

SURFACE SCIENCE LETTERS

**CALCULATION OF THE STRUCTURAL ENERGY OF THE
UNRECONSTRUCTED AND (1×2) RECONSTRUCTED Pt(110)
SURFACE**

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Describing the binding energy of both d and s valence electrons within the LCAO formalism, and by including repulsive Born–Mayer type interactions, we study the structural stability of the reconstructed and unreconstructed Pt(110) surfaces. Our main result is that amongst the various models for the (1×2) reconstruction the “Bonzel–Ferrer” model is unfavoured, while the “missing-row” model seems to be energetically degenerate with the unreconstructed surface. Our calculation predicts also a small surface concentration, which, however, has only a minor effect on the total energy of the system.

It is well established that the (110) surfaces of the late 5d metals Ir, Pt and Au show a (1×2) reconstruction at room temperature [1–3]. Various models have been proposed for the atomic arrangement at these surfaces [4,5]: the “paired rows”, the “buckled surface” and the “missing-row” model. Mainly based on a low-energy electron diffraction (LEED) data analysis, the “missing-row” model seems to be favoured at these surfaces [5]. Due to difficulties with regard to explaining the mass transport, Bonzel and Ferrer proposed an alternative sawtooth model [5] for the reconstructed surface. Recent scanning tunnelling microscopy (STM) and X-ray diffraction experiments suggest a disordered surface structure with “missing-row”-like domains [6,7].

In order to clarify the controversy about the equilibrium atomic structure at those fcc (110)- (1×2) surfaces, we calculated the total energy for the unreconstructed as well as for the “missing-row” and the “Bonzel–Ferrer” reconstructed Pt(110) surface. The structure models for these surfaces are schematically given as insets in fig. 1. In our calculation, the cohesive energy E_{coh} is given by an attractive band-structure term E_{BS} due to d- and s-electron cohesion, and by a repulsive Born–Mayer type interatomic interaction E_{R} mainly due to s-electron repulsion. Thus,

$$E_{\text{coh}} = E_{\text{BS}} + E_{\text{R}}, \quad (1)$$

where

$$E_{BS} = E_{BS}^d + E_{BS}^s. \quad (2)$$

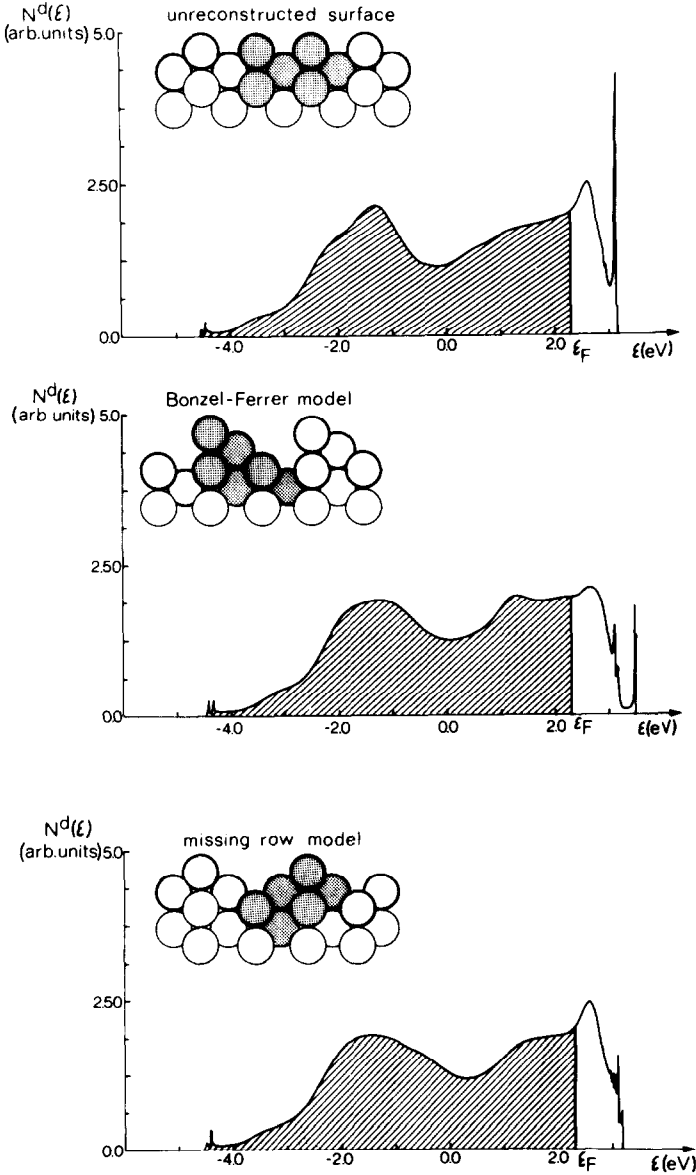


Fig. 1. Results for surface densities of d-states $N^d(\epsilon)$ for various surfaces. The insets illustrate the relevant model for the surface structure.

The d-electron band structure part is given by [8]

$$E_{\text{BS}}^{\text{d}} = \sum_i \int_{-\infty}^{\epsilon_{\text{F}}} d\epsilon (\epsilon - \epsilon_{0,i}^{\text{d}}) N_i^{\text{d}}(\epsilon), \quad (3)$$

where the summation extends over all sites i , $\epsilon_{0,i}^{\text{d}}$ is the local d-band center of gravity and $N_i^{\text{d}}(\epsilon)$ denotes the local density of d-states.

Owing to little structure in the s-electron density of states, the s-electron band structure energy $E_{\text{BS}}^{\text{s}}(i)$ at site i is proportional to the square root of the second moment $M_2^{\text{s}}(i)$ of its local density of states and can be related to the bulk band structure energy $E_{\text{BS}}^{\text{s}}(\text{bulk})$ by [9]

$$E_{\text{BS}}^{\text{s}}(i) = \frac{[M_2^{\text{s}}(i)]^{1/2}}{[M_2^{\text{s}}(\text{bulk})]^{1/2}} E_{\text{BS}}^{\text{s}}(\text{bulk}) \equiv \frac{\left[\sum'_j (t_{ij}^{\text{s}})^2 \right]^{1/2}}{\left[\sum'_j (t_{\text{bulk},j}^{\text{s}})^2 \right]^{1/2}} E_{\text{BS}}^{\text{s}}(\text{bulk}). \quad (4)$$

Here, the second moments $M_2^{\text{s}}(i)$ have been expressed in terms of s-hopping integrals t_{ij}^{s} between the site i and all its neighbours j . Defining the effective coordination number $Z_{\text{eff}}(i)$ by [9]

$$Z_{\text{eff}}(i) = \frac{1}{(t_{\text{nn}}^{\text{s}})^2} \sum'_j (t_{ij}^{\text{s}})^2 = Z_1(i) + \left(\frac{t_{ij}^{\text{s}}}{t_{\text{nn}}^{\text{s}}} \right)^2 Z_2(i) + \dots, \quad (5)$$

where t_{nn}^{s} is the nearest neighbour s-hopping integral and $Z_n(i)$ is the number of n th nearest neighbours of site i , the total s-electron band structure energy can be written as [9]

$$E_{\text{BS}}^{\text{s}} = \sum_i \left(\frac{Z_{\text{eff}}(i)}{Z_{\text{eff}}(\text{bulk})} \right)^{1/2} E_{\text{BS}}^{\text{s}}(\text{bulk}). \quad (6)$$

The s-band structure energy in the bulk can be obtained from a pseudopotential ansatz [10] using the Ashcroft empty-core potential, following a similar treatment for the 4d transition metals [10] as

$$E_{\text{BS}}^{\text{s}}(\text{bulk}) = -\frac{3Z_{\text{A}}N_{\text{s}}}{m_{\text{s}}} \frac{1}{S} \left[1 - \left(\frac{R_{\text{A}}}{S} \right)^2 \right] + \frac{3}{5} \left(\frac{9}{4} \pi N_{\text{s}} \right)^{2/3} \frac{N_{\text{s}}}{m_{\text{s}} S^2}. \quad (7)$$

Here, S is the Wigner–Seitz radius, Z_{A} and R_{A} denote the effective core charge and radius, respectively, N_{s} is the s-band occupancy and m_{s} is the effective s-electron mass.

The repulsive part E_{R} is a sum of pairwise repulsive interactions given by [9,11]

$$E_{\text{R}} = \frac{(q/p) E_{\text{coh}}(\text{bulk})}{(1 - q/p) Z(\text{bulk})} \sum'_{ij} \exp[-p(r_{ij}/r_0 - 1)]. \quad (8)$$

Here, Z is the coordination number and $r_{ij}(r_0)$ is the relaxed (unrelaxed or bulk) distance between the nearest neighbour sites i and j . When calculating E_{coh} for distorted or relaxed geometries, we assume the intersite d-hopping integrals $t_{ij}^d(r)$ to show an exponential distance dependence [11] given by

$$t_{ij}^d(r) = t_{ij}^d(r_0) \exp[-q(r/r_0 - 1)]. \quad (9)$$

Note that a similar distance dependence has been assumed in eq. (8) for the repulsive interaction, involving p in the exponent. For a given crystal geometry, the total energy of the reconstructed and unreconstructed system can now be obtained from eqs. (3) and (6)–(8).

Since it is not clear a priori that total energy differences between the unreconstructed and reconstructed system are not severely affected by a multilayer relaxation at the surface, we first estimate this relaxation from minimizing

$$E_{\text{coh}}^{\text{relax}} = E_{\text{BS}} + E_{\text{R}} \quad (10)$$

with respect to geometry. For this purpose we describe the Pt binding electrons by a model density of states which satisfies the first three moments and obtain for the energy to be minimized [9,11]

$$E_{\text{coh}}^{\text{relax}} = \frac{E_{\text{coh}}(\text{bulk})}{(1 - p/q)\sqrt{Z(\text{bulk})}} \sum_i \left[\left(\sum_j' e^{-2q(r_{ij}/r_0 - 1)} \right)^{1/2} - \frac{1}{\sqrt{Z(\text{bulk})}} \frac{q}{p} \sum_j' e^{-p(r_{ij}/r_0 - 1)} \right]. \quad (11)$$

The parameters involved in the calculation are obtained by adjusting the Slater–Koster parameterized d-hopping integrals to the calculated [12] bulk 5d bandwidth of Pt $W_{\text{d}} = 7.62$ eV, and we use the 5d occupancy [12] $N_{\text{5d}} = 8.22$ electrons. The s-band structure energy is calculated taking for the Pt 6s-band occupancy [12] $N_{\text{6s}} = 0.76$ and by extrapolating 4d-metal data [10] yielding $Z_{\text{A}} = 1.1$ a.u., $R_{\text{A}} = 1.12$ Å and $m_{\text{s}} = 0.95$. The parameters p and q describing the elastic behaviour of the crystal are chosen to reproduce data (referring to $T = 0$ K) for the bulk cohesive energy [13] $E_{\text{coh}}(\text{bulk}) = -5.86$ eV, the bulk modulus [14] $B_0 = 2.88 \times 10^{12}$ dyn/cm² and the nearest neighbour distance [15] in bulk Pt, $r_0 = 3.916$ Å, which yields $p = 13.7$ and $q = 5.0$.

Using these parameters, we first minimize $E_{\text{coh}}^{\text{relax}}$ in eq. (11) with respect to geometry. The estimated relaxations of the topmost layers of the unreconstructed and the (1×2) reconstructed surface models are shown in table 1.

Next, in order to compare the cohesive energies of the reconstructed and unreconstructed crystals, we subdivide the topmost layers of each surface into equivalent blocks of 6 atoms (see the hatched sites in the insets of fig. 1). We further assume that the contribution of the deeper-lying “bulk-like” atoms

Table 1

Vertical relaxation of the topmost layers at different Pt(110) surfaces as obtained from eq. (11)

	First layer	Second layer	Third layer
Pt(110)-(1×1) unreconstructed	-8.7% ^{a)}	+1.8%	
Pt(110)-(1×2) “missing row”	-7.4%	-2.3%	
Pt(110)-(1×2) “Bonzel–Ferrer”	-12.3%	-0.2%	-3.4%

^{a)} Relaxation of the interlayer spacing with respect to the bulk spacing. The negative sign denotes a contraction.

with a complete first and second nearest neighbour shell to total energy differences can be neglected. The local density of d-states is then calculated for the inequivalent sites in the block of surface atoms by using the recursion technique [16] for both the unrelaxed and the relaxed surface. Self-consistency is achieved by taking into account surface shifts of the d-levels $\epsilon_{0,i}^d$ in order to preserve local charge neutrality. Note, within a similar framework the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction observed on W and Mo(100) surfaces has been explained previously [17].

In order to minimize undesirable boundary effects in the calculation of the local density of states, we use large cubic-like clusters of about 1200 atoms. We truncate the continued fraction expansion of $N^d(\epsilon)$ after 10 levels (hence satisfying 20 moments of the local density of states) by using a moment-preserving quadratic terminator procedure [18] and determine the terminating coefficients alternatively from bulk band data and from a non-standard procedure due to Beer and Pettifor [19]. The results for the average surface density of states at the different Pt(110) surfaces studied are shown in fig. 1. The average s-band structure energy $\langle E_{BS}^s(\text{surface}) \rangle$ for the 6-atom blocks was evaluated by assuming the effective distance-dependence of the hopping integrals $t_{ij}^s(r)$ to vary between r^{-1} and r^{-3} in eq. (5). Allowing up to 9 nearest neighbour shells of the site i to contribute to $E_{BS}^s(i)$, we obtained $\langle E_{BS}^s(\text{surface}) \rangle / E_{BS}^s(\text{bulk}) = 0.854$ for the unreconstructed surface, 0.849 for the missing-row and 0.824 for the Bonzel–Ferrer reconstructed surface.

The results of our total energy calculation are presented in table 2. For both the unrelaxed and the relaxed surfaces we find the “Bonzel–Ferrer” model energetically unfavoured by ≈ 0.6 eV (per 6 surface atoms) with respect to the unreconstructed surface, whereas the “missing-row” model seems to be almost energetically degenerate ($\Delta E_{\text{coh}} \leq 0.1$ eV) with the Pt(110)-(1×1) structure. As can be seen from table 2, the influence of relaxation is to lower the total energy by ≈ 0.5 eV per block of surface atoms. Yet its inclusion and the influence of

Table 2

The cohesive energy E_{coh} and its contributions at relaxed and unrelaxed Pt(110) surfaces for different reconstruction models; E_{BS}^{d} and E_{BS}^{s} denote the d- and s-electron band structure contribution and E_{R} the repulsive energy due to Born–Mayer potentials; all energies refer to blocks of 6 surface atoms (marked in fig. 1) and are given in eV

	Relaxed ^{a)}				Unrelaxed			
	E_{coh}	E_{BS}^{d}	E_{BS}^{s}	E_{r}	E_{coh}	E_{BS}^{d}	E_{BS}^{s}	E_{R}
Pt(110)-(1 × 1) unreconstructed	-32.07	-26.28	-11.17	5.38	-31.58	-25.26	-11.17	4.85
Pt(110)-(1 × 2) “missing row”	-31.99	-26.21	-11.10	5.30	-31.58	-25.33	-11.10	4.85
Pt(110)-(1 × 2) “Bonzel–Ferrer”	-31.34	-25.72	-10.78	5.16	-30.72	-24.46	-10.78	4.53

^{a)} The assumed relaxations are given in table 1.

the parameters p and q on the energy differences is very small and does not affect our results [20].

A first qualitative understanding of these results can be obtained within a simple pair-bond model which also suggests the “Bonzel–Ferrer” model to be unfavoured with respect to the “missing-row” and the unreconstructed surface, independent of the respective metal. On these grounds, our main conclusions are expected to hold true also for the other late 5d metals Ir and Au, which show the same reconstruction pattern at the (110) surface [3].

The calculated energy differences of typically 0.1 eV per surface atom between the reconstruction models considered seem plausible and consistent with similar results [17] for the $\text{W}(100)-(1 \times 1) \rightleftharpoons (\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ transition. We find that these changes in energy are governed by a delicate energy balance between the attractive and the repulsive terms in E_{coh} . Also, our result that the “missing-row” reconstructed and the unreconstructed Pt(110) surfaces are close in energy is supported by the experimental evidence that the latter is only a metastable state of the reconstructed surface [21].

Concerning the accuracy of E_{BS}^{d} , we compare results obtained with different numbers of levels in the continued fraction expansion of $N^{\text{d}}(\epsilon)$ and determined the quadratic terminator coefficients from the bulk d-bandwidth or, alternatively, from the Beer–Pettifor procedure [19]. The uncertainty in energy proved to be of the order of 10^{-3} eV and hence does not affect our main conclusions. The d-level shifts introduced to preserve local charge neutrality are a manifestation of the surface potential and should coincide with core-level shifts. Indeed, the calculated shifts of -0.48 eV (top layer) and -0.21 eV (second layer) for the relaxed “missing-row” surface show an excellent agreement with observed core-level shifts [22] $\Delta_{\text{c}}^1 = -0.55$ eV (top layer) and $\Delta_{\text{c}}^2 = -0.21$ eV (second layer).

Unlike Terakura and Hamada [17] who investigate the reconstruction at the Mo and W (100) surfaces by a similar method and who trace the favourable $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstructed state back to a pronounced surface state in $N^d(\epsilon)$ near ϵ_F , we do not find any such feature in our local or averaged densities of states (see also fig. 1). Hence, from our calculation we cannot find any specific electronic origin of the Pt(110) reconstruction at zero temperature. On the other hand, since the (1×2) reconstructed state is found stable at nonzero temperatures [21], we speculate that surface entropy might be the driving force for reconstruction in this case. While the contribution of configurational entropy to free energy differences is negligible if the size of reconstructed domains is large enough, we expect the surface phonon entropy to be larger at the more open reconstructed surfaces as compared to the unreconstructed surface.

With respect to the above mentioned calculation for the Mo and W (100) surfaces [17], we improved the total energy expression by also considering the s-electrons, which were assumed to form a separate, rather structureless band. Clearly, the inclusion of s-d hybridization, neglected in the present calculation, is especially important in metals with a considerably different electronic configuration (s-d redistribution) at the surface and in the bulk. While this effect has to be considered when describing reconstruction at Au surfaces, it is expected to have only a minor influence on our numerical results and conclusions for Pt.

In our calculation for the "missing-row" model we tacitly assumed an infinitely extended surface with missing rows, in contrast to experimental evidence for limited domains with that structure [6,7]. We still expect our conclusions concerning the structure stability to hold true, if these domains are large enough and the domain boundary energies taken per surface atom are smaller than the energy difference driving the reconstruction at a perfectly periodic surface.

In this letter, the d-band structure energy has been calculated by using the (real-space) recursion method rather than a slab technique. The reason for our preference is the possibility to extend our investigations and compare our results to more realistic systems with structurally disordered reconstructed domains and to adsorbate- (e.g. CO)-covered systems [23].

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