Instability of the Ideal Tungsten (001) Surface

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The energetics of reconstruction models of the ideal W(001) and Ta(001) surfaces are studied by the general-potential linearized augmented plane-wave method. The ideal W(001) surface is found to be very unstable to the low-temperature Debe and King $c(2\times2)$ structure, gaining an energy of about 1200 K upon reconstruction. It is thus not likely that the high- (room-) temperature phase is in the ideal $p(1\times1)$ structure. It is determined that the instability is due to local bonding effects and not to a Fermi-surface instability.

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The tungsten (001) surface is probably the most studied metal surface. In spite of this, its atomic geometry and phase transitions are still not well understood. For temperatures greater than about 300 K the clean surface displays a $p(1\times1)$ LEED pattern characteristic of an ideal unreconstructed surface,[1-4] and much of the theoretical work and analysis of experimental data has assumed this structure (possibly with a surface interlayer contraction). There exist conflicting data, however,[5-8] especially from ion-channeling experiments.[5] In this Letter we report total-energy calculations which indicate that the high-temperature phase is not ideal $p(1\times1)$.

Whatever its actual structure, the W(001) high-temperature phase is known to be only marginally stable. A T-dependent reversible phase transition to a $c(2\times2)$ LEED pattern is observed on cooling of the clean surface below room temperature.[2,3] Very low hydrogen coverage also induces a reconstruction,[1,4,9] even at room temperature and above. Debe and King[3] (DK) have proposed a model of the T-dependent W(001) reconstruction in which the low-T phase is formed displacively from the ideal surface by alternating parallel ⟨110⟩ shifts of the top layer atoms to form zigzag chains, and theoretical LEED intensity analysis[10] indicates that the shifts are between 0.15 and 0.30 Å. This model has been challenged, however, by other experimental evidence.[5-8] By contrast with tungsten, LEED experiments on the (001) surface of tantalum (which has one less electron than tungsten) demonstrate that Ta *does not* reconstruct at least down to 15 K and, in addition, that low hydrogen coverages do not induce a reconstruction on it.[11,12]

To investigate the relative stability of the ideal W and Ta (001) surfaces, we have performed total-energy calculations for the low-T DK model using the self-consistent, general potential (no shape approximations), linearized augmented plane-wave (LAPW) method,[13-15] which is only briefly described here, within the framework of local-density-functional theory. In this method the valence-electron states are treated scalar relativistically while the core electrons are treated fully relativistically in an atomiclike[15] approximation. While most core states are highly localized within the muffin-tin spheres, the "tails" of overlapping core states (e.g., the $5p$ state) are treated correctly[15] without further approximations. The surface was modeled by a three-dimensional periodic structure (or supercell) consisting of thin slabs, five atomic layers thick, separated by five empty layers. [The charge density in the central vacuum layer was about $10^{-5}\,e/(\text{a.u.})^3$, more than three orders of magnitude smaller than on a muffin-tin sphere surface.] The Wigner exchange correlation potential[16] was used for the tungsten surfaces while the Hedin-Lundqvist form[17] was used for the tantalum surfaces. The calculations were done at lattice parameters of 3.161 Å for tungsten and 3.306 Å for tantalum. A basis of about 1000 LAPW's was used to calculate the energies on the tungsten surface with a muffin-tin radius of 2.362 36 a.u. Reducing the basis set to about 670 LAPW's resulted in relatively small changes of less than 0.5 mRy per surface atom in the energy differences and, accordingly, this size was used for the other calculations presented here. The muffin-tin radius for tantalum was set equal to 2.40 a.u. The Brillouin-zone sampling consisted of four special[18] k points. Since it was not certain whether the W(001) reconstruction was due to a Fermi-surface instability, we felt that it was important to check the adequacy of the Brillouin-zone sampling. We therefore repeated the calculation on the unrelaxed W(001) surface for $\delta=0.0$ and $\delta=0.06$ (see the inset of Fig. 1 which depicts the DK model) using a set of 16 special k points and found a negligible change in the energy difference despite the improved sampling.

This supercell approach reproduces earlier results obtained with the slab LAPW method for seven-layer W(001)[19] and five-layer Ta(001).[20] The surface energy for an unreconstructed tungsten surface was calculated with use of a five-atom supercell and yielded a value of 5.54 J/m^2 (experiment[21] yields 6.0 ± 0.9 J/m^2) in good agreement with the value of about 5.1 J/m^2 obtained by previous calculations.[22] The surface interlayer contraction was also obtained for the five-atom supercell and was in good agreement with that calculated for the $\delta=0$

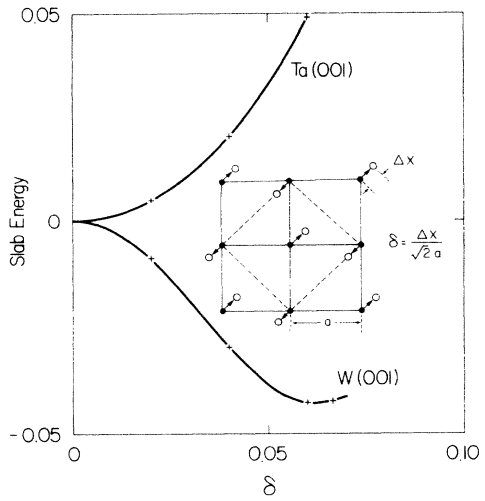


FIG. 1. Total energy (in rydbergs) for the ten-atom W and Ta slabs. Inset: Debe and King reconstruction model.

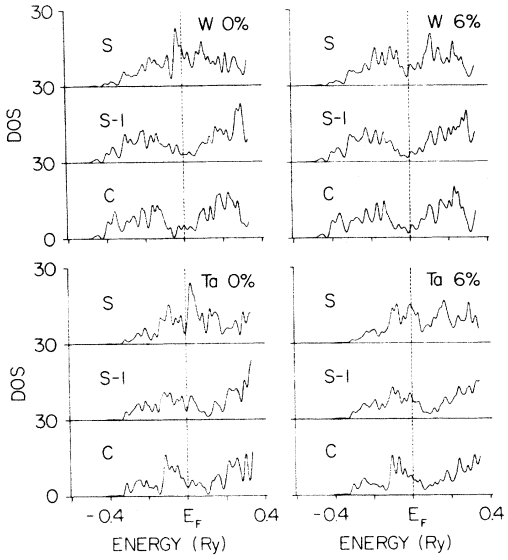


FIG. 2. Projected d-band density of states (DOS) (electrons/Ry-atom-spin) for the surface (S), subsurface ($S-1$), and central (C) layer atoms of the W and Ta slabs.

ten-atom supercell and with previous calculations.[23,24]

Our principal results for the energetics of the DK model are presented in Fig. 1 which shows the calculated slab energies as a function of the coordinate δ for the unrelaxed Ta(001) and W(001) surfaces. Since this model has two atoms per layer, the supercell contains ten atoms of which four are surface atoms. The energies in Fig. 1 must therefore be divided by four to obtain the energy change per surface atom. The Ta(001) surface is found to be stable while the W(001) surface is not, with the energy minimum on W(001) occurring for a shift of 0.28 Å and 10.9 mRy per surface atom below the energy of the ideal unrelaxed surface. The surface interlayer relaxation was calculated for $\delta=0$ and $\delta=0.06$ (or about 0.27 Å). For $\delta=0$, the topmost layer of W(001) is found to relax inward by 5% with a relaxation energy of 3.1 mRy per surface atom. For $\delta=0.06$ the relaxation is less than 1% with a negligible energy gain. The net effect is that relaxation acts to stabilize the unreconstructed surface, reducing the reconstruction energy to 7.8 mRy (1200 K) per surface atom.

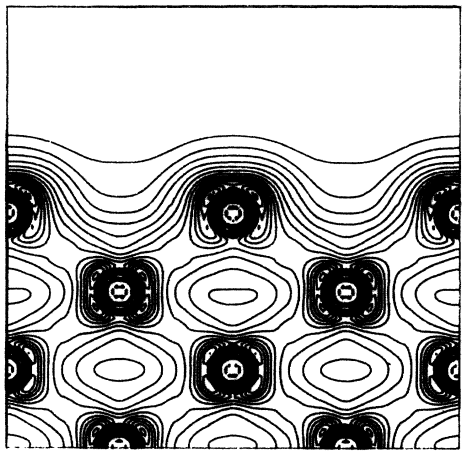
Previous total-energy calculations using the empirical tight-binding method[25] predicted a stable $p(1\times1)$ W surface while an *ab initio* LAPW calculation by Fu *et al.*[26] obtained a value of only 120 K, which is a factor of 10 *smaller* than that reported here. The discrepancy between our value and that of Fu *et al.* is due to their use of a restricted basis set. In order to deal with the overlapping "tails" of the W $5p$ core state, they treated it as a variational band state. As a consequence, essentially no $l=1$ component was allowed for the *valence* wave function within the muffin-tin spheres, resulting in restricted variational freedom for their valence-electron basis set. This resulted in their obtaining a surface interlayer relaxation energy in substantial disagreement with the results of their earlier calculation,[24] where they used a better basis, and with an independent pseudopotential calculation,[23] and with results reported here. In order to demonstrate that this basis-set restriction is the source of the discrepancy between our results and those of Ref. 26, we have performed calculations on the W(001) surface using their treatment of the $5p$ core state (in our supercell geometry) and reproduced their main result, i.e., that the ideal surface is predicted to be only marginally unstable. We also recalculated the unrelaxed $\delta=0$ and $\delta=0.06$ distortions treating the $5p$ electrons as valence electrons in a separate energy window (neglecting the $5p$ spin-orbit interaction but retaining full variational freedom for the valence states). In this case the ideal surface is found to be about 20% more unstable. Thus, the use of the restricted basis set in Fu *et al.*[26] results in large errors of about 1110 K per surface atom.

The energy gain obtained here of 1200 K is very large for a structural phase transition which occurs below room temperature and is not consistent with a model of the transition in which the high-T phase is the $p(1\times1)$ ideal surface. We stress this point by noting that the value of 1200 K is only a *lower limit* on the energy to be gained upon reconstruction; i.e., even if the DK model does not actually best describe the structure of the low-T phase, the true ground-state structure must be even lower in energy.

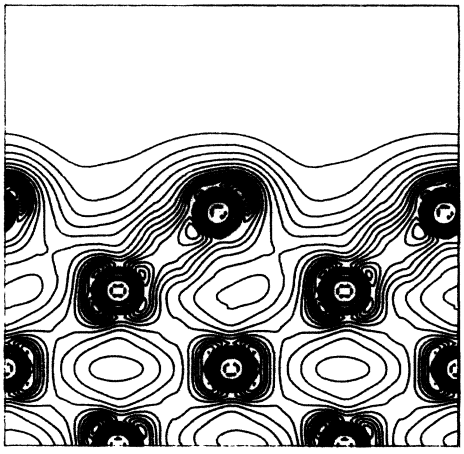
In Fig. 2 the layer-projected d densities of states are presented for the unrelaxed W(001) and Ta(001) surfaces with $\delta=0.0$ and $\delta=0.06$. The most striking feature of these is a large peak in the density of states, due largely to surface states, which is eliminated as the surfaces reconstruct. We associate this peak with the driving force for the reconstruction. The fact that it is above

the Fermi energy on Ta(001) is consistent with the fact that this surface does not reconstruct. On inspecting the band structures we find that the elimination of this peak is associated with the sweeping of bands (both bulk and surface states) away from the W(001) Fermi energy over a large portion of the Brillouin zone, consistent with our earlier observation regarding the k-point sampling. Since the effect of the reconstruction is not localized in the Brillouin zone one might expect it to be local in real space.

This is in fact the case. Examining the W(001) charge densities shown in Fig. 3 for $\delta=0$ and $\delta=0.06$, we note that on the ideal tungsten surface there is a rather prominent dangling-bond feature which is absent on tantalum (not shown). For semiconductor surfaces dangling bonds are often associated with instabilities. On the W(001) surface the reconstruction partially suppresses the dangling bonds and acts to enhance the surface-subsurface bond compressed by this distortion. We associate this charge redistribution with the elimination of the peak in the density of states. The compressed surface-subsurface bond is not enhanced on reconstructed Ta(001), but rather there is a repulsive charge build-up midway between the atoms.



(a)



(b)

FIG. 3. W charge-density contour plots for a (110) plane perpendicular to the surface. (a) Unreconstructed surface. (b) $\delta=6\%$ reconstruction. Adjacent contours are separated by 0.008 e/a.u.[3]

Previous explanations[19,27-29] for the W(001) reconstruction have often been formulated in terms of a charge-density-wave (CDW) mechanism[29] in which a Fermi-surface instability associated with nesting features of surface states and resonances drives the reconstruction. However, photoemission measurements[30,31] and calculations including the spin-orbit interaction[32] have undermined the CDW interpretation by finding surface-state dispersions which differ enough from those obtained scalar relativistically so as to remove the nesting feature. Inglesfield[27] had already suggested that such nesting features play a minor role and that the ideal surface is inherently unstable. Similarly Terakura and coworkers[33,34] have questioned the CDW mechanism, favoring instead a Jahn-Teller-like mechanism (here the terms Jahn-Teller and CDW are used in a qualitative sense to distinguish driving mechanisms related to local bonding effects from delocalized Fermi surface related mechanisms) whereby the energy is lowered by the elimination of a large peak in the surface density of states, as in Fig. 2. This view is supported by the present calculations.

In conclusion, the ideal relaxed tungsten surface is found to be very unstable because of a local chemical effect associated with dangling bonds present on the ideal W(001) surface [but absent on Ta(001)], and the reconstruction is not caused by a Fermi-surface instability as previously suggested.[19,29] The calculated energy difference (1200 K) between the ideal relaxed tungsten surface and the DK $c(2\times2)$ structure makes it highly unlikely that the room-temperature phase is in the ideal $p(1\times1)$ structure. One possible alternative is a disordered phase with random parallel shifts[35] but no long-range order, as this might be expected to reduce the energy difference. This possibility would be consistent with the observed LEED $p(1\times1)$ pattern and with ion-scattering experiments[5] which indicate that about $\frac{2}{3}$ of the surface atoms are displaced at room temperature. Another possibility is a different ordered phase with a lower energy [which must, however, preserve the observed $p(1\times1)$ LEED pattern]. Recently, Walker, Debe, and King[36] have suggested that the LEED data are consistent with a high-T phase consisting of a top layer shifted along the $\langle100\rangle$ direction. We have also calculated the energy change for this uniformly shifted surface (assuming a rigid subsurface layer) and found that the ideal W surface seems to be *stable* against this distortion. Clearly further work is required to characterize the structure of the W(001) surface.

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