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Properties of the surface region of a metal crystal

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Abstract

Total-energy calculations from first principles have been made on a seven-atomic-layer slab of Mo(001) as a function of the in-plane lattice parameter with full relaxation of the layer spacings. The energy minimum gives the equilibrium state of the slab, which contracts both in plane and out of plane between one and two per cent with respect to bulk. The energy changes under deformation from equilibrium are treated as strain energies and are fitted to a composite elastic model consisting of two surface regions and a bulk region, each with its structural and elastic parameters. These parameters are evaluated in a separate calculation for the bulk region, so that subtracting the known bulk strain energies from the total strain energy permits evaluation of the parameters of the surface region. Six deformations of the slab around equilibrium give the six elastic constants of the tetragonal surface regions. The surface region material is about two atomic layers deep, slightly prolate in its own equilibrium state, substantially elastically anisotropic compared to cubic symmetry, stable, but considerably weaker elastically and closer to instability than bulk.

1. Introduction

In previous papers [1, 2] we have calculated the total energy E of a seven-layer slab of Mo(001) by a first-principles method as a function of in-plane lattice constant a (in the (001) plane); [1] assumed uniform relaxation of layer spacings, but [2] used the more realistic assumption of independent relaxation of all layer spacings. The resulting function $E(a)$, called the epitaxial Bain path (EBP) of the slab [3, 4], has a minimum in the equilibrium state of the slab at $a = a_Q$. A composite elastic model of the slab consisting of two surface regions and a bulk region between them was fitted to the curvature of $E(a)$ at $a = a_Q$. Taking the elastic properties of the bulk region from a separate bulk calculation, the average value of Y'_s, the epitaxial Young's modulus of the surface region (defined later), was evaluated, along with the equilibrium in-plane lattice constant of the surface region a_{s0} (as a separate free material) and the thickness of each surface region t_s.

The present work extends the energy calculations on the slab to five deformations of the slab around equilibrium in addition to the EBP deformation, which give five elastic constants of the tetragonal surface region in addition to Y'_s. The complete set of six surface-region elastic

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constants is then compared with the stronger bulk constants. The surface region is shown to be stable, but less stable than bulk.

2. Procedures and results

All calculations were made with the band structure program WIEN97 [5] using a supercell of seven layers of Mo atoms and six layers of empty spheres, as described in [2]. The potential included the generalized gradient approximation and semi-relativistic corrections. The charge densities were adjusted at each iteration and when these densities converged the forces on the atoms were calculated. Then the atom positions were adjusted to reduce the forces and the process was repeated until the forces also converged. Iterations were continued until energy differences were less than 0.05 mRyd, charge density differences were less than 10^{-4} electrons/bohr^3 and forces were less than 1 mRyd/bohr on each atom.

2.1. Bulk calculations

First the parameters of bulk Mo were evaluated using procedures for the two-atom bcc cell that were similar to those used later for the seven-atom slab unit cell. The EBP of the bcc cell was determined at each a by finding the c satisfying $\partial E/\partial c = 0$ (the condition of zero stress in the out-of-plane or c direction), which is the epitaxial boundary condition, hence the name EBP. For the two-atom bcc cell of bulk Mo

$$\begin{aligned} E_b^{EBP} &= V_b Y_b' \varepsilon_{1b}^2 \\ V_b &= a^3 \\ Y_b' &= c_{11b} + c_{12b} - \frac{2c_{12b}^2}{c_{11b}} \\ \varepsilon_{1b} &\equiv \frac{a - a_{b0}}{a_{b0}}. \end{aligned} \tag{1}$$

In (1) a_{b0} is the equilibrium lattice constant of cubic bulk Mo and ε_{1b} is the isotropic in-plane strain. Then from (1)

$$\left(\frac{\mathrm{d}^2 E_b^{EBP}(a)}{\mathrm{d}a^2}\right)_Q = 2a_{b0}Y_b' \tag{2}$$

where subscript Q indicates evaluation at bulk equilibrium. Here and in later equations we assume the strains are small and make the linear elastic approximation that elastic constants are independent of strain.

Table 1 tabulates the points and energy changes along the EBP of the two-atom bulk bcc cell of Mo, and gives more complete data than table 1 of [1]. From table 1 $(\mathrm{d}^2 E_b^{EBP}(a)/\mathrm{d}a^2)_Q$ = 428.4 mRyd/bohr^3, a_{b0} = 5.9820 bohr, hence (2) gives Y_b' = 35.82 mRyd/bohr^3.

The condition defining the EBP, $\sigma_3 = 2c_{12}\varepsilon_1 + c_{11}\varepsilon_3 = 0$, gives

$$\left(\frac{\varepsilon_3}{\varepsilon_1}\right)_Q^{EBP} = \left(\frac{c}{a}\frac{\mathrm{d}c}{\mathrm{d}a}\right)_Q^{EBP} = -\frac{2c_{12b}}{c_{11b}}. \tag{3}$$

From the data in table 1 $(\mathrm{d}c/\mathrm{d}a)_Q^{EBP} = 0.690$, hence (3) gives $c_{12b} = 0.345c_{11b}$. Then (1) and (3) with Y_b' from (2) give c_{11b} = 32.35 mRyd/bohr^3 and c_{12b} = 11.16 mRyd/bohr^3.

From the general strain energy formula for a cubic crystal [6]

$$\frac{E^{str}}{V} = \frac{c_{11}}{2}(\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2) + c_{12}(\varepsilon_2\varepsilon_3 + \varepsilon_3\varepsilon_1 + \varepsilon_1\varepsilon_2) + \frac{c_{44}}{2}(\varepsilon_4^2 + \varepsilon_5^2 + \varepsilon_6^2) \tag{4}$$

Table 1. (1) Energies δE^{EBP} for the two-atom bcc cell of bulk Mo in mRyd relative to the bulk equilibrium energy against a and c lattice constants in bohr along the bulk EBP. (2) Strain energies δE^{str} for the two-atom bcc cell of bulk Mo from bulk equilibrium at $a_{b0} = 5.9820$ bohr in mRyd against the in-plane angle θ_{12} between lattice vectors a_1 and a_2 around $\pi/2$ radians.

(1)			(2)	
a	c	δE^{EBP}	θ_{12}	δE^{str}
5.8624	6.0801	3.156	1.5272 (87.5°)	3.034
5.9222	6.0263	0.736	1.5446 (88.5°)	1.100
5.9820	5.9822	0.000	1.5621 (89.5°)	0.120
6.0418	5.9423	0.808	1.5795 (90.5°)	0.122
6.1016	5.9031	3.008	1.5970 (91.5°)	1.080

Table 2. Experimental and theoretical values of equilibrium lattice constant of bulk Mo (bohr); $Y' = c_{11} + c_{12} - 2c_{12}^2/c_{11}$ is the in-plane epitaxial Young's modulus for epitaxial stress in (001) planes; $\gamma = 2c_{12}/c_{11}$ is the epitaxial Poisson ratio for in-plane epitaxial strain; $Y = c_{11} - 2c_{12}^2/(c_{11}+c_{12})$ is the Young's modulus for out-of-plane stress; $\nu = c_{12}/(c_{11}+c_{12})$ is the Poisson ratio for out-of-plane strain; percentage deviations of theory from experiment are shown in parentheses.

	Experiment[a,b]	Theory[c]
a_{b0}	5.9463	5.9820 (+0.6%)
c_{11b}	30.59	32.35 (+5.8%)
c_{12b}	11.75	11.16 (−5.0%)
c_{44b}	8.50	7.43 (−14.4%)
Y'_b	33.31	35.82 (+7.5%)
γ_b	0.768	0.690 (−11.3%)
Y_b	24.07	26.75 (+11.1%)
ν_b	0.278	0.256 (−7.9%)

[a] Taylor A F and Kagle Brenda J 1963 *Crystallographic Data on Metals and Alloys* (New York: Dover) (a_{b0}).
[b] Featherstone F H and Neighbors J R 1963 *Phys. Rev.* **130** 1324 (c_{ij}).
[c] The theoretical values have been recalculated and differ slightly from the values in [1].

we have

$$\left(\frac{\partial^2 E_b^{str}}{\partial \theta_{12}^2}\right) Q = a_{b0}^3 c_{44b} \tag{5}$$

where $\varepsilon_6 = 2\varepsilon_{12} = \delta\theta_{12}$ [6] and $\delta\theta_{12}$ is the in-plane change in angle of the square side of the unit cell around $\pi/2$ radians due to in-plane [100], [010] shear. Then from table 1 $(\partial^2 E^{str}/\partial\theta_{12})_Q = 1.5905$ mRyd and (5) gives $c_{44b} = 7.43$ mRyd/bohr^3. Table 2 lists the bulk Mo theoretical structural and elastic constants and compares them with experiment.

2.2. Slab calculations

The composite elastic model of the seven-layer Mo(001) slab has thickness t_N made up of two homogeneous surface regions of thickness t_s and a bulk region of thickness t_b

$$t_N = 2t_s + t_b. \tag{6}$$

Table 3 lists energies along the EBP and shows that at slab equilibrium

$$a_Q = 5.9124 \text{ bohr}$$
$$t_N = 7\overline{d} = 7 \times 2.931 = 20.517 \text{ bohr} \tag{7}$$

Table 3. (1) Energies δE^{EBP} for the seven-atom cell of the seven-layer slab of Mo(001) in mRyd relative to slab equilibrium against lattice constant a and average layer-spacing $\overline{d}$ in bohr along the EBP of the seven-layer slab. (2) Strain energies δE^{str} of the seven-atom slab cell relative to slab equilibrium against $a = a_1 = a_2$ with layer spacings at equilibrium values. (3) Strain energies of the seven-atom cell relative to slab equilibrium against a_1 at equilibrium values of a_2 and layer spacings.

(1)			(2)		(3)	
a	$\overline{d}$	δE^{EBP}	a	δE^{str}	a_1	δE^{str}
5.9620	2.901	1.228	5.6759	53.893	5.7942	4.546
5.9222	2.931	0.045	5.7942	12.307	5.8533	1.166
5.9124	2.931	0.000	5.9124	0.000	5.9124	0.000
5.8923	2.932	0.235	6.0306	10.366	5.9715	0.923
5.8624	2.952	1.419	6.1489	41.492	6.0306	3.751

where $\overline{d}$ is the average layer spacing and $\overline{d}/2$ is added beyond each end-atom position. These results for full layer-spacing relaxation were obtained in [2] and are partially repeated in table 3. By an analysis of the layer relaxations it was also estimated in [2] that $t_s = 6 \pm 1.5$ bohr. Hence the calculations here will use

$$t_s = 6 \text{ bohr} \qquad t_b = 8.517 \text{ bohr}. \tag{8}$$

In section 3 the effect of varying t_s over the estimated range on the properties of the surface region will be discussed.

The surface regions are considered to be under tensile stress, stretched from the unknown equilibrium in-plane lattice constant a_{s0} up to a_Q, while the bulk region is under compressive stress, compressed from the known bulk equilibrium value a_{b0} down to the known slab equilibrium value a_Q. The epitaxial Young's moduli Y'_s and Y'_b relate in-plane stress to in-plane epitaxial (biaxial) strains at any a by [2]

$$\sigma_{1s}(a) = Y'_s \varepsilon_{1s}(a) \qquad \sigma_{1b}(a) = Y'_b \varepsilon_{1b}(a) \tag{9}$$

$$\varepsilon_{1s}(a) \equiv \frac{(a - a_{s0})}{a_{s0}} \qquad \varepsilon_{1b}(a) \equiv \frac{(a - a_{b0})}{a_{b0}}. \tag{10}$$

At slab equilibrium the in-plane stresses σ_{1s} and σ_{1b} are related by the force balance equation of static equilibrium

$$2\sigma_{1s}(a_Q)t_s = -\sigma_{1b}(a_Q)t_b. \tag{11}$$

If t_s is given, (9) to (11) give a relation at a_Q between the unknown surface parameters a_{s0} and Y'_s, hence if Y'_s is known, a_{s0} is known. The elastic constant Y'_s is the first of the six elastic constants of the surface region that will now be found from the derivatives of the strain energy of the slab under six deformations.

Since the surface regions are tetragonal and the bulk region cubic, the strain energy from slab equilibrium is given by

$$\begin{aligned} E^{str} = a_Q^2 \Bigg\{ 2t_s \Bigg[& \frac{c_{11s}}{2}(\varepsilon_{1s}^2 + \varepsilon_{2s}^2) + c_{12s}\varepsilon_{1s}\varepsilon_{2s} + c_{13s}(\varepsilon_{3s}\varepsilon_{1s} + \varepsilon_{2s}\varepsilon_{3s}) \\ & + \frac{c_{33s}}{2}\varepsilon_{3s}^2 + \frac{c_{44s}}{2}(\varepsilon_{4s}^2 + \varepsilon_{5s}^2) + \frac{c_{66s}}{2}\varepsilon_{6s}^2 \Bigg] \\ & + t_b \Bigg[\frac{c_{11b}}{2}(\varepsilon_{1b}^2 + \varepsilon_{2b}^2 + \varepsilon_{3b}^2) + c_{12b}(\varepsilon_{2b}\varepsilon_{3b} + \varepsilon_{3b}\varepsilon_{1b} + \varepsilon_{1b}\varepsilon_{2b}) \\ & + \frac{c_{44b}}{2}(\varepsilon_{4b}^2 + \varepsilon_{5b}^2 + \varepsilon_{6b}^2) \Bigg] \Bigg\}. \end{aligned} \tag{12}$$

The first deformation from slab equilibrium is along the EBP, where $\varepsilon_1 (= \varepsilon_2)$ and ε_3 are related by $\sigma_3 = 0$, and $\varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0$, so that

$$E^{EBP}(a) = a_Q^2 [2t_s Y_s' \varepsilon_{1s}^2(a) + t_b Y_b' \varepsilon_{1b}^2(a)] \tag{13}$$

where Y_b' is given in (1), $\varepsilon_{1s}(a)$ and $\varepsilon_{1b}(a)$ are the isotropic strains defined in (10) and

$$Y_s' = c_{11s} + c_{12s} - \frac{2c_{13s}^2}{c_{33s}}. \tag{14}$$

Then the second derivative of $E^{EBP}(a)$ at slab equilibrium, treating the strains as small, gives

$$\left(\frac{\mathrm{d}^2 E^{EBP}(a)}{\mathrm{d}a^2}\right)_Q = 4t_s Y_s' + 2t_b Y_b'. \tag{15}$$

From the data in table 3 we have

$$\left(\frac{\mathrm{d}^2 E^{EBP}(a)}{\mathrm{d}a^2}\right)_Q = 1.070 \times 10^3 \frac{\mathrm{mRyd}}{\mathrm{bohr}^2}. \tag{16}$$

Then using (8) for t_s and t_b, table 2 for Y_b', (15) and (16) give

$$Y_s' = 19.16\ \mathrm{mRyd/bohr}^3. \tag{17}$$

Now put (17) into (9), (10) and (11), use (7) for a_Q and table 2 for a_{b0} to find

$$a_{s0} = 5.8225\ \mathrm{bohr}. \tag{18}$$

For the second deformation from slab equilibrium to put into (12) take $\varepsilon_1 = \varepsilon_2 = \delta a/a$ as given by (10), but keep d_{ij} and $\overline{d}$ at slab equilibrium values (unlike along the EBP), so that $\varepsilon_3 = \varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0$, then

$$\left(\frac{\partial^2 E^{str}(a, \overline{d})}{\partial a^2}\right)_Q = 4t_s(c_{11s} + c_{12s}) + 2t_b(c_{11b} + c_{12b}). \tag{19}$$

From the data in table 3

$$\left(\frac{\partial^2 E^{str}(a, \overline{d})}{\partial a^2}\right)_Q = 1.702 \times 10^3 \frac{\mathrm{mRyd}}{\mathrm{bohr}^2} \tag{20}$$

hence using (8) for t_s and t_b, with c_{11b} and c_{12b} from table 2, (19) and (20) give

$$c_{11s} + c_{12s} = 40.04\ \mathrm{mRyd/bohr}^3. \tag{21}$$

For the third deformation from slab equilibrium only $\varepsilon_1 \equiv \delta a_1/a_1$ is varied, but $a_2 = a_Q$ so that $\varepsilon_2 = \varepsilon_3 = \varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0$; then from (12) and table 3

$$\left(\frac{\partial^2 E^{str}(a_1, a_2, \overline{d})}{\partial a_1^2}\right)_Q = 2t_s c_{11s} + t_b c_{11b} = 589.9 \frac{\mathrm{mRyd}}{\mathrm{bohr}^2}. \tag{22}$$

Hence with c_{11b} from table 2

$$c_{11s} = 26.20\ \mathrm{mRyd/bohr}^3. \tag{23}$$

For the fourth deformation from slab equilibrium used to evaluate c_{33s} we vary the total thickness of the slab, keep $a = a_Q$, and at each thickness relax the layer spacings, so that $\varepsilon_1 = \varepsilon_2 = \varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0$. Then (12) becomes

$$E^{str}(a_Q, \overline{d}) = a_Q^2 \left[2t_s \frac{c_{33s}}{2} \varepsilon_{3s}^2 + t_b \frac{c_{33b}}{2} \varepsilon_{3b}^2\right] \tag{24}$$

where

$$\varepsilon_{3s} \equiv \frac{\overline{d_s} - \overline{d_{s0}}}{\overline{d_{s0}}} \qquad \varepsilon_{3b} \equiv \frac{d_b - d_{b0}}{d_{b0}}. \tag{25}$$

Table 4. (1) Strain energies δE^{str} of the seven-atom slab cell in mRyd relative to slab equilibrium against slab thickness with corresponding relaxed layer spacings d_{12}, d_{23}, d_{34}, and average layer spacing $\overline{d}$ in bohr keeping a_1, a_2 at equilibrium values. (2) Strain energies δE^{str} against θ_{23} in radians around equilibrium value $\pi/2$ with a_1, a_2, d_{ij} at equilibrium values. (3) Strain energies δE^{str} as in (2), but against θ_{12}.

(1)					(2)		(3)	
d_{12}	d_{23}	d_{34}	$\overline{d}$	δE^{str}	θ_{23}	δE^{str}	θ_{12}	δE^{str}
2.5667	2.9676	2.9098	2.8147	13.750	1.5359 (88°)	3.298	1.5359	3.234
2.6411	3.0167	2.9622	2.8733	2.651	1.5533 (89°)	0.810	1.5533	0.810
2.712	3.069	3.015	2.931	0.000	1.5708 (90°)	0.000	1.5708	0.000
2.7662	3.1304	3.0753	2.9906	2.923	1.5882 (91°)	0.793	1.5882	0.810
2.8467	3.1795	3.1217	3.0493	12.252	1.6057 (92°)	3.106	1.6057	3.237

In (25) $\overline{d_s}$ is the average layer spacing over the non-uniform relaxed values in the surface regions and $\overline{d_{s0}}$ is the value of $\overline{d_s}$ for the surface in free equilibrium. Similarly, d_b is the bulk region layer spacing, which is uniform, and d_{b0} is the value of d_b at the bulk equilibrium $d_{b0} = a_{b0}/2$.

To find c_{33s} from (24) we need to differentiate $E^{str}(a_Q, \overline{d})$ with respect to $\overline{d}$, which requires knowing how $\overline{d_s}$ and d_b vary with $\overline{d}$, and also requires evaluation of $\overline{d_{s0}}$. The procedure is more complicated than differentiation by a used previously when all regions had the same a.

The function $d_b(\overline{d})$ is given by $d_{34}(\overline{d})$ in table 4, since in [2] it is shown that d_{34}, the innermost layer spacing, behaves like bulk under the compression of a from a_{b0} to a_Q. Now $\overline{d_s}$ and d_b are related to $\overline{d}$ by the weighted average

$$\overline{d} = \frac{2t_s\overline{d_s} + t_b d_b}{2t_s + t_b} \tag{26}$$

hence $\overline{d_s}(\overline{d})$ is found from $d_b(\overline{d})$ by (26).

To evaluate d_{s0} first use (26) to evaluate $\overline{d_{sQ}}$, where $\overline{d_Q} = 2.931$ bohr is known from table 4, as is $d_{bQ} = d_{34}(\overline{d_Q}) = 3.0150$ bohr, hence

$$\overline{d_{sQ}} = 2.8714 \text{ bohr}. \tag{27}$$

Then relate $\overline{d_{sQ}}$ to d_{s0} by the epitaxial Poisson ratio γ_s, which relates the out-of-plane strain from $\overline{d_{s0}}$ to $\overline{d_{sQ}}$ to the epitaxial in-plane strain from a_{s0} to a_Q, namely

$$\overline{d_{sQ}} = \overline{d_{s0}}(1 - \gamma_s \varepsilon_{1s}(a_Q)) \tag{28}$$

where $\varepsilon_{1s}(a_Q)$ is given by (10), a_{s0} by (18) and a_Q by (7). From (27) and (28) and the assumption that

$$\gamma_s = \frac{2c_{13s}}{c_{33s}} = 1.55 \tag{29}$$

we find

$$\overline{d_{s0}} = 2.940 \text{ bohr}. \tag{30}$$

The value of γ_s assumed in (29) will later be shown consistent with calculated values of c_{13s} and c_{33s}.

Now from (24) and (25)

$$\left(\frac{\partial^2 E^{str}(a, \overline{d})}{\partial \overline{d}^2}\right)_Q = \frac{2a_Q^2 t_s}{\overline{d_{s0}}^2}\left(\frac{\partial \overline{d_s}}{\partial \overline{d}}\right)_Q^2 c_{33s} + \frac{a_Q^2 t_b c_{33b}}{d_{b0}^2}\left(\frac{\partial d_b}{\partial \overline{d}}\right)_Q^2. \tag{31}$$

Table 5. (1) Structural parameters of the surface region material in its free equilibrium state, a_{s0} and d_{s0} in bohr, percentage change from bulk in parentheses. (2) Theoretical elastic stiffness coefficients of surface region material in mRyd/bohr^3 at $t_s = 6$ bohr and in parentheses the average percentage deviation for $t_s = 4.5$ bohr (first sign) and for $t_s = 7.5$ bohr (second sign). (3) Corresponding values of the epitaxial Young's modulus Y_s' and the epitaxial Poisson ratio γ_s for the (001) plane, the out-of-plane Young's modulus $Y_s = c_{33s} - 2c_{13s}^2/(c_{11s}+c_{12s})$ and the Poisson ratio $\nu_s = c_{13s}/(c_{11s}+c_{12s})$ with percentage change from bulk in parentheses.

(1)		(2)		(3)	
a_{s0}	5.8225 (−2.7%)	c_{11s}	26.2 (− + 6.5%)	Y_s'	19.2 (−46%)
d_{s0}	2.939 (−1.2%)	c_{12s}	13.8 (+ − 5.0%)	γ_s	1.50 (+217%)
		c_{33s}	17.4 (− + 6.0%)	Y_s	7.84 (−67%)
		c_{13s}	13.5 (+ − 5.2%)	ν_s	0.35 (+37%)
		c_{44s}	7.13 (− + 1.1%)		
		c_{66s}	7.38 (− + 0.2%)		

From table 4 and (26)

$$\left(\frac{\partial^2 E^{str}(a,\overline{d})}{\partial \overline{d}^2}\right)_Q = 1.904 \times 10^3 \frac{\text{mRyd}}{\text{bohr}^2}$$
$$\left(\frac{\partial \overline{d_s}}{\partial \overline{d}}\right)_Q = 1.011 \tag{32}$$
$$\left(\frac{\partial \overline{d_b}}{\partial \overline{d}}\right)_Q = 0.985.$$

Putting (32) in (31) gives

$$c_{33s} = 17.35 \text{ mRyd/bohr}^3. \tag{33}$$

Now using (14), (17), (21) and (33) c_{13s} is given by

$$c_{13s} = \left[\frac{(c_{11s}+c_{12s}) - Y_s' c_{33s}}{2}\right]^{1/2} = 13.46 \frac{\text{mRyd}}{\text{bohr}^3}. \tag{34}$$

From (34) and (33) $\gamma_s = 2c_{13s}/c_{33s} = 1.55$ in agreement with the assumption in (29).

For the fifth deformation from slab equilibrium to put into (12), use $\varepsilon_4 = \delta\theta_{23}$ (as in (5)), where $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \varepsilon_5 = \varepsilon_6 = 0$

$$\left(\frac{\partial^2 E^{str}}{\partial \theta_{23}^2}\right)_Q = a_Q^2(2t_s c_{44s} + t_b c_{44b}) = 5.204 \times 10^3 \text{ mRyd} \tag{35}$$

on using the data in table 4. Then (35) with c_{44b} from table 2 gives

$$c_{44s} = 7.13 \text{ mRyd/bohr}^3. \tag{36}$$

Similarly, the sixth deformation from slab equilibrium varies $\varepsilon_6 = \delta\theta_{12}$, to give from (12)

$$\left(\frac{\partial^2 E^{str}}{\partial \theta_{12}^2}\right)_Q = a_Q^2(2t_s c_{66s} + t_b c_{44b}) = 5.308 \times 10^3 \text{ mRyd} \tag{37}$$

hence from (37)

$$c_{66s} = 7.38 \text{ mRyd/bohr}^3. \tag{38}$$

The surface region elastic stiffness coefficients are collected in table 5 along with the Young's moduli and Poisson ratios, in plane and out of plane, which are compared with bulk values.

3. Discussion

The main conclusions about the structural and elastic properties of the surface material compared to bulk material can be drawn from tables 2 and 5. In its own equilibrium state the surface material was found to have a structure which is 2.7% smaller in plane and 1.2% smaller out of plane than bulk, and the equilibrium unit cell is slightly prolate tetragonal.

However larger differences from bulk are shown by the elastic stiffness coefficients of the surface material, which are rather anisotropic compared to cubic symmetry, and are considerably weaker than bulk. The fact that Y_s' is 46% less than Y_b' means that a given in-plane epitaxial stress produces nearly twice the in-plane epitaxial strain in the surface material compared to bulk; the fact that γ_s is more than twice γ_b means that a given in-plane epitaxial strain produces more than twice the out-of-plane strain in the surface compared to bulk.

Similarly, the fact that Y_s is much smaller than Y_b means that a given out-of-plane stress produces much larger out-of-plane strains in the surface compared to bulk; that ν_s is larger than ν_b means that a given out-of-plane strain produces larger in-plane strains in the surface than in bulk.

The surface material satisfies the four stability conditions for tetragonal structures [6], namely

$$\begin{aligned} &c_{11s} - |c_{12s}| = 12.4 > 0 \\ &(c_{11s} + c_{12s})c_{33s} - 2c_{13s}^2 = 297.7 > 0 \\ &c_{44s} = 7.25 > 0 \\ &c_{66s} = 7.38 > 0. \end{aligned} \tag{39}$$

However the surface material is considerably closer to instability than bulk in satisfying the first two conditions in (39) (bulk values 21.2 and 1158.5, respectively).

Analysis of the layer-spacing relaxations in [2] indicated that the surface region ends between the second and third atomic layers, or $4.5 \leqslant t_s \leqslant 7.5$ bohr, since d_{34} expanded under compression like bulk material and d_{12} contracted strongly as if in strong tension. An absolute lower cutoff for t_s comes from the fact that the equations relating Y_s' and a_{s0} to t_s ((11) and (15)) have no physically reasonable solutions for $t_s \leqslant 3$ bohr. Calculation of the c_{ijs} over the range of t_s from 4.5 to 7.5 bohr shows the c_{ijs} vary on average by ± 4 or 5% from the values at $t_s = 6$ bohr (shown in table 5). These variations do not affect the general conclusions about the elastic properties of the surface material compared to bulk. Comparison of results on thicker slabs with the seven-layer results should fix t_s more precisely.

The elastic analysis used the linear elastic approximation, which assumes that the elastic constants are independent of strain, when the bulk elastic constants were applied to the energy curvatures around slab equilibrium in (15), (19) etc. The cubic fits to the energy between a_Q and the 1.2% larger a_{b0} indicate that the curvature at the compressed lattice constant a_Q is about 10% larger. Hence taking account of these nonlinear elastic effects would further decrease the surface stiffness coefficients. The nonlinear corrections could be systematically studied by more detailed energy calculations. Such a nonlinear correction would also enter in calculating the surface elastic constants at the bulk lattice constant a_{b0}, which corresponds to surfaces on thick crystals.

In summary a metal crystal of Mo appears to be covered by a coherent epitaxial film about two layers thick, which is under strong tension, and which has elastic stiffness coefficients that are anisotropic compared to cubic and much weaker than bulk Mo. Such a coating can be expected to affect all surface-sensitive properties.

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