

Thickness dependent structural and electronic properties of CuO grown on SrTiO₃(100): a hybrid density functional theory study

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Abstract

We discuss the structural and electronic properties of tetragonal CuO grown on SrTiO₃(100) by means of hybrid density functional theory. Our analysis explains the anomalously large Cu–O vertical distance observed in the experiments (≈ 2.7 Å) in terms of a peculiar frustration between two competing local Cu–O environments characterized by different in-plane and out-of-plane bond lengths and Cu electronic populations. The proper inclusion of substrate effects is crucial to understanding the tetragonal expansion and to reproduce correctly the measured valence band spectrum for a CuO thickness of 3–3.5 unit cells, in agreement with the experimentally estimated thickness.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The discovery of novel magnetic and electronic phases confined at the interface between two dissimilar materials (such as the formation of a two-dimensional electron gas sandwiched between two non-superconducting layers) and the continuously growing field of high-temperature superconductivity in the copper oxide perovskite family have boosted even further the already high interest in the search for new superconducting materials and to understand the still debated mechanism which governs superconductivity at elevated temperature. Motivated by the possible interplay between Jahn–Teller-like distortions and the electron–phonon coupling in highly symmetric CuO [1], Siemons *et al* were able to synthesize copper monoxide with a tetragonal (i.e. elongated rock salt) structure on a SrTiO₃(100) substrate and provided a preliminary discussion of its electronic properties [2]. This new tetragonal phase of CuO differs substantially from

the well-known native monoclinic phase of CuO that has been the subject of numerous experimental and theoretical investigations [3] disclosing the quite peculiar properties of cupric oxide, namely (i) unlike other transition metal monoxides CuO crystallizes with a monoclinic structure [4], (ii) it undergoes a paramagnetic to antiferromagnetic transition at about 230 K followed by a spin reorientation transition at 212 K towards a commensurate antiferromagnetic order with Cu spins alternating along the $[10\bar{1}]$ direction of the cubic unit cell [5], (iii) the observed magnetic moment is $0.68 \mu_B$, significantly smaller than $1 \mu_B$ expected from a spin-only Cu²⁺ ion [5] and (iv) a band gap of 1.7 eV is opened between Cu d_{z^2} and O p orbitals [6].

In a recent theoretical study [7] we investigated the ideal bulk phases of tetragonal CuO by applying a hybrid density functional theory approach, which is able to deal with the electronic, ionic and magnetic properties of such a system. Studying a variety of magnetic orderings we obtained two

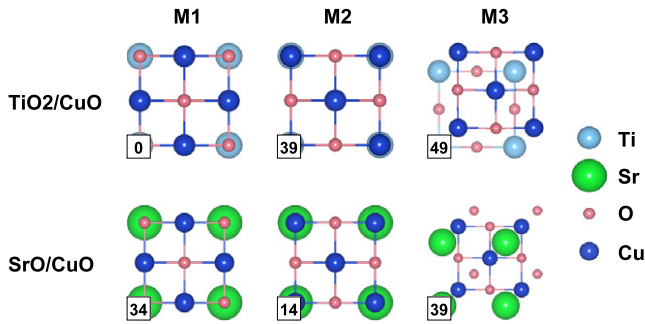


Figure 1. Top view of the interface models of the $(\text{CuO})_n/\text{SrTiO}_3(100)$ adsorbate system as studied by the present HSE approach. The numbers in the squares (bottom left corner of each structure) denote the calculated energy difference (in meV \AA^{-2}) relative to the TiO_2 terminated M1 stacking, which is the most stable arrangement.

energy minima as a function of tetragonal distortion. The antiferromagnetically ordered phase (denoted as TET2) with a tetragonal distortion of $c/a = 1.377$ appeared to be the most stable one with its lattice parameters being in very good agreement with the experimental results. Furthermore, by evaluating the interatomic exchange parameters for the TET2 phase using an effective Heisenberg Hamiltonian we predicted a very high Néel temperature (T_N) of 800 K [7], which would perfectly fit the trend of T_N for the 3d-transition metal monoxides [2]. Also, the calculated density of states of the TET2 phase agreed well with the experimental valence band spectrum with the exception of a few residual differences related to the structure of the main peak and the presence of an additional peak in the low energy spectrum which we have attributed to surface/substrate effects not taken into account in our previous analysis.

The aim of the present work is to corroborate our basic findings for the artificial TET2 phase by modeling experiments as realistically as possible by taking into consideration the effect of the $\text{SrTiO}_3(100)$ substrate and the thickness of the tetragonal CuO overstructure. With this aim, we describe the adsorbate system in terms of an $(\text{CuO})_n/\text{SrTiO}_3(100)$ slab for various thicknesses of CuO layers (with n denoting a CuO coverage of 2, 3, 3.5 and 4 unit cells (u.c.)).

Shortly after the publication of our bulk CuO study, a further theoretical study appeared which was based on the self-interaction-corrected local-density functional method [8]. Again, for a variety of magnetic orderings two energy minima were found as a function of the tetragonal distortion, but the c/a values were much closer to 1 than in our work, and consequently in worse agreement with the experimentally observed c/a ratio of 1.357. Therefore, the present study also serves the purpose of buttressing the theoretical capability of our applied hybrid density functional theory approach enabling an understanding of the nature of the exceptionally large vertical elongation observed in SrTiO_3 supported CuO .

2. Computational aspects

Because standard density functional theory applications fail to correctly describe the ground state of 3d-transition metal

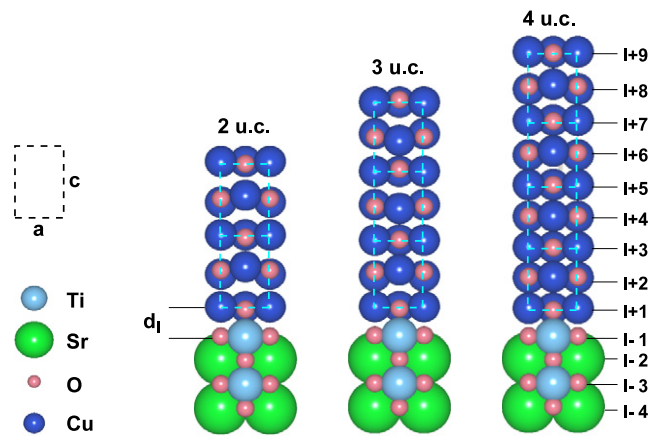


Figure 2. Side view of the $(\text{CuO})_n/\text{SrTiO}_3(100)$ slabs for a coverage by $n = 2, 3, 4$ u.c. of CuO as used in the HSE calculation. (The $n = 3.5$ coverage, which was also studied, is not shown.) Atomic arrangements are according to the TiO_2 terminated substrate and the M1 stacking of the CuO adsorbate (see figure 1). The layers are numbered with respect to the interface: $I + j$ denotes CuO layers, $I - j$ marks SrTiO_3 layers. The side projected two-dimensional unit cell with lattice parameters a and c is sketched by the dashed rectangle. Detailed structural data are listed in table 1.

monoxides, a more sophisticated (and much more costly) approach has to be chosen. Therefore, for the present study we apply hybrid density functional theory [9] based on the Heyd–Scuseria–Ernzerhof (HSE) method [10] as implemented in the Vienna *ab initio* simulation package (VASP) [11–13]. All the corresponding technical parameters were the same as in our recent study [7] of tetragonal bulk CuO . In particular, 1/4 of short-ranged Hartree–Fock exchange was admixed to the generalized-gradient-approximation exchange–correlation functional. The adsorbate systems $(\text{CuO})_n/\text{SrTiO}_3(100)$ ($n = 2, 3, 3.5$ and 4 u.c.) were modeled by a repeated slab scheme containing up to 62 atoms per slab for the highest coverage. Figures 1 and 2 sketch the basic layer-wise atomic arrangements. All atomic positions of CuO layers were fully relaxed, whereas for the SrTiO_3 substrate the lowest five bottom layers, corresponding to a full SrTiO_3 unit cell, were kept fixed. The lateral lattice parameter $a = 3.90 \text{ \AA}$ for SrTiO_3 was taken from the recent VASP-based HSE study by Wahl *et al* [14]. Indeed, the optimal HSE value of a is in very good agreement with the measured lattice constant $a_{\text{Expt}} = 3.900 \text{ \AA}$ [15]. In order to make the HSE computations feasible, ferromagnetic (FM) ordering was assumed, although a specific antiferromagnetic ordering appeared to be energetically more stable in the ideal tetragonal bulk phase [7]. Nevertheless, also because of the small magnetic Cu-moments of about $0.7 \mu_B$, we expect only a small influence of the magnetic ordering on the structural relaxations and valence band spectrum [16], which we aim to study in our present work on the $(\text{CuO})_n/\text{SrTiO}_3(100)$ substrate system. The \mathbf{k} -point integration for the structural optimization runs has been done by using a 4×4 two-dimensional Monkhorst–Pack grid, which was increased to 6×6 for the final electronic relaxation.

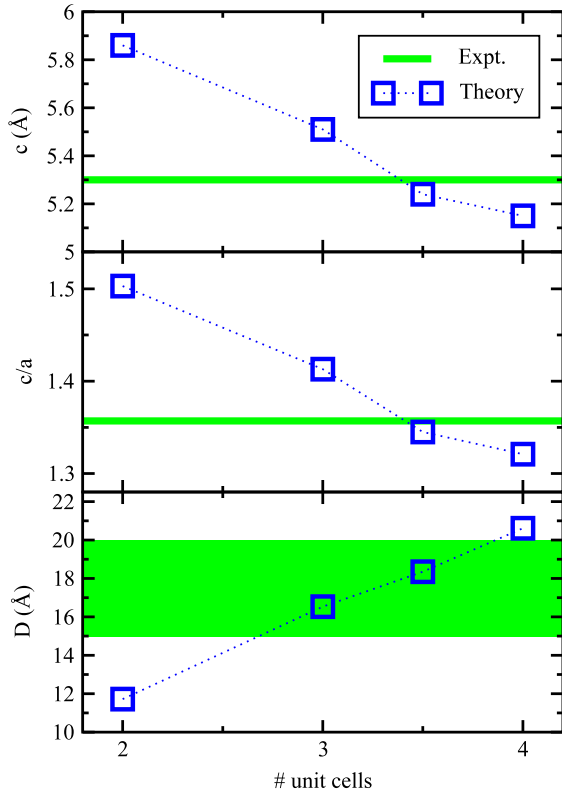


Figure 3. Thickness dependent variation of the structural parameters D , c/a and c of the CuO adsorbate on SrTiO₃(100) as listed in table 1. Horizontal bars illustrate the experimental data of [2].

3. Results and discussion

3.1. Structural properties

To find the energetically most stable atomic arrangement several terminations of the SrTiO₃(100) substrate and stacking of the CuO adsorbate were investigated. Figure 1 sketches all the studied cases: the substrate is either TiO₂ or SrO terminated. CuO layers may be accommodated in several ways: (i) Cu on top of oxygen atoms (M1), (ii) Cu on top of Ti or Sr atoms (M2), or (iii) Cu and O in hollow sites (M3). These (FM) calculations have been done by placing two CuO unit cells (five CuO layers) on SrTiO₃ (6 u.c.). Figure 1 shows that the TiO₂ terminated M1 structure is the most stable one. It should, however, be noted that rather close in energy (only 14 meV Å⁻² less stable) is the SrO terminated M2 stacking. From now on, we only discuss the TiO₂ terminated M1 structure. We study the evolution of the structural and electronic properties of the (CuO)_{*n*}/SrTiO₃(100) adsorbate system for a CuO coverage of $n = 2, 3, 3.5$ and 4 u.c.. This choice is based on the experimental estimate that a tetragonal CuO layer consisting of 3–4 u.c. can be grown on SrTiO₃(100) [2]. The corresponding structural models are displayed in figure 2.

The structural properties are summarized in figure 3 and table 1. Figure 3 illustrates that theoretical and experimental geometrical properties agree well when in the calculation the CuO coverage is 3.5 u.c., which is also in the estimated

Table 1. Geometrical data for (CuO)_{*n*}/SrTiO₃(100) for $n = 2, 3, 3.5$ and 4 CuO unit cells (u.c.). The data for c and c/a are based on averages of the vertical lattice parameter according to [2], and the lateral parameter $a = 3.90$ Å of SrTiO₃(100) is taken from another VASP-based HSE study [14]. The total thickness of adsorbed CuO is described by D . The interlayer distance between two subsequent layers, as illustrated in figure 2, is denoted by d , and $d_{l+1/l-1}$ indicates the interface separation between SrTiO₃ and CuO. Layers are labeled according to figure 2. The lattice parameters of the HSE calculation for the ideal TET2 phase [7] are $a = 3.908$ and $c = 5.381$ Å resulting in an ideal bulk-like layer distance of 2.69 Å. Experimental values are included when available. All length parameters are given in units of Å.

	2 u.c.	3 u.c.	3.5 u.c.	4 u.c.	Expt [2]
c	5.86	5.51	5.24	5.15	5.3
c/a	1.503	1.413	1.345	1.321	1.357
D	11.72	16.53	18.35	20.61	15–20
$d_{l+9/l+8}$				2.82	
$d_{l+8/l+7}$			2.87	2.70	
$d_{l+7/l+6}$		2.84	2.80	2.63	
$d_{l+6/l+5}$		2.78	2.61	2.56	
$d_{l+5/l+4}$	3.03	2.85	2.57	2.53	
$d_{l+4/l+3}$	2.93	2.72	2.49	2.46	
$d_{l+3/l+2}$	2.90	2.65	2.44	2.43	
$d_{l+2/l+1}$	2.93	2.73	2.58	2.49	
$d_{l+1/l-1}$	2.47	2.37	2.37	2.29	
$d_{l-1/l-2}$	1.88	1.88	1.86	1.82	
$d_{l-2/l-3}$	2.00	2.00	1.97	1.92	
$d_{l-3/l-4}$	1.95	1.94	1.94	1.90	
$d_{l-4/l-5}$	1.97	1.97	1.94	1.90	
$d_{l-5/l-6}$	1.98	1.94	1.95	1.92	
$d_{l-6/l-7}$	1.98	1.95	1.95	1.92	
$d_{l-7/l-8}$	1.95	1.95	1.96	1.94	
d_{bulk}	1.95	1.95	1.95	1.95	1.95

range of the experimentally derived thickness (parameter D in table 1). The experimental value of $c/a = 1.357$ is close to the theoretical value of 1.345, which compares favorably to $c/a = 1.377$ as obtained from the HSE study for the ideal bulk TET2 phase [7]. In general, when increasing the number of unit cells c and c/a decrease as shown in table 1.

The analysis of the interlayer distances reveals that inside the SrTiO₃ substrate the interface effects are healed out rather rapidly. Only the distance of the layer closest to the interface ($d_{l-1/l-2}$) experiences a distinct shortening, as is also the case for the CuO layer at the interface ($d_{l+1/l-1}$). On the other hand, the CuO layer distances appear to be quite sensitive to the thickness of adsorbed CuO. For a coverage of 2 and 3 u.c. the distances are significantly larger than the reference value of 2.69 Å which was derived from the ideal TET2 bulk study. For coverage larger than 3 u.c. the distances between the inner CuO layers are significantly shortened, whereas the top two layers expand outwards. This change in bond length is reflected by the change of ionicity of Cu, as will be discussed in the following.

3.2. Electronic properties

Figure 4 compares the HSE calculated density of states (DOS) with the experimental valence band spectrum. It is obvious that the total as well as the local CuO-projected DOS is

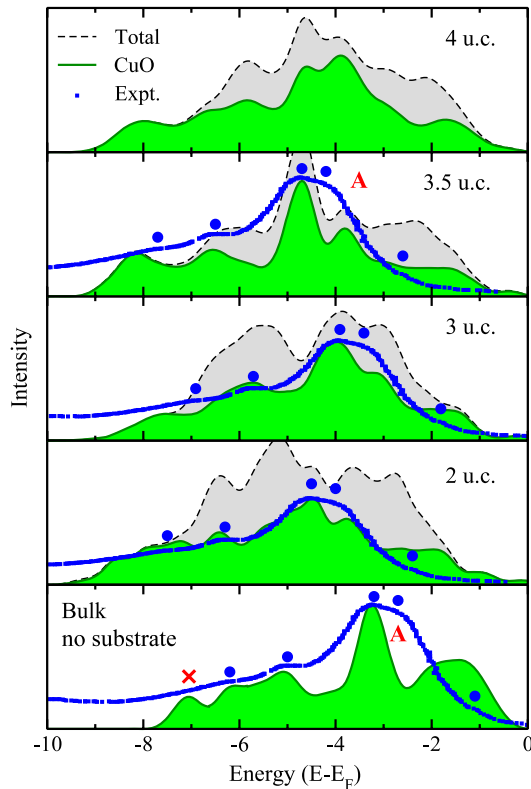


Figure 4. Results of the HSE calculations: total (light gray) and local CuO-projected (dark green) density of states for $(\text{CuO})_n/\text{SrTiO}_3$ ($n = 2, 3, 3.5$ and 4 u.c.) and for the ideal bulk tetragonal TET2 phase [7]. The experimental curve is the valence band spectrum of [2]. The circles and crosses indicate the position of the measured peaks. Energy zero is chosen to be the top of the valence band. The position of the maximum of the experimental spectrum is adjusted to the corresponding maximum of the HSE density of states. The calculated DOS is broadened by a Gaussian of half-width 0.2 eV.

rather sensitive to the thickness of the CuO block. Strikingly, the calculated DOS for the ideal TET2 bulk phase and for the system with a coverage of $n = 3\text{--}3.5$ u.c. agree well with experiment, in quite a contrast to other cases. Though the superstructure with two CuO unit cells already displays some film features which are not reproduced in the calculated bulk spectrum (such as the appearance of the peak A), the overall comparison with the measured curve is not satisfactory due to (i) a much too dominant presence of substrate-related states which weaken the intensity of the main CuO peaks around -4 eV and (ii) the lack of a one-to-one correspondence between theoretical and experimental peaks.

As was discussed for the bulk phase TET2 [7], the agreement with experiment is rather good with the exception of one missing peak (indicated by the letter A in figure 4) and one extra peak (indicated by the cross) in the calculated spectrum. From the DOS for $n = 3\text{--}3.5$ u.c. one clearly deduces that the experimental structure is reproduced very well (especially for 3.5 u.c.) and the overall agreement is improved with respect to the ideal bulk phase. In particular, a new peak (A) is found due to the CuO interface layer (the local CuO DOS has a very distinctive peak at this energy position, which is also reflected in the total DOS) and the spurious peak found in the

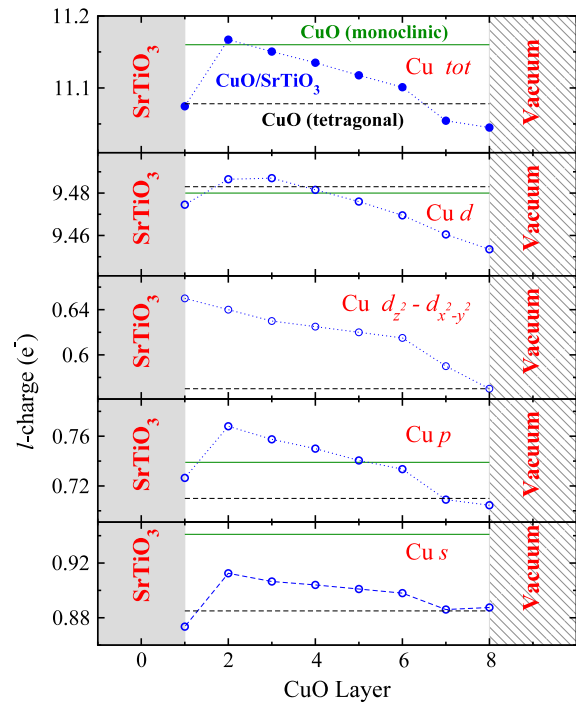


Figure 5. Layer by layer total and l -decomposed and eg -decomposed charge of Cu atoms (sphere radius of 1.16 Å) of $(\text{CuO})_{[3.5]}/\text{SrTiO}_3(100)$ in comparison to the corresponding values for bulk monoclinic CuO (tenorite structure) and the ideal bulk tetragonal TET2 phase [7]. The placements of the SrTiO₃ substrate and the vacuum regions are indicated.

ideal bulk phase disappears. Finally, according to the DOS for $n = 3.5$ u.c. in figure 4 the highest experimental peak, can now be mainly attributed to the substrate, because there the local CuO DOS shows a weak depression, again in line with the observed valence band spectrum.

Figure 5 illustrates the layer dependent change of ionicity of the Cu atoms decomposed over the orbital quantum number l , and the difference between the d_{z^2} and $d_{x^2-y^2}$ occupations. A comparison with the corresponding bulk values for both the monoclinic and tenorite structures is also given. Leaving out the layer distance at the interface there is a uniform trend to be seen: with increasing distance from the interface the Cu charge is reduced by about $0.15e^-$ (i.e. the ionicity of the positive Cu ions increases). This change in charge/valency (topmost panel) is mostly due to the change of p - and d -like charges (second and third panel from the top). For the two Cu layers closest to the surface the total Cu charge is even less than for the tetragonal bulk phase. This increase in valency is directly accompanied by an increase in the interlayer distance, as clearly illustrated by table 1.

In general, an increase in bond length corresponds to an increase in ionicity: typical Cu–O bond lengths involving Cu^{2+} ions are of the order of 2 Å whereas for Cu^{3+} the value might strongly increase up to 2.75 Å (see [17]). In our case, the increase in interlayer distance corresponds to the stretching of the Cu–O bond in the vertical direction (perpendicular to the Cu–O layers). According to table 1 for the topmost layer of the $n = 3.5$ u.c. case the bond length is 2.87 Å, being well in the

bond length regime of Cu^{3+} ionicity. On the other hand, the in-plane bond lengths—due to the SrTiO_3 substrate or the lattice parameter $a = 3.91 \text{ \AA}$ of the optimized bulk TET2 phase—correspond rather well to an ionicity of Cu^{2+} . On the basis of our present surface and recent bulk TET2 study it seems that the Cu atoms appear in two competing concurrent ionic states, depending on the directions of the Cu–O bonds.

Our interpretation of the layer dependent modulation of the Cu electronic population and Cu–O bond lengths suggesting a peculiar coexistence of Cu^{2+} -like and Cu^{3+} -like behavior is in line with the combined DFT and photoelectron spectroscopy study on copper oxide clusters presented by Wang *et al* [18]. By investigating the structural and electronic properties of Cu_2O_x ($x = 1-4$) these authors report a significant change both in the Cu–O bond length (0.05 \AA) and Cu charge ($0.1e^-$) going from Cu_2O_2 (Cu^{2+}) to Cu_2O_3 (Cu^{3+}).

Finalizing the discussion of the electronic structure, the gap of the ideal TET2 phase of 2.7 eV is strongly reduced when CuO is grown on SrTiO_3 : for a coverage of 3.5 u.c. the gap formed by CuO states is reduced to about 0.6 eV , which for the total system (now including substrate states) is even more reduced to about 0.5 eV . The average local magnetic moment for Cu is about $0.75 \mu_B$, which is enhanced in comparison to $0.63 \mu_B$ of the bulk TET2 phase. It should be noted that the present calculation for the surface system $(\text{CuO})_{[n]}/\text{SrTiO}_3(100)$ was made for ferromagnetic ordering (in order to make the HSE calculation feasible) whereas for the bulk TET2 calculation the most stable phase was found for some particular antiferromagnetic ordering [7]. However, in [7], which studied several magnetic orderings, it was found that the local Cu moment is rather insensitive to the specific alignment of spins.

3.3. Summary

To summarize, our first principles study on the $(\text{CuO})_{[n]}/\text{SrTiO}_3(100)$ adsorbate system based on a hybrid density functional theory approach describes and explains the recent experiments [2] rather well, which corroborates our findings and predictions for the ideal bulk (without SrTiO_3 substrate) TET2 phase [7]. The analysis of our calculated results for structural and electronic properties indicates that the physical properties of the Cu–O bonds are rather peculiar. In particular, we find that the enormous structural anisotropy of the Cu–O sublattice—which determines the experimentally observed tetragonal symmetry—can be understood in terms

of a layer dependent evolution of the Cu ionicity which increases progressively towards the surface. Ultimately, the local structural and electronic Cu–O environment appears very frustrated as a result of the coexistence between two concurrent states attributable to in-plane Cu^{2+} -like and out-of-plane Cu^{3+} -like arrangements.

Acknowledgments

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