Instability, Distortion, and Dynamics of the W(100) Surface

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A model for the reconstructions of the W(100) surface is presented. Four types of distortions are obtained, along ⟨011⟩, ⟨001⟩, ⟨100⟩ (commensurate), and (×10) (incommensurate). The ⟨011⟩ distortion, corresponding to the observed $(\sqrt{2}\times\sqrt{2})45°$ clean surface, is worked out in detail. A distortion magnitude of ~0.35 Å is found, and a surface coherence length $\xi \simeq 15$ Å close to experiment. The full vibrational spectrum, the distortion penetration, and the anisotropic surface anharmonic energies are also obtained.

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Reversible displacive phase transitions have been reported on W(100) [and Mo(100)] surfaces, both clean[1] and H covered.[1,2] A surface charge-density-wave[3] (SCDW) mechanism has been invoked to account for the low-temperature "reconstruction."[4] At higher temperature, entropy[5] favors the undistorted surface, which is richer in low-lying excited states, and eventually causes a two-dimensional (2D) transition at $T_0 \sim 300$ K. While a comprehensive treatment of this coupled electron-electron problem seems still beyond present possibilities,[6] we have found it possible to provide a realistic description of the $T=0$ surface lattice distortion, and of its properties. This Letter summarizes the essence of our technique and some of our results. The details will be given in a longer paper.[7]

Our basic assumption is to treat the SCDW as an "effective" lattice phenomenon. Electrons are renormalized out, their driving effect being represented by extra forces between surface atoms. Consistently, only vibrational entropies should be included for $T \neq 0$. This seems a better approximation than that—usual in 1D cases[8]—which focuses on electrons only. In 2D or 3D, there is only a well-defined gap in the phonon density of states, hence that aspect should prevail. Also, a lattice-vibration approach is amenable to quantitative calculations, as we now show.

A standard secular problem is solved for the $T=0$ phonon eigenvalues $\omega^2(\vec{q})$ and eigenvectors $u_{l\mu}(\vec{q})$ of an unrelaxed n-layer W(100) slab (n varies from 9 to 21, as necessary to decouple the two surfaces). The slab dynamical matrix $D_{ll'}{}^{\mu\nu}(\vec{q})$ is defined by[9,10]

$$\sum_{l'\nu} D_{ll'}{}^{\mu\nu}(\vec{q})u_{l'\nu} = \sum_{N\nu}[\alpha_N \delta_{\mu\nu} + (\beta_N - \alpha_N)R_N{}^{\mu}R_N{}^{\nu}|\vec{R}_N|^{-2}][u_{l\nu} - \exp(i\vec{q}\cdot\vec{R}_N)u_{l+N,\nu}], \quad (1)$$

where $\vec{q}$ is the 2D wave vector, l and $l'=1,\ldots,n$ denote atoms in each layer, μ and $\nu = x, y, z$ (x is orthogonal to the surface; y and z join atoms in it), N denotes a neighbor of atom l a distance $\vec{R}_N$ away from it, and $\alpha_N = R_N{}^{-1}[dU(R)/dR]_{R=R_N}$, $\beta_N = [d^2U(R)/dR^2]_{R=R_N}$ are force constants [$U(R)$ is some hypothetical W-W potential]. Their first- and second-neighbor values are fixed at $\alpha_1 = -0.04$ THz² g, $\beta_1 = 6.11$ THz² g and $\alpha_2 = -\alpha_1 = 0.04$ THz² g, $\beta_2 = 4.37$ THz² g (that fit well the bulk W phonons[10]) unless both atoms lie on the same surface.

In the latter case, they are given values α_s and β_s if first *surface* neighbors and zero otherwise (restriction to short-range forces is here purely a matter of convenience, and could be released if necessary). Our α_s, β_s, or specifically $\alpha_s - \alpha_2$ and $\beta_s - \beta_2$, embody all extra forces due to surface electrons. Here, they are treated as free parameters to be fixed later against experimental information.

A first-principles calculation of these quantities, as well as of other surface-induced modifications of long-range interatomic forces, will be possible only when a reliable total-energy scheme will become available for this surface. Meanwhile, our approximation, crude as it is, can be justified as follows. First, the 2D Fermi surface—which we suppose to drive the SCDW distortion[4]—implies intrasurface Friedel-type oscillations, whose periodicity is close to $a(1, 1)$, where a is the lattice parameter. That is, a much larger force is expected between first neighbors than between second surface neighbors. Second, all the mentioned long-range forces should be further reduced by the distortion itself, which acts precisely to eliminate the 2D Fermi surface. A chemical picture that can be proposed[3,4] for the SCDW-distorted surface is one where a weak bond is established, essentially between first surface neighbors—at least so long as the distortion is not too small—to eliminate the otherwise unsaturated d broken bonds.

With $\alpha_s = \alpha_2$, $\beta_s = \beta_2$, the stable surface phonon spectrum is reproduced.[10] By varying α_s and β_s, some frequencies become imaginary, at either $\vec{q} \equiv M = (2\pi/q)(\frac{1}{2}, \frac{1}{2})$, $\vec{q} \equiv L = (2\pi/a)(\frac{1}{2}, 0)$, or $\vec{q} \equiv \Lambda = (2\pi/a)(\frac{1}{2}, \delta)$. This signals a surface lattice instability, leading to a displacive reconstruction, as discussed, e.g., by Blandin, Castiel, and Dobrzynski[11] and by others.[3,10,12] The "phase diagram" thus obtained is shown in Fig. 1. For purposes of representation, boundaries between unstable phases are drawn where the two respective imaginary frequencies coincide. Five instability regions are found, corresponding to four types of unstable zone-boundary phonons. They are (i) M_5 (twofold degenerate), with $\vec{u}_l$ either (a) along $\langle 011 \rangle$, leading to a $(\sqrt{2} \times \sqrt{2})45°$ reconstruction, which is seen on clean neutral W(100) (Ref. 1); or (b) along $\langle 010 \rangle$, leading to a $c(2 \times 2)$ reconstruction analogous to that observed[1,2] at low H coverage on W(100); (ii) M_1, with $\vec{u}_l$ along $\langle 100 \rangle$, leading to $c(2 \times 2)$, observed on clean but positively charged W(100) (Ref. 13); (iii) L_2, with $\vec{u}_l$ along $\langle 010 \rangle$, leading to (2×1) or (2×2) reconstructions, not observed; (iv) Λ_1, with $\vec{u}_l$ along $\langle \epsilon 10 \rangle$, where $\epsilon \sim \delta(\frac{1}{2} - \delta)$ leading to *incommensurate* reconstructions of both the I_1 and I_2 regions. The last type of phase is observed[2] at larger H coverage on W(100).[14] On crossing the I_1 region, δ goes from $\frac{1}{2}$ to ~ 0.4 and back to $\frac{1}{2}$; on crossing I_2, δ goes from $\frac{1}{2}$ to 0. The deviation from commensurability has a continuous square-root behavior at all commensurate-incommensurate boundaries, which, however, do not need to be second-order lines, since there will generally be Lifshitz terms and discommensurations.[15] The M_5 distortion, we note, occurs for $\alpha_s < 0$, $\beta_s < 0$, corresponding to extra *attraction* between surface atoms. This is indeed expected from electronic SCDW, or chemical, reasoning,[3] since pairing of surface electrons can occur only if surface atoms come together. The subsurface amplitude of all unstable eigenvectors $|\vec{u}_l|$ decreases rapidly, with over 80% concentrated in the first layer. Our conclusion, that all W(100) reconstructions should be very nearly a first-layer affair, is compatible with available data[16] and awaits confirmation by further work.

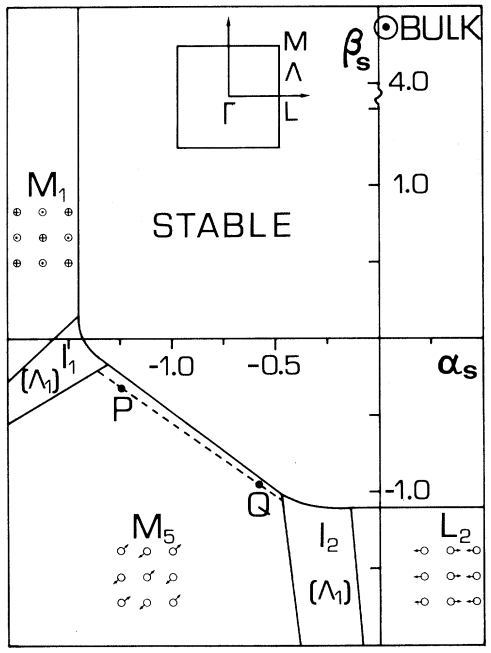

FIG. 1. $T = 0$ phase diagram as a function of surface forces α_s and β_s, in units of THz^2 g for W(100). The regions M_1, M_5, and L_2 are commensurate (first-layer distortions are sketched), while I_1 and I_2 are incommensurate, with a Λ_1-type distortion. The clean W(100)$(\sqrt{2} \times \sqrt{2})45°$ surface is described by a point on the P–Q line.

Our model permits a detailed description of

TABLE I. Summary of some calculated $T = 0$ properties of W(100)($\sqrt{2}\times\sqrt{2}$)45°, compared with experimental low-temperature estimates.

	P	Q	Expt.
α_s (THz^2 g)	-1.246	-0.572	
β_s (THz^2 g)	-0.318	-0.956	
$d_0 = \lvert\langle\vec{u}_1\rangle\rvert$ (Å)	0.331	0.384	0.15–0.3,[a] > 0.2[b]
$d_0 = \lvert\langle\vec{u}_2\rangle\rvert$ (Å)	0.085	0.098	
$d_0 = \lvert\langle\vec{u}_3\rangle\rvert$ (Å)	0.032	0.027	
ω_L (meV)	3.13	2.28	
ω_T (meV)	5.97	5.09	
ω_x (meV)	7.40	10.80	
ξ_{11} (Å)	15	18	~20[c]
ξ_{10} (Å)	11	11	
a [10^{20} g (sec cm)$^{-2}$]	1.6	0.6	
b [10^{20} g (sec cm)$^{-2}$]	16.9	12.4	

[a]See Ref. 16. [b]See Ref. 19. [c]See Refs. 1 and 2.

these phases. To illustrate, we have chosen the M_5 ($\sqrt{2}\times\sqrt{2}$)45° phase. We allow a $\langle 011\rangle$ static displacement of magnitude $d = \langle u_1\rangle$ of first-layer atoms—neglecting for simplicity the smaller displacements of other layers. We solve again for the phonons of the thus reconstructed surface, where now $l = 1, \ldots, 2n$, $\vec{R}_N \to \vec{R}_N + \delta\vec{R}_N(d)$, $\alpha_N \to \alpha_N + \beta_N\,\delta\vec{R}_N\cdot\vec{R}_N/R_N$, $\beta_N \to \beta_N$ [i.e., a parabolic $U(R)$ is assumed]. The mean-field equilibrium distortion magnitude $d_0 = d_0(\alpha_s, \beta_s)$ is determined with the help of the symmetry-based Landau energy expansion[6]

$$\mathcal{H} = m|\omega_5|^2(u^2+\bar{u}^2) + a(u^2+\bar{u}^2)^2 + bu^2\bar{u}^2, \tag{2}$$

where u and $\bar{u}$ are the $\langle 011\rangle$ and $\langle 01\bar{1}\rangle$ components of the M_5 order parameter, $\omega_5^2 < 0$ is the M_5 mode frequency for $d = 0$, the mass m is taken to be that of the W atom, and a and b are unknown "spherical" and "cubic" anharmonic coefficients. We specialize for $a > 0$, $b > 0$ [the alternative choice $a > 0$, $b < 0$ would instead be appropriate for the $c(2\times 2)$ phase of W(100)-H]. Mean-field minimization of (2) yields

$$d^2 \approx \langle u\rangle^2 = m|\omega_5|^2/2a \tag{3}$$

corresponding to an energy change

$$\Delta E_{\mathrm{MF}} = -\tfrac{1}{2}m|\omega_5|^2 d^2. \tag{4}$$

By further inserting into (2) small oscillating pieces $u = \langle u\rangle + \epsilon$, $\bar{u} = 0$ and $u = \langle u\rangle$, $\bar{u} = \epsilon$, we obtain "longitudinal" and "transverse" frequencies

$$\omega_L^2 = 2|\omega_5|^2, \tag{5}$$

$$\omega_T^2 = (b/2a)|\omega_5|^2. \tag{6}$$

Note now that ω_L^2 of (5) is independent of a and b. For any (α_s, β_s) inside the M_5 region, we first set $d = 0$ and find ω_5^2 with our slab calculation. Then, we set $d > 0$ and recalculate. The two modes ω_L^2, ω_T^2 are identified as $q = 0$ optical models of Γ_1, Γ_3 symmetry (the surface symmetry is lowered from C_{4v} to C_{2v}) that rise sharply from ω_5^2 as d increases. The sought equilibrium value d_0 is found when (5) is satisfied. From (3) and (6) we then obtain a and b, so that all parameters in (2) are determined for that (α_s, β_s).

We would finally like to know which point (α_s, β_s) inside M_5 best represents the clean W(100)($\sqrt{2}\times\sqrt{2}$)45° surface. In the absence of accurately known experimental quantities, we have developed a crude procedure that uses only the transition temperature T_0 as input. Consider $T \neq 0$ (all the preceding was for $T = 0$). Since the critical behavior—expected to be continuous, but nonclassical and nonuniversal[17]—is unknown, we assume it to be Gaussian as a simple starting point.

We can then write one more approximate relationship connecting T_0 with the changes of energy ΔE_{MF}, of zero-point energy ΔE_{ZP}, and of entropy ΔS_{MF} between $d = d_0$ and $d = 0$, as[18]

$$\Delta E_{\mathrm{MF}} + \Delta E_{\mathrm{ZP}} \sim T_0 \Delta S_{\mathrm{MF}}. \tag{7}$$

The first term is given by (4). The others are

calculated numerically as

$$\Delta E_{ZP} = \tfrac{1}{2} \sum_{\vec{q}\lambda} (\omega_{\vec{q}\lambda} - \omega_{\vec{q}\lambda}{}^{0})^2, \tag{8}$$

$$T_0 \Delta S_{MF} = T_0 \tfrac{1}{2} \sum_{\vec{q}\lambda} \ln\{[1 - \exp(-\omega_{\vec{q}\lambda}/k_B T)][1 - \exp(-\omega_{\vec{q}\lambda}{}^{0}/k_B T)]^{-1}\}, \tag{9}$$

where $\omega_{\vec{q}\lambda}$ and $\omega_{q}\lambda^{0}$ are slab frequencies at α_s, β_s, $d = d_0$ and at $\alpha_s{}^*$, $\beta_s{}^*$, $d = 0$, respectively ($\alpha_s{}^*$, $\beta_s{}^*$ is the closest point on the M_5-stable boundary). Here, $\vec{q}$ runs over the 2D zone, $\lambda = 1, \ldots, 6n$ labels branches, and $\frac{1}{2}$ accounts for two surfaces in the slab. For $T_0 = 300$ K, we find that the clean W(100)$(\sqrt{2}\times\sqrt{2})45°$ surface can correspond to any point on the dashed P–Q line of Fig. 1. The first-layer distortion d_0, which ranges from 0.33 Å at P to 0.38 Å at Q, is compatible with experimental estimates—also very uncertain—shown in Table I, together with other results. The surface anisotropy b/a is large, with ω_T about twice ω_L. These two $q = 0$ surface vibrations, together with the folded-in out-of-plane vibration ω_x, should be directly observable spectroscopically. Surface coherence lengths ξ_{11} (along ⟨011⟩) and ξ_{10} (along ⟨010⟩ are also derived from the surface phonon dispersion, in the form $\omega_L{}^2(q = 2\pi/\xi) = 2\omega_L{}^2(q = 0)$ and are found to be around 15 Å, close to experimental healing-length estimates.[1,2] This also suggests that the H-induced switching between $(\sqrt{2}\times\sqrt{2})45°$ and $c(2\times2)$ (Refs. 1 and 2) should occur for a coverage $(a/\xi)^2 \lesssim 1/25$.

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