Formation energy, stress, and relaxations of low-index Rh surfaces

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Ab initio local-density-functional-theory calculations of formation energies, stress, and relaxations are reported for the (111), (100), and (110) surfaces of Rh. The study is performed using ultrasoft pseudopotentials and plane waves in a parallel implementation.

I. INTRODUCTION

In this paper we report ab initio calculations of formation energies, stress and relaxations of low-index Rh surfaces. Our results provide, among others, original information on surface stress and surface anisotropy, confirming the recent findings by Feibelman for Pd and Pt [1]. This is a positive test of the feasibility and accuracy of such calculations within the pseudopotential method.

A proper understanding of the basic properties of clean metal surfaces is an essential step forward in the study of adatom diffusion and of catalysis of basic chemical reactions on metal surfaces, both topics of obvious fundamental and technological interest [2]. Ab initio calculations on transition metal surfaces can provide adsorption geometries, dissociation barriers, and diffusion paths for use within empirical methods (e.g. kinetic Montecarlo), and deeper insight into the basic governing mechanisms, and are therefore of the utmost importance.

With a view at studying diffusion barriers [3] and molecular dissociation [4] on low-index surfaces of transition metals, we have undertaken a series of ab initio calculations on the surfaces of Rh. Besides its interest as a catalyst, good experimental data exist for selfdiffusion on Rh, in particular for its (100) face [5]. Here we present surface formation energies, stress, and multilayer relaxations of the clean Rh low-index surfaces; work in progress on surface vacancy formation, homoadsorption and self-diffusion on Rh surfaces will be presented elsewhere. Our calculations were performed within local-density-functional-theory [6], using ultrasoft pseudopotentials [7] to describe ion-electron interaction, a plane-waves basis, and iterative diagonalization algorithms in an efficient parallel implementation [8]. A newly developed variant of the Vanderbilt scheme [9] has been used, whereby norm conservation is only released for those angular-momentum channels which would otherwise generate very hard potentials (the d-channel in the present case) [10].

For bulk Rh, the following computational parameters were found to give converged total energy differences and structural properties: plane-wave cutoff of 30 Ryd, 10 special-point mesh for the fcc lattice, Fermi-surface smearing of 0.05 Ryd, first-order approximation of Methfessel and Paxton [11] for the occupation numbers distribution function (an up-to-date, lucid discussion of this treatment of the metallic state in ab initio calculations has been given recently by de Gironcoli [12]). For all calculations, we used downfolded meshes equivalent to the one used for the bulk. The resulting bulk parameters are \(a_0 = 7.215 \text{ bohr}\) and \(B = 3.079 \text{ Mbar}\). The theoretical lattice constant was used in all calculations. The surface areas per atom are 26.03 \text{ bohr}^2, 22.54 \text{ bohr}^2 and 36.81 \text{ bohr}^2 for the (100), (111) and (110) surfaces, respectively. Our results, given below in eV/atom, should be divided by the above values to switch to eV/bohr^2.

II. RELAXED SURFACE GEOMETRIES

The topmost layers of most clean transition-metal surfaces are known to relax inward [2]. The intralayer spacing between the first two top layers, in particular, is appreciably reduced with respect to its bulk value. Such a relaxation is accompanied by smaller relaxations of the second and third layers, that may be directed both inward or outward.

The magnitude of the relaxations depends markedly on surface orientation. It is common knowledge that larger inward relaxations occur for rougher surfaces (i.e. with lower atomic density). Our results, reported for the three low-index clean surfaces of Rh in Table I confirm this tendency: the (110) surface shows the largest relaxations, the closest-packed (111) the smallest. Also, even the second and third layer in (110) relax noticeably, while for (100) and (111) only the top-layers show an appreciable shift.

The results in Table I were obtained with 7-layers slabs, whereby all layers have been relaxed to their equilibrium position. The relaxation pattern is insensitive to a further increase of the number of layer for the (100) and (111) surfaces. For the (110), changes are non-zero but marginal: using a 9-layers slab, \(\Delta \sigma_{12}\) is almost unchanged (–10.7 %), and \(\Delta d_{23}\) and \(\Delta d_{34}\) are only slightly reduced (3.5 % and –1.0 % respectively). We emphasize that results in Table I are variations in interlayer spacing, which include relaxation contributions from the layers above and below the one considered. For the top layer these values are equal to the deviation from the ideal position...
only when the underlying layers are kept fixed.

In Table I, our results are also compared with those of Methfessel et al. [13], who used the FP-LMTO method to calculate the top-layer relaxations while keeping all other layers fixed. While the relaxation trend as a function of roughness is the same in both calculations, a sizable quantitative difference appears for the (110) surface. To clarify this, we repeated our calculations relaxing only the first surface layer, obtaining a relaxation of ~7.5%. The deviation from our full results is thus due to the neglect of multilayer relaxation in Ref. [13]. Indeed, this relaxation mode is expected to play a role on the (110) face, where first-layer and third-layer atoms are nearest-neighbors. Our results show that the assumption (suggested in Ref. [14] for bcc (100) surfaces) that the top interlayer spacing remains unchanged irrespective of the movement of the layers below, is inappropriate for the fcc (110) surface.

We now briefly recall Pettifor’s [15] model for the trend systematization of the basic properties of transition-metal surfaces. In transition metals, according to this model, the bulk equilibrium lattice constant results from the competition of a negative (attractive) pressure due to bonding, localized, and directional d states, and of the repulsive pressure of the delocalized sp ones (which tend to decrease their kinetic energy). At the surface, sp electrons can spill out into vacuum, and the top layer is further driven inward by the d electron attraction. Within this model, one expects the top-layer relaxation to follow a roughly parabolic trend as a function of d occupation. (This feature was basically confirmed by the DFT-LDA calculations of Methfessel et al. [13], where further detailed discussions can be found.) At the end of a transition series, the s-d balance is reversed, with the s electrons providing cohesion and the d states functioning more and more as a closed shell as one approaches the noble metals. The fcc structure is typical of this section of the transition series. Rh is peculiar in that it is the first metal in the 4d transition series of the three surfaces, listed in Table I, are in line with these expectations.

Results are given for both relaxed and unrelaxed surfaces. Surface energies and work functions are only marginally affected by relaxations, even for the rough (110) surface. The discussion of this feature given in a previous work on W [14] applies to Rh as well. Our results are seen to compare well with those of Ref. [13]. Numerical deviations are quite minor, considering the difference between the two methods employed.

A technical point concerning the calculation of surface energies is in order here. It is generally assumed that surface energies can be extracted straightforwardly as differences of the energy of a slab mimicking the surface, and of an appropriate bulk energy. For the present case

$$\sigma = \lim_{N \to \infty} \frac{1}{2N} (E_{\text{slab}} - N E_{\text{bulk}}),$$

(1)

with N the number of layers and $E_{\text{bulk}}$ the bulk energy per atom. It has been recently proven by Boettger [17] that the surface energy diverges as a function of slab thickness if the incremental energy of the slab upon addition of an atom differs (however little) from the bulk energy $E_{\text{bulk}}$. While this results has not yet been widely appreciated, in a recent work it has been shown [18] that the problem is indeed relevant in practice even for technically state-of-the-art calculations. A simple solution to the problem was suggested [18]: the bulk energy to be used in Eq. (1) is the linear part of the slab total energy as a function of N. This choice of $E_{\text{bulk}}$, besides being the natural one, leads to fast convergence of $\sigma$ (see Ref. [18] for further details). In our calculations we indeed encountered essentially the same situation mentioned in Ref. [15] for Pt (100), and computed $\sigma$ by the method suggested there.

III. SURFACE FORMATION ENERGIES AND WORK FUNCTIONS

Surface roughness plays a key role in determining the general trends of formation energy, work function, and relaxations. One could pick any of these quantities as a quantitative measure of the roughness, since each of them exhibits well-defined trends as a function of roughness. Within the Smoluchowsky model [16], a rough surface presents a smaller inward-oriented electric dipole moment compared to a smoother surface of the same material.

One thus expects the (110) surface to have the largest formation energy (having the highest number of removed nearest neighbors) and the smallest work function; on the other hand, the close-packed (111) surface should have the smallest surface energy and the largest work function. Our results for the surface energies $\sigma$ and work functions $W$ of the three surfaces, listed in Table I, are in line with these expectations.

IV. SURFACE STRESS

Surface stress is an important quantity providing insight into surface structure, and useful trend information on a number of processes, such as surface reconstructions. For example, relief of tensile in-plane stress is believed to cause the quasi-hex reconstruction of the (100) surface of 5d fcc transition metals [13]; a contractive reconstruction observed recently on Cu (100) [2] has been attributed to the same cause [2]. The surface stress is defined as the strain derivative of surface energy per surface cell [1][2]. If all bulk contributions to the stress are zero, the surface stress is thus...
\[ \tau_{\alpha\beta}^{\text{surf}} \equiv \frac{1}{A} \frac{\partial \sigma}{\partial \epsilon_{\alpha\beta}} = \frac{\Omega}{2A} \tau_{\alpha\beta}, \]

where \( \tau_{\alpha\beta} \) is the volume-averaged stress tensor \(^{[22]}\) of the supercell. As usual the factor of 2 accounts for the two surfaces of the slab. A positive \( \tau_{\alpha\beta}^{\text{surf}} \) is a tensile stress favoring in-plane contraction of the surface, while a negative (compressive) stress favors surface expansion.

For the stress calculations, we used an energy cutoff of 45 Ryd, at which the bulk stress is essentially zero (\( \tau_{\alpha\beta}^{\text{bulk}} \approx 5 \times 10^{-6} \text{ eV/bohr}^3 \)), and dispensed therewith with bulk corrections to the surface stress \(^{[21]}\). If the bulk stress were non zero, it should be subtracted out much in the same way as in the calculation of the surface energy. In passing we verified that the surface energies calculated at 45 Ry deviate from those calculated at 30 Ry by less than 0.01 eV/atom.

In Table III we report the surface stress for the (111), (100) and (110) surfaces of Rh. For the unrelaxed surface the planar components of the stress are sizably larger than the vertical component. The latter is however non-zero, and in fact quite large for the very open (110) surface. Relaxation reduces appreciably the in-plane components of the stress are sizably larger than the vertical component. The latter is however non-zero, and in fact quite large for the very open (110) surface. Relaxation reduces appreciably the in-plane components (up to about 50 \%) and renders the z component of the supercell stress negligible in comparison to the planar components, as it should be.

As expected, the stress is anisotropic for the (110) surface. The ratio of the stress components along the [110] and [001] directions is 1.59 (1.09) for the relaxed (unrelaxed) surface. These appear consistent with the anisotropy values of 1.47 (1.05) for relaxed (unrelaxed) Pd (110), and 2.08 (1.47) for relaxed (unrelaxed) Pt (110) recently reported by Feibelman \(^{[1]}\). Both anisotropy and absolute values of the (110) stress components are comparable to those of Pd, but much smaller than for Pt. This seems consistent with the absence of missing-row reconstructions of clean Rh (110) and Pd (110), and its presence for Pt (110). Note also that anisotropy is strongly enhanced by relaxation due to a larger decrease of the stress along [001] (i.e. transversally to the surface channels), again in agreement with Feibelman’s results for Pt and Pd. Also, the stress values are quite insensitive to the number of layers used in its calculation, which is consistent with Feibelman’s finding that close to 99 \% of the stress on a Pt (111) surface originates from the top surface layer.

To our knowledge these are the first calculations of stress for Rh surfaces. The only other stress calculation for Rh we are aware of is that of Ref. \(^{[13]}\), in which a stress of 1.94 eV/atom was obtained for unrelaxed Rh (100). This compares well with the value of 2.03 eV/atom obtained here, especially in view of the very different computational methods used in the two cases.

\[ \tau_{\alpha\beta}^{\text{surf}} \equiv \frac{1}{A} \frac{\partial \sigma}{\partial \epsilon_{\alpha\beta}} = \frac{\Omega}{2A} \tau_{\alpha\beta}, \]

\[ \text{where } \tau_{\alpha\beta} \text{ is the volume-averaged stress tensor } \]
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| This work | Ref. [13] |
|-----------|-----------|
| (100)     | (110)     | (111)     | (100) | (110) | (111) |
| ∆d_{12}  | -3.4      | -10.5     | -1.6  | -3.5  | -7.5  | -2.5  |
| ∆d_{23}  | 0.5       | 4.4       | -0.4  |       |       |       |
| ∆d_{34}  | -0.3      | -1.6      | 0.3   |       |       |       |

TABLE I. Intra-layer relaxations (percentage variation with respect to ideal layer spacing) for the three low-index surfaces of Rh. Results from Ref. [13] are included for comparison.

| This work | Ref. [13] |
|-----------|-----------|
| (100)     | (110)     | (111)     | (100) | (110) | (111) |
| σ⁺⁺⁺⁺     | 1.34      | 1.96      | 0.98  |       |       |       |
| σ⁺⁺⁻⁻     | 1.32      | 1.89      | 0.97  | 1.27  | 1.84  | 0.99  |
| Δσ⁺⁺⁺⁺     | 0.02      | 0.07      | 0.01  |       |       |       |
| W⁺⁺⁺⁺     | 5.45      | 5.07      | 5.59  | 5.25  | 4.94  | 5.44  |

TABLE II. Surface energy σ, relaxation energy Δσ (the surface energy change upon relaxation) and work function for the three clean surfaces. ‘u’ and ‘r’ indicate unrelaxed and relaxed surfaces respectively. All results are in eV/atom. Results of Ref. [13] are included for comparison.