Surface relaxation and stress for 5d transition metals

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Abstract
Using the density functional theory, we present a systematic theoretical study of the layer
relaxation and surface stress of 5d transition metals. Our calculations predict layer contractions
for all surfaces, except for the (111) surface of face centered cubic Pt and Au, where slight
expansions are obtained similarly to the case of the 4d series. We also find that the relaxations
of the close packed surfaces decrease with increasing occupation number through the 5d series.
The surface stress for the relaxed, most closely packed surfaces shows similar atomic number
dependence as the surface energy. Using Cammarata's model and our calculated surface stress
and surface energy values, we examine the possibility of surface reconstructions, which is in
reasonable agreement with the experimental observations.

1. Introduction

The determination of the surface geometry of solid surfaces is one of the basic questions of surface science. Transition metal surfaces are of particular interest, since they act as catalysts in various reduction and hydrogenation reactions. It is well known that real surfaces of pure metals can adopt different structures from those of ideally truncated crystals. During relaxation only rigid inward or outward displacement of the atomic layers occurs, while in the case of reconstruction the displacement of atoms may alter the two-dimensional symmetry of the surface. Experimental studies have demonstrated that the surface layer of clean transition metal surfaces relaxes inward [1], i.e. the interlayer distance between the topmost two atomic layers is smaller than that of the bulk. Outward expansion of the top layer has also been found for some surfaces of noble metals. The top layer relaxation is often accompanied by relaxation of the subsurface atomic layers, resulting in an oscillatory multilayer relaxation.

Several theoretical models have been proposed to explain the surface relaxation of transition metals. Generally, the magnitude of relaxation is larger for rough surfaces than for smooth ones. The model, proposed by Finnis and Heine [2] based on Smoluchowski smoothing [3], states that, when cutting a perfect crystal, charge redistribution gives rise to an inward electrostatic force on the top layer nuclei. Since this effect increases with surface roughness, the above model confirms the general relationship between relaxation and surface roughness. It also explains the contraction found for most transition metal surfaces, but it fails to describe the noble metal surface relaxation. Pettifor [4] proposed that the crystal geometry is determined by the balance of the negative pressure of the localized d bonds and the homogeneous positive pressure of the sp electrons. According to Heine and Marks [5], at metal surfaces the mobile sp electrons can flow into the vacuum, while the d bonds between the first and second layers remain practically unchanged. Therefore, the d electrons give rise to an inward force on the surface atoms, which is proportional to the strength of the d bonds. Because the strength of the d bonds shows a well-known parabolic behavior across the transition

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metal series, the magnitude of the top layer relaxation is also expected to follow a parabolic trend [6]. This model predicts positive (outward) relaxation for noble metal surfaces. One possible way to approach the problem of surface relaxation is to treat the surface as a two-dimensional defect with a potential which is screened towards the bulk metal. It is well known that free surfaces cause Friedel oscillations in the charge density towards the bulk metal [7]. The periodicity of the Friedel oscillation is twice the Fermi wavevector k_F and it is generally incommensurate with the relevant lattice constant (interlayer distance) of the metal.

In contrast to the surface energy, the surface stress is drastically influenced by layer relaxation [8]. According to a simple model described by Ibach [9], upon cleaving a metal surface the electronic charge density of the broken bonds is redistributed between surface atoms and their backbonds. This leads to increased charge density between surface atoms. However, lattice constraint by subsurface layers hinders in-plane relaxation of surface atoms, resulting in the tensile (positive) surface stress on metal surfaces. The first-principles calculations performed so far confirm that the surface stress on clean metal surfaces is tensile. Furthermore, strengthening of the backbonds of surface atoms results in inward relaxation of the top layer. Nichols *et al* [10] explained the surface stress change during surface relaxation in terms of a jellium model and performed *ab initio* DFT calculations to describe the outward relaxation of the Au(111) surface. They have suggested that the shift of the energy bands to lower energies, i.e. the depleted surface density of states near the Fermi level, is the driving force for the expansion on the Au(111) surface.

In this paper, we present a systematic *ab initio* study of the top layer relaxation and surface stress in 5d transition metals. In section 2 we outline the method of the surface stress calculation, while in section 3 we summarize and discuss the results.

2. Computational method

The surface stress is the reversible work per area to stretch the surface elastically. It can be expressed by the Shuttleworth equation [11]:

$$\tau_{ij} = \frac{1}{A} \frac{\partial A\gamma}{\partial \varepsilon_{ij}} = \gamma \delta_{ij} + \frac{\partial \gamma}{\partial \varepsilon_{ij}}, \qquad (1)$$

where τ_{ij} denotes the components of the surface stress tensor, A is the surface area, ε_{ij} stands for a deformation tensor element and γ denotes the surface energy. The latter is defined as the reversible work per surface area to create a surface, i.e. $\gamma = (E^s - E^b)/A$, where E^s is the total energy of the surface region and E^b is the total energy of a bulk region, both of them referring to the same number of atoms. Throughout the paper, superscript s refers to surface and superscript b to bulk quantities.

In order to calculate the surface stress, we consider a slab formed by N atomic layers parallel to the surface. For surface calculations, the slab is embedded in vacuum, while for bulk calculations the slab is periodically repeated along the direction perpendicular to the atomic layers. We elongate the lattice

Table 1. Calculated bulk lattice parameters and optimized c/a ratios for the 5d elements.

Metal	Structure	a (Å)	c/a
La	hcp	3.7649	1.6189
Hf	hcp	3.1930	1.5790
Ta	bcc	3.3074	
W	bcc	3.1704	
Re	hcp	2.7730	1.6156
Os	hcp	2.7540	1.5776
Ir	fcc	3.8767	
Pt	fcc	3.9774	
Au	fcc	4.1740	

vectors lying in the surface plane by ε and keep the interlayer distances fixed. For this distortion, the deformation tensor has the form

$$\varepsilon_{ij} = \begin{bmatrix} \varepsilon & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & 0 \end{bmatrix}. \qquad (2)$$

The total energies of the surface and bulk slabs, i.e. E^s and E^b, are computed for five different deformations ($\varepsilon = 0$, ± 0.01 and ± 0.02) and fitted by a quadratic polynomial, i.e.

$$E^{s/b}(\varepsilon) \approx E^{s/b}(0) + c_1^{s/b}\varepsilon + c_2^{s/b}\varepsilon^2. \qquad (3)$$

Here $E^b(0)$ is the total energy of the undistorted bulk, calculated for the theoretical equilibrium volume. $E^s(0)$ is the total energy of the undistorted slab with in-plane lattice constants equal to the bulk equilibrium values, and with relaxed interlayer distances. The surface stress is determined from the linear coefficients of the slab and bulk energies, namely

$$\tau = \frac{c_1^s - c_1^b}{4A}, \qquad (4)$$

where the factor 4 arises from the two surfaces of the slab and the two deformed in-plane lattice vectors. Note that in the case of low symmetry surfaces equation (4) gives the average of the two main stress tensor components.

During the surface relaxation, we change the distance between the first and second atomic layers (λ_{12}^s) on both sides of the surface slab. To determine the equilibrium top layer relaxation, we calculate the total energy of the surface slab for several $\delta \equiv (\lambda_{12}^s - \lambda_{12}^b)/\lambda_{12}^b$ values, where λ_{12}^b is the bulk equilibrium interlayer distance. Then, to minimize the numerical noises, we make a quadratic regression on the mesh points and the minimum of the fitted curve gives the optimal δ or λ_{12}^s.

In the present application, the total energies have been calculated using density functional theory [12]. The Kohn–Sham equations [13] have been solved using the Vienna *ab initio* simulation package (VASP [14]) employing the Perdew–Burke–Ernzerhof generalized gradient approximation [15]. The projector augmented-wave method was applied using a 350 eV plane-wave cutoff energy. A $25 \times 25 \times 25$ k-point grid was used for bulk calculations and a $55 \times 55 \times 1$ k-point grid was used for surface calculations (with the surface being in the xy plane). The surface relaxations and stress calculations were performed for the (111) facet of the face centered cubic

Table 2. Calculated layer relaxations (in per cent) for single-layer (d_{12}^s) and multilayer (d_{ij}) relaxations of some low-index, close packed surfaces of 5d transition metals.

|			Multilayer				
	Surface	Single-layer d_{12}^s	d_{12}	d_{23}	d_{34}	d_{45}	d_{56}
La	hcp(0001)	−4.22	−4.77	4.33	−1.99	1.06	−0.91
Hf	hcp(0001)	−6.40	−6.86	3.49	−1.03	0.68	0.09
Ta	bcc(110)	−4.91	−4.87	0.24	0.01	0.11	0.31
	bcc(100)		−13.43	0.09	2.98	−1.37	0.20
W	bcc(110)	−3.71	−3.76	0.45	0.02	0.18	−0.16
	bcc(100)		−12.16	2.97	−1.34	0.20	0.10
Re	hcp(0001)	−5.33	−6.23	3.94	−2.72	2.93	−2.19
	hcp(10$\bar{1}$0)		−16.44	0.12	−1.85	1.79	−1.35
Os	hcp(0001)	−3.72	−3.79	0.04	0.89	−0.04	−0.47
	hcp(10$\bar{1}$0)		−17.20	0.63	−2.41	1.54	−1.32
Ir	fcc(111)	−2.05	−2.09	−0.51	0.32	−0.02	0.10
	fcc(100)		−5.42	0.99	0.35	−0.23	−0.17
Pt	fcc(111)	1.19	0.99	−0.49	−0.12	0.11	0.12
	fcc(100)		−2.54	−0.47	0.03	0.28	0.29
Au	fcc(111)	1.92	1.67	0.04	0.22	0.38	0.29
	fcc(100)		−1.52	0.10	0.32	0.09	0.04

(fcc) lattice, for the (110) facet of the body centered cubic (bcc) lattice, for the (0001) facet of the hcp lattice and for the (100) surface facets of the bcc and fcc metals. The free surfaces were modeled by slab geometries. Each slab contained 10 atomic layers and a vacuum layer of width equivalent to 5 atomic layers for the most closely packed geometries, while for the bcc and fcc (100) facets we have used 12 atomic layers. In all calculations, the in-plane lattice constants were fixed to the theoretical bulk equilibrium values and the interlayer distances (λ_{ij}, i and j are the layer indices) were allowed to relax.

3. Results and discussion

3.1. Relaxation and stress

The calculated bulk equilibrium lattice parameters and c/a ratios are listed in table 1. They are in perfect agreement with former theoretical results obtained using the same exchange–correlation functional [16]. In table 2, we list our results for the single-layer and multilayer relaxations obtained for some low-index surfaces of 5d transition metals. First, when we compare the single and multilayer relaxation cases we can conclude that there is no essential difference in the topmost layer relaxation. Examining the calculated multilayer relaxations seen in table 2, we see that for most 5d metals the relaxation decays relatively fast with the distance from the surface. The only striking exception is Re [17], where d_{56} has a similar magnitude as the top layer relaxation (d_{12}). A similar anomalous behavior was found in the case of hcp Tc [8].

The calculated surface energy, stress and excess surface stress are listed in table 3 for the relaxed, most closely packed and cubic (100) surfaces of 5d transition metals. For the most closely packed surfaces the surface energy and stress are compared in figure 1. At the beginning of the series the magnitude of the surface stress values are similar (or smaller) to those of the surface energy: in some cases the excess surface
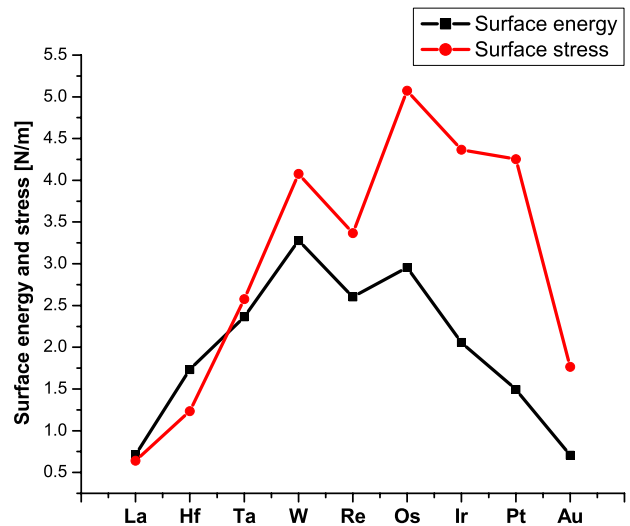
Figure 1. Calculated surface energy and surface stress values for the relaxed, most closely packed surface facets of the 5d series.

(This figure is in colour only in the electronic version)

stress ($\frac{\partial \gamma}{\partial \varepsilon_{ij}}$ from equation (4)) is negative. For the second half of the series the excess surface stress can be exceptionally high, like for Ir and Pt, which has consequences for the possible surface reconstructions, as we will see later.

3.2. Stability of close packed surfaces

Intuitively it is straightforward to assume that a large surface stress can result in a surface reconstruction. This idea is described quantitatively in Cammarata's model (first proposed by Herring [18], and later extended by Cammarata [19]). Several effects should be taken into account in order to predict if a surface will reconstruct or not. First of all it is obvious that there is a remarkable energy gain if a surface with tensile

Table 3. Calculated surface energy (γ), total (τ) and excess ($\tau - \gamma$) surface stress (in J m^{-2}) for the most closely packed and cubic (100) surfaces of 5d transition metals. The results correspond to the fully layer-relaxed geometry. For the most closely packed surfaces 10-layer slab geometry was used, while for the (100) surfaces 12-layer slab geometry was used.

	Surface	γ	τ	$(\tau - \gamma)$
La	hcp(0001)	0.713	0.642	−0.07
Hf	hcp(0001)	1.733	1.235	−0.50
Ta	bcc(110)	2.365	2.576	0.21
	bcc(100)	2.469	1.784	−0.68
W	bcc(110)	3.279	4.076	0.80
	bcc(100)	4.021	2.706	−1.31
Re	hcp(0001)	2.605	3.366	0.73
Os	hcp(0001)	2.956	5.073	2.12
Ir	fcc(111)	2.057	4.367	2.31
	fcc(100)	2.840	3.246	0.41
Pt	fcc(111)	1.493	4.252	2.76
	fcc(100)	1.848	3.323	1.47
Au	fcc(111)	0.707	1.766	1.06
	fcc(100)	0.864	2.073	1.21

Table 4. Estimated elastic energy change in the continuum model during reconstruction—'creating a dislocation'—for the most closely packed surfaces (mcp) of Re–Au and for the fcc(100) surfaces of Ir, Pt and Au. mcp stands for (0001) for Re and Os and (111) for Ir, Pt and Au. The corresponding excess surface stress values are also shown.

	$(\tau - \gamma)_{\mathrm{mcp}}$ (J m^{-2})	$(\tau - \gamma)_{100}$ (J m^{-2})	G (GPa)	b (Å)	$Gb/10$ (J m^{-2})
Re	0.73	—	180	2.773	5.0
Os	2.12	—	223	2.754	6.1
Ir	2.31	0.41	209	2.741	5.7
Pt	2.76	1.47	61	2.812	1.7
Au	1.06	1.21	26	2.951	0.8

energy and stress values, and pointed out the exceptionally high excess surface stress for the second half of the series and its consequences for the possible surface reconstructions.

Acknowledgments

stress is compressed and the surface strain energy is reduced. This energy gain is proportional to the surface stress τ. At the same time, however, the density of atoms at the surface is increased, i.e. atoms should be transferred from the bulk to the surface, which is roughly proportional to the surface energy γ. Therefore the driving force for surface reconstruction is proportional to the excess surface stress $\tau - \gamma$. This energy gain should be compared to the energy contribution associated with the energetically unfavorable sites in the reconstructed layer. In Cammarata's model this energy contribution is described by the energy change due to the formation of a dislocation using the continuum elastic theory: αGb, where G stands for the shear modulus, b is the magnitude of the Burgers' vector of the reconstruction and $\alpha \cong (4\pi(1 - \nu))^{-1} \cong 0.1$ (ν stands for Poisson's ratio). Reconstruction is expected if $\tau - \gamma \geqslant \alpha Gb$.

In table 4 we have listed these elastic energy contributions for Re–Au. According to these, reconstruction is expected for Au(111), (100), Pt(111) and perhaps Pt(100). In all other cases the excess stress is not enough to compensate for the elastic energy loss. It is interesting to compare these results with the experimentally observed surface reconstructions [20], like Ir(100) [21], Pt(100) [22], Au(100) [23], Au(111) [24, 25] and Pt(111) [26–28]. For the Ir(100) we have no explanation for the reconstruction, although in this case we do not expect that the formation of a quasi-hexagonal, close packed top surface layer is properly described by Cammarata's model. For all other cases our predictions are in good agreement with the experimental observations.

4. Conclusions

We have presented a systematic theoretical study of the top layer relaxation and surface stress of 5d transition metals. We have examined the atomic number dependence of the surface

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