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Stability of the Missing-Row Reconstruction on fcc (110) Transition-Metal Surfaces

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Analysis of the results from first-principles calculations produces physical insights on the stability of the missing-row reconstruction on the Au(110) surface. The absence of the missing-row reconstruction on the (110) faces of other fcc metals and the possibility to induce the reconstruction by charge transfer are also explained.

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Reconstruction of crystal surfaces indicates a change in the interatomic forces in the different environment at the surface. Understanding the physical mechanism driving the reconstruction can help us understand the properties of the surface and also give information about its interaction with adsorbed atoms. One of the more intriguing cases is the missing-row reconstruction (Fig. 1) which occurs on the (1×2) (110) surface of the fcc transition metals Au, Pt, and Ir. The structures of these surfaces have been the subject of intensive experimental and theoretical studies.[1-18] Although the geometry of the reconstruction is well understood, the basic mechanism stabilizing such a geometry is not clear. The fact that the reconstruction occurs for elements with different numbers of valence electrons indicates that it cannot be due to a Fermi-surface effect. More intriguing is the fact that the reconstruction does not occur on the clean (110) surfaces of the corresponding isoelectronic $4d$ elements Ag, Pd, and Rh but can be induced to occur by the deposition of a small fraction of a monolayer of alkali metal.[19-23]

To elucidate the basic mechanism stabilizing the missing-row reconstruction, we have analyzed the results from our recent first-principles pseudopotential density-functional calculations for the Au(110) surface.[24] In these calculations, the surface is represented by periodic slabs seven atomic layers thick and separated by three to five layers of vacuum. Calculations were performed for both the (1×1) bulk-truncation geometry and (1×2) reconstructed missing-row model. Our results show that the surface energy for the missing-row geometry is lower than that of the (1×1) surface (Table I). Using forces calculated by the Hellmann-Feynman theorem, we determined the relaxed equilibrium geometry for both the (1×1) and the (1×2) surfaces. We find that the relaxation energy again favors the (1×2) surface (Table I). The equilibrium geometry determined from our calculations indicates a contraction of the first interlayer spacing for the missing-row surface with lateral displacements in the second layer and a buckling of the third layer (see Fig. 1), in good agreement with results from LEED[5] and ion-scattering experiments.[10]

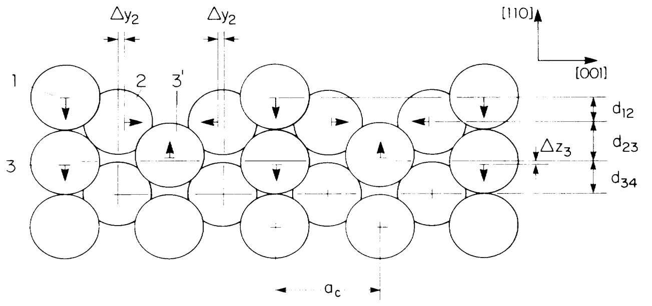

FIG. 1. Schematic drawing of the geometry of the missing-row structure for the (1×2) reconstructed Au(110) surface.

Experimentally, the missing-row reconstruction is stable on the (110) face of the fcc $5d$ metals Au, Pt, and Ir but unstable for the corresponding $4d$ metals—Rh, Pd, and Ag. This difference in behavior suggests the importance of the d electrons in stabilizing the missing-row reconstruction. The $5d$ electronic wave functions are more delocalized than the $4d$ wave functions leading to larger hybridization for the $5d$ band. This results in a stronger contribution of the d electrons to the bonding of

TABLE I. Surface energy for the Au(110) surface (in joules per square meter).

Unrelaxed (1×1)	1.43
Unrelaxed (1×2)	1.40
Relaxed (1×1)	1.38
Relaxed (1×2)	1.31
Expt. (Ref. 25)	1.5

TABLE II. Structural properties of bulk Au and Ag. The calculated values are for Au and a modified Au pseudopotential with the *d* attraction increased by 5%. The experimental values are from Ref. 27.

	Expt.		Calc.	
	Ag	Au	Au	Au(mod)
Cohesive energy (eV)	2.95	3.81	3.45	2.42
Lattice constant (Å)	4.09	4.08	4.10	4.15
Bulk modulus (Mb)	1.01	1.73	1.71	1.25

the crystal[26] which shows up in the bulk properties—the 5*d* metals have substantially bigger cohesive energies and bulk moduli (Table II). The lattice constants of Au and Ag, of Pt and Pd, and of Rh and Ir are very close to each other (within 1%; in fact, Au has a slightly smaller lattice constant than Ag) although the 5*d* metals have a bigger core radius. This is another indication that the bonding is stronger in the 5*d* metals than in the 4*d* metals. To demonstrate the importance of the *d* electrons we have repeated our calculations using a pseudopotential in which the $l=2$ part of the pseudopotential is deepened so that the *d* states become more localized. With a 5% increase in *d* attraction, we can reduce the cohesive energy by 1 eV, expand the lattice parameter by 1.2% and produce a modified Au with bulk modulus which lies between Au and Ag (Table II). When we repeat the surface-energy calculations for the modified pseudopotential, we find that the relative stability of the missing row and bulk-truncation geometry has been reversed.

To obtain a clear microscopic picture, we have listed in Table III the contributions to the surface energies of the (1×1) and (1×2) surfaces coming from the electronic kinetic energy, exchange-correlation energy, and electrostatic potential energy. The missing-row surface is stabilized over the bulk-truncated surface by having a smaller electronic kinetic energy.

There are two factors contributing to the surface kinetic energy of the electrons. The first is the breaking of surface *d* bonds which leads to an increase in the surface kinetic energy with an accompanying decrease in potential energy as the *d* electrons relax back into the core at the surface. This disruption of the *d* bonds at the surface is demonstrated in Fig. 2 which shows the local density of *d* states on the surface atoms [the top two layers for the (1×1) geometry and atoms 1,2,3′ for the (1×2) geometry as in Fig. 1]. The *d* states are narrowed for both the (1×1) and the (1×2) surfaces and the center of gravity of the *d* states is shifted upward relative to the bulk density of *d* electronic states indicating a decrease in the hybridization of the *d* electrons and hence a decrease in the *d* bonding at the surface.

TABLE III. Various contributions to the surface energy (in joules per square meter).

	Unrelaxed			Relaxed
	(1×1)	(1×2)	$(1\times 2)-(1\times 1)$	(1×2)
Kinetic energy	2.21	1.36	−0.85	0.11
Exchange-correlation	3.39	3.50	0.10	3.52
Potential energy	−4.18	−3.47	0.71	−2.34

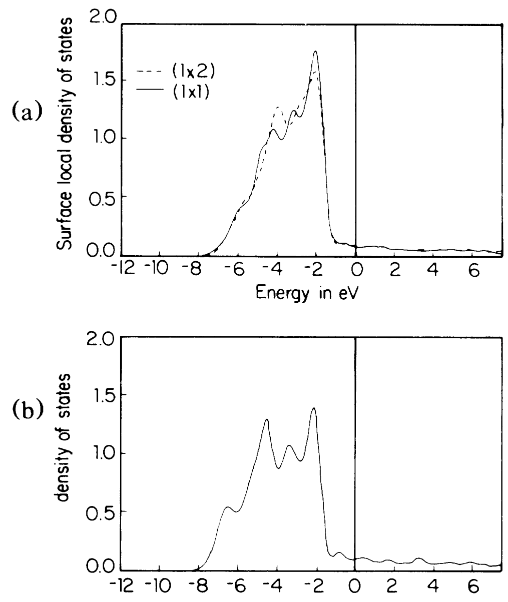

FIG. 2. (a) Local density of states of *d* electrons at Au(110) surfaces obtained by weighting the electronic density of states with the amount of surface local *d*-like orbitals contained in the wave function of each state. The zero of the energy scale represent the Fermi level. (b) Density of *d* states in bulk.

The second factor which contributes to the surface kinetic energy (and the most important factor which affects the relative stability of the two surfaces) is the lowering of the kinetic energy of the *s* and *p* electrons at the surface. This is most evident in plots of the average kinetic energy per state as a function of band energy for bulk Au and the (1×1) and (1×2) surfaces (Fig. 3). The kinetic energy is lowered for electrons near the Fermi level.[28] This behavior is characteristic of delocalized electrons because the electronic wave functions for these electrons become more spread out at the surface. In fact, for a jellium surface, this decrease in surface kinetic energy causes the surface energy to become negative for high electron concentrations ($r_s < 2.3$).[29] This is because kinetic energy varies as r_s^{-2} and dominates the surface energy at high electron densities.

Of course, a system with negative surface energy is unstable and cannot be observed physically. However,

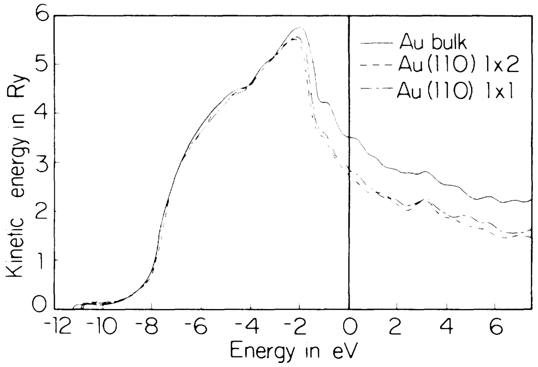

FIG. 3. Average electronic kinetic energy per state as a function of band energy.

for the $5d$ metals, the surface energy can be heuristically separated into a part coming from the delocalized electrons and a part from the d electrons. In this way, the delocalized electrons can be compressed to densities higher than the jellium instability limit without the total surface energy becoming negative. The surface is stabilized by the bonding of the d electrons—the energy required to break the d bonds keeps the surface energy positive. However, if the system can increase its area without breaking extra d bonds it would do so with a lowering of the total surface energy. The missing-row geometry provides a solution to the problem of minimizing the kinetic energy of the s electrons while retaining as much of the bulk cohesion as possible—the (1×2) surface has the same number of broken nearest-neighbor bonds as the (1×1) surface but provides more room for the electrons to spread out and lower their kinetic energies.

We have also performed calculations for modified lattice constants and observed a direct correlation of the stability of the missing-row reconstruction at the surface with the average interstitial charge density in the bulk.[30] The crossover point corresponds to an interstitial r_s roughly equal to 2. The interstitial charge densities of bulk Au and Ag lie on different sides of the crossover; thus the missing-row reconstruction is stable on the Au(110) surface but not on the Ag(110) surface. The difference in behavior between the $5d$ and $4d$ metals comes from the stronger d bonding in the $5d$ metals (as mentioned above), leading to a bigger contraction of the lattice and causing a bigger compression of the sp electrons in the bulk.[31] Therefore it may be possible to stabilize the missing-row reconstruction on fcc (110) surfaces by increasing the surface s-electron concentration —for example, by deposition of submonolayers of alkali metals.[19-23]

In conclusion, we have shown that the participation of d electrons in bonding in the solid and the decrease of the kinetic energy of delocalized electrons at the surface play decisive roles in the stabilization of the missing-row geometry on fcc transition-metal (110) surfaces. Our calculations also give insight into the stable surface geometry for these surfaces under conditions of surface charging and when the surface layer is expanded or contracted.

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[26] The contribution of the d electrons to the bonding comes from two sources: One is the $d-d$ bonding due to overlap of d electrons on different atoms, the other is the hybridization of the d electrons with the sp electrons which leads to a lowering of the energy of the occupied d states.

[27] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1986), 6th ed., Tables 1.3, 3.1, and 3.3.

[28] The increase in surface kinetic energy of the d electrons shows up as a shift of the surface d states towards the upper part of the d band where the kinetic energy is highest.

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[30] This result has interesting implications for the stability of the missing-row reconstruction on epitaxial layers of transition metals where the lattice constants might be different from the bulk.

[31] There is also more compression of the sp electrons in the $5d$ metals because the delocalized electrons have to be orthogonal to the d states at each site and the $5d$ orbitals, being more extended, exclude more space.