

Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual Physical Review standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Surface strain of tungsten (001)

Jing Chen and H. Krakauer

Department of Physics, College of William and Mary, Williamsburg, Virginia 23185

D. J. Singh

Complex Systems Theory Branch, Naval Research Laboratory, Washington, D.C. 20375-5000

(Received 5 July 1990)

We report the results of *ab initio* local-density-functional total-energy calculations of W(001) slabs of varying thickness as a function of the in-plane or surface lattice parameter. The results are used to isolate the surface strain energy of the ideal surface. We find that the ideal W(001) surface is softer than the bulk and has a small tensile strain of about 1% with a strain energy of less than 1 mRy/(surface atom). A comparison of the strain energy with the energy associated with the reconstruction leads to the conclusions that the interaction between the ideal surface atoms is *weakly attractive* and the instability of the ideal W(001) surface is *not* the result of a large surface strain.

Despite the fact that the clean W(001) surface has been extensively studied using a variety of experimental and theoretical techniques, a detailed understanding of its low-temperature reconstruction^{1,2} and associated phase transition has yet to be achieved. At room temperature and above this surface displays a (1×1) low-energy electron diffraction (LEED) pattern, characteristic of an ideal surface, though there are now strong indications that this phase is disordered.³⁻¹⁰ In any case, at low temperatures a c(2×2) LEED pattern is observed indicating the presence of a reconstruction. Several of the unanswered questions about the phase transition hinge on an understanding of the interactions between the surface atoms. In particular, in order to achieve a detailed picture of the phase transition, it is necessary to determine to what extent long-range interactions are important and to determine the nature of the short-range interactions. Fasolino, Santoro, and Tosatti¹¹ have used short-range potential models to calculate the W(001) photon spectrum; based on their calculations and the known reconstruction of W(001) surface, they concluded that the interactions between surface atoms are *repulsive*. Joubert¹² has carried out a detailed tight-binding analysis of the interactions of surface atoms of W(001) which indicate that the dangling-bond peak in its density of states leads to an *attractive* interaction between the surface atoms which drives the W(001) reconstruction. Our previous total-energy calculations^{4,5} have indicated that the instability of the ideal surface is due primarily to short-range interactions involving bond formation, though the detailed form of the interactions could not be determined. Here

we report total energy calculations performed in order to isolate the surface strain energy of the ideal W(001) surface and thus determine what role if any surface strain plays in its instability.

The total energies were calculated within the local-density-functional approximation (LDA) using the general potential linearized augmented-plane-wave (LAPW) method^{13,14} with the Wigner¹⁵ exchange correlation potential. This method has been described in detail previously.¹⁴ Since our aim is to investigate the possibility that the surface strain energy of the ideal W(001) surface contributes to the reconstruction, we use unreconstructed p(1×1) slabs to model the surface. The interlayer separation of these slabs is kept at the bulk equilibrium lattice parameter value of 5.973 a.u., except for a fixed surface interlayer relaxation of 6% (the calculated relaxation value for the ideal surface). A muffin-tin radius R_{MT} , of 1.25 Å and a basis set cut off at $R_{\text{MT}}K_{\text{max}}=8.0$ were used. It was determined that adequate Brillouin zone sampling was achieved using a set of 10 special k points in the irreducible wedge.¹⁶ The calculated changes in total energy between two basis sets cut off at $R_{\text{MT}}K_{\text{max}}=8.0$ and 8.6 for a five-layer slab were small, about 0.1%, in equilibrium lattice constant. Differences in the calculated total energy are covered to better than 0.1 mRy per atom.

In order to isolate the surface strain energy we express the total energy E_t of a slab consisting of n layers and with surface lattice parameter a_s ,

$$\Delta E_t(a_s, n) = (n-2)\Delta E_b(a_s) + 2\Delta E_s(a_s, n), \quad (1)$$

where

$$\Delta E(a_s) \equiv E(a_s) - E(a_{s0}) \quad (2)$$

and a_{s0} is the surface lattice parameter corresponding to the equilibrium bulk lattice parameter. E_b is the energy of a bulk layer, and E_s is the effective energy of a surface layer (note that it includes modifications to inner layers due to the presence of the surface). By definition E_b is independent of n and may be obtained from a total energy calculation for bulk tungsten. On the other hand, E_s may depend on both n and a_s . We note, however, that the component depending on n arises from interactions between opposite faces of the slab and should become negligible for large enough n . In this case we may write

$$\Delta E_s(a_s) = \frac{1}{2} [\Delta E_t(a_s) - (n-2)\Delta E_b(a_s)] \quad (3)$$

The effective energy of a surface layer of W(001) can be derived according to Eq. (3) from the calculated total energy for a slab and that for the bulk. The total energy for the bulk is calculated as a function of in-plane lattice parameter in a two-atom tetragonal cell. [A special k -point set consisting of 40 points, commensurate with the slab of two-dimensional 10 k -point set, is used. This yields well-converged results not only for the equilibrium in-plane lattice parameter $a_{s0} = 5.9957$ a.u., which is within 0.4% of the bulk equilibrium lattice parameter, but also for the elastic constant $(C_{11} + C_{12}) = 701$ GPa, in good agreement with the experimental value of 738 GPa. Other convergence parameters were kept the same as in the slab calculation to facilitate accurate subtraction.] The calcu-

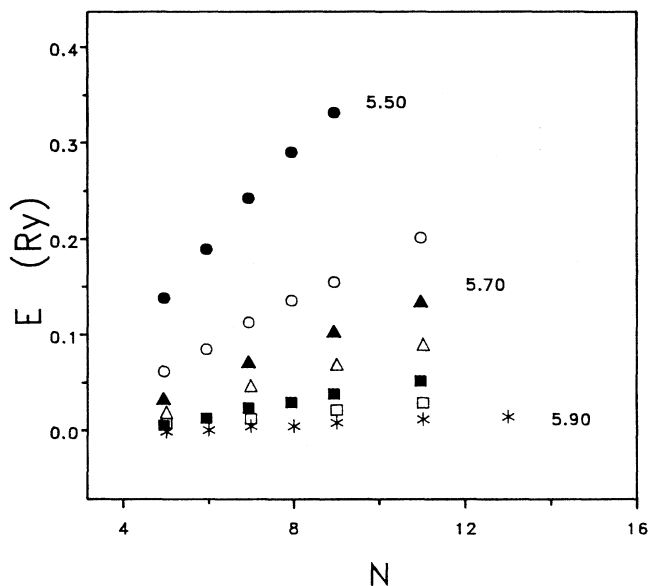


FIG. 1. The solid and open circles, the solid and open triangles, the solid and open squares, and the stars are calculated total energies for a function of slab thickness N and surface lattice parameter of 5.5, 5.65, 5.70, 5.75, 5.80, 5.85, and 5.90 a.u., respectively. The values are given relative to the energies at the bulk equilibrium lattice parameter which is 7708.400 97 Ry.

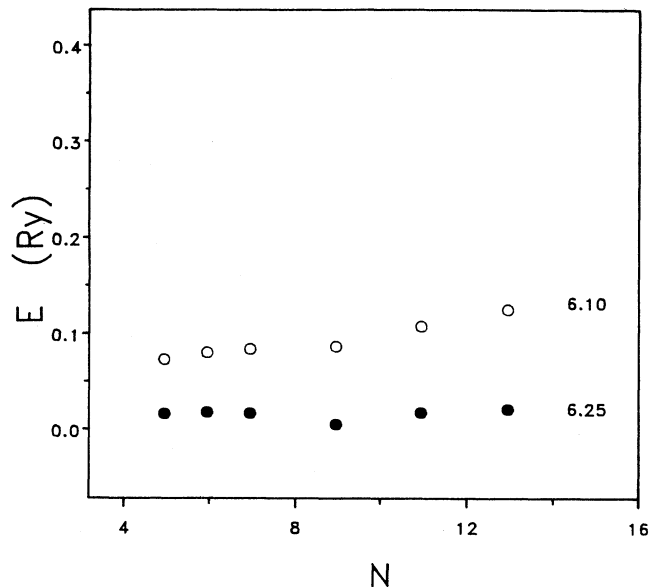


FIG. 2. The solid and open circles are calculated total energies for a function of slab thickness N and surface lattice parameter of 6.10 and 6.25 a.u., respectively. The values are given relative to the same reference as in Fig. 1.

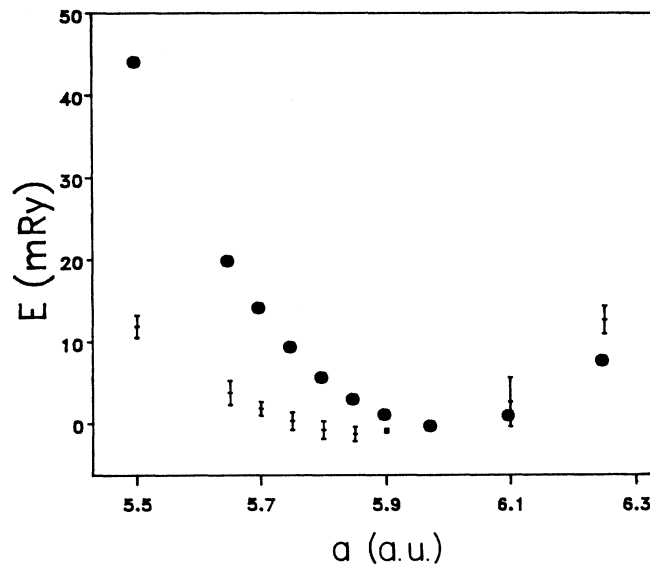


FIG. 3. Total energy as a function of surface lattice parameter. The solid circles denote the total energy of a bulk layer, while the dots with error bars denote the total energy of the surface layer. The values are given relative to the energy at the bulk equilibrium lattice parameter.

lated total energies are shown in Figs. 1 and 2 as a function of slab thickness n , for various surface lattice parameters a_s . Results for slabs with smaller lattice parameters than the equilibrium lattice parameter of bulk W (which is 5.973 a.u.) are shown in Fig. 1 while those with larger parameter are shown in Fig. 2. Note the approximate linear dependence on the number of layers n especially for the thicker slabs. The energies of a surface layer so derived for the three thickest slabs among those shown in Figs. 1 and 2 are averaged and shown in Fig. 3 as a function of surface lattice parameter. The error for the averaged energy of a surface layer ranges from 3 to 0.3 mRy. Also shown in Fig. 3 is the energy of bulk W (derived from the two-atom tetragonal cell) for comparison.

Least-squares fits to E_s yield the equilibrium surface lattice parameter of 5.90 a.u. corresponding to a tensile surface strain of about 1% and a strain energy of about 0.9 mRy which is almost an order of magnitude smaller than the calculated reconstruction energy.⁵ This implies that surface strain cannot account for the W(001) reconstruction. However, examination of the results presented in Fig. 3 reveals that the surface layer is considerably softer than the bulk. This is in accord with theoretical

work suggesting that the ideal W(001) surface is relatively soft against a variety of distortions.^{5,17-19} It is also consistent with the observation of a disordered high-temperature phase.

In summary, total energies for W(001) slabs were calculated as a function of slab thickness and surface lattice parameter. The surface strain energy of the ideal surface is isolated from the slab energies and bulk energies and is found to be less than 1 mRy. Results show that the equilibrium lattice parameter of the ideal surface is smaller than that of the bulk with the surface strain of about 1%, and that the surface is much softer than the bulk. Comparing the strain energy with the energy associated with the reconstruction, it is concluded that the interaction between ideal surface atoms is weakly attractive and the instability of the ideal W(001) surface is not the result of a large surface strain.

This work was supported by the National Science Foundation through Grant No. DMR-87-18535 and by the Office of Naval Research. Computations were carried out on an IBM 3090 at the Cornell National Supercomputer Facility.

-
- ¹T. E. Felter, R. A. Barker, and P. J. Estrup, Phys. Rev. Lett. **38**, 1138 (1977).
²M. K. Debe and D. A. King, Phys. Rev. Lett. **39**, 708 (1977); Surf. Sci. **81**, 193 (1979).
³I. Stensgaard, L. C. Feldman, and P. J. Silverman, Phys. Rev. Lett. **42**, 247 (1979).
⁴D. Singh, S. H. Huai, and H. Krakauer, Phys. Rev. Lett. **57**, 3292 (1986).
⁵D. Singh and H. Krakauer, Phys. Rev. B **37**, 3999 (1988).
⁶L. D. Roelofs and J. F. Wendelken, Phys. Rev. B **34**, 3319 (1986); L. D. Roelofs, T. Ramseyer, L. N. Taylor, D. Singh, and H. Krakauer, *ibid.* **40**, 9147 (1989).
⁷J. W. Chung, K. Evans-Lutterodt, E. D. Specht, R. J. Birgeneau, P. J. Estrup, and A. R. Kortan, Phys. Rev. Lett. **59**, 2192 (1987).
⁸I. Stensgaard, K. G. Purcell, and D. A. King, Phys. Rev. B **39**, 897 (1989).
⁹I. K. Robinson, A. A. MacDowell, M. S. Altman, P. J. Estrup, K. Evans-Lutterodt, J. D. Brock, and R. J. Birgeneau, Phys. Rev. Lett. **62**, 1294 (1989).
¹⁰J. Jupille, K. G. Purcell, and D. A. King, Phys. Rev. B **39**, 6871 (1989).
¹¹A. Fasolino, G. Santoro, and E. Tosatti, Phys. Rev. Lett. **44**, 1684 (1980); A. Fasolino and E. Tosatti, Phys. Rev. B **35**, 4264 (1987).
¹²D. P. Joubert, J. Phys. C **20**, 1899 (1987).
¹³O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); D. D. Koelling and G. O. Arbman, J. Phys. F **5**, 2041 (1975); D. R. Hamann, Phys. Rev. Lett. **42**, 662 (1979); E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981).
¹⁴S. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985); S. Wei, H. Krakauer, and M. Weinert, Phys. Rev. B **32**, 7792 (1985).
¹⁵E. Wigner, Phys. Rev. B **46**, 1002 (1934).
¹⁶H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976); J. D. Pack and H. J. Monkhorst *ibid.* **16**, 1748 (1977).
¹⁷J. E. Inglesfield, J. Phys. C **12**, 149 (1979).
¹⁸K. Terakura, I. Terakura, and Y. Teraoka, Surf. Sci. **86**, 535 (1979).
¹⁹D. P. Joubert, J. Phys. C **21**, 4233 (1988).