$ uc for the interface to become conducting.

This behavior has to be associated with a change of the anisotropy in the $3d$ electronic states as a function of the
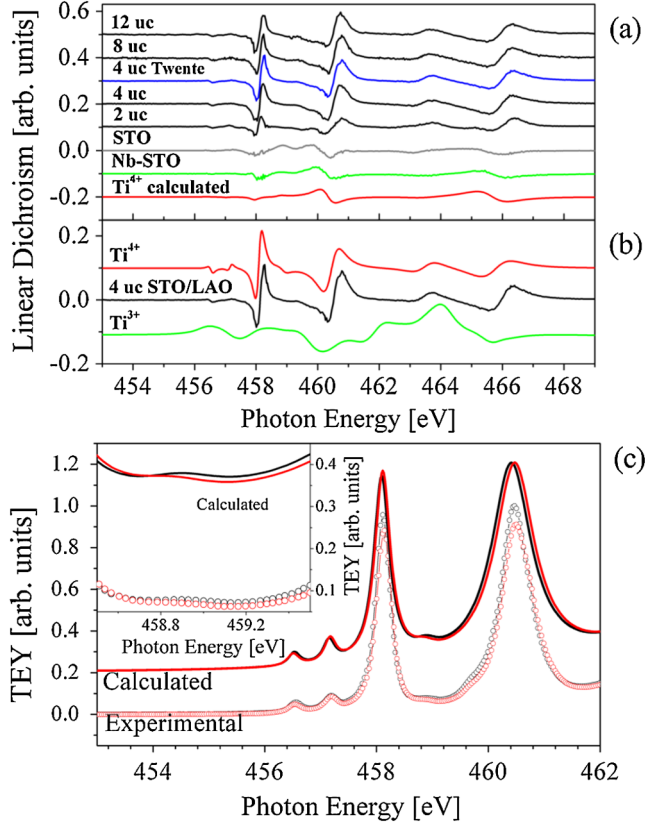
FIG. 2 (color online). (a) Total electron yield linear dichroism acquired at 300 K on STO (gray line), Nb-STO (green line), and LAO/STO as a function of the LAO thickness (black lines, Augsburg samples grown at 8×10^{-5} mbar; blue line, Twente 4 uc sample grown at 2×10^{-3} mbar). The calculated linear dichroism reproducing the data on bare STO or Nb-STO is shown as a red line. (b) Comparison between the calculated linear dichroism of Ti^{4+} (red line) and Ti^{3+} (green line) and the data on 4 uc STO/LAO (black line). The splitting between in-plane and out-of-plane t_{2g} and e_g levels is assumed to be the same for the Ti^{3+} and Ti^{4+} cases. (c) Comparison between I_{ab} (black line) and I_c (red line) experimental TEY spectra on 4 uc LAO/STO (open circles) and calculated ones for a bilayer assuming a Ti^{4+} configuration which reproduces the dichroism (continuous lines). The region between a_1 and b_1 peaks is better visible in the inset. For clarity, the curves in (a) and (b) are plotted with regular, artificial y offsets.

LAO thickness. As a first hypothesis, one could argue that the anisotropy is due to transfer of carriers to $3d_{xy}$ states of Ti ions. The Ti ions will then assume a Ti^{3+} oxidation state, thereby breaking the cubic symmetry. Another possibility is that the dichroism is caused by a distortion of the TiO_6 octahedra located at the interface. This distortion would induce an energy splitting between in-plane and out-of-plane $3d$ levels of the Ti^{4+} ions at the center of the TiO_6 octahedra. The two situations give rise to a different dichroism and have been compared to the experimental LD in Fig. 2(b). For the calculation we use here a similar energy splitting for the two different situations which suggest an interface composed by Ti^{3+} and Ti^{4+} ions,

respectively. In particular, even for a relatively small negative splitting of -25 meV between d_{xy} and the (d_{xz}, d_{yz}) orbitals and of -50 meV between the $d_{x^2-y^2}$ and d_{z^2} states, it is found that the LD of the Ti^{3+} system is large but substantially different from the data. On the contrary, the experimental results are nicely explained by an anisotropic Ti^{4+} system. The best agreement between the data and the theory is obtained by assuming an interface composed of at least 90% of Ti^{4+} ions characterized by in-plane d_{xy} and $d_{x^2-y^2}$ orbitals having a smaller energy than the out-of-plane (d_{xz}, d_{yz}) and d_{z^2} orbitals by $\sim$50 and $\sim$100 meV, respectively. By using these parameters, also the details of the XAS spectra are well reproduced by the calculation [Fig. 2(c) and inset]. The presence of a linear dichroism produces an energy shift of the positions of the main peaks in the I_c and I_{ab} spectra to higher energies. This shift is particularly evident for the peak b_1 in both I_{ab} and I_c spectra [Fig. 3], while the position of the a_1 peak (not shown) changes only slightly as a function of the LAO thickness. This result is another indication that the experimental data are explained by a change of the anisotropy in the $3d$ electronic states. Indeed, in agreement with the calculations presented in Fig. 2(c), the effects of a structural distortion of the TiO_6 are more pronounced for the $3d$ states which directly point toward the oxygen ions in the octahedra. These are the e_g states (peak b_1).

Finally, we note that the shift of the peaks correlates with the change of the LD as a function of the thickness. Indeed, both the integral of the absolute dichroism $\int |I_c - I_{ab}| dE$ and the position of the b_1 peaks from the I_{ab} and I_c spectra show a sudden change as a function of the number of $LaAlO_3$ layers, in particular, between 2 and 4 uc, i.e., for the thickness at which the interface becomes conducting [Fig. 3]. Above 4 uc, these quantities remain approximately constant.

To further investigate the electronic properties of the STO/LAO interface, we have performed measurements on each sample at different temperatures between 300 and 9 K. The orbital reconstruction is found to be robust and almost temperature independent. Moreover, the reconstruction is extremely similar in samples grown under different oxygen conditions.

We conclude that, for LAO thicknesses close to the conductance threshold, a pronounced anisotropy of the $3d$ energy levels is induced. This behavior is correlated with the formation of the 2D electron gas and therefore reveals that an orbital reconstruction occurs when mobile carriers appear at the interface. These results are consistent with signatures of electronic reconstructions that have recently been reported for LAO/STO superlattices investigated by resonant x-ray scattering [17] and for LAO/STO bilayers studied by second harmonic generation [18].

Our results suggest that a structural distortion at the interface occurs. Structural modifications of both STO and LAO unit cells, close to the interface, were indeed reported by transmission electron microscopy and x-ray
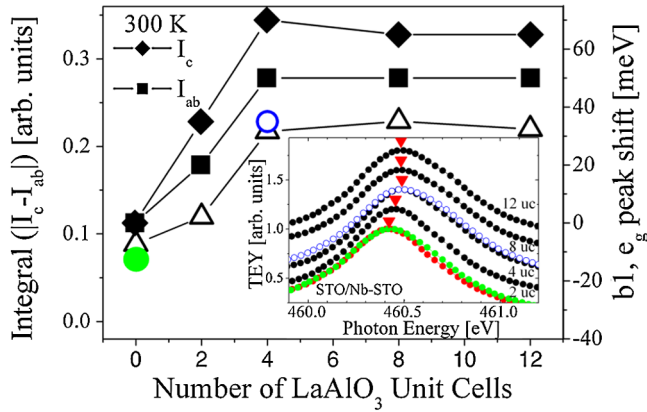
FIG. 3 (color online). The integral of the absolute dichroism (open triangles, Augsburg samples and STO; blue circle, Twente sample; green circle, Nb-STO sample) and the position of the b_1 peaks from the I_{ab} (filled squares) and I_c (filled diamonds) spectra as a function of the number of LaAlO$_3$ layers. In the figure, the left scale refers to the dichroism data, while the right scale relates to the shift of the b_1 peaks. The inset shows the region of the TEY XAS spectra around the peak b_1 for STO (red circles), Nb-STO (green circles), and LAO/STO. Red triangles in the inset mark the position of the peak.

diffraction studies [19–21]. On the other hand, structural distortions of oxide interfaces are predicted by theoretical calculation as a consequence of the electronic reconstruction. Describing the generation of the electron gas at the LaTiO$_3$/SrTiO$_3$ interface, Okamoto, Millis, and Spaldin have proposed a ferroelectriclike distortion of the TiO$_6$ [22]. Their calculation also shows that this kind of structural relaxation could provide an orbital ferrodistortive ordering of the $3d_{xy}$ Ti states, so that these states become the lowest empty levels for conducting electrons. Similar conclusions are reported in Ref. [23] for the same system and in Ref. [24] for the LaAlO$_3$/SrTiO$_3$ superlattice. On the other hand, recent local-density approximation (LDA) and LDA $+ U$ [25] calculations on the LaAlO$_3$/SrTiO$_3$ predict an antiferrodistortive ordering as found in GdFeO$_3$. In this case the conducting electrons would have only partially a $3d_{xy}$ character, which would be conflicting with the experimental data that reveal the $3d_{xy}$ orbital to be the first available state.

The calculations performed on superlattices predict an electronic reconstruction and a conducting interface also for a one unit cell LAO thin layer, a result experimentally verified in LAO/STO multilayers [26]. However, the situation of a bilayer differs considerably due to the proximity of the interface to the LaAlO$_3$ surface. As shown in Ref. [27], the dipole field inside the LaAlO$_3$ can be partially accommodated by relaxation and consequent polar distortion of the lanthanum and oxygen ions. Therefore, until a critical thickness threshold, the polar distortion in the LaAlO$_3$ can compensate partially the electrostatic energy. Above the threshold, this mechanism is no more

efficient and an orbital reconstruction takes place. Our data demonstrate that an orbital reconstruction indeed occurs in the bilayers only above a thickness threshold. In particular, interface sidebands with $3d_{xy}$ character appear. Remarkably, within our resolution, the carriers do not appear to be localized in Ti^{3+} states, suggesting some degree of covalency.

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