Electronic charge and orbital reconstruction at cuprate-titanate interfaces

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Abstract In complex transition metal oxide heterostructures of physically dissimilar perovskite compounds, interface phenomena can lead to novel physical properties not observed in either of their constituents. This remarkable feature opens new prospects for technological applications in oxide electronic devices based on nm-thin oxide films. Here we report on a significant electronic charge and orbital reconstruction at interfaces between YBa$_2$Cu$_3$O$_6$ and SrTiO$_3$ studied using local spin density approximation (LSDA) with intra-atomic Coulomb repulsion (LSDA+U). We show that the interface polarity results in the metallicity of cuprate-titanate superlattices with the hole carriers concentrated predominantly in the CuO$_2$ and BaO layers and in the first interface TiO$_2$ and SrO planes. We also find that the interface structural relaxation causes a strong change of orbital occupation of Cu 3$d$ orbitals in the CuO$_2$ layers. The concomitant change of Cu valency from $+2$ to $+3$ is related to the partial occupation of the Cu 3$d_{3z^2-r^2}$ orbitals at the interface with SrO planes terminating SrTiO$_3$. Interface-induced predoping and orbital reconstruction in CuO$_2$ layers are key mechanisms which control the superconducting properties of field-effect devices developed on the basis of cuprate-titanate heterostructures.
1 Introduction

It is well known that the rich properties of transition metal oxides like ferroelectricity, magnetism or superconductivity are closely associated with the physics of d-orbitals [1]. In heterostructures of physically different transition metal oxides, the local structural deformations and uncompensated charge at the interfaces result in properties well beyond a simple combination of the characteristics of their constituents [2, 3, 4]. A prominent example is the titanate superlattice of insulating perovskites SrTiO$_3$ and LaTiO$_3$ where the metallic conductivity is caused by the mixed valence (+3/ +4) of Ti and by electronic charge reconstruction at polar interfaces [5]. The new electron states appearing in such heterostructures can be tuned by external electromagnetic fields which opens new prospects for engineered oxide electronic devices based on nm-thin transition metal oxide films.

In heterostructures with high-$T_c$ cuprate films, the external electrostatic fields tune the surface/interface charge density and in this way lead to transitions between conducting (or superconducting) and insulating states. Such heterostructures consist of YBa$_2$Cu$_3$O$_{7-\delta}$-films grown on SrTiO$_3$ layers and are of central importance in superconducting field-effect devices [6, 7, 9]. In the existing literature, the shift of $T_c$ achieved with increasing electrostatic field is often understood in terms of an electrostatic doping concept without detailed consideration of the microstructure of the interfaces between YBa$_2$Cu$_3$O$_{7-\delta}$-film and SrTiO$_3$ [7, 9]. Several experimental facts, however, indicate an interface-related modification of the electronic states in the cuprate/perovskite oxide heterostructures. For example, recent studies on under-doped cuprate films produced a $T_c$-shift of about 5–15 K, whereas in the overdoped films no shifts were observed, a fact, which cannot be explained satisfactorily by field-doping [9]. Despite the important role of interfaces in the physical properties of such oxide heterostructures, no direct experimental studies of the electronic properties of interfaces between copper and titanium oxides are currently available. This is partially related to extreme experimental difficulties in distinguishing the direct interface- and bulk-contributions in the experimental data [8]. On the other hand, due to the high complexity of the cuprate and titanate structures, extensive theoretical studies of the cuprate-titanate interfaces [11, 12, 13, 14, 15, 16] are a challenging task which requires extremely demanding computational resources [17, 18].

The goal of the current project is the development of interface models for microstructures of strongly correlated cuprates and titanates. The analyses of novel electronic states are based on the density functional theory within LSDA and LSDA+$U$ implementations. Due to the insufficient structural information about atomic arrangements at cuprate-titanate interfaces, the theoretical investigations include the theoretical modeling of heterostructures with different structurally compatible surface terminations of SrTiO$_3$ and YBa$_2$Cu$_3$O$_6$ and relaxation of interface atomic structures. In this context, the main amount of the computer time is used for high-performance theoretical engineering of multilayer oxide supercells and for structural optimization.

In our extensive analyses, we find a metallic state in cuprate-titanate interfaces which is characterized by significant hole predoping of cuprate films [17]. In the
field-effect experiments, such an interface-caused predoping occurs even before the electrostatic injection of charge and is of essential importance for functional properties of superconducting field-effect devices. Furthermore, our results not only allow to obtain a clear answer to the question about the electronic charging of the cuprate-titanate heterostructures, but also to make important predictions how to increase the performance of field-effect devices. Our studies directly show that despite the extreme computational resources required for optimization procedures, the interface structural relaxation is of crucial importance for understanding the physics of transition metal oxide heterostructures. In the copper oxide layers of cuprate-titanate superlattices, we find that the interface-caused local structural deformations strongly affect electronic occupancies of \( d \)-orbitals of Cu and can lead to a change of its electronic valence state. Due to the central role of \( d \)-orbitals in the magnetic and superconducting properties of transition metal oxides, the obtained interface-induced orbital reconstruction should have dramatic consequences for the functionality of field-effect devices based on cuprate-titanate superlattices.

2 Description of the methods

Our extensive studies of oxide surfaces are based on the density functional theory within the local spin density approximation (LSDA) with intra-atomic Coulomb repulsion (LSDA+\( U \)) [19]. The calculations of the electronic densities of states, structural relaxation in terms of minimization of total energy and forces have been performed using the linearized augmented plane wave method (LAPW) implemented in the WIEN2k package [20]. The most numerically intensive parts of the package code are executed in parallel, namely full potential calculations, iterative solution of eigenvalues and eigenvector problems of the generated Hamiltonian matrix and calculations of electronic charge density expansions. Parallelization is achieved on the \( k \)-point level by distributing subsets of the k-mesh to different processors and is based on parallelization libraries including MPI, Scalapack, and BLACS.

The small amount of the computational resources was spent for the development of interface-related extensions to the WIEN2K-code which are aimed at specific studies of the local electronic structure and the charge density profiles across the interfaces in heterostructures. For instance, to obtain the profiles of the hole density across the polar interfaces, we had to generate the charge densities in the energy window between the Fermi level and the top of the valence bond and to perform a subsequent planar integration of these profiles. In this way, not only the charge distribution, but also the effective thickness of the interface, where the charge density deviates from its usual bulk-type behavior, can be estimated.

The main part of the resources was absorbed by computationally demanding structural optimization and LDA+\( U \)-calculations of the optimized superlattices. Specifically, for superlattices of \( \text{YBa}_2\text{Cu}_3\text{O}_6/\text{SrTiO}_3 \) and \( \text{CuO}_2/\text{SrTiO}_3 \) containing from 18 to 22 atoms in a supercell, a single run of LDA+\( U \) included from 50 to 80 iteration steps until the final convergence with respect to the electronic charge.
and total energy could be reached. With 15–20 processors used for the parallel $k$-points calculations, each converged LDA+$U$ run usually required up to 25,000 CPU hours. In addition, in each superlattice, the relaxation of the interface distances could be achieved by performing up to 10 single LSDA runs which required about 10,000 CPU hours. Due to a wide range of superlattices analyzed in our project (YBCO/STO-sandwiches, CuO$_2$/STO-slubs, Sr$_2$CuO$_2$Cl$_2$/STO superlattices), such computationally demanding calculations have used about 150,000 CPU hours in the first 6 months after beginning the project.

The further stages of calculations of interfaces require a full optimization of all local atomic coordinates in the superlattices and the increase of the number of elementary unit cells of the constituent compounds in each supercell. Consequently, the computational time required for a structural optimization drastically increased up to 25,000 CPU hours for a single superlattice, whereas each LDA+$U$ single run requires about 35–40,000 CPU hours for a supercell with 33 different atoms. Without the exceptional computational resources provided by HLRB, the performance of such demanding calculations would not be a feasible task and could not have been achieved in a realistic time period.

3 Electronic properties of cuprate-titanate superlattices

The recent X-ray studies of the interface arrangement [21, 8] give clear indications of incompletely grown unit cells of the cuprate film on the SrTiO$_3$ substrate. Whereas the bulk unit cell of YBa$_2$Cu$_3$O$_{7-\delta}$ is terminated by CuO chains, responsible for the charge doping of cuprates, the CuO chains near the interface are missing which makes the corresponding unit cell incomplete. This structural rearrangement should strongly affect the superconducting properties of cuprate thin films. Therefore, we focus in our studies on the consequence of the effective ‘substitution’ of electrostatically charged CuO-chains with electrostatically neutral (001) layers of SrTiO$_3$. As the superlattices, which result from such a structural rearrangement, will be polar, the overall charge neutrality requires extra hole carriers to be distributed near the cuprate-titanate interface. Our results clearly show that in YBa$_2$Cu$_3$O$_6$-SrTiO$_3$ heterostructures such interface induced hole predoping may drastically change the interfacial electronic properties.

In YBa$_2$Cu$_3$O$_6$-SrTiO$_3$ heterostructures, the chemical bonding at the (001) interface with the cuprate film will be determined by the first termination plane of SrTiO$_3$, which can be either TiO$_2$ or SrO. Below we demonstrate the consequences of interface electronic reconstruction for these two basic cases of SrTiO$_3$ termination.
3.1 Case study: TiO\textsubscript{2} termination at interface

In the case when the substrate of SrTiO\textsubscript{3} is terminated by a TiO\textsubscript{2}-layer, the determined interface arrangement is typically a stack of .../TiO\textsubscript{2}/BaO/CuO\textsubscript{2}/Y/CuO\textsubscript{2}/... layers. Such structural stacks suggest an interface chemical bonding Ti-O-Cu with the oxygen of the BaO-layers shared between the CuO\textsubscript{2} and TiO\textsubscript{2}-planes. From the electrostatical point of view, the initial ‘bulk-type’ electronic charging of the constituent layers indicated in the left panel of Fig. 1 would result in 1 extra hole which is needed in order to compensate the polarity. In the sandwich-type supercell shown in Fig. 1, this compensation leads to a doping of upper and lower symmetric blocks .../SrO/TiO\textsubscript{2}/BaO/CuO\textsubscript{2} by 0.5 holes.

![Fig. 1 Scheme of a YBaCuO/SrTiO\textsubscript{3}-sandwich where the polar interfaces appear due to the incomplete Ba\textsubscript{2}Cu\textsubscript{2}O\textsubscript{6}-unit cell with an interface structural configuration shown in detail on the right.](image)

For the YBaCuO/SrTiO sandwich-type supercells, we performed calculations of the electronic structure using the SIC variant of the LSDA+U method on a $9 \times 9 \times 1$ \textit{k}-point grid with $U = 8$ eV and $J = 0.8$ eV on the Cu 3\textit{d} orbitals. The lattice constants of the supercell were fixed to the lattice constant $a = b = 3.898$ Å of cubic SrTiO\textsubscript{3}. The interface distance $\Delta$ between the nearest BaO and TiO\textsubscript{2} planes was optimized by minimization of the total energy which leads to the value $\Delta = 1.85$ Å between the apical oxygens of BaO and the TiO\textsubscript{2} plane.

From the calculated density of states, shown in Fig. 2, we can identify the metallic state with hole carriers originating from the oxygen \textit{p} states. Like in the bulk YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6}, the Cu $d_{z^2-r^2}$ states are separated by a gap of 1.34 eV from the oxygen 2\textit{p} states. It should also be noted that for this type of interface arrangement, the orbitals Cu $d_{z^2-r^2}$ and $t_{2g}$ are occupied and remain below the Fermi level. Fig. 2 demonstrates that the significant amount of hole charge is located in the interfacial TiO\textsubscript{2}, BaO and more distant SrO layers. Also, a substantial amount of hole charge is distributed over the CuO\textsubscript{2} planes.
More detailed information about the distribution of the charge-compensating hole density is presented in Fig. 3. Through an integration of the hole carrier density along the interfacial $z$-direction we obtain that the major part of hole carriers is distributed along the BaO (25%) and the first TiO$_2$ (48%) and SrO (12%) layers. Furthermore, about 5% of the total interface hole charge 0.5 e is located in CuO$_2$ planes. This suggests a finite metallic conductivity in the titanate, BaO, and copper oxide planes. It is noteworthy that the structural relaxation for this type of interface leads to a reduction of the hole density in the BaO plane and to its slight redistribution within the interface SrO and more distance planes, whereas the hole density and orbital occupation in the CuO$_2$ planes remains almost unaffected.

Fig. 3 Hole density distribution near the YBa$_2$Cu$_3$O$_6$/SrTiO$_3$-interface for optimized ($\Delta = 1.85$ Å) and unrelaxed ($\Delta = 1.94$ Å) cases. The position $z = 0$ is at the bottom TiO$_2$-plane of the SrTiO$_3$/YBa$_2$Cu$_3$O$_6$/SrTiO$_3$-sandwich.
Our results for the hole charge in the copper oxide planes clearly show that, apart from chemical doping, the interface polarity is another decisive factor that modulates the doping level in the cuprate films. In superconducting field-effect devices, operated by electrostatic charging, such initial interface-induced predoping levels may have dramatic consequences for their performance. From the point of view of superconductivity, the most important feature is the shift of $T_c$ with electrostatic doping which will be directly affected by the obtained predoping ($x = 0.025$) in the copper oxide film. Moreover, in other structural configurations at YBCO/SrTiO interfaces, much higher hole predoping levels and dramatic changes of electronic occupancies of Cu $3d$ orbitals in CuO$_2$ planes can appear as a result of electronic and orbital interface reconstruction.

### 3.2 Case study: SrO termination at interface

To analyze the structurally different SrO termination of the substrate SrTiO$_3$, we consider a model case in which a copper oxide plane is directly deposited on SrTiO$_3$ (Fig. 4). The direct deposition of the single Cu$^{2+}$O$_4^-$ plane on the electrostatically neutral titanate layer would require two extra holes to maintain the overall charge neutrality. To achieve such an extremely high doping level, interface electronic reconstruction is inevitably required. Apart from the electronic mechanism, other forms of interface reconstruction like oxygen vacancies or cation intermixing could modify the chemical composition. However, it is still instructive to enforce atomically flat and stoichiometric surfaces in order to study comprehensively different mechanisms of the electronic reconstruction.
In our work, in order to focus on the effect of electronic reconstruction, we have introduced a decoupling vacuum layer of 13 Å thickness between the CuO$_2$ surfaces in the slab geometry shown in Fig. 4. We have also performed an optimization of the superlattice structure where a relaxed interface distance $\Delta = 1.83$ Å between the CuO$_2$ and SrO corresponds to a minimum of the total energy.

Fig. 5  Hole density distribution in the interface planes of the CuO$_2$/SrTiO$_3$ superlattice. Here $z = 0$ corresponds to the location of the lower CuO$_2$-plane.

In contrast to the case of TiO$_2$ termination, the effect of the structural relaxation on the distribution of the interface-predoped hole density is crucial for the CuO$_2$/SrO interface (Fig. 5). To demonstrate this fact, we show in Fig. 5 the distribution of hole carrier density for the optimized ($\Delta = 1.83$ Å) and unrelaxed ($\Delta = 2.2$ Å) interfaces. The density plots across the interface are obtained by the integration of generated charge density in the energy window between the Fermi level and the top of the O 2$p$ bands. As can be seen in Fig. 5 the relaxation of the interface distance $\Delta$ leads to a dramatic decrease of the hole density $n_h$ in the CuO$_2$ layers. The integration of $n_h$ along the interfacial $z$ direction shows that the total predoped hole charge $N_h$ accumulated predominantly in the 2$p$ orbitals of O and hybridized with 3$d$ Cu orbitals, amounts exactly to 2 holes in the unrelaxed ($\Delta = 2.2$ Å) supercell. In contrast to this, in the relaxed structure the density integration gives $N_h = 1$ hole for the total hole charge. Such a strong difference between $N_h$ in relaxed and unrelaxed cases appears due to the additional orbital mechanism of the polarity compensation. It becomes important due to the interface structural relaxation.

The new mechanism of the orbital reconstruction becomes evident when we compare the partial densities of states of 3$d$ orbitals calculated for optimized and unrelaxed supercells demonstrated in Fig. 6. The figure shows that the $3d_{x^2−y^2}$ and $3d_{xy}$ orbitals of Cu are affected only slightly by the decrease of the [CuO$_2$-SrO] distance $\Delta$. Specifically, the orbitals $3d_{xy}$ are fully occupied and located well below the Fermi level independently of $\Delta$. Furthermore, a significant amount of holes is found in the states $3d_{x^2−y^2}$ which are split due to the charge transfer gap of about 1.5 eV. The charge transfer gap becomes narrower with the decrease of $\Delta$. The most striking effect, which appears for the relaxed $\Delta = 1.83$ Å, is the reconstruction of Cu $3d_{3z^2−r^2}$ orbitals. While for $\Delta = 2.2$ Å both Cu $3d_{3z^2−r^2}$ orbitals are located about 4−5 eV
below the Fermi level, the decrease of $\Delta$ leads to their splitting. This splitting results in the “displacement” of one $d_{3z^2-r^2}$ orbital (spin down case in Fig. 6) to about 1 eV above the Fermi level which implies that this orbital becomes empty. Such a strong change of the occupation of $d_{3z^2-r^2}$ corresponds to an increase of the valency of Cu from +2 to +3. It occurs due to the change of the Coulomb potential for the decreasing [CuO$_2$-SrO] distance and the corresponding deformation of interfacial CuO$_6$ octahedra. As a result of the orbital reconstruction, the local electron configurations of Cu atoms in the antiferromagnetically ordered interface CuO$_2$ planes can be represented by an altering sequence of $\{3d^{13}_3;3d^{13}_5\}$ local spin states. Such an arrangement leads to an enhancement of the local magnetic moment on Cu up to 33% which is also consistent with the corresponding Hund rules of electronic orbital arrangement.

Consequently, at the CuO$_2$-SrO interfaces, two basic reconstruction mechanisms are involved in order to compensate the interface polarity: (i) electronic charge compensation which leads to the hole charge predoping of total amount $N_h = 1$ with holes located predominantly in the O 2$p$ orbitals hybridized with Cu 3$d_{3z^2-r^2}$ in the CuO$_2$ planes; (ii) orbital reconstruction associated with changes of the occupancy of Cu 3$d_{3z^2-r^2}$ orbitals so that exactly one of these orbitals becomes unoccupied by electrons. In contrast to the unrelaxed interfaces where only the first charge-predoping mechanism is responsible for the electrostatic neutrality, the relaxation of the neutral supercell leads to a combination of two (charge and orbital) mechanisms which become equally important in order to achieve the stability of the system.
The new reconstruction mechanism also involves a redistribution of the partial density of states for the O 2p orbitals in the CuO2 planes as shown in Fig. 7. In the unrelaxed heterostructure the Fermi level is located at a distance of about 0.7 eV below the top of the O 2p bands implying high hole densities. The interface relaxation leads to a shift of the Fermi level closer to the top of the 2p bands which leads to the decrease of the hole charge. It is remarkable that such a modification of the structure near the Fermi level is also accompanied by a significant reduction of the energy gap between O 2p and Cu 3d orbitals, an effect which is observed in the total DOS, displayed in Fig. 8. Such a reduction of the gap is caused by the location of the empty Cu 3d_{x^2−y^2} band at a distance less then 1 eV above the Fermi level which is a clear manifestation of the orbital reconstruction mechanism in the structurally relaxed heterostructure.

It should be noted that up to now, the growth of high quality YBaCuO films on the substrates of structurally compatible transition metal oxides remains a challenging task due to their roughness caused partially by ionic compensation of interface polarities. The existing difficulties with assembling heterostructures as well as with probing the interfacial physics directly make the theoretical calculations a powerful alternative tool for studies of oxide interfaces. In fact, the importance of the presented results is supported by recent resonant X-ray spectroscopic studies of interfaces between YBa2Cu3O7 and La2/3Ca1/3MnO3 for which evidence of orbital reconstruction with partial occupation of Cu 3d_{x^2−y^2} orbitals has been provided. Our theoretical studies identify a possible mechanism of such orbital reconstructions. In this context, the presented HLRB project contributes new and fascinating results in the rapidly developing field of the physics of transition metal oxide surfaces/interfaces.

Fig. 7 Projected O 2d orbital density of states in the CuO2 planes at the interface with SrTiO3 terminated by SrO (LSDA+U studies). The zero of energy is at the Fermi level. The top and bottom panels correspond to the case of unrelaxed (Δ = 2.2 Å) and optimized (Δ = 1.83 Å) interfacial distances.
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Fig. 8 Total density of states of the superlattice with CuO$_2$ deposited on SrTiO$_3$, terminated by SrO (LSDA+$U$ studies). The zero of energy is at the Fermi level. The top and bottom panels correspond to the case of unrelaxed ($\Delta = 2.2$ Å) and optimized ($\Delta = 1.83$ Å) interfacial distances.

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