Interface structure of SrTiO₃/LaAlO₃ at elevated temperatures studied *in situ* by synchrotron x rays

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The atomic interface structure between SrTiO₃ and LaAlO₃ was studied at elevated temperatures employing *in situ* surface x-ray diffraction. The results at 473 K indicate that the lattice distorts significantly in two ways. First, the interatomic distances between the cations across the interface become as large as 4.03(2) Å. Second, the TiO₆ octahedra at the interface contract their principal axis along the surface normal considerably and the Ti displaces off center. These distortions can be ascribed to the charge inbalance introduced by the change in atomic species across the interface and to a Jahn-Teller effect. The latter distortion suggests the presence of extra electrons at the interface, which is important for understanding the electronic properties of this system.

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I. INTRODUCTION

Perovskite transition metal oxides possess a wealth of physical properties, comprising ferromagnetism, ferroelectricity, semiconductivity, conductivity, nonconductivity, and superconductivity, making these materials extremely interesting for technological applications.[1] Depending on the composition, having the general chemical formula ABO_3 (*A* and *B* cations), structural differences between different compounds are very subtle, whereas the properties may alter completely. Recently it has been shown in several papers, that by careful interface-strain engineering, the properties of perovskite thin films may be altered. In the case of ferroelectric superlattice heterostructures made of BaTiO₃/SrTiO₃/CaTiO₃, a 50% enhancement of the polarization compared to bulk BaTiO₃ was found.[2,3] Another example is that of substrate-induced strain making thin SrTiO₃ films ferroelectric.[4]

Besides strain effects, the different bond configuration at heterointerfaces may result in surprising conduction phenomena. Since the general structure of the perovskites can be seen as a stack of alternating layers of AO and BO_2 in one of the principal crystallographic directions, a heterointerface will introduce polarity discontinuities when both *A* and *B* have different valence states on either side of the interface. The resulting properties of these kinds of interfaces were discussed already in the early days of heteroepitaxy.[5,6] Recently, Ohtomo and Hwang[7] found different electronic behavior for thin LaAlO₃ (LAO) films on either SrO or TiO₂ terminated SrTiO₃ (STO) substrates, the former interface being insulating and the latter conducting. Here, using the formal valence states, the polarity discontinuities are formed by either the $(SrO)^0$-$(AlO_2)^-$ or $(TiO_2)^0$-$(LaO)^+$ sequence.[8] Similar behavior was found for the LaTiO₃/SrTiO₃ interface.[9] The intriguing phenomenon of conductivity at the interface between two *insulating* materials has become known as "electronic reconstruction," and progress is being made in a theoretical description.[8,10–12]

It is well known that the atomic structure of surfaces and interfaces differs in general from the bulk. In order to better understand and model the exotic properties of the aforementioned heterointerfaces, it is important to determine the atomic structure. For this purpose, *ab initio* structure calculations of these interfaces have been performed recently,[13,14] showing that considerable atomic displacements occur. So far, experimental studies devoted to clarify the three-dimensional (3D) atomic interface structure have been obtained only via microscopy techniques,[15,16] having an intrinsic resolution on the verge of what is needed. Surface x-ray diffraction (SXRD) is a well-established technique for high-resolution structure determination of surfaces and interfaces.[17]

Here we present SXRD studies on the STO/LAO heterointerface during its formation by pulsed laser deposition (PLD). *In situ* studies enable to clarify the atomic heterointerface structure of perovskite materials at deposition conditions, which is important for understanding the growth. The atomic interface structure and morphology depend strongly on several parameters, of which the difference in lattice parameters between the materials on either side of the interface is very important.[2] Although the lattice mismatch between STO and LAO is about 3%, pseudomorphic films up to 22 nm thickness have been reported.[15] This means that strain relaxation is expected to occur for thicker films and more importantly that the structure of films thinner than 22 nm are expected not to change too much as a function of thickness. Therefore, this system seems very suited to study the difficult problem of the atomic structure during nucleation and growth of heteroepitaxial systems. Furthermore, it is expected that the interface structure and surface morphology may differ as a function of temperature. Knowledge about the structure at deposition temperatures is important in relation to the question if lattice defects and even charge states, leading to the unexpected conduction phenomena, are formed during growth. These questions can be addressed by studying submonolayer coverages of LAO on STO, thereby also serving as a first step in the pursuit of understanding the electronic properties of embedded interfaces.

The aim of the present study is thus twofold: a more general case study of the atomic heterointerface structure of perovskites at high temperatures and, more specific, a study of the atomic structure of an electronically reconstructed heterointerface.

TABLE I. Details of the two datasets at two different temperatures and the final results of the refinement of the model as described in the text. The refined atomic positions are listed in Table II.

	1123 K	473 K
Number of points	60	45
CTR's	10,11,20,21	10,11,20
θ_1	0.38(2)	0.48(1)
θ_2	0.57(1)	0.50(1)
$\theta_1 + \theta_2$	0.95(2)	0.97(2)
χ^2	2.1	2.6

II. EXPERIMENT

The experiments were carried out using a specially designed PLD chamber,[18] which was mounted on a 2+3 type surface diffractometer with vertical scattering geometry at BM26 (DUBBLE)[19] at the European Synchrotron Radiation Facility (ESRF). The x-ray beam was monochromatized to a wavelength of 0.775(1) Å. Optically polished SrTiO$_3$ (001) [space group $Pm\bar{3}m$ with a=3.901(1) Å at room temperature[20]] substrates were obtained from Surfacenet GmbH, Rheine, Germany. A special treatment of these substrates results in single TiO$_2$-terminated surfaces.[21] The target consisted of a single crystal of LaAlO$_3$ (LAO). The bulk crystal structure of LAO, having space group $R\bar{3}c$ with a=5.364 62(4) Å and c=13.1096(1) Å at room temperature,[22] can be represented by a pseudocubic unit cell with $a_{\text{cub}}=\sqrt{\frac{1}{3}a_{\text{hex}}^2+\frac{1}{36}c_{\text{hex}}^2}$ resulting in a_{cub}=3.790 Å.

During deposition the substrate temperature was kept at 1123 K, while the pressure in the chamber was around 10^{-4} mbar, close to the ideal conditions for LAO growth.[23] At a grazing angle for the incoming x-ray beam, the intensity of the surface-sensitive reciprocal space point (0,0,0.175) in STO lattice units was monitored while depositing. During the first intensity oscillation, i.e., before completion of one complete smooth unit cell layer, the deposition was stopped. One sample was then cooled to 473 K while another sample was kept at the deposition temperature of 1123 K. For both samples several crystal truncation rods (CTR's) were measured. In order to monitor the stability of the structure at 1123 K, the reciprocal point (2,0,1.9) was recorded several times during data collection. Over 6 hours the integrated intensity of this particular point fluctuated 4% around its average value, which is an indication that at least the crystal structure of the partial monolayer maintained stable. For the sample that was cooled to 473 K, the reflectivity ridge scan before and after the data collection showed no significant differences, indicating that also this sample was stable.

III. RESULTS

The details of the CTR measurements are given in Table I. The measured diffraction profiles were integrated and corrected in a standard way in order to obtain structure factors.[24]

Due to the sample chamber, access to reciprocal space was limited and it was therefore not possible to measure symmetry related reflections. In the absence of redundancy of the measured data, the systematic errors were estimated at 15%, a value which is deduced from previous data collections on bare STO substrates using the same setup.[25]

Next, the measured data were described by a structural model, in which a TiO$_2$-terminated STO substrate is partly covered by a unit cell layer of LAO. The part of the substrate that is covered by LAO, is *a priori* not known. Since it is conceivable that the surface atoms in the STO lattice in the part of the substrate that is covered by LAO will distort, a model is needed in which the total interference sum of both distorted and undistorted part is taken by

$$F_{\text{sum}} = \frac{F_{\text{sto}}}{1 - e^{-i2\pi l}} + \theta_1 F_{\text{sto}} + \theta_2 (F'_{\text{sto}} + F_{\text{lao}}). \quad (1)$$

Here, F_{sto} is the structure factor of bulk STO, and the first term on the right-hand side renders the well-known CTR of the bulk STO substrate. The fraction θ_1 is the part of the undistorted substrate surface and θ_2 is the fraction of the distorted substrate surface (F'_{sto}) that is covered by LAO (F_{lao}). From previous room-temperature measurements on the bare STO surface it is known that the relaxations of the outermost atoms are very small.[25,26] *In situ* annealing experiments have revealed that at moderate temperatures the STO(001) surface changes, but when increasing the temperature to typical deposition values the surface restores again.[27,28] More detailed analysis of a complete set of CTR data indicates that at high temperatures the room-temperature model gives a good description.[28] Therefore, to a good approximation, the uncovered part of the substrate is supposed to be bulk terminated. Indeed, running fit routines that allowed the uncovered part to relax as well resulted in negligible relaxations. In order to reduce the number of parameters the above-mentioned model was then used.

The program ROD (Ref. 29) was used to refine the atomic positions against the experimental data. The results of the refined atomic positions are listed in Table II and the measured and calculated CTR's are shown in Fig. 1. The fractional occupancies θ_1 and θ_2 were refined independently, and their values are listed in Table I. Finally, a schematic view of the atomic positions of the refined model at 473 K is shown along one principal crystallographic direction in Fig. 2.

Other models different from the model discussed in the preceding section were tested as well. These consisted of atomic stackings such as bulk-SrO-AlO$_2$-LaO, bulk-SrO-LaO-AlO$_2$ (Ruddlesden-Popper phase[30]), bulk-TiO$_2$-AlO-LaO$_2$, and bulk-TiO$_2$-AlO$_2$-LaO [where the AlO$_2$-LaO layer is displaced by the in-plane vector $(\frac{1}{2},\frac{1}{2},0)$]. Each of these models did not describe the data very accurately. As a comparison with the best-fit model, Fig. 1 shows CTR's that are calculated by using two bulklike terminated models as well. In those two cases, the interatomic distances across the STO-LAO interface are kept at the pseudocubic bulk LAO lattice parameter. In one case a stacking with a TiO$_2$-terminated substrate is used, and for the other a SrO termination. Allowing more STO unit cell layers in the bulk

TABLE II. Refined fractional coordinates of the best-fit model as described in the text for two different samples at two temperatures as well as the isotropic thermal parameters (B) that were used in the refinement procedures.

Layer	Atom	x	y	$z_{1123\ K}$	$z_{473\ K}$	$B_{1123\ K}$ (Å^2)	$B_{473\ K}$ (Å^2)
AlO$_2$	Al	$\frac{1}{2}$	$\frac{1}{2}$	1.99(1)	2.031(8)	2.0	1.0
	O1	$\frac{1}{2}$	0	1.99(2)	1.88(2)	3.0	2.0
LaO	La	0	0	1.536(4)	1.565(2)	2.0	1.0
	O2	$\frac{1}{2}$	$\frac{1}{2}$	1.58(5)	1.40(2)	3.0	2.0
TiO$_2$	Ti	$\frac{1}{2}$	$\frac{1}{2}$	1.01(1)	0.997(6)	1.6	0.7
	O3	$\frac{1}{2}$	0	1.04(2)	0.92(2)	2.6	1.5
SrO	Sr	0	0	0.513(5)	0.536(3)	2.2	1.2
	O4	$\frac{1}{2}$	$\frac{1}{2}$	0.57(3)	0.51(2)	2.6	1.5

to relax as well in the best-fit model, resulted in negligible atomic displacements for these layers. In order to reduce the number of fit parameters only the first STO unit cell layer was allowed to distort in the final fit. Attempting to refine the thermal parameters resulted in very large estimated standard deviations (e.s.d.'s). Therefore, the thermal parameters were kept at bulklike values (see Table II) inferred from the literature.[20,22]

IV. DISCUSSION

In the following the results obtained from the SXRD measurements will be discussed. In order to distinguish between the structural model and its relation to physical properties the discussion is segmented into two parts. First the results of the refined atomic positions are compared with related bulk crystal structures. Then the origin and implications of these results are discussed in relation to the literature that appeared on structural phase transitions, conducting properties and thickness dependence.

A. Structural model

Table II shows that almost all the atomic positions in the high-temperature interface (1123 K) structure, are within 2 times the e.s.d. from a bulk STO lattice site. For the low-temperature (473 K) interface structure however, the displacements from the bulk STO lattice sites become statistically more relevant. Starting from the bulk underneath, the Ti are both at high and low temperature in a bulk position. The Al, that follows on top of the Ti in a crystallographically similar position, is at low temperature displaced away from the surface and bulk STO lattice site. The Sr and La, that are on the A sites of the general ABO$_3$ structure, seem to behave differently. Again at high temperature both the Sr and La are practically on bulk STO lattice sites, whereas at 473 K the atoms displace away from the surface, resulting in quite large distances compared with the bulk lattice parameters of both LAO and STO. The oxygens show similar behavior, i.e., the displacements are much larger at low temperature. At high temperature they reside practically at bulk STO lattice sites.

However, the anions displace in the opposite direction from the cations and furthermore the displacements are much larger.

The results of the distances between the cations obtained for the 473 K interface structure here, shown in Table III, compare very well with results obtained by Maurice *et al.*[15] They studied thin LAO films of several nanometers on STO substrates by high resolution transmission electron microscopy (HRTEM). The measurements obtained in those studies revealed that on either side of the STO/LAO interface the atomic layers are dilated. Their results indicate that at room temperature several unit cell layers, both on the STO as well as the LAO side, expand up to 4.05 Å (see also Sec. IV B). Here, the studied interfaces are composed of a partially occupied unit cell layer, which might be the cause of the distortions to be found only in the last unit cell layer of STO. Nevertheless, the distances Al-Ti and La-Sr across the 473 K interface compare very well with the HRTEM results. Also *ab initio* calculations, performed on the LaTiO$_3$/SrTiO$_3$ interface, result in atomic displacements at the interface in the range 0.1–0.2 Å compared to their ideal lattice sites.[13,14]

In the quadrupole perovskite Sr$_2$La$_2$CuTi$_3$O$_{12}$ an atomic stacking very similar to the current interface occurs.[31] Although in that compound the A sites are randomly occupied by Sr and La, a comparison with the present results seems instructive. The selected bond distances, listed in Table III, show that the TiO$_6$ octahedra distort similarly in the present structure and bulk Sr$_2$La$_2$CuTi$_3$O$_{12}$. The distances Ti-O3 and Ti-O4 are, within the error bars, identical for the present 473 K structure and the reported Sr$_2$La$_2$CuTi$_3$O$_{12}$ (SLCTO). Although the distances Ti-O2 are different for the present 473 K structure and SLCTO, in both cases it is significantly shorter than the two other Ti-O distances. The obvious reasons for this difference may be the current presence of a surface and the aforementioned disorder of Sr/La over the A sites, which in the present case is unlikely to occur. Nevertheless, qualitatively the distortions of the TiO$_6$ octahedra are similar, that is the axis along the growth direction becomes shorter and the Ti is displaced off center. The latter distortion can be expressed by the buckling of the O-Ti-O chains, which is 0.30(8) Å and 0.21(5) Å in the present and bulk case, respectively. These distortions are a combination of two
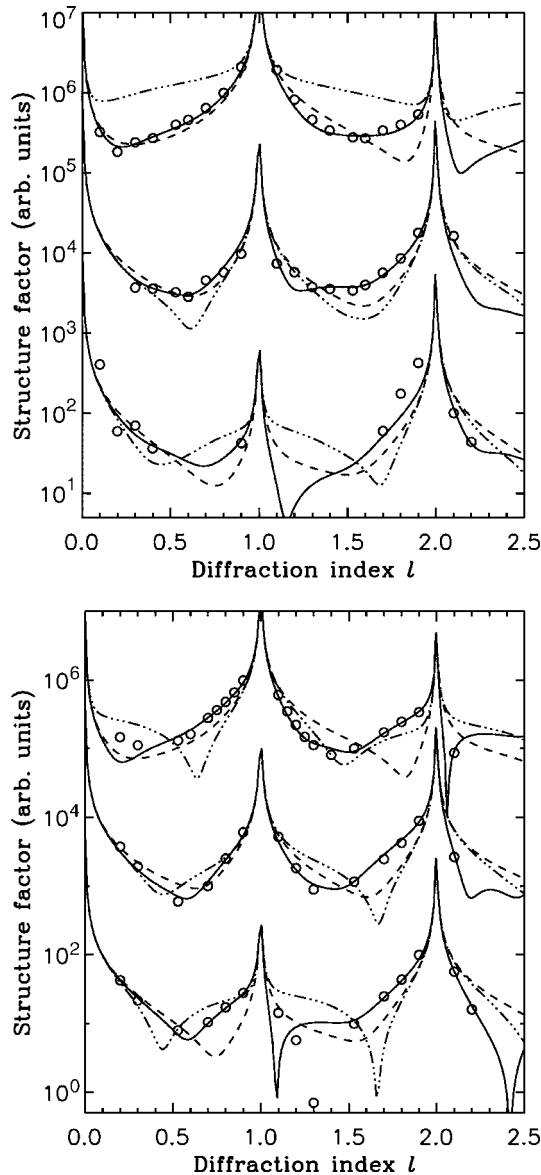
FIG. 1. Measured data points for the sample at 1123 K (upper) and 473 K (lower). For both temperatures are shown the 10 (top), 11 (middle), and 20 (bottom) rods. The solid lines are the CTR's calculated by using Eq. (1) and the atomic positions as listed in Table II. As a comparison, the CTR's calculated by assuming a bulklike termination are shown as well, for the bulk-TiO_2-LaO-AlO_2 (dashed line) and bulk-SrO-AlO_2-LaO (dashed-dotted line) interface stackings. Clearly one can distinguish between the two different interfaces, showing the sensitivity of SXRD.

commonly observed distortions from the perfect cubic perovskite structure:[32] Jahn-Teller distortion and ferroelectric-like. The term ferroelectric should not be taken strictly as being the ability to switch between two different polarization states. The term is used here only to address the similarity with, for example, $BaTiO_3$, where the Ti displaces off center in the oxygen octahedra in the ferroelectric state. The distorted oxygen octahedron originating from a Jahn-Teller effect was discussed by Maurice *et al.* and ascribed to the valence state of half the interface Ti atoms changing from 4+ to 3+, which means that the extra electron occupies a
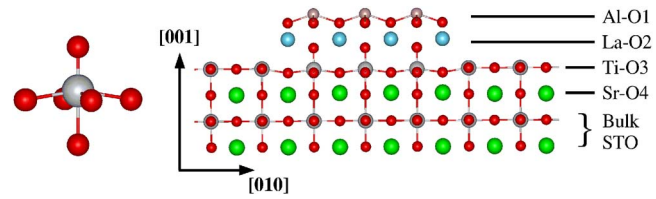

FIG. 2. (Color online) Schematic view of the model with the interface stacking bulk-TiO_2-LaO-AlO_2 after refinement against the dataset obtained at 473 K. For clarity the projection along the [100] direction is shown. The atomic fractional coordinates are listed in Table II. On the left-hand side the distorted surface TiO_6 octahedron is enlarged for clarity.

previously unoccupied *d*-shell state. However, from their measurements it was concluded that the octahedron axis *elongated*, which would, as they discussed, lead to a twofold degenerate lowest energy level after the splitting of the t_{2g} levels. The present finding of a *contraction* of the octahedron axis would therefore be exactly what is expected in view of the Jahn-Teller theory. The conclusion drawn by Maurice *et al.* concerning the octahedron elongating in the growth direction, rests on their experimental finding of dilated atomic layers. The present results show that although the interatomic distances between the cations compare very well with the HRTEM results, the octahedra distort differently. The apparent difference might be due to limitations in the resolution that can be achieved by HRTEM, unlike the present method of SXRD.

Recently, several papers discussed the Jahn-Teller effect in $LaTiO_3$,[33–35] that in the bulk already contains a $3d^1$ Ti atom. In the present interface, similar bond configurations as in $LaTiO_3$ are forced to occur, which might explain the observed displacements.

B. Structure and physical properties

From charge considerations in the ionic limit, it follows that one-half of the interface Ti atoms have an extra electron.[7] This raises an interesting question concerning the nature of a possible Jahn-Teller (JT) effect being static or dynamic. Although the present results point towards extra charge carriers at the interface, of course the used method of SXRD does not probe the carrier mobility. In this context it is informative to compare results obtained for thicker structures. Recently, Thiel *et al.*[36] found that LAO on STO showed to be conducting only for film thicknesses of 4 unit cells and more. However, Huijben *et al.*[16] find conduction even for a single LAO unit cell layer sandwiched between STO. Seemingly, the occurence of Ti^{+3} at a deeply embedded interface or at (near) a free surface results in different conduction properties. A possible Jahn-Teller distortion will be much influenced by the presence of a surface, which alters the crystal field and will introduce dangling bonds. Thick LAO films up to 22 nm seem to show structural distortions in the first few unit cell layers only,[15] and seem therefore to coincide with the reported thickness dependence of the electronic properties.[16,36] Again from charge considerations it is highly unlikely that the Ti atoms other than the ones at the

TABLE III. Selected interatomic distances obtained from the refinement of the model as described in the text and those of the room-temperature structure of $Sr_2La_2CuTi_3O_{12}$. The bulk lattice parameters of STO (a_{sto}) and LAO (c) for both temperatures are given. For $Sr_2La_2CuTi_3O_{12}$ the value c is a fourth of the room-temperature c axis ($c_{bulk}/4$) from Ref. 31. The same numbering for the atoms is used as in Table II and Fig. 2.

	1123 K (Å)	473 K (Å)	$Sr_2La_2CuTi_3O_{12}$
a_{sto}	3.935(5)	3.915(5)	
c	3.824	3.797	3.9485(3)
Al-Ti	3.86(4)	4.03(4)	
La-Sr	4.03(2)	4.03(2)	3.95(1)
O1-O3	3.7(1)	3.8(1)	
O2-O4	4.0(2)	3.5(1)	3.77(9)
Ti-O2	2.2(2)	1.58(8)	1.81(8)
Ti-O3 (×4)	1.97(9)	1.98(8)	1.97(5)
Ti-O4	1.7(1)	1.90(8)	1.96(5)

interface have an extra electron, i.e., that a JT distortion occurs in more than one unit cell layer. More likely is that the structural distortion at the interface extends up to several unit cell layers into both the STO and LAO, much like a strain field. Therefore, the atomic interface structure of the sub-monolayer films studied here is apparently representative for thicker films. However, the *mobility* of the extra charge seems to depend on the layer thickness, or, more general, whether it is embedded in a thicker structure. To further investigate the interplay between atomic structure, thickness and electronic properties it would be very useful to conduct SXRD measurements on similar and thicker structures focusing on fractional order reflections, that would indicate charge order. Since temperature influences the signal-to-noise ratio in diffraction experiments, these experiments should be carried out at low temperatures ($T < 200$ K), which in turn enables to study possible structural phase transitions.

If the high-temperature interface structure does not differ too much from having a STO bulk terminated crystal in which the topmost Ti and Sr atoms are replaced by Al and La respectively, the present results would indicate a structural phase transition temperature somewhere between 1123 K and 473 K. Understanding the interface structure and the differences between the high- and low-temperature interface might be complicated further by the temperature dependence of the bulk structure of LAO. At room temperature, LAO has the rhombohedral structure, which differs from the perfect cubic structure by the rotation of the oxygen octahedra about their threefold axis. At 821 K the structure transforms to become cubic ($Pm\bar{3}m$).[37] Although the rhombohedral structure differs only little from cubic (less than the distortions found here), the driving force for the phase transition might be of importance to understand the observed distortions. Also the LaAlO₃(001) atomic surface structure has been found to be temperature dependent. Yao *et al.*[38] claim that at temperatures below 423 K the surface is AlO₂ terminated while for temperatures higher than 523 K the termination switches to LaO. On the other hand, Francis *et al.*[39] conclude to no such termination switch at high temperatures, but rather to large in-plane atomic displacements in the topmost layers. In ei-

ther case, the atomic surface termination of LAO(001) seems to change drastically at high temperatures, and may play a role for understanding the structure of the current heterointerface.

V. CONCLUSION

High-temperature SXRD was employed on LAO/STO interfaces just after their PLD growth. Two crystallographic data sets from two different samples were obtained; one at the deposition temperature of 1123 K and the other at 473 K. The model that fits the experimental data best, is that of a fractionally covered TiO₂-terminated substrate. The uncovered part of the substrate remains bulk terminated while the interface atoms of the covered part relax. At high temperatures, the atomic displacements from ideal bulk STO lattice sites in the interface region are comparable with the error bars. At the lower temperature of 473 K, the distortions do become significant, whereby the anions displace towards and the cations away from the underlying substrate. The interatomic distances across the interface between the cations in the range of 4.0–4.1 Å found here, compare very well with HRTEM measurements performed on similar interfaces by Maurice *et al.*[15] The opposite displacements of cations and anions, seen as strong buckling of the atomic layers, result in the TiO₆ octahedra at the interface to contract their axis in the surface normal direction. The present distortions compare rather well with the bulk structure of $Sr_2La_2CuTi_3O_{12}$, which has a similar atomic stacking.[31] These results strongly suggest to originate from a Jahn-Teller effect: the initially unoccupied d-shells of one-half of the interface Ti atoms, receive one electron. This is an important result in view of the exotic electronic properties of these kinds of interfaces, since it could explain the origin of charge carriers at the interface.

The results obtained here suggest that at deposition temperature the atoms in the interface region occupy positions very close to bulk STO lattice sites. This might be an indication to why the ideal deposition temperature is found to be around 1123 K: the lattice distorts very little, even during growth.

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