Rule for Structures of Open Metal Surfaces

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We present a clear and simple rule for determining the relaxation sequences on open (stepped, vicinal, or high-Miller-index) metal surfaces. At the bulk-truncated configuration of a surface, a *surface slab* is defined where the coordination of atoms is reduced from the bulk. The rule predicts that the interlayer spacings within this slab contract, while the interlayer spacing between this slab and the substrate expands. By first-principles calculations, we show that this rule is obeyed on all open Cu surfaces with interlayer spacings down to about 0.5 Å. We also illustrate a direct relation of the relaxation sequences to the charge redistribution on these surfaces, which is demonstrated to be driving the multilayer relaxations. The applicability of the rule can be extended to other fcc and bcc metals, including unreconstructed and missing-row surfaces.

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Cutting a crystal at a small angle away from a low-Miller-index plane creates two vicinal (or high-Miller-index) surfaces. Such surfaces exhibit atomic terraces orienting to the low-index plane, and the terraces are separated by either straight or kinked atomic steps, for which they are also described as *stepped* surfaces. Despite their high surface free energy, stepped metal surfaces are found to be stable when clean with respect to reconstruction up to near the melting point [1,2]. The step and kink sites are known to play key roles in many physical and chemical processes, such as phase changes, heterogeneous catalysis and crystal growth [1]. Elucidating the atomic structures of the stepped surfaces is, therefore, important because the structural information of a surface is essential for studying its other properties.

Many attempts to understand the mechanism of ionic relaxations on single crystal metal surfaces have been made in the past few decades. Based on experimental results, the topmost atomic layer on low-index metal surfaces can relax both inwards and outwards. Extensive theoretical studies have focused on formulating a general rule on top layer relaxations experimentally observed [3–5]. As made clear by Feibelman [5], a physical picture and a chemical picture exist to describe the top layer relaxations. The former originated from the theory of Finnis and Heine [3] using Smoluchowski's concept of charge smoothing [6]. The latter, put forward by Feibelman, is based on the promotion-hybridization idea [5]. In contrast to low-index surfaces, all high-index metal surfaces experimentally studied exhibit, without exception, a contraction in the first interlayer spacing. Another feature of high-index metal surfaces is that *multilayer* relaxations are usually more significant. Recently, the multilayer relaxations on high-index metal surfaces have become a new focus of the theoretical studies [7–9]. Empirical rules for predicting *a priori* the relaxation sequence have been deduced from existing experimental and theoretical results [10,11]. However, the validity of these rules is still subject to systematic tests. More importantly, why certain high-index metal surfaces follow a specific relaxation sequence is still an open question. In this Letter, we first show that the relaxation sequences on all open Cu surfaces with their interlayer spacings down to about 0.5 Å obey our proposed rule. Second, we quantitatively illustrate how the relaxation sequence is related to the change in the coordination of the atoms near the surface and how the charge redistribution drives the multilayer relaxations.

We propose that the relaxation sequence on open metal surfaces [12] follows the rule: At bulk-truncated configuration, define a *surface slab* in which the nearest neighbors of all atoms are fewer than those in the bulk; in the process of relaxation, the interlayer spacing between each pair of atomic layers within this slab contracts, while the spacing between this slab and the substrate expands [11]. In Table I, we list the open Cu surfaces ranked by the interlayer spacing which serves as a measure of openness. We take these surfaces as the benchmark to evaluate the proposed rule. The interlayer spacings of the surfaces in Table I at their bulk-truncated configurations can be obtained by $d_{\mathrm{bulk}} = a_0/(\delta\sqrt{h^2 + k^2 + l^2})$, where a_0 is the lattice constant, (hkl) is the Miller indices, and δ equals two if there is at least one even number in the indices and one otherwise. Table I also shows the nearest neighbor sequences, from which one can determine the number of atomic layers in the *surface slab* (N_s), and the relaxation sequences of these surfaces, which are predicted from the proposed rule. A nearest neighbor sequence $(n_1, n_2, n_3, 12, \ldots)$ means that, at bulk-truncated configuration, the atoms in the first layer have n_1 nearest neighbors, the second layer n_2, the third n_3, and, from the fourth layer downwards, the number recovers to 12, i.e., the value in the bulk fcc structure. For a surface having a nearest neighbor sequence of $(n_1, n_2, n_3, 12, \ldots)$, the *surface slab* consists of three layers and, according to the rule, the interlayer spacings within this slab, i.e., d_{12} and

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TABLE I. Open Cu surfaces and their relaxation sequences predicted from the nearest neighbor sequences according to the proposed rule. N_s is the number of atomic layers in the surface slab.

Surface	Nearest neighbor sequence	N_s	Relaxation sequence
Cu(110)	(7, 11, 12, ...)	2	$- + \cdots$
Cu(311)	(7, 10, 12, ...)	2	$- + \cdots$
Cu(331)	(7, 9, 11, 12, ...)	3	$- - + \cdots$
Cu(210)	(6, 9, 11, 12, ...)	3	$- - + \cdots$
Cu(211)	(7, 9, 10, 12, ...)	3	$- - + \cdots$
Cu(511)	(7, 8, 10, 12, ...)	3	$- - + \cdots$
Cu(531)	(6, 8, 10, 11, 12, ...)	4	$- - - + \cdots$
Cu(221)	(7, 9, 9, 11, 12, ...)	4	$- - - + \cdots$
Cu(310)	(6, 8, 9, 11, 12, ...)	4	$- - - + \cdots$
Cu(533)	(7, 9, 9, 10, 12, ...)	4	$- - - + \cdots$
Cu(711)	(7, 8, 8, 10, 12, ...)	4	$- - - + \cdots$
Cu(551)	(7, 7, 9, 11, 11, 12, ...)	5	$- - - - + \cdots$
Cu(320)	(6, 7, 9, 11, 11, 12, ...)	5	$- - - - + \cdots$

d_{23}, contract (denoted by the "$-$" sign), while the spacing between this slab and the substrate, i.e., d_{34}, expands (denoted by the "$+$" sign).

It is worth noting that Cu(711) and Cu(551) have the same interlayer spacing and the same surface unit cell, but different stacking, i.e., different interlayer vector. This different stacking results in the different nearest neighbor sequence, i.e., (7, 8, 8, 10, 12, ...) for (711) and (7, 7, 9, 11, 11, 12, ...) for (551). This means that the surface slab of Cu(711) consists of four atomic layers while Cu(551) consists of five. Hence, different relaxation sequences are predicted on the two surfaces.

We conducted first-principles calculations to evaluate the proposed rule. Our calculations are based on the density functional theory and the generalized gradient approximation to the exchange-correlation functional [13]. Plane waves are employed as the basis functions and the interactions between the ion cores and valence electrons are described by the Vanderbilt-type ultrasoft pseudopotential [14,15]. The surfaces are simulated by symmetric atomic slabs separated by vacuum layers. The ionic relaxations are guided by the calculated Hellmann-Feynman forces. The Vienna *ab initio* simulation package (VASP) [16] is adopted to carry out the calculations throughout this work.

The calculated multilayer relaxations of open Cu surfaces are listed in Table II. Since the lateral relaxations of all these surfaces are relatively small (about 2% or less), only the vertical relaxations of the interlayer spacings are given. Comparing Table II with Table I, it can be seen that the relaxation sequences on all the 13 surfaces comply with the proposed rule, i.e., $N_s - 1$ contractions followed by an expansion. Note that, as expected, Cu(711) and Cu(551) exhibit different relaxation sequences although they have the same interlayer spacing and surface unit cell.

Some of the relaxations in Table II, namely Δd_{34} on Cu(531), Δd_{23} on Cu(533), and Δd_{45} on Cu(551), are too small to be said unambiguously as having a contraction. Nevertheless, it can be noticed that the relaxation sequences are actually characterized by the positions where the expansions take place. From this point of view, there is no ambiguity since the first expansions on all the 13 surfaces are significant.

Next, the relaxation rule proposed will be understood from the charge redistribution on these surfaces, i.e., the physical picture [3]. For this purpose, we calculated the electric charge within a sphere centered at the nuclei of all atoms in the simulating slabs. The sphere radius, 1.42 Å, is chosen to be the Wigner-Seitz radius, which makes the volume of the sphere equal to that of the Wigner-Seitz cell. For comparison, the radius (1.29 Å) that makes the spheres touch each other was also tested. The same trend as given below has been observed. All calculations were done on slabs at bulk-truncated configurations. This also allows the study of the initial forces applied on the atoms when the surface is created. The plots of the number of charges within a sphere against the layer depth are given in Fig. 1.

In Fig. 1, the 13 surfaces are divided into four groups according to their relaxation sequences (or N_s). We have two observations from this figure. First, the charge per atomic sphere decreases considerably for the atoms near

TABLE II. Multilayer relaxations of open Cu surfaces from first-principles calculations.

	(110)	(311)	(331)	(210)	(211)	(511)	(531)	(221)	(310)	(533)	(711)	(551)	(320)
Δd_{12} (%)	−9.9	−13.7	−13.6	−16.2	−13.1	−10.4	−16.7	−14.3	−11.8	−15.9	−12.3	−7.5	−11.5
Δd_{23} (%)	+4.4	+4.5	−5.1	−5.6	−9.9	−13.6	−12.3	−6.8	−15.4	−2.2	−4.1	−18.0	−16.5
Δd_{34} (%)	−1.0	−0.4	+8.0	+6.9	+9.5	+9.4	−1.3	−5.9	−4.1	−13.0	−18.0	−5.5	−6.3
Δd_{45} (%)	+0.7	−0.2	−2.5	−0.5	−1.6	−3.8	+8.6	+12.7	+10.2	+14.6	+15.7	−1.3	−3.9
Δd_{56} (%)	+0.1	+0.9	−0.2	−0.6	−1.0	+2.0	−0.3	−4.6	−2.0	−0.4	−3.1	+13.9	+13.7
Δd_{67} (%)			+0.2	+0.3	+0.8	−0.3	−1.0	−1.4	−0.8	−4.4	−4.6	−1.8	−1.4
Δd_{78} (%)							−1.0	+1.8	+0.2	−0.4	+3.4	−3.3	−1.4
Δd_{89} (%)												−1.9	−0.5

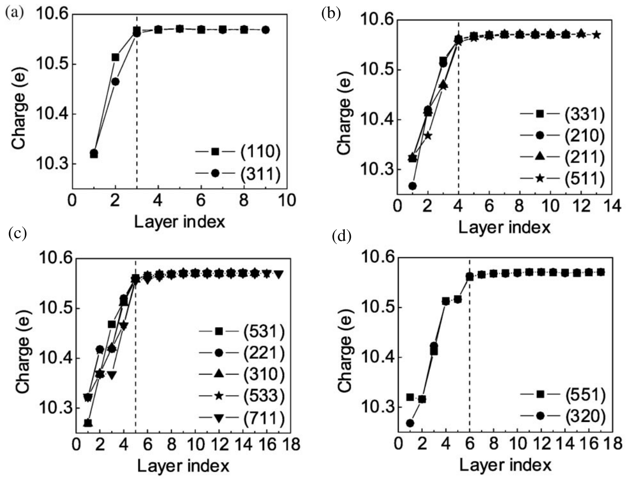

FIG. 1. Plots of charge per atomic sphere against the layer depth on open Cu surfaces at bulk-truncated configurations. The surfaces are grouped according to N_s as given in Table I.

TABLE III. Initial forces (component perpendicular to the surface) on the atoms calculated at the bulk-truncated configurations. f_n denotes the force on the atoms in the nth layer. The unit used is eV/Å.

Surface	f_1	f_2	f_3	f_4	f_5	f_6
Cu(110)	+0.41	−0.38	−0.04			
Cu(311)	+0.46	−0.27	−0.23			
Cu(331)	+0.45	−0.06	−0.32	−0.06		
Cu(210)	+0.60	−0.08	−0.41	−0.19		
Cu(211)	+0.45	+0.01	−0.23	−0.22		
Cu(511)	+0.45	+0.16	−0.26	−0.28		
Cu(531)	+0.64	+0.14	−0.27	−0.34	−0.23	
Cu(221)	+0.44	+0.02	−0.01	−0.31	−0.07	
Cu(310)	+0.58	+0.19	−0.07	−0.41	−0.27	
Cu(533)	+0.40	−0.01	+0.04	−0.21	−0.15	
Cu(711)	+0.41	+0.15	+0.15	−0.25	−0.25	
Cu(551)	+0.42	+0.38	−0.07	−0.35	−0.31	−0.00
Cu(320)	+0.60	+0.38	−0.07	−0.43	−0.34	−0.17

the surface. This charge redistribution can be understood in the light of Smoluchowski's concept of charge smoothing. According to this concept, at metal surfaces, the nearly free electrons tend to spread towards regions of low charge density and smooth the corrugation formed by the ion cores in order to lower the kinetic energy. Second, the number of layers in which the charge per atomic sphere decreases, coincides with N_s given in Table I, as guided by the dashed lines in Fig. 1. This indicates a direct relation of the relaxation sequence to the charge smoothing effect. In the process of charge smoothing, the movement of electrons induces ionic relaxations. For more open surfaces, electrons from the deeper layers contribute to the smoothing; hence more layers relax.

The effect of charge redistribution can be quantitatively seen from the calculated initial forces on the atoms at bulk-truncated configurations as listed in Table III, where a "+" sign denotes a force pointing into the surface and "−" out of the surface. From this table, it can be seen that, for all the surfaces, the topmost layer feels an inward force, which is always of the largest magnitude, and the N_sth layer feels an outward force, while the forces on the layers in between are not definite. This means that the two sides of the surface slab feel compression forces, which lead to contractions within the surface slab. If the magnitude of f_{N_s+1} is always smaller than f_{N_s}, the expansion of the spacing between the surface slab and the substrate can also be explained readily. However, we found $|f_4| > |f_3|$ on Cu(511) and $|f_5| \approx |f_4|$ on Cu(711). This implies that dynamically monitoring the forces in the process of the simulated relaxation, instead of solely studying the initial forces, is necessary in order to explain the expansion. Figure 2 illustrates the force changes in simulated relaxations on Cu(511) and Cu(711). It can be seen that all forces vanish in a monotonic way except for f_{N_s+1}, which changes from negative to positive after two relaxation steps. This illustration using Cu(511) and Cu(711) is representative of all other surfaces studied and is independent of the algorithm (conjugate gradient and variable metric methods are tested) used in the relaxation. It is the opposite sign of f_{N_s} and f_{N_s+1} that is responsible for the expansion.

It is noted that the proposed rule is also consistent with the bond-order–bond-length relation, i.e., the chemical picture [5]. Based on this relation, when the number of neighbors of an atom is reduced, the bonds become stronger; hence the bond length is shortened. In the surface slab, all atoms have fewer nearest neighbors than those in the bulk. Hence, the interlayer spacings (the bond length) within it become shorter. If considering the surface slab as a whole with respect to the substrate, the top layers of the substrate actually see more neighbors due to the contractions in the surface slab. This results in a weakened bonding between the surface slab and the substrate and may explain the expansion between them.

Finally, we postulate that the proposed rule may also apply to metals of bcc structure and even reconstructed surfaces. In Table IV, we list the relaxation sequences on all open Fe surfaces studied by quantitative low-energy

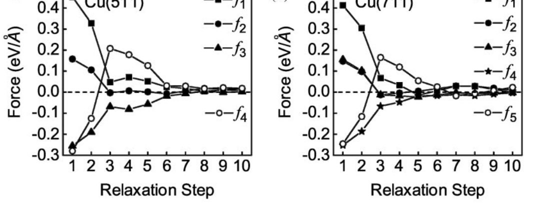

FIG. 2. Force changes in simulated relaxations on Cu(511) and Cu(711).

TABLE IV. Testing of the proposed rule on open Fe surfaces.

Surface	Nearest neighbor sequence	N_s	Relaxation sequence	Reference
Fe(211)	(5, 7, 8, ...)	2	$- + \cdots$	[17]
Fe(310)	(4, 6, 8, ...)	2	$- + \cdots$	[18]
Fe(111)	(4, 7, 7, 8, ...)	3	$- - + \cdots$	[19]
Fe(210)	(4, 6, 6, 8, ...)	3	$- - + \cdots$	[20]

electron diffraction analysis [17–20]. It can be seen that these relaxation sequences are consistent with the proposed rule. For missing-row (110)-(1 × 2) and (311)-(1 × 2) surfaces of fcc metals, the surface slabs consist of one more atomic layer than those in the unreconstructed configurations due to the missing rows. The expansions are, therefore, expected to be delayed to one layer deeper, i.e., to Δd_{34}. Indeed, this is found to be true for Pt by first-principles calculations [21]. Moreover, it has been shown that the surfaces of the same orientation, but of different metals, tend to have the same relaxation sequence [22]. Based on the evidence above, it is expected that the proposed rule is universally applicable to open metal surfaces.

In summary, an empirical rule for predicting the multilayer relaxation sequences on open metal surfaces has been proposed and systematically evaluated on a series of open Cu surfaces by first-principles calculations. It has been shown that the relaxation sequence on all these surfaces obey the rule. This rule can be understood using both physical and chemical arguments, which warrants an extension of this rule in the understanding of all open metal surfaces.

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