Frozen-Phonon Total-Energy Determination of Structural Surface Phase Transitions: W(001)

C. L. Fu, A. J. Freeman, and E. Wimmer[(a)]
Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201

and

M. Weinert
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973
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The prototypical W(001) structural phase transition is investigated by all-electron, frozen-phonon, total-energy calculations. The strong coupling between surface states and the $\overline{M}_5$ phonons plays a decisive role in favoring the reconstructed $c(2\times 2)$ structure with a lateral $\langle 110\rangle$ zig-zag displacement of 0.18 ±0.01 Å (in excellent agreement with experiment) and no interlayer relaxation. The transition from the (1×1) into the $c(2\times 2)$ phase proceeds over a very flat region of the energy hypersurface and suppresses the relaxation.

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The richness, variety, and complexity of surface phenomena—notably geometric and electronic structure properties—have stimulated a great number of investigations. The focus of much of the effort at understanding transition-metal surfaces has been directed at tungsten, which plays the same prototypical role for metal surfaces as does Si for semiconductor surfaces. Despite extensive investigations and considerable progress in elucidating a number of electronic structure properties, an understanding of the structural phase transition in W(001) is far from complete and still a subject of disagreement. Originally, Felter, Baker, and Estrup[1] suggested the possibility of an alternating displacement of the atoms perpendicular to the surface. Currently, the most widely accepted model to explain the observed reconstruction[1,2] upon cooling below room temperature from a (1×1) into a $c(2\times 2)$ structure, namely alternating *lateral* displacements of W atoms along the $\langle 110\rangle$ directions to form zig-zag chains with a $(\sqrt{2}\times\sqrt{2})R45°$ structure,[2] has met with conflicting experimental results. Melmed *et al.* and Tung, Graham, and Melmed[3] observed the occurrence of preferential field evaporation of alternate surface atoms, and thus concluded that W(001) is reconstructed with alternating *vertical* displacements of the surface atoms from 15 to 580 K. On the other hand, results of megaelectronvolt ion-scattering experiments[4] supported neither a lateral nor vertical displacive model for the reconstructed surface and provided evidence instead for a disorder-order phase transition on this surface. Theoretical model calculations based on two-dimensional surface response functions,[5,6] lattice dynamics,[7] and the matched Green's-function method[8] concluded that a reconstructed surface exists at low *T*; however, a stable (1×1) surface was obtained with empirical tight-binding total-energy approaches.[9] Despite its obvious importance, no *ab initio* electronic structure study of surface reconstruction has been reported on this transition-metal surface, and little is known about the energetics involved in this phase transition.

In this Letter, we present the first all-electron local-density-functional (LDF) study of the surface reconstruction on the W(001) surface employing the full-potential linearized augmented plane wave[10] (FLAPW) total-energy approach.[11] On the basis of the "frozen-phonon" method (adiabatic approximation), we have studied lateral displacements via the longitudinal phonon mode $\overline{M}_5$ $[q=(\pi/a)(1,1)$, where $a=3.16$ Å$]$ which leads to a $(\sqrt{2}\times\sqrt{2})R45°$ structure [Fig. 1(a)], and vertical displacements via the buckled-phonon mode $\overline{M}_1$ [Fig. 1(b)]. The results support the conclusion that W(001) is reconstructed at low temperature according to the Debe and King[2] model with an in-plane displacement in the $\langle 110\rangle$ direction by 0.18 ±0.01 Å. Evidence is given that the strong coupling between surface states and $\overline{M}_5$ phonons near the Fermi level (E_F) is the driving mechanism of this phase transition. In disagreement with the conclusions drawn from earlier observations[3] we find that the (1×1) structure is stable with respect to the $\overline{M}_1$ phonon distortion. The reconstructed surface is found to exhibit essentially no relaxation of the surface atoms and this demonstrates, for the first time, that surface reconstruction may act to suppress surface relaxation or even reverse the surface relaxation from a contraction into an expansion The transition from the relaxed (1×1) phase into the reconstructed $c(2\times 2)$ phase proceeds over a very flat region of the energy hypersurface before the system is stabilized in a shallow harmonic potential. These results shed new light on the proposed order-disorder transition and the difference between the low-energy electron-diffraction (LEED) and field-ion microscopy (FIM) observations.

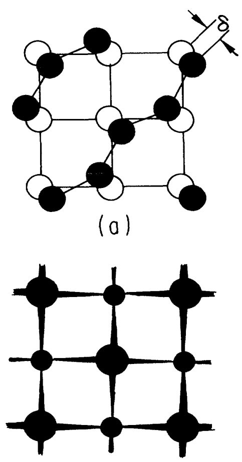

FIG. 1. Atomic displacements for (a) $\overline{M}_5$ phonon with displacements in the ⟨110⟩ direction (open circles indicate bulklike positions); (b) $\overline{M}_1$ phonon with alternating vertical displacements perpendicular to the surface.

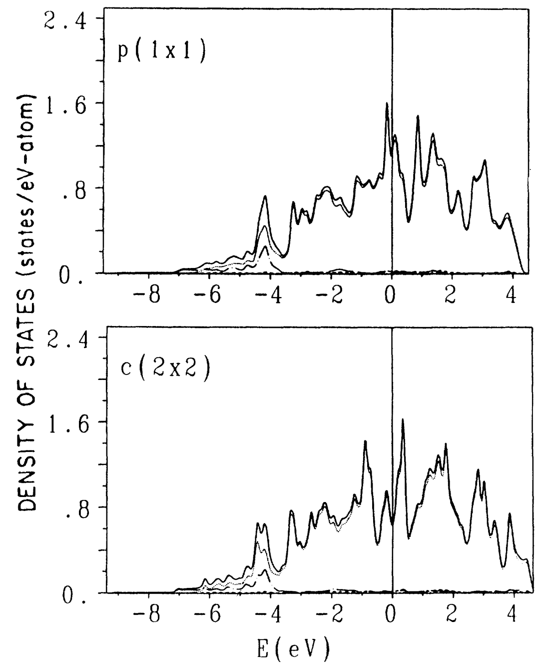

FIG. 2. The surface-layer partial DOS (in states/eV) for $p(1\times1)$ and $c(2\times2)$ structures. The total and d (s-p) partial DOS are given by solid and dotted (broken) lines.

Finally, these studies of delicate energetic processes portend a new generation of detailed predictions based on theoretical-computational calculations now made possible by the application of new methods and algorithms on supercomputers like the Cray.

The W(001) surface is represented by a thin slab of five atomic layers—thick enough to describe the electronic structure,[12] the multilayer relaxation,[13] and the surface energy of this surface.[14] The Kohn-Sham LDF equations incorporating the Wigner exchange-correlation potential[15] are solved self-consistently by use of the all-electron FLAPW thin-film method.[13] For both the $\overline{M}_5$ and $\overline{M}_1$ phonons, the new two-dimensional (2D) periodicity has two atoms per layer; thus 10 atoms/cell are included in this calculation. The experimental lattice constant $a = 5.973$ a.u. is used, which is within 0.5% of that obtained in an independent FLAPW total-energy calculation on bulk tungsten.[16] With a muffin-tin radius of 2.3 a.u., a total of 1000 LAPW basis functions are used. All electrons are treated self-consistently, the core fully relativistically and the valence electrons semirelativistically.[17]

The total energy (E_t) is calculated as a function of two independent quantities—the percentage change (Δ_{12}) of the first interlayer spacing (relaxation) relative to its bulk value and the "frozen-phonon" displacement (δ). A contraction of the first interlayer spacing by 4% for the (1×1) surface is found in this calculation.[18] For the $\overline{M}_1$ phonon mode, frozen-phonon E_t calculations were performed with a vertical displacement of $\pm0.02a$ for alternate surface atoms as referred to their equilibrium positions in the relaxed (1×1) structure. Negligible changes of the density of states (DOS) at E_F and in the work function are found which reflects a rather weak coupling of the surface states (SS) with the $\overline{M}_1$ phonon. Therefore, the (1×1) structure is stable with respect to the $\overline{M}_1$ phonon distortion; a phonon frequency amounting to 4.4 THz is obtained with the harmonic approximation. This result disagrees with conclusions drawn from FIM experiments,[3] which ascribed a stable reconstructed surface to vertical displacement components.

For the $\overline{M}_5$ phonon mode, frozen-phonon E_t calculations were performed for $\Delta_{12} = -6\%$, -3%, 0%, and 3% vs a lateral displacement, δ, in the ⟨110⟩ direction ≤ 0.3 Å. Consider first a comparison of the surface-layer partial DOS for the unrelaxed (1×1) and $c(2\times2)$ structures shown in Fig. 2. The high surface-layer DOS at E_F obtained also in earlier calculations[12,19] was taken as evidence for an instability of the (1×1) phase. The results shown in Fig. 2 demonstrate that the surface states at the E_F couple strongly with the $\overline{M}_5$ phonon mode and lead (i) to a dramatic reduction of the DOS at E_F and (ii) to a splitting into an occupied and an unoccupied peak in the DOS, separated by 1.3 eV. The band gapping found for the $\overline{M}_5$ displacement occurs only in the region near the new Brillouin zone boundary of the reconstructed structure in the ⟨11⟩ direction, and is dominated by SS with d_{xz}, d_{yz}, and $d_{x^2-y^2}$ orbitals. (Unlike the case of relaxation, which is demonstrably a multilayer process,[13] the high DOS that exists only in the surface layer assures that the reconstruction process is localized to the surface layer.) Further, it is important to note that because of the bonding enhancement between surface and subsurface atoms caused by reconstruction, the work function increases by 70 meV for the reconstructed surface—in excellent agreement with the experimental increase[20] of 50 ± 5 meV.

The upper panel of Fig. 3 shows the total energy E_t relative to the unrelaxed (1×1) structure along the minimum-energy path from the relaxed (1×1) phase into the essentially unrelaxed $c(2\times2)$ phase. The lower panel of Fig. 3 displays the relaxation Δ_{12} $(E_{\min})$, which corresponds to the lowest total energy for a given displacement. The results clearly indicate that at low temperatures the (1×1) structure is unstable with respect to the $\overline{M}_5$ phonon distortion. This distortion leads to a $(\sqrt{2}\times\sqrt{2})R45°$ structure and a predicted lateral atomic displacement of 0.18 ±0.01 Å along the ⟨110⟩ direction to form a zig-zag chain structure, with the first interlayer spacing remaining within 0.5% of its bulk value. The theoretical in-plane lateral displacement is in excellent agreement with LEED analyses by Barker *et al.*[21] (δ = 0.15–0.3 Å) and by Walker, Debe, and King[22] (δ = 0.16 Å). The reconstruction is found to accompany a uniform dilation of the first interlayer spacing from its relaxed

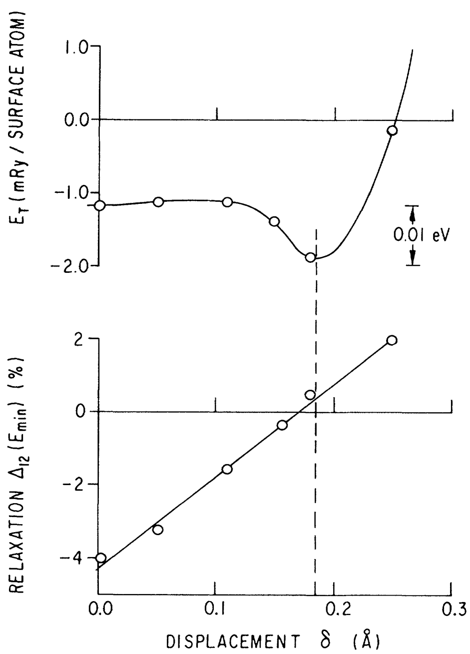

FIG. 3. Upper panel: Total energy (as referred to the unrelaxed and unreconstructed surface) along the transition path from the relaxed (1×1) phase into the reconstructed $c(2\times2)$ phase. Lower panel: Relaxation (relative to the interlayer spacing in the bulk) as a function of displacement. Note that at equilibrium (vertical broken line) the relaxation is essentially zero.

(1×1) surface value back to its bulk value as the lateral displacement increases, which gives a prediction of *no* vertical relaxation for a reconstructed surface. We obtain a reconstruction energy of about 10 meV (120 K) [defined as the difference in E_t per surface atom between a relaxed (1×1) surface and the reconstructed surface]. The approximate transition temperature is consistent with the experimental observation of sharp, intense half-order beams of LEED pattern on cooling below[23] 200 K. Now, the part of the energy hypersurface shown in Fig. 3 allows a straightforward interpretation of the thermally induced reconstruction of the W(001) surface: At low T, the ground state is in the reconstructed $c(2\times2)$ phase, where the atoms are held in a potential well with a depth of about 0.01 eV. As T is increased, anharmonic effects start to play an important role. Eventually the oscillation around δ = 0.18 Å changes into a strongly anharmonic large-amplitude oscillation in a soft $\overline{M}_5$ phonon-mode potential well with the center of gravity at δ = 0.

The unexpectedly flat region of the energy hypersurface around the relaxed and unreconstructed positions of the surface atoms out to δ = 0.1 Å displacements (cf. Fig. 3) has the following implications for the interpretation of LEED, FIM, and ion-backscattering experiments reported for the W(001) surface, notably in the regime just above the phase transition (i.e., at room temperature): (i) The disagreement between our $\overline{M}_1$ results and FIM experiments may be taken as evidence to show the validity of the oft-cited argument that in FIM experiments[3] strong electric fields are present perpendicular to the surface and so, through polarization effects, these fields may stabilize the "buckled" $c(2\times2)$ surface (vertical displacements) which exhibit an ionic superstructure[7,24] coupling to the external fields. (ii) The surface atoms can perform large-amplitude oscillations along ⟨110⟩, and since this may wash out the LEED reflection signals, only the subsurface atoms may be seen. We thus speculate that the assignment of the "surface layer" in the LEED intensity analysis may become ambiguous. (iii) The possible large amplitudes in the lateral oscillations may give rise to order-disorder transition phenomena as suggested earlier.[4] Since the phase transition is second order in nature (cf. the flat region of the energy hypersurface shown in Fig. 3), short-range ordering as probed by the photoemission experiments may well persist above T_c.

A simple physical picture emerges from these all-electron total-energy calculations: The transition from the $p(1\times1)$ into the $c(2\times2)$ phase involves two competing effects—lowering of the E_t either by relaxation or by reconstruction. Surface relaxation barely reduces the surface layer DOS at E_F without appreciable change of the electronic structure. On the other hand, a larger electronic energy is gained through the surface reconstruction by surface band gapping around E_F. Therefore, the system tends to minimize its electronic energy by increasing the lateral atomic displacement (cf. Fig. 3) and avoids the energetically unfavorable nuclear repulsion due to the decreased atomic distances in the relaxed phase by expanding the first interlayer spacing. The result is that surface relaxation is suppressed for the reconstructed surface.

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[a]Present address: Cray Research, Inc., 1440 Northland Dr., Mendota Heights, Minn. 55120.

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