Reconstruction Mechanism of fcc Transition Metal (001) Surfaces

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(Received 24 May 1993)

Ab initio studies of the reconstruction mechanism of (001) fcc transition metal surfaces are presented, showing that a close-packed quasihexagonal reconstruction is possible for the late 5d metals Ir, Pt, and Au, while it is disfavored in the isovalent 4d metals Rh, Pd, and Ag. The driving mechanism is identified in the tensile *excess* stress of the unreconstructed surfaces. The stress overcomes the substrate resistance to reconstruction only in 5d metals, where it is much larger than in 4d metals because of the stronger relativistic effects. The origin of surface stress is a d charge depletion from the surface layer.

PACS numbers: 68.35.Bs, 68.35.Md

The (001) surfaces of some fcc transition and noble metals are known to reconstruct to a close-packed quasihexagonal (hex) overlayer arrangement, periodically matching the (001) square substrate [1]. Because of the different symmetries of overlayer and substrate, commensurate hex geometries have rather long periodicities, typical observed surface cells being 5×1 and 20×5. The phenomenon presents a number of interesting aspects. First, the reconstruction is seen only at the end of the 5d transition series, for the metals Ir, Pt, and Au, while their 4d isoelectronic upper neighbors Rh, Pd, and Ag do not reconstruct. Second, the observed reconstructions of Ir, Pt, and Au, though not identical, are qualitatively very similar; in view of the differences in the electronic structures of those materials, this strongly suggests that surface electronic-structure details are not of primary importance. Third, it is known [1] that (001) surfaces of late 5d metals can be rather easily forced to switch between the unreconstructed and the reconstructed phases by deposition or removal of small amounts of adsorbates, which indicates that the energy difference between the two phases is small.

The aim of this Letter is to study this class of reconstructions by a density-functional-theory treatment [2–4], and to understand the underlying physical mechanism establishing a simple picture of the energetics of the phenomenon. In the following, we first present a direct calculation of the heat of reconstruction of the (1×1) to (5×1) reconstructive transition for the (001) surfaces of the isoelectronic pair Pd and Pt, showing that reconstruction is disfavored in the former (4d) and permitted in the latter (5d), in accordance with experiment. To clarify the reconstruction mechanism, we calculate the surface energy and stress for the relevant *unreconstructed* surfaces, showing that they are subjected to a large tensile stress—that is, they tend to prefer a smaller in-plane lattice constant and a higher in-plane atomic density. While indeed achieving close packing of the surface layer, the quasihexagonal reconstruction also causes a modification of the surface-substrate bonding topology, effectively reducing the average atomic coordination; we demonstrate that (a) the reconstruction is determined by the balance

between the energy gain associated with the increase in atomic density at the surface, and the energy lost upon reconstruction due to the disruption or stretching of bonds between mismatched top and subsurface layers, and that (b) only in 5d metals is the surface energy gain due to surface density increase large enough to outweigh the mismatch energy loss, thus making the reconstruction favorable in those elements only. This is due to the fact that the surfaces of end-of-series 5d metals (Ir, Pt, Au) are subject to twice as large a tensile stress as those of the isovalent 4d metals (Rh, Pd, Ag), and thus gain much more energy upon close packing. We then discuss the origin of surface stress, which is due to depletion of d charge from the surface, and the relativistic effects responsible for the enhancement of this mechanism in the fifth row.

Technical aspects.—The calculations were performed using density functional theory (DFT) together with the local density approximation (LDA) [2] and the all-electron full-potential linear muffin tin orbital (LMTO) method [3]. The unreconstructed (1×1) surface is simulated by seven-layer slabs, separated by about ten layers of vacuum, the k-point summations being done on a 15-point mesh in the irreducible part of the surface Brillouin zone (ISBZ) of the (1×1) surface cell. For the (5×1) surface, the summation was performed on a somewhat denser grid [32 points in the (5×1) ISBZ], and a five-layer slab was used. Details on the method and on its previous applications to surfaces can be found in Ref. [4], while a full report of the present calculations will be given elsewhere [5].

Part of the calculations described in the following are basically concerned with the elastic response of the surface. The appropriate reference system is therefore the stress-free crystal at theoretical equilibrium. It is worth pointing out a general problem of DFT-LDA calculations for transition metals. Scalar-relativistic calculations [5,6] give excellent results for the equilibrium properties of bulk 5d metals, and such treatment appears indeed to be vital for a proper description of these systems; in 4d metals, on the other hand, the relativistic treatment gives lattice constants about 2%–2.5% too small, and as a conse-

quence it produces considerable errors in the theoretical bulk moduli (about 30% to 40% too large), while nonrelativistic calculations give excellent equilibrium crystal properties (in $3d$ metals the scalar-relativistic treatment gives even worse results). Although these errors may be considered acceptable (they are at the commonly accepted limit of LDA standard accuracy), one is nevertheless confronted with the fact that, for the elements in question, a relativistic treatment may induce spurious effects in the elastic response, deriving from the incorrect equilibrium crystal ground state it produces. We therefore chose to present here nonrelativistic results for the $4d$ metals. Accurate tests, to be discussed elsewhere [5], show indeed that the picture presented here remains unaltered if a scalar-relativistic treatment is adopted for the $4d$ metals.

(5×1) reconstruction.— For the computational study of this prototypical hex-overlayer system, we assumed the structure inferred from low energy electron diffraction (LEED) data [7], in which six surface atoms are packed together on top of each five substrate atoms in a (11) direction on the (001) surface, as sketched in Fig. 1. To obtain a safer comparison, we also calculated the *unreconstructed* (5×1) surface [i.e., a (1×1) cell repeated 5 times] with the same technical ingredients, obtaining a surface energy within 2% of that calculated using the (1×1) surface cell. No relaxation has been attempted with respect to the experimentally determined geometry. In view of the accuracy limits of LEED structural determination [7], and of typical energy changes upon relaxation [4], we estimate the overall error bar of the calculation to be in the order of 0.05 eV per (1×1) area (or 6 meV/Å^2 for Pd and Pt).

The heat of reconstruction E_r is defined to be the difference of the total energies of the unreconstructed slab plus two bulk atoms and of the reconstructed slab, divided by 10 to refer the energy to the area of the (1×1)-(001) surface cell. A positive value thus indicates the reconstruction to be energetically favored. The nu-

merical result is $E_r = -0.21$ eV in Pd and $E_r = -0.03$ eV in Pt, indicating that Pd will not reconstruct, whereas in Pt the reconstructed and unreconstructed phases have equal energies within the accuracy of the calculation. This result agrees with the fact that both phases are observed for Pt depending on the experimental conditions, while the reconstruction has not been observed in Pd.

Since the reconstruction increases the surface atomic density, atoms have to be added to the surface layer. In equilibrium conditions, it can be assumed that the additional atoms come from the bulk, which actually means that they come from kink sites at surface steps. Indeed, the atom chemical potential in thermal equilibrium equals the crystal cohesive energy. We note in passing that if the surface were coupled, in nonequilibrium conditions, to a reservoir with a lower chemical potential [8], the energy cost per additional atom would be lower, and the heat of reconstruction would increase (i.e., the reconstruction would be more favored).

Surface stress versus surface-substrate mismatch. — To gain insight into the mechanism driving the reconstruction, we calculated the surface energies, stresses, and relaxations for the *unreconstructed* (001) surfaces of the relevant fcc metals. From calculated total energies of slabs and bulk at various in-plane lattice constants, we obtain the strain derivative of the surface energy, $\tau = d\sigma/d\epsilon$. Because of the fourfold symmetry of the system, τ is isotropic and can be expressed as the derivative $\tau = d\sigma/da$ with respect to the area $a = A/A_0$ normalized to the equilibrium area A_0 of the unreconstructed (1×1) surface cell. We name τ the *excess* surface stress, as it gives a quantitative measure of the *change* in surface energy, $\sigma(A) - \sigma(A_0) = \tau\,\delta a$, which would result from a relative area variation $\delta a = (A - A_0)/A_0$. We note that, in a related context, use has been made in the past of the total surface stress [9] of the unreconstructed surface, which is the sum of τ and of the surface energy σ at zero strain. Though, the relevant quantity here is indeed the excess part of the stress, since, while σ itself is a fixed cost of formation for the unreconstructed surface at the in-plane lattice constant determined by the underlying bulk, the value and sign of τ indicate the tendency to reduce the surface energy by changing the surface atomic density. In particular, a positive (or tensile) excess stress indicates that the surface tends to contract and to attain a higher atomic density. Of course, as discussed below, the bonds to the substrate will strongly counteract the surface layer tendency to change its in-plane lattice constant [10]. A further energy cost originates, as seen above, from the need to increase the atomic density of the surface layer.

Our results are presented in Table I. The excess surface stress is tensile in all cases, and it increases considerably going from the fourth to the fifth row. We now show that the large tensile excess surface stress is the driving force of the quasihexagonal reconstruction of the
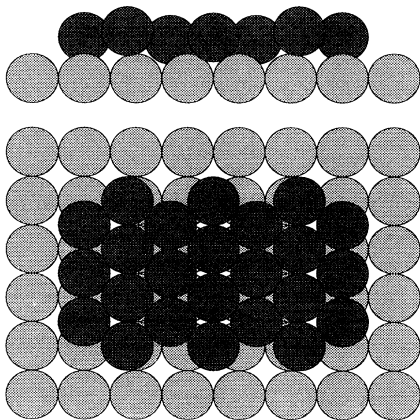

FIG. 1. Side and top view of the (5×1) reconstruction.

TABLE I. Surface energy and excess stress [in eV per (1×1) cell area], top-layer relaxation (percentage of interlayer spacing), and work function (eV) of the unreconstructed (001) surfaces of $4d$ and $5d$ fcc transition and noble metals. The variation of total, sp, and d charge between bulk and surface (electrons) obtained by Mulliken analysis is given.

	σ	τ	Δd_{12}	W	δQ	δQ^{sp}	δQ^d
Rh	1.26	1.94	−4.5	5.24	−0.30	0.08	−0.38
Pd	0.91	1.05	−0.8	5.30	−0.19	−0.08	−0.11
Ag	0.59	0.88	−1.9	4.43	−0.11	0.02	−0.13
Ir	1.73	2.94	−3.0	4.92	−0.42	0.24	−0.66
Pt	1.21	2.69	0.0	6.11	−0.36	0.15	−0.51
Au	0.75	1.62	−1.0	5.61	−0.20	0.10	−0.30

Ir, Pt, and Au (001) surfaces. To attain close packing, the surface layer has to rearrange to a different geometry and must thereby overcome the energy cost of bond rearrangement; we estimate this cost by ideally splitting the heat of reconstruction into a "gain" and a "loss"; the latter, the bond rearrangement contribution ΔE_b to the heat of reconstruction E_r, is obtained by subtracting from E_r the stress-related surface energy gain $\delta\sigma = -\tau\,\delta a$ obtained by a reduction of the surface area per atom to the value of the (111) surface (i.e., about 14%; the sign of $\delta\sigma$ is chosen consistently with our convention for the heat of reconstruction).

The values for the fourth and fifth row are rather close: $\Delta E_b = -0.36$ eV for Pd, and $\Delta E_b = -0.41$ eV for Pt, referred to (1×1) area. We conclude that the favorable balance for the reconstruction in $5d$ metals as opposed to $4d$ metals is indeed determined by an exceptionally large stress-related energy gain in the former case, driving the reconstruction against a bond rearranging cost which is about the same in both series. Inspection of the reconstructed geometry reveals a reduction in the number of bonds between surface and first substrate layer. Thus, the bond rearrangement cost is mostly due to the *average* coordination of subsurface and surface atoms being decreased, despite the increase of in-plane coordination in the reconstructed top layer.

It is worth noticing that the balance between surface contraction and surface-substrate mismatch is favorable in $5d$ metals and unfavorable in $4d$ metals because of the *magnitude* of the surface excess stress; the mere *sign* of the latter is in itself not sufficient to decide whether or not the reconstruction will actually take place [10]. Further, we emphasize that even the magnitude of the stress is meaningful as a reconstruction predictor only when related to the substrate bonding resistance to the reconstruction. This is especially relevant when considering systems in different positions in the transition series: For instance, Rh(001) has a larger stress than Au(001), but the d bonding to the substrate is very much stronger in the former case, so that indeed Rh(001) is not able to reconstruct, while Au is.

Origin of surface stress enhancement. — For d metals, an explanation of the surface stress and of its magnitude can be found in the competition between sp and d bonding, and how the balance is modified at the surface. The accepted description of bonding for a transition metal series [11] is that as the d occupation n_d increases from 0 to 10, bonding, nonbonding, and antibonding states are successively filled. Neglecting sp electrons, this leads to a parabolic bond strength as a function of n_d, with a maximum around $n_d \approx 5$. Including sp electrons in the picture, it is found that throughout most of the series the d electrons form localized bonds which tend to contract the crystal, while the more diffuse sp electrons exert an outwards pressure [12]. This balance is reversed when the d band is nearly full; the sp electrons now bind the crystal, while the full d shell tends to resist lattice contraction.

As an indication of how the balance in the bulk is perturbed by the surface, we inspect the sp and d charges at the surface and in the bulk. A Mulliken population analysis [13] shows that the total charge Q_S at the surface is smaller than the charge Q_B in the bulk, i.e., $\delta Q = Q_S - Q_B < 0$. More specifically, this depletion is mostly of d character $(\delta Q^d = Q_S^d - Q_B^d < 0)$, while the sp charge has slight net increase $(\delta Q^{sp} = Q_S^{sp} - Q_B^{sp} \geq 0)$. The total layer charge as a function of position into the slab shows first a depletion (mostly d), then an enhancement in the first sublayer (mostly d), and finally it rapidly saturates to its bulk value. As seen from Table I, the magnitude of the stress correlates with the amount of charge depletion from the surface layer. Since the depleted charge is predominantly of d character, the tensile surface stress in the late transition metals $(n_d > 5)$ can be explained as a consequence of deoccupying antibonding d states at the high-energy end of the surface density of states (DOS). Thereby, the bond strength between surface atoms is increased. Direct inspection of the charge density shows that d_{xy} orbitals are indeed depleted with respect to bulk occupation; the depletion takes place by partial charge transfer to other sp-hybridized d states [5]. The mechanism giving rise to surface stress is an "internal conversion" in the d shell assisted and enhanced by hybridization with sp orbitals [5], and is thus quite different from that causing the stress of nearly-free-electron metal surfaces [9]. In particular, due to the key role of d states, jellium-based descriptions might be

inapplicable to the present cases.

Given the above findings, the sizably larger surface stress in the fifth-row metals is easy to understand: The origin is the strong relativistic effects in these systems. It is known that the lattice constants of Ir, Pt, and Au are about the same as those of Rh, Pd, and Ag despite the much larger size of the d shell in $5d$ elements, and the $5d$ bulk moduli are larger than those of $4d$ by a factor of about 1.5–2. This is a consequence of the enhanced bonding in fifth-row metals as compared to $4d$ metals, due to relativistic effects [14]. As a result of the action of mass-velocity terms (both direct, and through orthogonalization to deep s core states), the $6s$ and $6p$ states contract and lower their energy, so that sp occupation is increased. As a consequence antibonding d states are emptied; thus the bonding is overall enhanced. In terms of the DOS, this increased bonding sp-d hybridization in a $5d$ metal corresponds to a longer sp tail, and to a d-band complex which is wider and closer in energy to the Fermi level than in a $4d$ one. Hence in $5d$ metals the narrowing and upward shift of the DOS at the surface will produce a larger d depletion (partly in favor of sp charge) [15]. A direct demonstration of the effect is provided by a nonrelativistic calculation for Pt. The lattice constant is 5% larger than experimentally observed, and the bulk modulus is only 60% of its actual value, i.e., close to that of Pd. Most importantly, the surface stress is indeed found to decrease by a factor of 2 and the surface energy by 30%, while the bulk-to-surface charge differences are also significantly smaller: Overall the surface quantities for nonrelativistic Pt resemble rather closely those of Pd [5]. The strength of relativistic effects thus appears to be the relevant difference between the fourth- and fifth-row metals in this context, and it may be identified as the ultimate cause for the reconstruction of fifth-row fcc (001) surfaces.

Summary.— We have calculated the quasihexagonal reconstruction of the (001) surfaces of representative fcc transition metals, finding it to be favored for the late $5d$ metals and not for $4d$ metals, in accordance with experiment. A correlation has been established between reconstruction and magnitude of the surface stress calculated *ab initio* for the unreconstructed surfaces: The reconstruction results from a delicate balance between surface-substrate mismatch and stress-related energy gain. Only in the case of $5d$ metals is the latter gain large enough to actually drive the reconstruction against the substrate resistance to misregistry, which is comparable for isoelectronic systems (e.g., Pd and Pt). The origin of the surface stress is the d charge depletion at the surface, caused by enhanced sp hybridization; the remarkable stress enhancement in $5d$ metals is due to the major relativistic effects on the $6s$ and $6p$ shells.

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