Surface stress of Ni adlayers on W(110): the critical role of the surface atomic structure

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Abstract
Puzzling trends in surface stress have been reported experimentally for Ni/W(110) as a function of Ni coverage. In order to explain this behavior, we have performed a density-functional-theory study of the surface stress and atomic structure of the pseudomorphic and several different possible $1 \times 7$ configurations for this system. For the $1 \times 7$ phase, we predict a different, more regular atomic structure than previously proposed based on surface x-ray diffraction. At the same time, we reproduce the unexpected experimental change of surface stress between the pseudomorphic and $1 \times 7$ configuration along the crystallographic surface direction which does not undergo density changes. We show that the observed behavior in the surface stress is dominated by the effect of a change in Ni adsorption/coordination sites on the W(110) surface.

(Some figures may appear in colour only in the online journal)

1. Introduction
The importance of surface stress has been demonstrated for many surface processes, such as nanopatterning, surface reconstruction, interfacial mixing, and segregation [1–9]. In spite of its importance, however, a general understanding of the key factors governing the dependence of surface stress on the atomic structure of the surface is still lacking. This applies, in particular, to the case of heteroepitaxy and to the growth of metal adlayers on metal surfaces, where lattice mismatch is often assumed to be the prevailing factor controlling surface stress [10].

Specifically, in the case of metal adlayers on metal surfaces, puzzling changes in surface stress, as a function of adlayer coverage, have been observed experimentally [11–14]. Such changes are at variance with predictions based on lattice misfit arguments and model elasticity theory [11–14]. One interesting example is the Ni adlayer on W(110), whose surface stress was examined in some detail experimentally [13, 14]. In this system, the surface-stress changes along two orthogonal directions of the tungsten surface, [110] and [001], were measured as a function of Ni coverage [13, 14]. With increasing coverage, Ni goes through a range of phases [15, 16], a pseudomorphic (PS) $1 \times 1$ configuration, $1 \times 8$ and $1 \times 7$ coincidence structures, and finally a fcc(111)-like Ni overlayer with Nishiyama–Wassermann orientation on W(110) [15]. The epitaxial strain of the Ni(111) layer decreases with increasing coverage, from $\sim 27\%$ in the PS to $\sim -1\%$ in the $1 \times 7$ structure along W[001], while it remains constant ($\sim 4\%$) in these two phases along W[110]. The atomic density increases to nine Ni per seven W atoms along [001] in the $1 \times 7$ structure, whereas no change in periodicity relative to the PS configuration occurs in the perpendicular direction [17]. Interestingly, it was measured that the stress change between PS and $1 \times 7$ along [110] is considerably greater than that along [001], where actually a change of strain occurs. It remains unclear what the
microscopic changes are in the Ni/W(110) atomic structure related to this surprising behavior.

The structural properties of Ni/W(110) have been investigated experimentally by various techniques [15–23]. The types of reconstructions are known from low-energy electron diffraction (LEED) [15, 17] and scanning tunneling microscopy (STM) [16], but the actual details of the atomic structures are not well known or have large uncertainties. A model for the $1 \times 7$ coincidence structure has been proposed based on surface x-ray diffraction (SXRD) measurements [14]. It is characterized by distorted Ni hexagons and by a surprisingly large motion (up to 0.5 Å) of the subsurface-layer W atoms. Such displacements of the W atoms were suggested to be responsible for the anomalous behavior of the Ni/W stress [14]. However, because of the coexistence of various Ni phases at the deposition temperature used in [14], there is significant uncertainty on the structural details derived from the SXRD [14].

Ni/W is a prototype bimetallic system [15–31]. Such systems are particularly interesting due to their catalytic properties [21, 27–33], which often closely depend on surface structural changes. In addition, Ni has a very small atomic radius (the smallest of all fcc metals), so the study of its growth on bcc surfaces, such as the W surface, is especially helpful for understanding fcc/bcc metal interfaces [34, 15]. Ni/W systems have also been studied widely for its interesting magnetic properties [24–26, 35].

In this paper, we address the surface stress and atomic structure of the Ni/W $1 \times 1$ and $1 \times 7$ phases by means of first-principles density-functional-theory (DFT) calculations. In particular, we investigate the dependence of the surface stress on the atomic structure, with the aim of better understanding the key factors controlling the stress behavior in this type of bimetallic system. Ni/W(110) is an interesting case for this type of study as a surprising and unexplained stress change (related to unidentified structural modifications) between the two phases has been measured experimentally. For the $1 \times 7$ phase we predict a different, more regular atomic structure than the one proposed on the basis of the SXRD analysis [14]. The surface stresses we obtain for the theoretical lowest-energy $1 \times 1$ and $1 \times 7$ configurations account well for the stress behavior observed experimentally. Moreover, the change in surface stress between the $1 \times 1$ and $1 \times 7$ structure is shown to be dominated by the effect of a change in the Ni adsorption/coordination sites on the W(110) surface. This is in contrast to the situations where surface stress is determined mostly by elastic strains or charge transfer, which can be excluded in this system.

2. Methods

The DFT calculations were performed using pseudopotentials and a plane-wave basis, as implemented in the PWscf code, a part of the Quantum ESPRESSO distribution [36]. The local-density approximation (LDA) in the Perdew–Zunger parametrization [37] was adopted for the exchange and correlation functional. To simulate surfaces with different adlayer configurations we used a supercell method, for which we constructed an asymmetric slab with one Ni layer on five layers of W substrate (the bottom two W layers were fixed) and nine equivalent vacuum layers, both for relaxations and subsequent stress calculations. Laterally, we used a $1 \times 7$ cell. For the calculation of the adsorption sites we used 15-layer asymmetric $1 \times 1$ slabs, in which 12 layers were allowed to relax.

Vanderbilt ultra-soft pseudopotentials [38] were generated from the 3d$^9$4s$^1$ atomic configuration of Ni and from the 5s$^2$5p$^6$5d$^4$6s$^2$ configuration of W. The core-cutoff radii for Ni were $r_s = 2.0$ au and $r_d = 1.6$ au, and for W $r_{s,p} = 2.2, r_d = 2.4$ au. Our kinetic energy cutoff was 35 Ryd for the wavefunctions and 350 Ryd for the charge density. A $38 \times 38 \times 1$ $k$-point Monkhorst–Pack mesh [39] centered at $\Gamma$ was used for the $1 \times 1$ surface unit cell and a grid of comparable density $24 \times 6 \times 1$ for the $1 \times 7$ surface unit cell. We employed a Gaussian level smearing of 0.01 Ryd. The calculations were performed with the theoretical W lattice constant of 3.14 Å which is 1.6% different from the experimental lattice constant of 3.16 Å. The use of the theoretical equilibrium lattice constant ensures that no spurious stresses are present on the surface [40]. Total energy differences were converged to better than 0.1 meV. The forces in the $1 \times 7$ calculations, used as a criterion for the structural relaxation, were converged to better than 2 mRyd Å$^{-1}$ and the estimated uncertainties in the positions were 0.007 Å along $[110]$ and 0.010 Å along $[001]$. For the clean W(110) and Ni/W(110) PS calculations, the forces were converged to better than 0.2 mRyd Å$^{-1}$ and we estimated the uncertainties in positions to be around 0.001 Å in both directions.

We also performed calculations for the clean Ni(111) surface (non-magnetic) which were necessary for the interpretation of our results. For the calculation of the Ni(111) surface, we used our optimized lattice constant of 3.42 Å and a slab of 11 Ni layers. From our preliminary calculations we found the Ni PS layer on W(110) to be non-magnetic; the initial ferromagnetic Ni/W(110) configuration converged into a non-magnetic structure. This is consistent with findings in [41] and [42]. Hence, in the remaining part of this work all calculations refer to non-magnetic configurations.

Surface stresses were computed using the analytical expression derived by Nielsen and Martin [40], based on the Hellmann–Feynman theorem. The surface-stress uncertainty was estimated to be $\sim 0.3$ N m$^{-1}$ on the basis of convergence tests regarding the wavefunction and charge-density cutoffs, the number of $k$-points, and the number of vacuum layers [43]. As we used asymmetric slabs (with Ni on top and frozen W on the bottom), in order to obtain surface-stress values for the Ni-terminated surface, we subtracted the reference-surface stress of the frozen W surface.

3. Results and discussion

3.1. Pseudomorphic phase

The pseudomorphic Ni monolayer on W(110) may be viewed as a fcc-Ni(111) layer, oriented with the in-plane Ni[110]...
axis parallel to the W[001] in-plane direction, and laterally stretched along the W[001] and W[1\bar{1}]0 orthogonal directions. The Ni atoms can sit at or near any of the possible high-symmetry adsorption sites of W(110): ‘hollow’ (H) in the central-symmetric position, in a perfect continuation of the W bulk lattice, ‘three-fold’ (T) for which the Ni atoms are shifted along [1\bar{1}]0 to increase their coordination to the three nearest W neighbors, or ‘bridge’ (B) where the Ni atoms are located mid-way between two W atoms along [1\bar{1}]1. The sites H, T and B are shown in figure 1(a). A recent LEED I–V study [44] found that Ni atoms in the PS structure prefer to sit somewhere off the H site with a displacement toward the T site. This is in apparent contrast to the case of the PS Fe on W(110), where the Fe atom has been reported to sit at an intermediate position between the H and B site. The B site is clearly very unfavorable (~0.36 eV per Ni surface atom higher than T site). Figure 1(b) shows the lowest-energy pseudomorphic structure (T'). The Ni is close to the H site, but displaced along [1\bar{1}]0 at slightly less than 1/2 of the H–T distance. All results in table 1 are for the 15-layer asymmetric slabs (the bottom three layers are fixed to the bulk positions, while the remaining 12 layers are allowed to relax). We note that the Δx displacements in table 1 are given with respect to the bulk coordinates.

Our results are thus consistent with the slight displacement of the H site observed by LEED I–V. The T' site for Ni/W(110) may come as a surprise if one assumes a strong influence of the substrate in determining the adsorption site. Actually, for unreconstructed one-monolayer adsorbate surfaces it is often simply assumed that the adsorption will occur as a continuation of the bulk. On the other hand, one can reason that Ni(111) has a hexagonal in-plane structure with a three-fold coordination, which might influence a shift away from the hollow site.

### 3.2. 1 × 7 coincidence phase

The Ni/W(110) 1 × 7 structure is characterized by higher Ni density than the PS. As established experimentally [17], it has nine Ni atoms per seven substrate unit cells (the corresponding unit cell is illustrated in figure 2). The additional atoms are along the [001] direction, while along [110] it remains pseudomorphic.

We obtained three different stable and meta-stable solutions depending on the initial configuration for the structural relaxation. They are shown in figure 2. Starting from an ‘ideal’, equidistant Ni-row arrangement along [001] and

### Table 1. Energy difference between the equilibrium pseudomorphic configurations obtained by structural relaxations starting from the Ni atom at the H, T and B adsorption sites, respectively. The relaxations of the interlayer distances (Δd_{n,n+1}) and, for the T' configuration, the displacements along [1\bar{1}]0 (Δx), relative to the ideal hollow site (or the ideal bulk sites for the W) are also reported. ΔE is in meV per Ni surface atom, Δx in Å, while Δd_{n,n+1} is given in % of the bulk W–W interlayer spacing.

|        | H     | T'    | B     |
|--------|-------|-------|-------|
| ΔE     |       |       | 359   |
| Δd_{n,n+1} | Δx   | Δd_{n,n+1} | Δd_{n,n+1} |
| Ni     | -18.9 | 0.26  | -18.6 | -11.4 |
| W-first| 0.4   | 0.00  | 0.3   | 0.0   |
| W-second| 0.1  | 0.01  | -0.1  | 0.0   |
| W-third| 0.1   | 0.01  | 0.0   | 0.0   |

Figure 1. Possible adsorption sites for Ni/W(110) (a). T denotes three-fold, H hollow, B bridge site and Q denotes the site at one quarter of the W–W distance along [1\bar{1}]0. Black circles denote underlying W atoms, while an open circle stands for a Ni atom. Calculated pseudomorphic structure of Ni/W(110) (b). W atoms are shown in black and Ni atoms in green (gray).
Figure 2. Relaxed $1 \times 7$ structures of Ni/W(110). Atomic colors and directions are as in figure 1. The surface unit cell is also indicated (thick black solid lines) and shown enlarged in the right column for each structure.

[1\bar{1}0], configuration C1 (figure 2(a)) has been obtained. The C2 structure (figure 2(b)) was obtained starting from several different initial structures, including the SXRD structure from [14]. The C3 structure (figure 2(c)) resulted instead from a relaxation starting from a structure similar to the model superstructure of [14], but slightly less disordered, keeping only the distorted Ni hexagons. The C2 is the ground state; it is 196 and 244 meV per $1 \times 1$ W surface units lower than the C3 and C1 configurations, respectively.

The Ni layer in the C1 structure is very corrugated (with Ni sublayer separations, $\Delta z$, as large as 0.57 Å), as some of the Ni atoms sit on top of the underlying W atoms. The C2 structure (figure 2(b) and atomic coordinates in the appendix) can be described by oscillating chains of Ni atoms, oriented parallel to the W[001] direction, and with their axis projection on the W surface located mid-way between adjacent [001] rows of W atoms. The Ni layer in the C2 structure is corrugated only slightly ($\Delta z$ less than 0.15 Å).
and is very similar to the bulk Ni(111) layer—the same average nearest-neighbor (NN) distance of 2.51 Å, with a root-mean-square (rms) deviation of 0.12 Å, and an angular rms deviation of 4.9° with respect to the average NN angle of 60°. The C3 structure, instead, as shown in figure 2(c), has a more complicated structure, with distinct distorted Ni hexagons.

Based on SXRD measurements, Meyerheim et al [14] proposed a rather disordered structure, characterized by distorted Ni hexagons and Ni atoms located mostly at or close to the bridge sites between W atoms. We note that C2 does not resemble it much. We find from our calculations that the bridge-site configuration is energetically very unfavorable. A possible explanation for the discrepancy between our theoretical structure and the SXRD-derived atomic structure is the coexistence of various phases with domain sizes of a few nanometers [17, 16] observed under the growth conditions used in the SXRD measurement [14]. For such small domains, the structural relaxations at the domain boundaries are expected to be significant [43]. Furthermore, the coexistence of phases with similar periodicity, i.e. $1 \times 8$ and $1 \times 7$ phases, combined with the small domain sizes, possibly makes it difficult to distinguish the corresponding reciprocal-space features in the diffraction measurements. The disorder, which was essential in fitting the diffraction data in the mentioned SXRD study [14], is consistent with these observations. We note that such a disorder, resulting from room-temperature measurements, cannot be obtained from coexistence of the C1, C2 and C3 configurations due to the large energy differences between C2 and the other two structures. However, we cannot exclude the possibility that the C2 structure could represent a better model to fit the SXRD data, as the study in [14] does not seem to take into account a C2-like structure in searching for the optimal fit.

Our C2 structure, instead, corresponds to and is very much like the theoretical model prediction of [34] for the $1 \times 7$ structure of Ni/Mo(110) and the experimental and theoretical $1 \times 8$ structure of Co/W(110) [46, 47]. In our case, the amplitude of the oscillations of the Ni chains is about 0.34 Å. Mo and W are both bcc metals and have almost identical lattice parameters (the difference is about 0.6%). Clearly, the model predictions for the Ni/Mo(110) are also very relevant for Ni/W(110), as our optimized structure demonstrates. Similarly, the nearest-neighbor distances for bulk Ni and Co are very close (~0.5% difference), and one could expect some similarities of their adsorbate structures on W(110). Therefore, based on our results on Ni/W(110), one could expect that the $1 \times 7$ phase of Co/W(110) should also exist for coverages within the interval determined by the $1 \times 1$ and $1 \times 8$ phases.

### Table 2. The first two interlayer distances for the $1 \times 7$ configurations, compared to the PS and clean W(110).

|       | C1   | C2   | C3   | PS   | W    |
|-------|------|------|------|------|------|
| $d_{01}$ (%) | −6.1 | −10.1| −9.5 | −18.6| −3.6 |
| $d_{12}$ (%) | 1.1  | 0.0  | 0.5  | 0.3  | −3.6 |

In table 2 we compare the first two average interlayer distances of the three $1 \times 7$ configurations with the PS and clean W(110) surface. PS has the largest contraction of the first layer, roughly two times larger than the $1 \times 7$ configurations. Of those, C1’s first layer is the least contracted due to the on-top position of the Ni atoms in a part of the surface unit cell. In all the $1 \times 7$ and $1 \times 1$ adsorbate structures considered, the W top-layer relaxation of $−3.6\%$ is removed. Only the C1 structure displays a non-negligible $d_{12}$ relaxation, due to a relatively distant top layer. We note that although C2 and C3 have similar values for $d_{01}$, C2’s interlayer spacing of 2.00 Å is more similar (with less than 1% difference) to the first-layer spacing of the Ni(111) surface, which has a very small relaxation (we calculated it to be $−0.4\%$).

#### 3.3. Surface stress

In figure 3 we present the calculated surface stresses, along the W[110] and W[001] directions, for the clean W(110) surface and for our ground state PS and $1 \times 7$ Ni/W(110) surfaces. They are displayed as a function of Ni coverage. The values for the clean W(110) surface are consistent with previous DFT values [43, 48].

A first observation is that the stresses are tensile (positive) for all the configurations, which means that the stress relaxation would cause contraction of interatomic distances on the surface. This is not surprising, as tensile stress occurs at most metal surfaces due to a charge redistribution upon

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1 We note that our calculated W(110) relaxations are given in [43] and that the first two relaxations are identical for the five-layer W film used in the present work and a thicker film from [45].
2 Almost all Ni/W(110) structures considered in this work (the only exception is the H-site PS structure) also have some shear stress components, the magnitudes of which are always smaller than 1 N m$^{-1}$ and of which the largest is for the C3 structure.
Table 3. Surface stress for the $1 \times 1$ structures characterized by different adsorption sites. All stresses are in N m$^{-1}$.

| H    | T'   | T   | Q   | B   |
|------|------|-----|-----|-----|
| $I_{[110]}$ | 8.9  | 7.9 | 6.1 | 5.1 | 5.9 |
| $I_{[001]}$ | 2.9  | 3.6 | 5.8 | 8.4 | 7.5 |

Table 4. Surface stress for the three $1 \times 7$ structures. All stresses are in N m$^{-1}$.

| C1   | C2   | C3   |
|------|------|------|
| $I_{[110]}$ | 9.5  | 4.0  | 0.2  |
| $I_{[001]}$ | 2.7  | 4.1  | 3.5  |

bulk termination. From W to PS Ni/W the stress is increasing along $[110]$, whereas it is decreasing along $[001]$, which is somewhat surprising. Considering the lattice mismatch, the Ni layer is under a strongly tensile (experimentally: 27%, theoretically 30%) epitaxial strain along $[001]$ (and experimentally under a 4% strain, theoretically under a 6% strain along $[110]$). This would suggest a strongly tensile (positive), rather than compressive, change in the stress along $[001]$. In fact, the continuum elasticity estimates would yield tensile stresses along both directions $[13, 14]$, with the stress along $[001]$ roughly twice as large.

Moreover, we notice a large change (decrease) in stress along $[110]$ and almost no change along $[001]$ from the PS to the $1 \times 7$ configuration, although the change in strain (insertion of atoms, i.e. compressive change in strain) is occurring along $[001]$. In this case, the estimated change (decrease) of stress from the elasticity-theory model would be three times larger along $[001]$ than along $[110]$ $[10]$. Similar surprising trends in the stress were detected experimentally $[14]$. In fact, there is a good general agreement between theory and experiment $[13, 14]$: most of the main features and changes of trends are reproduced, although our calculated change in the $[001]$ stress from clean W to PS ($-2.0$ N m$^{-1}$) is smaller in magnitude than the reported measured value in $[13]$ ($-2.9$ N m$^{-1}$) and our $[001]$ stress change from clean W to $1 \times 7$ ($-1.3$ N m$^{-1}$) is larger/smaller in magnitude than the measured value reported in $[13]$ ($-0.8$ N m$^{-1}$) $[14]$ ($-2.1$ N m$^{-1}$) $[3]$. It should be noted that different degrees of coexistence of Ni phases, other than the reference $1 \times 7$ phase, are likely to be responsible for the difference in the experimental values in $[13]$ and $[14]$.

In order to understand the influence of the surface structure on the stress in figure 3, we also evaluated the surface stress of the other PS and $1 \times 7$ structures we considered in the previous subsections. The results are reported in table 3 (for the $1 \times 1$ structures) and table 4 (for the $1 \times 7$ structures). The results for the $1 \times 1$ structure in table 3 show that the Ni adsorption site has a critical influence on the surface stress. The H site (close to T') is characterized by an especially large stress (8.9 N m$^{-1}$) along $[110]$ and low stress (2.9 N m$^{-2}$) along $[001]$, which account for the stress behavior of the ground state (T') PS structure in figure 3. The B site, instead, has a larger stress along $[001]$ (7.5 N m$^{-1}$) than along $[110]$ (5.9 N m$^{-1}$), whereas the T site is characterized by a more isotropic (‘averaged’) stress (5.8–6.1 N m$^{-1}$). The stress is exactly isotropic somewhere off the T site, toward the Q site, which has reversed stresses, i.e. larger stress (8.4 N m$^{-1}$) is along $[001]$. At this site, along $[110]$ the stress (5.1 N m$^{-1}$) is the smallest of all considered $1 \times 1$ structures, as it is steadily decreasing from the H site to the Q site.

Similar trends are observed for the $1 \times 7$ structure in table 4, from which one can draw a relation between the stress of the predominant type of adsorption site and the stress of the $1 \times 7$ structures. In particular, the C1 structure is characterized by an especially large stress (9.5 N m$^{-1}$) along $[110]$ and low stress (2.7 N m$^{-1}$) along $[001]$. This is similar to the behavior of the H structure, suggesting a dominant influence of the H site in determining the stress of the C1 structure. Similar to the T structure, the C2 structure (including many Ni T-like sites) displays a nearly isotropic stress (4.0–4.1 N m$^{-1}$). This suggests a dominant influence, in this case, of T-like sites (figure 2(b)) on the behavior of the C2 stress. We also note that the C2 stress is somewhat lower than the T stress, which is consistent with a higher-density (more compressed) Ni layer in the C2 structure, compared to the T structure. For the C3 structure, instead, the crucial element for the interpretation of the stress in table 4 appears to be the presence of the 2 Ni atomic rows squeezed into one along $[110]$, which causes compressive stress along $[110]$.

We can apply the above findings to an explanation of the anomalous trend (with respect to the expectations from the model elasticity theory) observed in figure 3 and in the experiment, from PS to $1 \times 7$ configurations. From elasticity theory, an essentially constant stress along $[110]$ and a significant decrease of stress along $[001]$ are expected, while in both experiment and our calculations, we observe the opposite: there is a strong decrease along $[001]$ and a slight increase along $[110]$. The observed trends can be rationalized, however, by considering the change in Ni adsorption sites, from H-like or T' site (i.e. essentially two-fold coordinated sites) in the PS configuration to mainly three-fold coordinated T-like sites in the C2 configuration. In fact, the results in table 3 demonstrate a major influence of the type of site occupied by the Ni on the stress. They also indicate that the two-fold H-like sites tend to yield highly anisotropic stresses, with $T_{[110]} \gg T_{[001]}$, whereas the three-fold T-like sites tend to produce an isotropic stress, whose value is equal to the average over the two perpendicular directions of the Ni stress components (for the same Ni density). On the basis of these considerations, the stress from PS to $1 \times 7$ is expected to increase along $[001]$ and decrease along $[110]$, with the decrease being larger in magnitude, due to the effect of a larger Ni density in the $1 \times 7$ than in the PS case. We would like to emphasize that, in our case, unlike the case of alkali-metal
The trends in the stress changes are not driven by a charge transfer effect. In fact, we evaluated the work function change (which is a measure of charge transfer) between the 1×1 and 1×7 phases. The work function change between the T′ 1×1 and C2 configurations is 0.2 eV. The small change of the work function, as calculated, indicates a very small charge transfer, which cannot explain the large change in stress when the Ni site changes.

Meyerheim et al [14] also emphasized the importance of the displacement of the first W layer for their proposed structure, which had significant displacements of W atoms. We have checked the influence of the first W layer on the surface stress in the C3 structure, the most disordered 1×7 structure we obtained theoretically. In the proposed structure based on the SXRD, the W in-plane displacements are extremely large, reaching even 0.5 Å. In our structure, the maximum displacements are about 10 times smaller. We fixed W positions in this layer to the ideal bulk positions, keeping the interlayer spacing unchanged. The stress of the C3 structure thus changed by only –0.4 N m⁻¹ in both directions, indicating that the W displacements are probably not the cause of the drastic stress change of the C3 structure with respect to PS, and instead it is likely that the influence of Ni atoms and their configuration is the essential one.

Finally, we note that the C2 structure may be defined with two harmonic functions, which describe the atomic displacements along [110] and [001] [34], and create nearly regular hexagons. The resulting stress is actually almost isotropic, so one could hypothesize that although the system is not necessarily relaxing the surface stress, it is approaching the limit of a clean Ni surface. Even our calculated values are rather close, around 4 N m⁻¹ for C2 and 3.5 N m⁻¹ for the non-magnetic Ni(111). Therefore, it seems that in the case of the Ni/W(110) 1×7 reconstruction the minimum-energy configuration coincides with highly isotropic arrangement of Ni atoms whose average stress also corresponds to the clean Ni(111) surface.

4 We also evaluated the work function change between the clean W(110) and 1×1 phases: the change is –0.4 eV for the T′ and H sites and –0.6 eV for the B site. This is almost identical to the previous LDA [50] and GGA [42] findings and somewhat different (by 0.3–0.4 eV in magnitude) from the experimental value [18]. However, from both theoretical and experimental values of the work function change, which is considerably smaller in magnitude than for Li/Mo(110) [12], one can deduce that the charge transfer is not responsible for the drastic surface-stress changes.

4 Conclusion

Motivated by puzzling measured stress changes in Ni/W(110), we performed a first-principles DFT study of the surface stress and structural properties of the PS and 1×7 coincidence phase. We determined the ground state 1×7 structure which is different from the one proposed based on SXRD. The latter structure is very irregular, with many distorted Ni hexagons, while ours includes a highly isotropic Ni(111)-like layer and can be described by oscillating Ni[001] chains with their axis projection on the W surface located mid-way between adjacent rows of [001] W atoms. The ground state 1×7 coincidence structure we obtain is, instead, similar to the model-theory prediction for the 1×8 Ni/Mo(110) structure and to the experimentally and theoretically described 1×8 phase of Co/W(110).

Furthermore, our calculated stresses qualitatively follow the measured stress changes with Ni coverage and reproduce the surprising trend of a larger stress change along the direction perpendicular to the Ni atomic density change. We explained the trends in the stress changes in terms of a dominant influence on stress of the Ni adsorption/coordination sites, as opposed to the interpretations based on the continuum elasticity theory or charge transfer. We expect our conclusions concerning the stress dependence on the adsorption/coordination sites to apply more generally to other related bimetallic systems involving transition-metal atoms.

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Appendix. 1×7 atomic positions

In table A.1 we list the atomic coordinates of the upper three layers for the lowest-energy 1×7 configuration, C2.

|       | x    | y    | z    |       | x    | y    | z    |       | x    | y    | z    |
|-------|------|------|------|-------|------|------|------|-------|------|------|------|
| Ni1   | 16.86| 10.68| 24.12| W1    | 19.92| 10.99| 22.14| W6    | 2.20 | 0.00 | 19.92|
| Ni2   | 3.38 | 0.89 | 24.20| W2    | 2.20 | 1.57 | 22.18| W9    | 4.42 | 1.57 | 19.93|
| Ni3   | 5.35 | 2.15 | 24.17| W3    | 4.44 | 3.14 | 22.12| W10   | 6.65 | 3.14 | 19.91|
| Ni4   | 5.17 | 4.60 | 24.06| W4    | 6.66 | 4.70 | 22.11| W11   | 8.87 | 4.71 | 19.91|
| Ni5   | 7.41 | 3.35 | 24.08| W5    | 8.86 | 6.28 | 22.17| W12   | 11.08| 6.28 | 19.92|
| Ni6   | 11.95| 5.81 | 24.15| W6    | 11.05| 7.84 | 22.16| W13   | 13.26| 7.85 | 19.92|
| Ni7   | 9.96 | 7.03 | 24.21| W7    | 13.26| 9.42 | 22.12| W14   | 15.51| 9.42 | 19.92|
| Ni8   | 12.40| 8.25 | 24.14|       |      |      |      |       |      |      |      |
| Ni9   | 14.72| 9.44 | 24.08|       |      |      |      |       |      |      |      |

Table A.1. Atomic positions in Å for the upper three layers for 1×7. x is along [110] and y along [001].
References

[1] Haiss W 2001 Rep. Prog. Phys. 64 591
[2] Ibach H 1997 Surf. Sci. Rep. 29 195
[3] Narasimhan S and Vanderbilt D 1992 Phys. Rev. Lett. 69 1564
[4] Nielsen L P, Besenbacher F, Stensgaard I, Laegsgaard E, Engdahl C, Stoltze P and Norskov J K 1995 Phys. Rev. Lett. 74 1159
[5] Cammarata R C and Sieradzki K 1994 Annu. Rev. Mater. Sci. 24 215
[6] Mentes T O, Stojic N, Locatelli A, Aballe L, Binggeli N, Niño M A, Kiskinova M and Bauer E 2011 Europhys. Lett. 94 38003
[7] Needs R J, Godfrey M J and Mansfield M 1991 Surf. Sci. 242 215–21
[8] Sander D, Tian Z and Kirschner J 2009 J. Phys.: Condens. Matter 21 134015
[9] Blanco-Rey M and Jenkins S J 2010 J. Phys.: Condens. Matter 22 135007
[10] Sander D 1999 Rep. Prog. Phys. 62 809
[11] Sander D, Enders A and Kirschner J 1999 Europhys. Lett. 45 208
[12] Müller J E, Dahmen K and Ibach H 2002 Phys. Rev. B 66 235407
[13] Sander D, Schmidtths C, Enders A and Kirschner J 1998 Phys. Rev. B 57 1406
[14] Meyerheim H L, Sander D, Popescu R, Kirschner J, Robach O, Ferrer S and Steadman P 2003 Phys. Rev. B 67 155422
[15] Kolaczkiewicz J and Bauer E 1984 Surf. Sci. 144 495
[16] Schmidtths C, Sander D, Enders A and Kirschner J 1998 Surf. Sci. 417 361
[17] Schmidthals C, Enders A, Sander D and Kirschner J 1998 Surf. Sci. 402 636
[18] Kolaczkiewicz J and Bauer E 1985 Surf. Sci. 160 1
[19] Kämper K-P, Schmitt W, Güntherodt G and Kühnlenbeck H 1988 Phys. Rev. B 38 9451–6
[20] Kosiol C, Lilenkamp G and Bauer E 1990 Phys. Rev. B 41 3364–71
[21] Campbell R A, Rodriguez J A and Goodman D W 1990 Surf. Sci. 240 71
[22] Bauer E 1999 J. Phys.: Condens. Matter 11 9365
[23] Riffe D M, Franckowiak R T, Shin N D, Kim B, Kim K J and Kang T-H 2008 Surf. Sci. 602 2039
[24] Farle M, Berghaus A, Li Yi and Baberschke K 1990 Phys. Rev. B 42 4873–6
[25] Li Yi and Baberschke K 1992 Phys. Rev. Lett. 68 1208–11
[26] Bovenziepen U, Rultc C, Pouloupoulos P and Baberschke K 2001 J. Magn. Magn. Mater. 231 65
[27] Berlowitz P J and Goodman D W 1987 Surf. Sci. 187 463
[28] Greenleif C M, Berlowitz P J, Goodman D W and White J M 1987 J. Phys. Chem. 91 6669
[29] Maciejewski P, Wuth W, Köstlemeier S, Pacchioni G and Rosch N 1995 Surf. Sci. 330 156
[30] Khan N A and Chen J G 2003 J. Phys. Chem. B 107 4334
[31] Khan N A and Chen J G 2003 J. Vac. Sci. Technol. A 21 1302
[32] Campbell C T 1990 Ann. Phys. Rev. Phys. Chem. 21 134015
[33] Rodriguez J A 1996 Surf. Sci. Rep. 24 223
[34] van der Merwe J H, Bauer E, Tönsing D L and Stoop P M 1994 Phys. Rev. B 49 2127
[35] van der Merwe J H, Bauer E, Tönsing D L and Stoop P M 1994 Phys. Rev. B 49 2137
[36] Li Yi, Farle M and Baberschke K 1990 Phys. Rev. B 41 9596–9
[37] Giannozzi P et al 2009 J. Phys.: Condens. Matter 21 395502
[38] Perdew J P and Zunger A 1981 Phys. Rev. B 23 5048
[39] Vanderbilt D 1990 Phys. Rev. B 41 7892
[40] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[41] Nielsen O H and Martin R M 1983 Phys. Rev. Lett. 50 697
[42] Galanakis I, Debernardi A, Alouani M and Dreyszé H 2001 Surf. Sci. 482–485 1030
[43] Huang S F, Chang R S, Leung T C and Chan C T 2005 Phys. Rev. B 72 075433
[44] Mentes T O, Stojic N, Binggeli N, Niño M A, Locatelli A, Aballe L, Kiskinova M and Bauer E 2008 Phys. Rev. B 77 155414
[45] Ardini J and Locatelli A 2011 private communication
[46] Tober E D, Yznunza R X, Palomares F J, Wang Z, Hussain Z, Van Hove M A and Fadley C S 1997 Phys. Rev. Lett. 79 2085–8
[47] Pratzer M, Elmers H J and Getzlaff M 2003 Phys. Rev. B 67 153405
[48] Spišák D and Hafner J 2004 Phys. Rev. B 70 014430
[49] Harrison M J, Woodruff D P and Robinson J 2008 Surf. Sci. 602 226
[50] Stojic N, Mentes T O, Binggeli N, Niño M A, Locatelli A and Bauer E 2010 Phys. Rev. B 81 115437
[51] Leung T C, Kao C L, Su W S, Feng Y J and Chan C T 2003 Phys. Rev. B 68 195408