Reconstructions of Ir (110) and (100): an ab initio study

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Prediction criteria for surface reconstructions are discussed, with reference to ab initio calculations of the (110)-1×2 missing-row and (100)-5×1 quasi-hexagonal reconstructions of Ir and Rh.

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The low index surfaces of most metals undergo symmetry-conserving multilayer relaxations and, occasionally, surface reconstructions (either symmetry-breaking or -conserving), possibly accompanied by a change in atomic density in the topmost layer. Despite the good phenomenological characterization of the reconstructed phases, a general picture of the driving mechanisms is still missing. To some extent, it is not even clear if such a picture can be established at all. Of course, different phases can always be compared in terms of the respective free energies, but this implies a direct calculation for the reconstructed phase. A worthwile undertaking is therefore finding out which, if any, computable quantities pertaining to the *unreconstructed* surface can be of help in rationalizing and possibly predicting instabilities of the ideal (relaxed) surface towards a reconstructed phase; in other words, whether or not surfaces can predict their own stability [1]. Obvious candidate indicators are surface energy, stress [2], and strain [3]. For instance, the hex (100) reconstructions of Ir, Pt, and Au, whereby the top layer densifies into an hexagonal layer laid on top of the (100) square lattice, has been modeled in terms of the relief of surface stress [4], whereas faceting (i.e. a "surface-energy driven" transformation) has been suggested as the origin of the $n\times1$ reconstruction of Au (110) [5].

In this paper we take a first step towards the above goal by calculating the formation energies, relaxed geometries, and surface stresses of unreconstructed and reconstructed low-index surfaces of Ir and Rh. For both Ir (100) and (110), reconstruction is found to be favorable. The same reconstructions for Rh are found to be disfavored, in agreement with experiment; results and technical details for the ideal Rh surfaces have been reported elsewhere [6]. For Ir, we performed local-density-functional-theory [7] total energy and force calculations, using iterative diagonalization in a parallel implementation [8], smooth scalar-relativistic norm-conserving pseudopotentials, plane waves cut off at 40 Ryd, k-points sets downfolded from the 10-point fcc mesh, Fermi-surface smearing of 0.05 Ryd with the first-order Methfessel-Paxton approximation [9] for the occupation function. The resulting bulk parameters are $a_0 = 7.289$ bohr and $B = 4.2$ Mbar. Slabs are used encompassing 7 atomic layers for the (100) and (111) surfaces, 9 layers for the ideal and reconstructed (110), and 5 layers for the (100)-5×1. The vacuum region between slabs is equivalent to 5 atomic layers (3 layers for the 5×1). All structures are relaxed according to Hellmann-Feynman forces with a threshold of 1 mRyd/bohr ~ 0.05 eV/Å. We found it convenient to use the method of Ref. [10] to accelerate the selfconsistency convergence of forces, and the method of Ref. [11] to calculate surface energies.

In Table I we list surface energies, relaxations, work functions, and stress of the three low-index (1×1) surfaces of Ir. They are in agreement with the usual picture for cubic transition metal surfaces: inward surface relaxations occur, increasing with surface roughness, while workfunctions follow the opposite trend. As pointed out previously [4], many properties of Ir, and more generally the qualitative differences between $5d$ and $4d$ metals, can be traced back to relativistic effects. Despite the much larger core and in particular the larger d shell, Ir (both atomic and crystalline) has about the same size as Rh. This is due to the relativistic contraction of the outer s shell (caused by mass-velocity terms and $s-$core orthogonalization), having a pronounced maximum at nearby Au [12]. This results in large bulk modulus, compact lattice, large surface stress, and frequent surface reconstruction.

We now come to describe the reconstructions. Here we focus on Ir, but qualitative conclusions also apply to Pt and Au. The missing-row reconstruction of the (110) surface consists in the removal of one every two rows of atoms along the $[1\bar{1}0]$ direction. The calculated reconstruction energy (the gain in energy upon reconstruction) is 0.03 eV/(1×1 area), similar to the ab initio value of 0.05 eV for Au [13], and to the semiempirical tight-binding result of 0.04 eV for Pt [14]. The atomic relaxations (listed in Table II) are similar to those of the ideal (110) surface. The third-layer atoms corresponding to the missing surface rows move upwards, those neighboring the remaining top rows move downward, as expected. The displacements tend to reduce the surface roughness, in accordance with the stress across the surface rows of the surface being tensile. The components in the vertical direction are made to vanish by relaxation.

Does surface stress help in predicting this reconstruction ? We suggest that it does not: on the reconstructed surface, the stress (2.14 and 3.71 eV/atom in the two independent directions across and along the surface troughs) is appreciably larger than on the unreconstructed one (1.70 and 3.21 eV/atom), so stress relief cannot meaningfully be invoked in this case. This is not too surprising at a closer look, since the reconstruction

removes one top row, but exposes *two additional* ((111)-like) rows in the process. Stress might be removed from the topmost rows (although there is no way to tell this from just the integrated stress) but apparently it is just transfered to lower layers. This multilayer nature of surface stress of fcc (110) is confirmed by preliminary results of a layer-by-layer decomposition of the surface stress, to be presented in detail elsewhere.

A more useful alternative is that of viewing the reconstructed surface as a sequel of adjacent (111) microfacets at alternate angles of about $\pm 35^\circ$ from the vertical axis. While the upper and lower edge atoms will behave differently from atoms on a clean (111) face, it seems reasonable to argue that the *average* local environment is that of a (111) surface. This will be all the more true for a generic $n \times 1$ reconstruction in which $n-m$ every n surface rows are removed from the m-th layer ($n-1$ in the first layer, $n-2$ in the second, down to 1 in the $n-1$-th layer), and all layers down to the $n+1$-th expose atoms at the surface. It is then straightforward to predict the reconstruction on the basis of ideal-surface quantities only. The surface energy per atom of the reconstructed surface is expressed as

$$\sigma^{rec} = \frac{\sigma_{(111)}}{A^{1\times1}_{(111)}} \frac{a_0\sqrt{a_0^2+d^2}}{\sqrt{2}} \qquad (1)$$

where a_0 is the bulk lattice costant, and d the inter-layer distance. For the unrelaxed structure $d = a_0/\sqrt{2}$ and $\sigma_{rec} = 2\ \sigma_{(111)}$. With relaxation, d gets shorter and the surface energy is lowered. In the same spirit we can calculate the surface stress per cell by taking the stress per unit area equal to that of the the clean (111) surface. The in-plane $[1\overline{1}1]$ component (i.e. parallel to the chains) is simply obtained by

$$\tau^{rec}_{[1\overline{1}1]} = \frac{\tau^{surf}_{(111)}}{A^{1\times1}_{(111)}} \frac{a_0\sqrt{a_0^2+d^2}}{\sqrt{2}} \qquad (2)$$

while the [100] component in the relaxed configuration can be calculated by projecting the planar component of (111) surface along the [100] direction.

The faceting model gives a reconstruction energy of 0.04 eV/atom respectively, which compares well with the ab initio value of 0.03; the model also gives surface stresses of 2.20 and 3.82 eV/atom in the two independent surface directions, to be compared with ab initio values of 2.14 and 3.71 eV/atom. Two points are important: first, using only (1×1)-surface quantities, the model predicts *directly* the faceting of Ir (110) into (111) microfacets; second, it predicts accurately both surface energy and stress, at least in comparison with ab initio values. A further indication of the plausibility of the faceting picture is that the work function *increases* by about 0.3 eV upon reconstruction: while this looks strange if one views the 1×2 phase as just a rougher (110), this indicator of surface smoothening fits naturally into the (111)-microfaceting picture. Generally speaking, this picture is also in agreement with previous electronic kinetic-energy reduction arguments [13]. One more point to note is that the above arguments imply that the $n \times 1$ reconstruction should occur for any n. This agrees with the simultaneous observation of $n\times1$ domains with n up to 4 for Au (110). On the other hand, the formation of $n\times1$ domains implies the existence of domain walls consisting of steps or step bunches of total heigth $n-1$, the cost of which becomes rapidly too large for the surface to afford a large-n reconstruction.

The (100)-5×1 reconstruction presents quite different features. The atomic density increases due to a contraction of the atomic rows along the [100] direction, so that 6 atoms can be placed into 5 times a 1×1 cell area. The atoms are arranged in a buckled close-packed quasi-hexagonal structure. We calculate surface energies, relaxations, and stress for the "two-bridge" (TB) and the "top-center" (TC) configurations [15]. Both the TB and TC reconstructed configurations are found to be favorable, with a reconstruction energy of 0.14 eV/(1×1 area), and 0.11 eV/(1×1 area), respectively. The TB configuration is the most favored, in agreement with dynamical LEED results [15]; the geometry of the hex layer agrees reasonably with that predicted by LEED, although we obtain a smaller buckling. The relaxation energies with respect to the experimental positions are about 0.1 eV for both the configurations; also, Rh (100) is found not to reconstruct (rec energy ~ -0.1 eV). These latter results confirm further the conclusions of Ref. [4] on Pd and Pt, which were based on calculations for the experimental configuration.

Unlike the (110) missing-row, the "quasi-hex" reconstruction enhances the surface roughness, as signaled by a decrease in the workfunction of about 0.2 eV with respect to the (1×1) phase, in good agreement with the experimental drop [16] of ~ 0.15 eV. This behavior may seem unexpected for a transition to a close-packed structure. However the quasi-hexagonal overlayer matches poorly the square (100) substrate, and is strongly buckled (by 15 to 40 % of the ideal interlayer spacing). The net effect is a decrease of the surface dipole.

The surface stress of the (1×1) surface has been invoked as driving the 5×1 reconstruction [4]. The lowering of in-plane symmetry causes an anisotropy of the surface stress; the atomic density increases along the [110] direction, resulting in a large relief of surface stress ($\sim$ 40 %). On the other hand, along $[1\overline{1}0]$ the first neighbor distance remains unaltered on the reconstructed surface, and four new neighbors contribute to the stress along that direction. As a consequence, the stress along $[1\overline{1}0]$ is indeed found to increase (by about the same amount). A symmetry-breaking distortion, such as the domain rotations occurring at high temperature, will allow further stress relief to set in along this direction.

In any event, a direct comparison between the in-plane stress of the clean and reconstructed surfaces is again not really helpful. The integrated stress of the (1×1) surface gives information about the "driving force" (the in-plane

stress in the surface layer). This stress is relieved to to some unknown extent upon reconstruction. The integrated stress in the reconstructed phase contains additional contributions from bonds between the substrate and the mismatched overlayer which were not present in the (1×1) phase – that is, it contains information about both the residual "driving" force, and the "resisting" forces, in proportions that cannot be disentagled. Basically, as in previous studies, the problem of extracting an independent value for the mismatch energy remains unsolved. We suppose that a more useful reconstruction indicator would be the surface strain of the (1×1) phase as defined in Ref. [3]; this is in a way the strain effectively imposed onto the top layer by the infinite bulk to make the former fit onto the substrate. If the strain thus determined is larger than a critical strain extracted from e.g. elasticity theory, a transition behavior of the surface layer from a coherent (unreconstructed) to an incoherent (reconstructed) state can be expected. We are currently addressing this point and will discuss it elsewhere.

It may be useful to note that there is a further basic difference between the two reconstructions discussed above: the density increases in the 5×1 and decreases in the 1×2. The choice of the thermodynamic reservoir for atoms to be added (5×1) or removed (1×2) from the surface is therefore essential. We used (quite naturally) the bulk chemical potential which is the most unfavorable choice for the 5×1 reconstruction in equilibrium with the bulk phase. With a "less expensive" additional atom (for example, an isolated homoadatom), the reconstruction would be easier. On the contrary, the same choice is most favorable for the (110) 1×2 reconstruction.

In conclusions, calculations for Ir and Rh surfaces support the view that no unique quantity (energy, or stress, e.g.) can be invoked as a general driving force of surface reconstruction for metals. We found evidence for microfaceting of Ir (110). The results for reconstructed surfaces are in agreement with existing experiments.

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	Δd_{12}	Δd_{23}	Δd_{34}	σ	W	$\tau_{xx}^{\rm surf}$	$\tau_{yy}^{\rm surf}$
(111)	–1.3	–0.2	0.0	1.31	5.92	1.96	
(100)	–3.8	1.0	–0.5	1.85	5.92	1.86	
(110)	–11.6	5.4	–1.3	2.59	5.45	1.70	3.21

TABLE I. Inter-layer relaxations (percentage variation with respect to ideal layer spacing), surface energy σ (eV), work function W (eV) and surface stress τ (eV/atom) for the three low-index clean surfaces of Ir. All values refer to the fully relaxed structures.

	Δz_1	Δz_2	Δz_{3a}	Δz_{3b}	Δz_4	Δx_2	Δx_4
Rh	–10.8	–2.5	–1.6	3.0	–1.3	–0.3	–0.2
Ir	–10.3	–1.9	–2.5	5.2	–0.8	1.0	–0.8

TABLE II. Relaxations of 1×2 (110) reconstructed surface. Δz_n and Δx_n are vertical and planar changes, respectively, of the n-th layer atoms from ideal positions, (% of the ideal inter-layer spacing). For the third layer, two kinds of shift occur (see text).