

SIMPLE CRITERION FOR THE RECONSTRUCTION OF CLEAN AND ADSORBATE-COVERED METAL SURFACES

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A simple criterion is introduced which allows one to estimate the tendency of metal surfaces to reconstruct. At clean surfaces changes in surface tension γ^0 are estimated from a simple formula based on a tight-binding hamiltonian, yielding surface multilayer relaxations as by-product. The effect of adsorbates to induce or to suppress reconstruction is described by adsorbate-dependent modifications of γ^0 . The calculation successfully describes reconstruction at clean and adsorbate-covered (110) and (100) surfaces of Ir, Pt and Au.

Recently it has been shown that many surface properties such as surface energies and heats of adsorption show a universal behaviour which can be related to their bulk properties [1,2]. The objective of this letter is to show that in many cases similar behaviour is also expected for the surface reconstruction. This transformation is caused by the decrease in the surface free energy upon changes of the surface Wigner-Seitz cell. At the extensively studied bcc(100) surfaces details in the electronic structure have been made responsible [3] for the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction of W and the absence of such reconstruction in the neighbouring Ta. On the other hand, similarities in the reconstruction behaviour observed at the (100) and (110) surfaces of Ir, Pt and Au [4-7] suggest a general trend originating in the surface geometry rather than details of the electronic structure to be responsible for the equilibrium structure of these surfaces. While e.g. for the fcc(100)-(1x1) → (hex) transition the decrease in the surface tension γ^0 upon close-packing the topmost layer seems to be the driving force for reconstruction, this energy gain will generally be counter-acted by the energy due to the misregistry between the topmost and underlying layers. Similar forces drive also the commensurate-incommensurate transition during the interface formation between two different metals.

At surfaces with different atom types, the surface tension γ (per surface atom) is defined by

$$\gamma = \frac{1}{N_S} \sum_{i=1}^{N_{\text{tot}}} [E_{\text{coh}}(\text{bulk}) - E_{\text{coh}}(i)] , \quad (1)$$

as the energy in unsaturated bonds. The summation is performed over all N_{tot} crystal atoms (the number of surface atoms N_S is related to the surface area considered), and E_{coh} is the binding energy of atoms at different sites. At clean surfaces the heat of reconstruction E_R^0 is the gain in surface tension between the unreconstructed and reconstructed surface,

$$E_R^0 = \gamma_R^0 - \gamma_U^0 . \quad (2)$$

In presence of adsorbates E_R^0 has to be modified by an adsorbate term

$$\Delta\gamma^{\text{ads}} = \theta(E_{\text{ads,R}} - E_{\text{ads,U}}) , \quad (3)$$

which considers differences in the heat of adsorption E_{ads} between the reconstructed and unreconstructed surface and the adsorbate coverage θ . Hence, the general criterion for reconstruction at $T = 0$ K is

$$E_R = (\gamma_R^0 - \gamma_U^0) - \theta(E_{\text{ads,R}} - E_{\text{ads,U}}) < 0 . \quad (4)$$

For systems where E_R^0 and $\Delta\gamma^{\text{ads}}$ are known eq. (4) also contains a quantitative description of the adsorbate induced or suppressed reconstruction.

In order to obtain E_R^0 from eqs. (1) and (2) at dif-

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ferent surfaces, we calculate $E_{\text{coh}}(i)$ by assuming a single-band solid, local charge neutrality and the same band shape (except for a rescaled band-width) at the surface as in the bulk [8], and include repulsive Born–Mayer interactions [2], as [8]

$$E_{\text{coh}}(i) = \frac{E_{\text{coh}}(\text{bulk})}{(1 - q/p)Z_{\text{bulk}}^{1/2}} \times \left[\left(\sum_j' \exp[-2q(r_{ij}/r_0 - 1)] \right)^{1/2} \times Z_{\text{bulk}}^{-1/2} \frac{q}{p} \sum_j' \exp[-p(r_{ij}/r_0 - 1)] \right]. \quad (5)$$

Here, $r_{ij}(r_0)$ are the nearest-neighbor (equilibrium) distances, Z_{bulk} is the bulk coordination number and the summations extend over the nearest neighbors of i . The parameters q and p describe the distance dependence of the hopping integrals and the repulsive interactions, respectively, and are related to bulk elastic properties. For a given surface structure p and q only influence the multilayer relaxations, which are obtained from minimizing γ with respect to $\{r_{ij}\}$. For constant p and q , $E_{\text{coh}}(i)$ and hence γ scales with $E_{\text{coh}}(\text{bulk})$. Note that eq. (5) is especially expected to reproduce correctly energy differences due to local rearrangements at surfaces which occur e.g. during reconstruction.

We apply this equation first to obtain the surface tension γ^0 and surface multilayer relaxations Δd_{ij} at clean unreconstructed and (1×2) reconstructed fcc(110) surfaces. In our calculation for Pt, we use $E_{\text{coh}}(\text{bulk}) = 5.86$ eV, $r_0 = 2.77$ Å, and from the bulk modulus $B = 2.88 \times 10^{12}$ dyn/cm² we obtain [2,9] $p = 11.1$ and $q = 3.7$. Since very similar p, q values [2]

apply to Ir and Au, we expect the same multilayer relaxations and the surface energies to scale with $E_{\text{coh}}(\text{bulk})$ for these metals.

For the reconstructed surfaces we only consider the missing row and the Bonzel–Ferrer model which experimentally emerged as most favourable [4]. With respect to our earlier recursion technique calculation [10] the number of surface layers has been doubled and the number of inequivalent sites considered increased to 12. The resulting multilayer relaxations Δd_{ij} and surface energy values γ^0 are shown in table 1. The damped oscillatory behaviour of the surface multilayer relaxations agrees both in sign and in magnitude very well with experiments performed on the (unreconstructed) Ni(110), Cu(110), Ag(110) and Al(110) surfaces⁺¹. The surface tension slightly favours the missing row surface by 0.04 eV and strongly discards the Bonzel–Ferrer model by 0.76 eV.

The longstanding controversy about the diffusion processes necessary to create a missing row surface [4] has been resolved by a simple domain formation mechanism [5] which is schematically shown in fig. 1. In order to reconstruct, the domain wall formation energy $\Delta\gamma_{\text{DW}}^0$ must not exceed the gain in surface tension $E_{\text{R}}^0 = -0.04$ eV. In our calculation we obtain $\Delta\gamma_{\text{DW}}^0 = +0.32$ eV and conclude that even at $T = 0$ K the missing row reconstruction with domains would be favourable for domain sizes of 10 and more atoms in the $[1\bar{1}0]$ direction (fig. 1), in apparent agreement with experiment [5].

The complex (hex) reconstruction of Ir, Pt and

⁺¹ See ref. [11] and references cited therein, especially for deeper lying layers.

Table 1
Surface relaxations and surface energies at unreconstructed and (1×2) reconstructed Pt(110) surfaces.

	Relaxations (%)				Energies (eV)	
	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}	γ^0	E_{R}^0
unreconstructed (110) surface	-9.5	+1.7	-0.6	+0.3	1.84 ^{b)}	-
missing row model	-8.5	-2.1	-0.4	+0.3	1.77	-0.04
Bonzel–Ferrer model	-13.6	-1.0 ^{a)}	-3.2 ^{a)}	+0.3	2.53	+0.76

a) Average over inequivalent sites in the same layer.

b) γ^0 was evaluated in a doubled Wigner–Seitz cell for the sake of comparison with reconstructed surfaces.

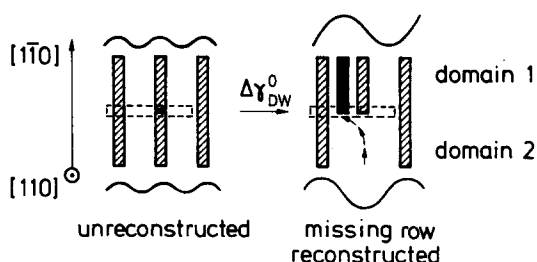


Fig. 1. Domain formation mechanism for the (1×2) reconstruction at fcc(110) surfaces discussed in ref. [5]. Cross-hatched bars denote topmost layer rows on the unreconstructed surface and the black bar the layer above. Surface corrugation is given on the top and bottom of the figure. The dashed area shows the atoms considered in the domain wall formation energy $\Delta\gamma_{DW}^0$.

Au(100) surfaces has been interpreted by the topmost layer forming a hexagonal close-packed arrangement on the square substrate lattice [6,7]. The general observation is a local (1×5) reconstruction arising from a 4% contraction along the $[01\bar{1}]$ direction, while the atomic spacing in the $[011]$ direction stays commensurate with the substrate, allowing for "top" or "bridge" arrangements [6,7] of topmost atoms. Further contraction by 4% in the $[011]$ direction and slight topmost layer rotations by $\varphi \lesssim 1^\circ$, which have been observed [6,7] on Pt and Au(100)-(hex) surfaces, give rise to large surface unit cells up to a size c (26×68) with hundreds of inequivalent sites. Since the total number of atoms is conserved during the reconstruction, $\gamma_R^0(\text{hex})$ must be compared to γ_U^0 for an unreconstructed surface with $\approx 20\%$ more adatoms in different arrangements.

Our energy results for the unreconstructed and re-

constructed surfaces are given in table 2. In our calculation we first varied the contraction in the $[01\bar{1}]$ direction for both the "top" and "bridge" arrangements and found a 4% contraction to be most favourable. This leads to a local (1×5) reconstruction with a very slight preference for the "bridge" arrangement. The assumption of further relaxations in the $[011]$ direction also yielded a 4% contraction to be most favourable, which further decreased γ_R^0 by 0.04 eV. As can be inferred from table 2, the heat of reconstruction with respect to an unreconstructed surface with isolated adatoms is $E_R^0 = -0.09$ eV for the (hex) phase and smaller in magnitude for the (1×5) phase. In these calculations, for each contraction an independent relaxation of all surface atoms in the unit cell was allowed and the resulting atomic positions showed agreement with the experiment [7]. The predicted lateral as well as vertical contractions are believed to arise from hybridization losses at metal surfaces [12].

In the case of the observed [13] CO-suppressed reconstruction on Pt(100), following eq. (4), E_R^0 has to be modified by $\Delta\gamma_{ads}$. Using experimental values for $E_{ads}(\text{CO}/\text{Pt}(100))$ shown in table 2, we obtain a critical value $\theta_{crit}(\text{CO}) \approx 0.2$ in very good agreement with the observed value [13] $\theta_{crit}(\text{CO}) \approx 0.05$, which is an average value and neglects CO island formation.

Since our above predictions of surface reconstruction are essentially material-independent, we have to explain the failure of our model in other 3d and 4d fcc metals which do not reconstruct without adsorbates. As mentioned earlier, the driving force for reconstruction is the gain in topmost layer energy, which is proportional to $E_{coh}(\text{bulk})$, and the counteracting force is the misregistry energy, which will de-

Table 2
Energies involved in the reconstruction of clean and CO-covered Pt(100) surfaces.

	Clean surface		Adsorbate-covered surface	
	γ^0 (eV)	E_R^0 (eV)	$E_{ads}(\text{CO})$ (eV)	$\Delta\gamma_{ads}(\theta = 0.2)$ (eV)
unreconstructed surface	0.69	-	1.63 ^{a)}	-
(1×5) reconstructed surface				
"top"	0.64	-0.05		
"bridge"	0.63	-0.06		
(hex) reconstructed surface	0.60	-0.09	1.19 ^{a)}	-0.09

^{a)} Ref. [13].

Table 3

Ratio $G/E_{\text{coh}}(\text{bulk})$ for fcc transition metals (in 10^{28} m^{-3}). $G = C_{44}$ is used for the shear modulus [14] in the [100] direction on the (100) plane. $T = 0 \text{ K}$.

Co: 11.5	Ni: 18.5	Cu: 14.7	↑ difficult
Rh: ?	Pd: 11.4	Ag: 10.8	reconstruction
Ir: 24.1	Pt: 8.2	Au: 7.4	↓ easy

pend on the shear modulus G . It should be noted that G (and hence γ^0) has been underestimated [2] in eq. (5), since the hopping integrals have been assumed to be isotropic. Generally, small values of $G/E_{\text{coh}}(\text{bulk})$ should be favourable for reconstruction and large values unfavourable. From a comparison of these values in table 3 we infer a general trend towards easy reconstruction when going from 3d to 5d metals ^{#2}.

In conclusion, a general formula has been used to evaluate surface energies and relaxations at unreconstructed and reconstructed metal surfaces. The predicted damped oscillatory behaviour of the multilayer relaxations showed very good agreement with experiment. Similar behaviour could be obtained within the same formalism for the horizontal and vertical relaxations at high Miller index bcc surfaces [12]. Reconstruction trends predicted for clean fcc(110) and (100) surfaces agreed very well with equilibrium structures observed at Ir, Pt and Au surfaces. Deviations from this behaviour in the 3d and 4d metals were explained by material dependent trends reflected in the ratio of the shear modulus and bulk cohesive energy. At adsorbate-covered surfaces, CO-suppressed and hydrogen-induced [12] reconstruction could be derived from a general criterion based on surface and adsorption energies.

^{#2} A similar criterion using the melting and Debye temperature has been used in ref. [6].

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