Equilibrium state of a metal slab and surface stress

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First-principles full-potential all-electron total-energy calculations on a seven-layer Mo(001) slab have found the equilibrium state of the slab and the energies of nearby states produced by isotropic two-dimensional (epitaxial) strain. In the slab equilibrium state, the in-plane lattice constant contracts 1.7% and the out-of-plane lattice constant contracts 0.7% from bulk values. The energy differences of these nearby states strained from equilibrium have been fitted to a composite elastic model of the slab which has two surface regions and a bulk region, each with three elastic parameters. The parameters of the surface regions determined by fitting the energy differences permit evaluation of the surface stress as 5.28 m Ry/bohr$^2 = 4.11$ J/m^2. The surface region material is found to be less stiff than the bulk. [S0163-1829(99)13247-8]

I. INTRODUCTION

First-principles total-energy full-potential calculations on metal slabs by supercell procedures can be made with sufficient accuracy to find energy differences per cell of a fraction of a m Ry. The total energy E of an N-atom cell of an N-layer body-centered-tetragonal metal slab with an in-plane lattice constant a and out-of-plane lattice constant c can be evaluated as a function of a and c. The equilibrium state of the slab is the state with the minimum value of $E(a,c)$.

In the present work this equilibrium state of the slab has been found, and small energy differences from this equilibrium state have been evaluated for states produced by isotropic epitaxial or two-dimensional strain on a seven-layer slab of Mo(001), which preserves tetragonal structure. These energy differences have been interpreted as linear elastic strain energies, and have been fitted to the strain energy of a composite elastic model made up of two surface regions and a bulk region (Fig. 1). The surface stress can then be expressed in terms of the elastic parameters of the surface region and evaluated.

Previous first-principles calculations of surface stress have found the surface energy of a slab as a difference between the slab total energy and the total energy of the same number of atoms of the bulk crystal. The surface stress is then found from the derivative of the surface energy with respect to strain by calculating the change in the surface energy when the slab is strained.[1] In the present work the surface energy is not required. The energy differences between special strained states of the slab and the equilibrium state are fitted to the composite elastic model mentioned above. The special strained states are the states produced by epitaxial strain on the slab. These states of epitaxial strain make up the epitaxial Bain path (EBP) of the slab.[2] For a tetragonal material small energy changes along this path are described by a single elastic constant—to be called the epitaxial elastic constant. The material of the Mo(001) surface regions is in general tetragonal in equilibrium, even if the bulk equilibrium state is cubic, because of the bonding anisotropy produced by the surface. This single elastic constant

is then one of the fitting parameters of the surface region used to fit the energy changes along the EBP of the slab.

Surface stress characterizes the state of stress in the surface layers of a thick crystal. For surfaces of square symmetry it is a single number associated with the surface of a thick crystal. In the present work we give the surface stress an atomic-level description in which the average stress over a specified atomic depth is found and the surface stress is the integrated stress over that depth. The tetragonal surface region in which the stress occurs acquires an equilibrium in-plane lattice constant and an epitaxial elastic constant which are both different from the bulk values.

II. FORMULATION OF THE COMPOSITE ELASTIC MODEL

The slab is assumed to have two surface regions of thickness t_s and a bulk region of thickness t_b as in Fig. 1. The
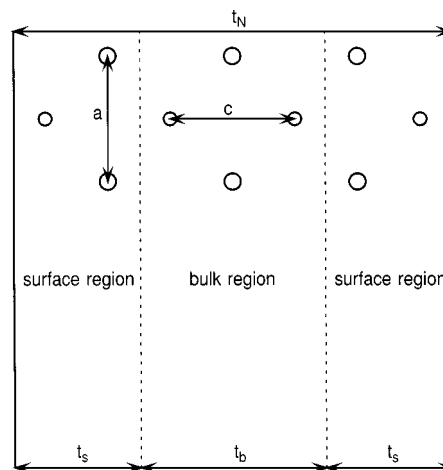

FIG. 1. Cross-section view of the composite elastic model of a seven-layer Mo(001) slab. Seven layers of atoms are shown (open circles); the slab thickness is t_N; the in-plane lattice constant is a; the out-of-plane lattice constant is c; the thickness of each surface region is t_s; and the bulk region thickness is t_b. The boundaries of the surface regions (dotted lines) correspond to $t_{sQ} = 6$ bohr when $t_N = 20.8$ bohr (the equilibrium value).

thickness of the seven-layer Mo(001) slab with out-of-plane lattice constant c is taken as $t_N = 7c/2$, which allows for extension by half a layer spacing beyond the plane of the outer-layer nuclei. Each region is assumed to be a homogeneous continuum with three parameters needed to find its elastic strain energy, i.e., for the surface regions these are t_s, and a_{s0}, the equilibrium in-plane lattice constant, and Y'_s the epitaxial elastic constant. The corresponding parameters for the bulk region are t_b, Y'_b, a_{b0}; Y'_b and a_{b0} are evaluated by bulk total-energy calculations, and t_b is given by

$$t_b + 2t_s = t_N. \qquad (1)$$

The epitaxial elastic constant Y' of a tetragonal material may be related to the usual two-index elastic constants c_{ij} for tetragonal structures as follows. Start with the general expression for the strain energy for tetragonal strains around a tetragonal equilibrium state of volume V, under the assumption of linear elastic behavior[3]

$$E^{\text{str}} = V \left[(c_{11} + c_{12}) \varepsilon_1^2 + 2c_{13} \varepsilon_1 \varepsilon_3 + \frac{c_{33}}{2} \varepsilon_3^2 \right], \qquad (2)$$

where $\varepsilon_1 = \varepsilon_2$ are the in-plane strains along crystal axes and ε_3 is the out-of-plane strain. For an epitaxial strain, which has the boundary condition of zero out-of-plane stress, we have

$$\sigma_3 = c_{13} \varepsilon_1 + c_{13} \varepsilon_2 + c_{33} \varepsilon_3 = 0; \qquad (3)$$

hence substituting for ε_3 in Eq. (2) and in the equation for σ_1 gives

$$E^{\text{str}} = V \varepsilon_1^2 (c_{11} + c_{12} - 2c_{13}^2/c_{33}) \equiv VY' \varepsilon_1^2,$$
$$\sigma_1 = (c_{11} + c_{12}) \varepsilon_1 + c_{13} \varepsilon_3 = Y' \varepsilon_1. \qquad (4)$$

For cubic structures $c_{13} = c_{12}$, $c_{33} = c_{11}$ and

$$Y' = \frac{(c_{11} - c_{12})(c_{11} + 2c_{12})}{c_{11}} = \frac{Y}{(1 - \nu)}. \qquad (5)$$

where Y is Young's modulus and ν is Poisson's ratio.

The strain energy of a seven-atom cell of volume $V = a^2 t_N$ in the composite elastic model is then

$$E^{\text{str}}(a) = a^2 (2t_s Y'_s \varepsilon_s^2 + t_b Y'_b \varepsilon_b^2), \qquad (6)$$

where the strains in the surface and bulk regions are

$$\varepsilon_s \equiv \frac{(a - a_{s0})}{a_{s0}}, \quad \varepsilon_b \equiv \frac{(a - a_{b0})}{a_{b0}}, \qquad (7)$$

respectively. The parameters t_s, Y'_s, and a_{s0} will be chosen to fit the strain energies given by Eq. (6) to the calculated slab energy differences from equilibrium. The fitting process uses two relations among the parameters.

The first relation among the three unknown parameters of the surface regions is the force-balance equation at slab equilibrium. Designating the in-plane stresses and strains in the surface and bulk regions at equilibrium by σ_{sQ}, ε_{sQ}, σ_{bQ}, and ε_{bQ} this relation becomes

$$2t_{sQ} \sigma_{sQ} = -t_{bQ} \sigma_{bQ}, $$

$$\sigma_{sQ} = Y'_s \varepsilon_{sQ} \equiv Y'_s \frac{(a_{NQ} - a_{s0})}{a_{s0}}, $$

$$\sigma_{bQ} = Y'_b \varepsilon_{bQ} \equiv Y'_b \frac{(a_{NQ} - a_{b0})}{a_{b0}}, \qquad (8)$$

$$t_{bQ} = t_{NQ} - 2t_{sQ}, $$

where the subscript Q has been used to indicate quantities evaluated at equilibrium. In Eqs. (8) the slab equilibrium in-plane lattice constant has been designated a_{NQ} and is a compromise between the surface region equilibrium constant a_{s0} and the bulk region constant a_{b0}, since tension in the surface region balances compression in the bulk region to give zero net force.

The second equation relating the surface region parameters comes from equating the calculated value of $d^2 E^{\text{EBP}}/da^2$ at equilibrium to $d^2 E^{\text{str}}/da^2$ at equilibrium from Eq. (6), where $E^{\text{EBP}}(a)$ is the slab total energy of a seven-atom cell under epitaxial strain. In Eq. (6) we first take account of the changes in c along the EBP as a changes by putting

$$t_X = t_{XQ} \left[1 - \gamma \frac{(a - a_{NQ})}{a_{NQ}} \right], \quad X = N, s, b. \qquad (9)$$

In the total-energy calculations all six layer spacings have been kept equal to each other at any a and c, i.e., relaxations of the layer spacings have been neglected, so γ is a Poisson-ratio-type quantity which is an average over the surface and bulk regions; it is evaluated from the slab calculations. Then the unknown surface region parameter t_s (which is a function of a) can be replaced by the single quantity t_{sQ}.

Putting Eq. (9) into Eq. (6) gives

$$E^{\text{str}}(a) = a^2 \left[1 - \gamma \frac{(a - a_{NQ})}{a_{NQ}} \right] (2t_{sQ} Y'_s \varepsilon_s^2 + t_{bQ} Y'_b \varepsilon_b^2). \qquad (10)$$

Differentiating Eq. (10), we can write the second derivative of E^{str} at equilibrium as

$$\left(\frac{d^2 E^{\text{str}}(a)}{da^2} \right)_{a = a_{NQ}} = 2B_Q (1 - 2\gamma) + 2a_{NQ} B'_Q (2 - \gamma)$$
$$+ a_{NQ}^2 B''_Q, \qquad (11)$$

where

$$B_Q \equiv 2t_{sQ} Y'_s \varepsilon_{sQ}^2 + t_{bQ} Y'_b \varepsilon_{bQ}^2, $$

$$B'_Q \equiv 4t_{sQ} Y'_s \varepsilon_{sQ}/a_{s0} + 2t_{bQ} Y'_b \varepsilon_{bQ}/a_{b0}, $$

$$B''_Q \equiv 4t_{sQ} Y'_s/a_{s0}^2 + 2t_{bQ} Y'_b/a_{b0}^2, \qquad (12)$$

and the strains in surface and bulk regions are

$$\varepsilon_{sQ} \equiv \frac{(a_{NQ} - a_{s0})}{a_{s0}}, \quad \varepsilon_{bQ} \equiv \frac{(a_{NQ} - a_{b0})}{a_{b0}}. \qquad (13)$$

The two equations—Eq. (11) set equal to the calculated value of $d^2 E^{\text{EBP}}/da^2$ at equilibrium, and Eq. (8)—reduce the three unknown parameters to one independent parameter.

TABLE I. Bulk states of Mo(001) on the EBP. Bulk Mo under epitaxial strain in the (001) plane becomes tetragonal; a is the in-plane lattice constant, and c is the out-of-plane lattice constant of the two-atom body-centered-tetragonal cell (in bohr); E is the total energy per atom of the strained crystal (in Ry); ΔE in (m Ry/atom) is the energy difference per atom from the bcc structure, which has the minimum E.

a (bohr)	c (bohr)	$(E+8100)$ (Ry/atom)	ΔE (m Ry/atom)
5.9820	5.9820	−0.585 724	0.000
5.9220	6.0500	−0.585 396	0.328
5.8620	6.1000	−0.584 164	1.560
5.8300	6.1098	−0.583 300	2.424
5.8030	6.1300	−0.582 300	3.424

III. CALCULATION PROCEDURES AND RESULTS

A. Bulk and slab calculations

The total-energy calculations were made with the all-electron full-potential linearized augmented plane wave method embodied in the WIEN97 code.[4] The Kohn-Sham equations were solved with two corrections—the semirelativistic correction (fully relativistic core and scalar-relativistic valence electrons) and the generalized gradient approximation (GGA). Spherical harmonics up to $l=10$ were used inside the muffin-tin sphere and up to $l=4$ in the interstitial region. The muffin-tin radius of Mo atoms was chosen to be 2.40 bohr in both bulk and slab calculations.

Bulk calculations were carried out with a bcc cell of Mo to find a_{b0} the equilibrium lattice constant and Y'_b the epitaxial elastic constant of bulk Mo. Total energies E of states along the EBP of bulk Mo were found by choosing a set of a values around a_{b0}, and at each a the value of c was varied to find the minimum of E at that a. The values of a and c at each minimum gave a point on the EBP of bulk Mo, and are listed in Table I. A second minimization of E along the bulk EBP gave the bulk equilibrium point and the value of a_{b0}. The minimizations were done by fitting a cubic to the values of $E^{\text{EBP}}(a)$ and finding where the first derivative of $E^{\text{EBP}}(a)$ vanished. The second derivative of the cubic in a was then fitted to the EBP points to give Y'_b, since, from Eq. (4),

$$E^{\text{EBP}}(a) = VY'_b\left(\frac{(a-a_{b0})}{a_{b0}}\right)^2; \qquad (14)$$

hence

$$\left(\frac{d^2E^{\text{EBP}}}{da^2}\right)_{a=a_{b0}} = a_{b0}Y'_b. \qquad (15)$$

This procedure gave $a_{b0}=5.9820$ bohr, 0.6% larger than the experimental value[5] 5.946 bohr, and $Y'_b=36.21$ mRy/bohr^3 $=5.33$ Mbar, 8.8% larger than the experimental value[6] of 4.90 Mbar.

For the bulk calculations more than 3000 k points in the Brillouin zone were used. Convergence was achieved when on successive iterations the total energy difference was less than 5×10^{-5} Ry, and charge differences were less than 1 $\times10^{-4}e$/bohr^3.

TABLE II. States on the EBP of the seven-layer Mo(001) slab. a is the in-plane lattice constant (in bohr); c is the out-of-plane lattice constant (in bohr), which is the same for all layers; E is the total energy per seven-atom cell (in Ry); and ΔE is the energy difference from the minimum E (last-line) of the seven-atom cell (in m Ry).

a (bohr)	c (bohr)	$(E+56703)$ (Ry)	ΔE (m Ry)
5.9222	5.9120	−0.799837	1.117
5.8923	5.9293	−0.800854	0.100
5.8624	5.9549	−0.800775	0.179
5.8324	5.9789	−0.799635	1.319
5.7726	6.0491	−0.793522	7.432
5.8785[a]	5.9400[a]	−0.800954[a]	0.000

[a]Equilibrium values at the minimum of E.

The EBP of the seven-layer slab of Mo was found by a procedure similar to the one used for the bulk EBP, but with a supercell of seven layers of Mo and six layers of vacuum. The number of k points in the two-dimensional mesh was 24×24, and the number of k points in the irreducible zone was 156. The energy cutoff of the plane waves was 14 Ry and of the kinetic energy was 196 Ry. The same convergence criteria were used for the slab as for the bulk calculations.

Some 25 slab total energies were used at five values of a. The first minimization at each a with respect to c gave the slab EBP points in Table II. The second minimization with respect to a along the EBP gave the slab properties in the equilibrium state: $a_{NQ}=5.8785$ bohr, $t_{NQ}=3.5\times5.94$ $=20.8$ bohr, and $d^2E^{\text{EBP}}/da^2=1201$ m Ry/bohr^2.

The equilibrium state of the slab compared to bulk shows that a decreased by 1.7% and c decreased by 0.7%. Table II also shows that as a decreases along the EBP, c increases, so that $\gamma\equiv-[(\delta c/c)/(\delta a/a)]=0.907$.

B. Fitting the slab EBP to an elastic model

If the slab is considered to be a single homogeneous tetragonal crystal, but with a different epitaxial elastic constant due to the rebonding caused by the surfaces, we can find the effective epitaxial elastic constant Y'. From Eq. (4) the strain energy of the homogeneous seven-atom cell is E^{str} $=t_Na^2Y'[(a-a_{NQ})/a_{NQ}]^2$, hence at $a=a_{NQ}$ we have $d^2E^{\text{str}}/da^2=2t_{NQ}Y'$. Then $Y'=1201/(20.8\times2)$ $=28.9$ m Ry/bohr^3, which is less than the bulk theoretical value $Y'_b=36.2$ m Ry/bohr^3.

A value of the effective Poisson ratio v of the homogeneous slab can also be found, since along the EBP for cubic structures γ is related to v by[7] $\gamma=2v/(1-v)$. Hence $\gamma=0.907$ gives $v=0.31$, which is larger than the theoretical bulk value 0.29 obtained similarly from the bulk EBP (the experimental value of v is 0.26).

These average elastic properties of the slab—smaller Y' and larger v than the bulk—indicate that the average effect of the surfaces on the slab is to make the slab less stiff than bulk. However, the seven-layer slab is thick enough to show the inhomogeneous effects of the surfaces, which should affect only a few atomic layers at each surface. These layers should then be affected more strongly than the average effects obtained when the slab is treated homogeneously.
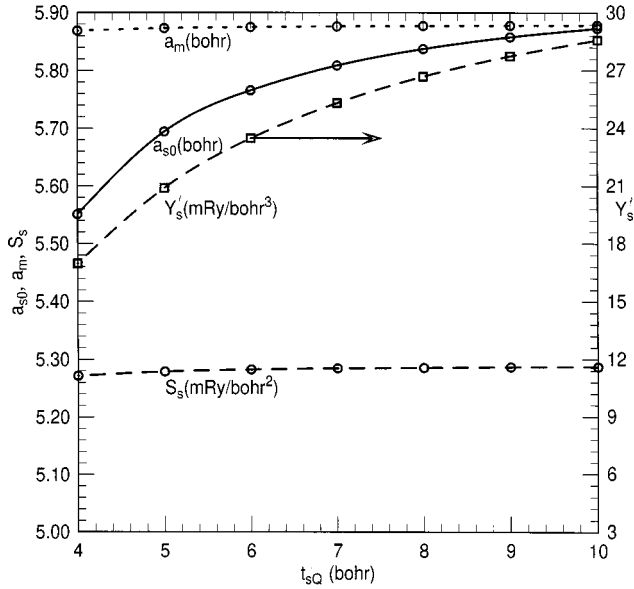
FIG. 2. Variation of the parameters of the surface region with equilibrium thickness of the surface regions t_{sQ} in bohr; a_{s0} is the equilibrium in-plane lattice constant of the surface region material in bohr (solid line); Y'_s is the epitaxial elastic constant of the surface region material in m Ry/bohr^3 (long dashes, scale on the right); S_s is the surface stress in m Ry/bohr^2 (long dashes); and a_m is the in-plane lattice constant of the slab with minimum strain energy in bohr (short dashes).

The composite elastic model of Sec. II can be applied to the EBP of the slab by using Eq. (8) to express Y'_s in terms of a_{s0} and t_{sQ}, and thereby eliminate Y'_s from Eq. (11). Then $d^2 E^{str}/da^2$ at $a = a_{NQ}$ from Eq. (11) is equated to 1201 m Ry/bohr^2, the curvature of the EBP at equilibrium, relates a_{s0} to t_{sQ}. At given t_{sQ} the complete elastic description of the slab can now be found. This description includes the values of the stresses σ_s in the surface region and σ_b in the bulk region, the value of Y'_s, and the value of the surface stress S_s. These elastic properties are given by

$$\sigma_s = Y'_s(a_{NQ} - a_{s0})/a_{s0},$$

$$\sigma_b = Y'_b(a_{NQ} - a_{b0})/a_{b0}, \qquad (16)$$

$$S_s = t_{sQ} Y'_s(a_{b0} - a_{s0})/a_{s0}.$$

The surface stress is given in Eqs. (16) as the stress in the surface region of a thick crystal times the thickness of the surface region. Note that the stress in the surface region of a thick crystal is greater than in the surface region of a thin crystal, such as the seven-layer slab used here, because the surface region is stretched from a_{s0} to a_{b0}, not just to a_{NQ}. The strain energy can also be found as a function of a from Eq. (10), and a_m, the value of a at the energy minimum can be determined.

Carrying out the procedure in the preceding paragraph gives Fig. 2, which plots a_{s0}, Y'_s, and S_s, and a_m vs t_{sQ}. First note that a_m is very close to $a_{NQ} = 5.8785$ bohr, so that we cannot fix the best t_{sQ} by the closest fit of a_m to a_{NQ}. But note that S_s is almost independent of t_{sQ} over the reasonable range of t_{sQ}, i.e., for $t_{sQ} < 2.5$ bohr there is no solution of the equation which equates Eq. (11) to 1201 m Ry/bohr^2 and for
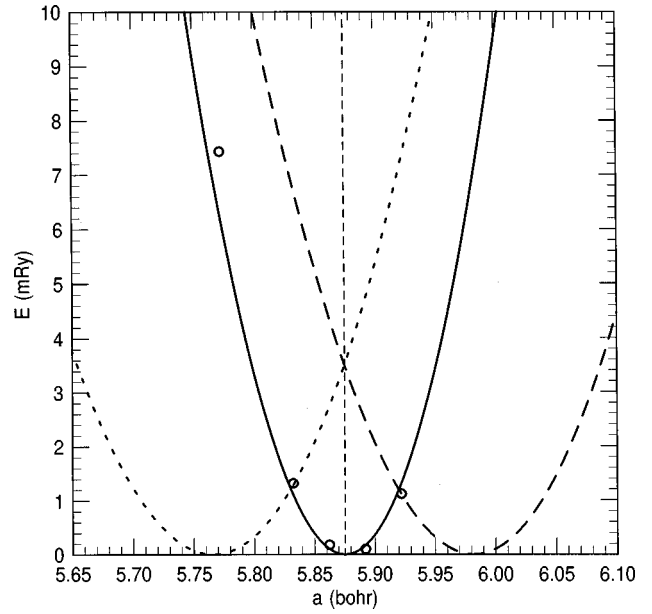

FIG. 3. Strain energy E of the seven-atom cell along the slab epitaxial Bain path vs in-plane lattice constant a (solid line) in bohr at $t_{sQ} = 6$ bohr; the minimum energy is set to zero; calculated total energies of the seven-atom cell on the EBP in m Ry are referred to zero at the minimum (open circles); the total strain energy in the two surface regions (small dashes); and the strain energy in the bulk region (long dashes). The vertical line is at the minimum of the strain energy at $a_m = 5.8754$ bohr.

$t_{sQ} > 10.4$ bohr the slab would be all surface region. Hence the value $S_s = 5.28 \pm 0.01$ m Ry/bohr^2 is well-determined. However a_{s0} and Y'_s vary substantially with t_{sQ}, but at all t_{sQ} the value of Y'_s lies below both the bulk value and the homogeneous slab value. As t_{sQ} approaches 10.4 bohr, where the bulk region vanishes, Y'_s approaches the homogeneous slab value and a_{s0} approaches a_{NQ}.

A plausible value of t_{sQ} is 6 bohr, which lies between the second and third atomic layers (as shown in Fig. 1), since the rebonding should occur principally in the first two layers. The values of the elastic parameters will be illustrated for $t_{sQ} = 6$ bohr. In Fig. 3 the strain energy at $t_{sQ} = 6$ bohr is plotted (solid line) along with the calculated slab EBP energies (open circles) as functions of a. The separate strain energies in the two surface regions (short dashes) and in the bulk region (long dashes) are also plotted; their sum has a minimum at a_m (vertical line) and the sum is shifted down by 7.01 m Ry to have the same zero value as has been given to the calculated EBP points at the minimum. That 7.01 m Ry is in fact the locked-in strain energy of the slab in equilibrium. The stress in the surface regions is $\sigma_s = 67.5$ kbar, and in the bulk region is $\sigma_b = -92.2$ kbar. The surface region has a tensile strain of 1.9% when $t_{sQ} = 6$ bohr and the bulk region has a compressive strain of 1.7%, which is independent of t_{sQ}. At $t_{sQ} = 6$ bohr where $a_{s0} = 5.7658$ bohr and $Y'_s = 23.48$ m Ry/bohr^3, the tensile stress in the surface region of a thick crystal will be $\sigma_s = Y'_s(a_{b0} - a_{s0})/a_{s0} = 0.880$ m Ry/bohr$^3 = 130$ kbar.

IV. DISCUSSION

Finding the slab equilibrium state by a double minimization of the energy with respect to first c and then a assumed

the accuracy of the Kohn-Sham equations of density-functional theory with the nonlocal GGA and the semirelativistic corrections. Also assumed was the equality of the six slab layer spacings at any a and c. The accuracy of the first assumption for nonmagnetic Mo is shown by the good agreement noted in Sec. III A of theory with the experimental values of the bulk lattice constant and the bulk epitaxial elastic constant. The second assumption remains to be tested by further calculations in which relaxation is allowed and the effect on the surface stress is determined. Note that the effects both of relaxation of layer spacings and of the addition of adsorbed layers are immediately described by the present composite elastic model with surface regions and a bulk region. The surface regions then comprise all layers that differ from bulk, and the fitted parameters give the average elastic properties over the surface region.

The application of the composite elastic model made the further approximation of linear elastic behavior, i.e., that the values of Y' are independent of strain. For strains less than about 2% (as is the case for $t_{sQ} = 6$ bohr) nonlinear effects are small.[3] One test of the linear approximation is provided by the fit of the parabolic strain energy (solid line in Fig. 3) to the EBP points over a range in a of $\pm 2\%$ from equilibrium. The elastic strain energy (6) assumed that each region followed its individual EBP as a changed. However, the constraint of constant c forced each region to adopt a c slightly different from the value along its EBP. Nevertheless, within the linear elastic assumption these deviations from the individual EBP's due to out-of-plane stress will not affect the value of $d^2 E^{EBP}/da^2$ given by the slab EBP at equilibrium, and used with Eq. (11) to fix the surface region parameters.

The equilibrium state and its parameters were needed because the two equations relating the three unknown surface-region parameters t_{sQ}, a_{s0} and Y'_s applied at equilibrium. The contraction of a at equilibrium from the bulk value is then explained by a_{NQ} being a compromise between a_{s0} and a_{b0}. The net contraction of the single value of c over the slab can be understood by the dominance of the *contraction* of c due to in-plane tension in the surface region over *expansion* of c due to in-plane compression in the bulk region on averaging c over the slab. The dominance of the surface region is due to an increase of the Poisson ratio of the surface-region material compared to bulk. An estimate of the value of the surface-region Poisson ratio ν_s can be made from the calculated contraction of the thickness of the slab compared to seven layers of bulk. That contraction is 0.15 bohr, and at $t_{sQ} = 6$ bohr with $\nu_b = 0.29$ (the theoretical value) we must have $\nu_s = 0.37$ to achieve that net contraction. That value of ν_s is well above the bulk value, and also above the value 0.31 found when the slab is treated homogeneously.

Although the calculations on the seven-layer slab did not fix the thickness of the surface region t_{sQ}, the surface stress S_s was well determined at 5.28 m Ry/bohr^2. This value of S_s may be compared with the published value[8] for Mo(001) of 2.241 J/m$^2 = 2.88$ m Ry/bohr^2 calculated by empirical potentials of uncertain reliability. The first-principles value is 83% higher. However, note that in two cases in which both first-principles results and empirical-method results have been made for the same surface, the same discrepancy exists,[8] i.e., the first principles result for Pt(111) is 96% higher and for Au(111) is 83% higher.

It should be possible to fix the value of t_{sQ} with total-energy calculations on a thicker slab, say with $N = 9$. Then assuming the surface parameters t_{sQ}, Y'_s, and a_{s0} are about the same for both slabs, which must be true for sufficiently thick slabs, a t_{sQ} is sought for which a_{s0} and Y'_s are the same for both slabs.

Finally note that the surface energy of the seven-layer film can be found from the difference between the total energy of the seven-atom cell when $a = a_{b0} = 5.982$ bohr (and the bulk region is not strained), which is $-56\,703.795\,151$ Ry, and the total energy of seven atoms of bulk in equilibrium, which is $-7 \times 8100.585\,724$ Ry. The energy of the slab seven-atom cell is 304.9 m Ry higher, which is much larger than the strain energies of the slab seven-atom cell in Table II of a few m Ry. This surface energy of the cell is not strain energy, but corresponds to the changes in cohesive energy of the rebonded slab. The surface energy per unit area on each face of the slab is then $304.9/(2 \times 5.982^2)$ $= 4.26$ m Ry/bohr$^2 = 3.32$ J/m^2, which is comparable to the surface stress of 5.28 m Ry/bohr^2. This surface energy may be compared with the value for Mo(001) in Ref. 9 of 3.52 J/m^2. The value in Ref. 9 includes relaxation of the first layer spacing not considered here, but does not include the GGA and semirelativistic corrections used here. Also, the surface energy found here is the difference of two energies calculated with different unit cells and is not as accurate as the strain energies for small changes in a and c calculated with the same unit cell.

ACKNOWLEDGMENTS

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