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First-principles investigation of the role of registry relaxations on stepped Cu(100) surfaces

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The multilayer relaxations of the (311), (511), (711), and (911) Cu surfaces are investigated using the all-electron full-potential linearized augmented plane-wave (FLAPW) method. We found relaxation sequences like $-+-\cdots$, $--+-\cdots$, $---+-\cdots$, and $----+-\cdots$ for (311), (511), (711), and (911), respectively, where the $-$ and $+$ signs indicate contraction and expansion, respectively, of the interlayer spacing. Furthermore, we found that the first-neighbor distances between the Cu atoms in the step edges do not depend on the surface termination, i.e., $d_{\mathrm{SC-CC}}$ is the same for all studied surfaces. Our FLAPW relaxation sequences are in full agreement with quantitative low-energy electron diffraction (LEED) results, as well as with the multilayer relaxation-coordination trend proposed recently. However, large discrepancies are found for the magnitude of the interlayer relaxations, particularly for those involving atoms at the step edges. From our calculations, we suggest that these discrepancies are due to the fact that the atomic displacements parallel to the surface were not take into account in the quantitative analysis of the LEED intensities, which we found to play an important role for a quantitative description of the stepped Cu $(2n-1,\ 11)$ surfaces.

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Surface defects, namely adatoms, vacancies, steps, kinks, etc., play a major role in the morphology and reactivity of solid surfaces.[1] Quantitative low-energy electron diffraction (QLEED) intensity analysis[2–6] and theoretical calculations[7–13] have played a key role in the study of the multilayer relaxations of stepped metal surfaces. However, the quantitative agreement between the LEED and theoretical results is quite poor for many stepped metal surfaces compared with the level of agreement obtained for flat surfaces.[10] Furthermore, for particular systems, even a qualitative agreement between independent first-principles calculations is not obtained for the multilayer relaxation sequence.[8,9] Several examples of those discrepancies are listed below for the particular case of stepped Cu surfaces.

For the Cu(511) surface, first-principles calculations[8,9] and QLEED intensity analysis[5] agree in the sign of the contractions and expansions of the topmost interlayer spacing, however, there are large discrepancies in the magnitude of the interlayer relaxations, e.g., LEED found a contraction of -6.1% for d_{23} (see Fig. 1), while first-principles calculations[8] found -16.4%. Similar results are reported for Cu(711). Spišak[8] and Heid *et al.*[9] found that d_{34} (see Fig. 1) contracts by -21.8% and -14.8%, respectively, while LEED studies[6] reported a contraction of -10%. For Cu(911), Tian and Rahman[7] used the embedded atom method and found a sequence of contractions and expansions like $----+-\cdots$. However, Spišak[8] and Heid *et al.*[9] used first-principles calculations and found $-+--+-\cdots$ and $--+-+-\cdots$, respectively. The $-$ and $+$ signs indicate contraction and expansion, respectively, of the interlayer spacing. To our knowledge, there is no QLEED study for Cu(911), and hence it is unclear which is the true multilayer relaxation sequence of the Cu(911) surface.

To our knowledge, the reasons for such discrepancies are unclear and have not been discussed in the literature. To contribute to the clarification of the above-mentioned discrepancies, as well as to obtain a further understanding of the atomic structure of stepped metal surfaces, we performed a systematic first-principles investigation of the multilayer relaxations of the stepped (311), (511), (711), and (911) Cu surfaces. Our calculations were performed using the density-functional theory[14,15] (DFT) within the generalized gradient approximation.[16] The Kohn-Sham equations are solved using the all-electron full-potential linearized augmented plane-wave (FLAPW) method,[17] as implemented in the FLEUR code.[18] The same FLAPW computational parameters reported in Refs. 10 and 11 were used in the present work.

The (311), (511), (711), and (911) Cu surfaces were modeled using (1×1) unit cells and slabs with a thickness of ≈ 11 Å, which correspond to 11, 17, 23, and 29 layers, respectively. The theoretical equilibrium lattice constant ($a_0=3.63$ Å) was used in our calculations.[10] The lattice parameters of the surface unit cells are summarized in Table I. The integration over the surface Brillouin zone was performed using a Monkhorst-Pack grid,[19] namely (14×8), (14×5), (14×4), and (14×3) for (311), (511), (711), and (911), respectively. Convergence tests similar to those reported in Refs. 10 and 11 were performed for the above-mentioned surfaces.

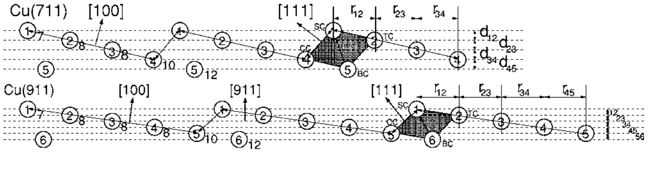

FIG. 1. Schematic side view of the unrelaxed stepped (311), (511), (711), and (911) Cu surfaces. The Cu atoms are indicated by open circles and the numbers inside indicate the atomic layer number (increasing for deeper layers). The numbers outside of the circles indicate the first-neighbor coordination. SC, TC, CC, and BC indicate Cu atoms with step, terrace, corner, and bulk coordination, respectively, i.e., 7, 8, 10, and 12. The interlayer and registry distances are also indicated.

TABLE I. Lattice parameters of the (1×1) surface unit cells. The primitive vectors are $\vec{a}=(\sqrt{2}a_0/2)\vec{i}$, $\vec{b}=-(\sqrt{2}a_0/4)\vec{i}+b_y\vec{j}$, where $\vec{j}$ is perpendicular to the steps. d_0 is the unrelaxed interlayer distance between the two adjacent surface layers parallel to the surface, while r_0 is the unrelaxed registry distance (planar) along of the direction $\vec{j}$. a_0 is the lattice constant.

	Cu(311)	Cu(511)	Cu(711)	Cu(911)
b_y/a_0	$\sqrt{22}/4$	$\sqrt{27}/4$	$\sqrt{51}/4$	$\sqrt{83}/4$
d_0/a_0	$1/\sqrt{11}$	$1/\sqrt{27}$	$1/\sqrt{51}$	$1/\sqrt{83}$
r_0/a_0	$5\sqrt{22}/44$	$5\sqrt{54}/54$	$7\sqrt{102}/102$	$9\sqrt{166}/166$

As indicated in Fig. 1, the stepped Cu$(2n-1,11)$ surfaces consist of a periodic succession of (100) terraces with n atom rows and (111)-oriented steps along the [110] direction. The atomic displacements perpendicular to the surface, $\Delta d_{i,i+1}$, and along the direction perpendicular to the steps (registry), $\Delta r_{i,i+1}$, are given in percent with respect to the ideal clean surfaces, which can be compared directly with QLEED results. That is, $\Delta d_{i,i+1}=100(d_{i,i+1}-d_0)/d_0$ and $\Delta r_{i,i+1}=100(r_{i,i+1}-r_0)/r_0$, respectively, where d_0 and r_0 are the unrelaxed interlayer and registry distances, respectively (see Table I). The multilayer relaxations are summarized in Tables II and III along with published results.

We found that the multilayer relaxation sequences of the (311), (511), (711), and (911) Cu surfaces can be represented by $-+-\cdots$, $--+-\cdots$, $---+-\cdots$, and $----+-\cdots$, respectively. These results provide a strong support for the relaxation-sequence coordination trend reported in Refs. 11 and 12. For example, for a stepped metal surface in which the topmost l surface atomic layers have a first-neighbor coordination smaller than for the bulk crystal (calculated for the ideal unrelaxed surfaces), the topmost $(l-1)$ interlayer spacings, i.e., $(d_{12},\cdots,d_{l-1,l})$, contract compared with the unrelaxed interlayer spacing, while the lth and $(l+1)$th interlayer spacings, i.e., $d_{l,l+1}$ and $d_{l+1,l+2}$, expand and contract, respectively.

Our sequences of contractions and expansions are in full agreement with available QLEED studies.[2,3,5,6] For Cu(311), the amplitude of the relaxations decays with an increase of distance from the surface, i.e., $|\Delta d_{i,i+1}|>|\Delta d_{i+1,i+2}|$ for $\Delta r_{i,i+1}\neq 0\,\forall\, i$, which is in agreement with the QLEED studies.[2,3] A similar trend is not found for Cu(511), Cu(711), and Cu(911). The magnitude of the topmost interlayer spacing is closer to the QLEED result reported in Ref. 3, however, our value for Δd_{23} is larger than the QLEED result. The opposite is found for the LEED results reported in Ref. 2. The agreement with other first-principles calculations[8] is in general good, in particular for the two topmost interlayer spacings.

TABLE II. Interlayer, $\Delta d_{i,i+1}$, relaxations of the stepped Cu$(2n-1,\ 11)$ Cu surfaces.

Surface	Method Reference	Δd_{12} (%)	Δd_{23} (%)	Δd_{34} (%)	Δd_{45} (%)	Δd_{56} (%)	Δd_{67} (%)	Δd_{78} (%)	Δd_{89} (%)	$\Delta d_{9,10}$ (%)	$\Delta d_{10,11}$ (%)	$\Delta d_{11,12}$ (%)	$\Delta d_{12,13}$ (%)	$\Delta d_{13,14}$ (%)
Cu(311)	This work[a]	−12.95	+4.16	−0.60	+0.23	+0.39								
	This work[b]	−13.69	+4.53	−1.05	+0.53	+0.16								
	PAW (Ref. 8)	−15.0	+4.0	−0.6	−1.1	+0.4	−0.7							
	LEED (Ref. 2)	−7.3	+3.7	0.0										
	LEED (Ref. 3)	−11.9	+1.8											
Cu(511)	This work[a]	−10.55	−9.81	+6.17	−4.30	+2.84	+1.33	−2.34	+1.67					
	This work[b]	−11.22	−13.74	+10.60	−5.68	+1.74	+2.19	−2.18	+1.38					
	FLAPW (Ref. 13)	−17.1	−13.8	+11.0	−7.4	+0.6	−0.8	−3.7	+0.7	−1.7				
	PAW (Ref. 8)	−11.1	−16.4	+8.4	−4.6	+2.3	−1.5	+0.2	+0.8	+0.3	−0.6			
	PPPW (Ref. 9)	−9.3	−10.7	+7.2	−2.9	+1.1	+1.7	−1.5	+1.6	−0.5				
	LEED (Ref. 4)	−13.2	−6.1	+5.2	−0.1	+2.7								
	Surface x ray (Ref. 5)	−15.4	+8.1	−1.1	−10.3	+5.4	−0.7	−6.9						
Cu(711)	This work[a]	−11.50	−3.06	−11.54	+7.23	−3.70	−2.08	+5.05	+0.49	−1.16	−1.21	+2.21		
	This work[b]	−10.99	−4.88	−18.99	+16.29	−3.12	−6.38	+4.51	+3.44	−2.44	−1.24	+2.25		
	PAW (Ref. 8)	−9.3	−7.7	−21.8	+14.3	−3.0	−9.1	+5.6	−0.2	−1.1	−3.2	+0.9	−0.6	−0.1
	PPPW (Ref. 9)	−7.3	−1.5	−14.8	+8.0	−1.0	−1.1	+1.4	+1.7	−1.5	−0.40	+2.0	+0.3	
	LEED (Ref. 6)	−13.0	−2.0	−10.0	+7.0	−1.0	−4.0	+7.0						
Cu(911)	This work[a]	−14.32	−1.39	−2.57	−13.85	+7.42	−3.75	−0.86	−2.54	+6.68	+0.05	−1.29	−1.16	−0.65
	This work[b]	−13.81	−2.84	−3.93	−24.03	+20.67	−3.61	−2.51	−6.86	+5.99	+5.10	−1.60	−3.76	−0.71
	PAW (Ref. 8)	−7.4	+0.8	−10.5	−23.3	+25.9	−0.5	−4.1	−10.5	+5.3	+4.7	−1.2	−2.4	−1.3
	PPPW (Ref. 9)	−11.2	−2.2	+0.6	−13.9	+5.4	−1.3	−4.1	+4.5	+3.0	−0.5	−2.5	+1.2	+1.6

[a] Only displacements perpendicular to the surface were included, i.e., $\Delta r_{i,i+1}=0\,\forall\, i$.

[b] Displacements parallel and perpendicular to the surface were included $(\Delta r_{i,i+1}\neq 0)$, i.e., full optimization.

TABLE III. Registry, $\Delta r_{i,i+1}$, relaxations of the stepped Cu($2n-1$, 11) surfaces.

Surface	Method Reference	Δr_{12} (%)	Δr_{23} (%)	Δr_{34} (%)	Δr_{45} (%)	Δr_{56} (%)	Δr_{67} (%)	Δr_{78} (%)	Δr_{89} (%)	$\Delta r_{9,10}$ (%)	$\Delta r_{10,11}$ (%)	$\Delta r_{11,12}$ (%)	$\Delta r_{12,13}$ (%)	$\Delta r_{13,14}$ (%)
Cu(311)	This work[a]	−0.02	−1.32	+1.02	+0.23	+0.25								
	PAW (Ref. 8)	−2.7	+1.9	−0.5	0.0	+0.4	+0.2	0.0						
Cu(511)	This work[a]	−1.46	−0.60	+1.35	+0.57	−0.92	+0.28	−0.28	−0.12					
	FLAPW (Ref. 13)	−0.65	−1.47	+2.17	+0.37	−0.92	+0.18	−0.18	+0.06	+0.01				
	PAW (Ref. 8)	−1.8	−1.7	+1.9	+0.7	−0.8	−0.2	−0.3	−0.1	+0.1	+0.2	0.0		
	PPPW (Ref. 9)	−1.17	−1.21	+0.98	+0.25	−0.31	+0.01	0.00	−0.14					
Cu(711)	This work[a]	−1.30	−1.33	−0.32	+1.43	+0.15	+0.56	−1.05	+0.40	+0.16	−0.55	+0.20		
	PAW (Ref. 8)	−1.6	−1.2	−1.1	+1.7	+0.5	+0.3	−1.0	+0.4	+0.6	−0.8	+0.3	+0.3	−0.1
	PPPW (Ref. 9)	−1.37	−0.32	−0.41	+0.77	+0.23	+0.82	−0.89	−0.01	−0.31	−0.20	+0.11		
Cu(911)	This work[a]	−1.35	−0.82	−0.74	−0.37	+1.58	−0.01	−0.08	+0.56	−1.00	+0.40	+0.09	−0.11	−0.32
	PAW (Ref. 8)	−2.4	−2.1	−1.0	−1.1	+1.9	−0.4	+0.1	0.0	−1.2	+0.2	+0.4	+0.2	−0.8
	PPPW (Ref. 9)	+0.99	−0.40	+0.28	−0.60	+0.38	−0.01	+0.55	+0.16	−0.44	−0.14	+0.40	−0.23	−0.25

[a] Displacements parallel and perpendicular to the surface were included ($\Delta r_{i,i+1} \neq 0$), i.e., full optimization.

Our results for Cu(511) provide extra evidence that the surface x-ray diffraction results reported in Ref. 4 are incorrect. We note that our relaxations are larger than the QLEED results, e.g., $\Delta d_{23}=-13.74\%$ (this work) −6.1% (QLEED). A similar trend is obtained for Cu(711). That is, there is excellent agreement between our DFT and QLEED results for the relaxation sequence, however, there are discrepancies for the magnitude of the relaxations, e.g., $\Delta d_{45}=+16.29\%$ (this work) +7.0% (QLEED). In general, the discrepancies are larger for the interlayer spacings involving atoms at the step edges. To our knowledge, there is no QLEED study for Cu(911).

It has been reported that most of the QLEED intensity analysis for stepped metal surfaces, including those studies performed for Cu(311), Cu(511), and Cu(711), did not take into account the atomic displacements parallel to the surface in the quantitative analysis of the LEED intensities.[2–6] To obtain a clear understanding of the discrepancies between our FLAPW calculations and the QLEED results mentioned above, we performed calculations in which the Cu atoms were not allowed to relax parallel to the surface, i.e., $\Delta r_{i,i+1}=0\,\forall\, i$. These results are also summarized in Table II.

For the case in which the lateral relaxations are not taken into account, we found that the largest interlayer relaxation in absolute value occurs for the topmost interlayer spacing for all studied surfaces. However, we found that the largest relaxation in absolute value for (311), (511), (711), and (911) takes into account registry relaxations that occur for d_{12}, d_{23}, d_{34}, and d_{45}, respectively. Hence our results clearly show that the common assumption that the atomic displacements parallel to the surface do not make an important contribution to the magnitude of the relaxations perpendicular to the surface is not true in general. It might be valid for stepped surfaces with two atom rows in the terrace, e.g., Cu(311), however, this assumption is not valid for stepped Cu surfaces with a larger number of atom rows in the terraces such as Cu(711) and Cu(911) (see Table II). For example, the relaxations of the interlayer spacings involving atoms close to the step edge (see Fig. 1) can increase up to a factor of 3 when registry relaxations are taken into account (see Table II).

It can be seen in Table II that our results obtained without taking into account the registry relaxations are closer to the QLEED results, e.g., for Cu(711) $\Delta d_{45}=+7.23\%$ (this work using $\Delta r_{i,i+1}=0$) +7.0% (QLEED). Therefore, based on our calculations, we suggest that the discrepancies between our DFT calculations and the QLEED results for the above-mentioned stepped Cu surfaces might be due to the fact that the QLEED studies did not take into account the relaxations parallel to the surface, which are important for a quantitative description of the atomic structure of stepped surfaces. Thus the present work provides insights into the discrepancies between DFT and LEED results for the stepped Cu($2n-1$,11) surfaces, which was not explained in previous first-principle studies.[8,9]

The agreement between our calculations and previous first-principles calculations is not good in general. Several discrepancies are found (see Tables II and III). For example, our relaxation sequence for Cu(911) is not in agreement with the results obtained by Spišak[8]($-+--+---++\cdots$) using the PAW method. There is a discrepancy for the sign of the second interlayer spacing for which we obtained a contraction and Spišak reported an expansion. Furthermore, our relaxation sequence is not in agreement with the relaxation sequence obtained by Heid *et al.*[9]($--+-+--++-\cdots$), also using first-principle calculations. We found large discrepancies in the magnitude of the multilayer relaxations between our results and those reported in Ref. 9, in particular for Δd_{34}, Δd_{45}, and Δd_{56}. Heid *et al.*[9] reported that the interlayer relaxations of the inner interlayer spacings of Cu(911) should be taken with caution, as the convergence criteria for this particular surface was not as good as for Cu(511) and Cu(711).

To obtain a further understanding of the multilayer relaxation phenomenon, we analyzed the first-neighbor distances

TABLE IV. First-neighbor distances of the atoms involved in the step edges of the stepped Cu($2n-1$, 11) surfaces. SC, TC, CC, and BC indicates Cu atoms with step, terrace, corner, and bulk coordination (see Fig. 1). The first-neighbor distance in the bulk Cu is 2.57 Å.

	$d_{\text{SC–TC}}$ (Å)	$d_{\text{SC–CC}}$ (Å)	$d_{\text{SC–BC}}$ (Å)	$d_{\text{TC–BC}}$ (Å)	$d_{\text{CC–BC}}$ (Å)
Cu(311)	2.51	2.51	2.49	2.57	2.61
Cu(511)	2.51	2.51	2.48	2.54	2.62
Cu(711)	2.52	2.51	2.48	2.55	2.62
Cu(911)	2.52	2.51	2.48	2.55	2.62

of the atoms involved in the step edges, which are indicated by SC (7), TC (8), CC (10), and BC (12) in Fig. 1. The numbers in parentheses indicate the first-neighbor coordination. In Table IV we summarize the first-neighbor distances of the fully relaxed stepped Cu surfaces. Our calculations indicate that the first-neighbor distances of the Cu atoms in the step edges do not depend on the termination of the studied Cu($2n-1$, 11) surfaces, however, it depends on the first-neighbors coordination. For example, the first-neighbor distance between the step (SC) and corner (CC) atoms is 2.51 Å for all studied surfaces, while in the bulk Cu is 2.57 Å, i.e., a contraction of 2.33%. An expansion of 1.95% is found for the first-neighbor distance between the corner and bulk atoms, i.e., $d_{\text{CC–BC}}$.

In summary, using the FLAPW method we found a multilayer relaxation sequence like $-+-\cdots$, $--+-\cdots$, $---+-\cdots$, and $----+-\cdots$ for the (311), (511), (711), and (911) Cu surfaces, respectively. These results provide clear support for the coordination-relaxation trend recently reported.[11,12] We found that the registry relaxations change the magnitude of the interlayer relaxations by a large value for the interlayer spacings involving atoms close to the step edges, which increases with an increase in the number of atom rows in the terraces. As a consequence of the registry relaxations, we found that the largest interlayer relaxations in absolute value for (311), (511), (711), and (911) occur for the interlayer spacings indicated by d_{12}, d_{23}, d_{34}, and d_{45}, respectively (see Fig. 1). Furthermore, we found that the first-neighbor distances involving Cu atoms in step edges, e.g., SC, TC, CC, and BC (see Fig. 1) do not depend on the surface termination, i.e., $d_{\text{SC–CC}}$ is the same for all studied surfaces. For (311), (511), and (711) Cu surfaces, for which QLEED studies are available,[2,3,6,5] our multilayer relaxation sequences are in perfect agreement with the QLEED results. However, several discrepancies are found for the magnitude of the interlayer relaxations, particularly for those involving atoms at the step edges. From the analysis of our calculations, we concluded that these discrepancies are due to the fact that the reported LEED results did not take into account the registry relaxations, which we show to be important for a quantitative description of the atomic structure of stepped Cu surfaces.

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