

All-electron local-density determination of the surface energy of transition metals: W(001) and V(001)

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The surface energies of W(001) and V(001) are determined theoretically within local-density-functional theory employing the all-electron full-potential linearized augmented-plane-wave method. The calculated values are 5.1 J/m^2 for W(001)—in good agreement with experiment—and 3.4 J/m^2 for V(001). Multilayer surface-relaxation calculations show that the surface-relaxation energy is small and amounts to only a few percent of the surface energy. The surface entropy at sufficient high temperatures for the W(001) surface, as deduced from a comparison of our calculated result and high-temperature experimental surface-energy values, is large ($1.5 \times 10^{-3} \text{ J/m}^2 \text{ deg}$).

The energy of a free surface plays an important role in such physical and chemical processes on solid surfaces as fracture, catalysis, and epitaxial growth. Unfortunately, experimental measurements of the surface energy are difficult to perform. They are mostly constrained to the determination of surface energies at high temperatures and are subject to numerous errors due to surface-active contaminants. For example, although the tungsten surface has been the most studied metal surface in the last decade, the experimentally measured surface energies at high temperature scatter widely from (Refs. 1–5) 1.8 to 5 J/m^2 . On the other hand, the surface energy of solid vanadium has not even been measured experimentally owing to the difficulty in preparing a clean surface because of oxygen contamination.⁶ Similarly, theoretical determinations of the surface energy face a formidable challenge. Previous theoretical efforts focused on simple metals using either first-order pseudopotential perturbation theory⁷ or nonperturbative variational methods.⁸ Only recently have first-principles calculations of the surface energy of such complex systems as the transition metals presented in this paper become feasible and realistic.^{9,10}

In this paper, we report theoretical determinations of the surface energies of W(100) and V(100) based on all-electron self-consistent first-principles calculations within local-density-functional theory¹¹ using the full-potential linearized augmented-plane-wave¹² (FLAPW) total-energy method.¹³ The W(001) and V(001) surfaces are described in a single slab geometry with five and seven atomic layers. (Because our slabs have two surfaces, the surface energy is one-half of the total-energy difference between a film and the corresponding value for the same number of atoms in a bulk crystal.) The convergence of the surface energy with respect to film thickness depends on how well the inner layers of the film approach the bulk. This is examined by comparing the total energy of the bulk atoms and the corresponding value obtained from the total-energy difference between the five- and seven-layer films. Thus, we have incorporated results obtained with both the FLAPW thin-film method¹² and an independent FLAPW bulk method¹⁴ into the surface energy determinations. These methods have been applied previously to the study of the electronic band structure^{14,15} and total energy of bulk tungsten¹⁴ and of its surface, including a multilayer surface relaxation,¹⁶ and have yielded results in excellent agreement with experiment. In

order to test the variation of the surface energy with respect to different forms of the exchange-correlation potential, both the Hedin-Lundqvist¹⁷ (HL) and the Wigner¹⁸ exchange-correlation potentials have been used. The former is known to be more exact in the metallic density region, while the latter is more appropriate for diffuse regions such as those near the surface. The effect of the surface lattice relaxation was examined for both tungsten¹⁶ and vanadium.¹⁹ We have used the experimental lattice constants²⁰ of 3.16 \AA for bulk bcc tungsten and 3.03 \AA for bcc bulk vanadium in the calculations for the surface energy.

Our calculated values of the surface energies are 5.1 J/m^2 for W(001) and 3.4 J/m^2 for V(100), respectively. We find that (i) owing to the highly local screening interaction, the seven-layer films are thick enough to explore the surface energy of transition metals with a convergence well within 5 mRy and (ii) the dominant contributions are from the surface and subsurface atoms. Also, we show from multilayer relaxation studies¹⁵ that the surface-relaxation energy constitutes only a small fraction of the surface energy [less than 2% for W(100) and less than 4.5% for V(001)]. Finally, the high-temperature surface entropy is discussed for the W(100) surface.

The results of our calculations are summarized in Table I for different forms of assumed exchange-correlation potential (HL and Wigner) and for the various numbers of basis functions used in the calculations. The theoretical values of the surface energies E_s are found to be large $\sim 230 \text{ mRy}$ (or 5.1 J/m^2) for W(001) and $\sim 145 \text{ mRy}$ (or 3.4 J/m^2) for V(001). A large value for E_s in W(001) is not surprising in view of its anomalously stable atomic structure (which is reflected in the ratio of the cohesive energy to atomic surface area²¹) and its high density of surface states near the Fermi level.²² Various features of the calculations are examined with a view towards understanding their effects on the results obtained.

The effect of a finite film thickness can be examined by considering the quantity ΔE , which is defined as the total-energy difference per atom between the bulk crystal and the center of a seven-layer film (obtained from taking one-half of the total-energy difference between a seven-layer and a five-layer slab). As shown in Table I, the values of ΔE are small (less than 5% of the calculated surface energies) for both elements. The smallness of ΔE not only indicates the

TABLE I. FLAPW ground-state surface energies (E_s) for W(001) and V(001): E_r is the surface relaxation energy. E_{bulk} , $E(5\text{-L})$, and $E(7\text{-L})$ denote the total energy for bulk crystal (per atom), five-layer slab, and seven-layer slab. Numbers of basis functions used in the calculation are 480 (380) and 420 (320) for seven- (five-) layer films for tungsten and vanadium, respectively; values in the square brackets denote the results with larger basis set (see text for details).

	W(001)		V(001)	
	Wigner	HL	Wigner	HL
E_s (mRy)	5-L 232 [231]	237	142	151 [149]
(unrelaxed surface)	7-L 235 [237]	238	146	155 [154]
E_r (mRy)	4.5			6
E_s (mRy)	~ 230 (5.1 J/m ²)			~ 145 (3.4 J/m ²)
(relaxed surface)				
$[E(7\text{-L})-E(5\text{-L})]/2$ (Ry)	-32 306.350	-32 321.960	-1893.415	-1894.777
	[-32 306.356]			[-1894.781]
E_{bulk} (Ry)	-32 306.353	-32 312.961	-1893.419	-1894.781
	[-32 306.362]			[-1894.786]
ΔE (mRy)	3 [6]	1	4	4 [5]

convergence of the surface energies with film thickness, but also demonstrates the high-precision capability of the FLAPW method to yield essentially identical results for two independent codes (a two-dimensional thin-film method¹² and a three-dimensional bulk method¹⁴). Finally, the calculated surface energies are only weakly dependent on the form of the exchange-correlation potentials. The well-known misrepresentation of image forces in the local-density approximation mainly affects the low-density vacuum regions and, hence, has little effect on the total energy of the system. On the other hand, the work function Φ , is possibly more sensitive since it measures the potential difference across this region. Consequently, the dependence of Φ on the form of the exchange and correlation potential is larger. Thus, for W(001), we find $\Phi = 4.6$ eV (Wigner), 4.4 eV (HL) vs 4.63 eV (expt),²³ and for V(001), $\Phi = 4.3$ eV (Wigner), 4.2 eV (HL) vs 4.12 eV (expt),²⁴ showing that the differences between the experimental and theoretical values can be explained by effects which are only approximately included in the local-density approximation.

A larger LAPW basis set gives a better description of the wave functions of surface states extended into inner layers, and this results in a slight increase of the inner layer energy difference ΔE for the seven-layer films. The results shown in square brackets in Table I are obtained from calculations employing a nearly doubled number of basis functions for both elements and this only causes ΔE to increase by less than 3 mRy. This again indicates the very good convergence of the surface energies in our calculation. Also, it should be noted that even a five-layer film can yield the surface energy within 5 mRy of the value for a seven-layer film, i.e., the main contributions to the surface energy are from surface and subsurface atoms due to the short-range screening effects at transition metal surfaces.

The effect of multilayer surface relaxation was studied for both W(001) and V(001). For W(001),¹⁶ these all-electron FLAPW calculations showed a contraction of the topmost layer by 5.5% and expansion of the second and third interlayer spacings by 2.4% and 1.2%, respectively. The surface-relaxation energy is found to be 4.5 mRy, which amounts to only 2% of the surface energy. Thus, the effect of surface relaxation does not lead to a significant change of the surface energy. For V(001) (Ref. 19)—in good agreement with experiment⁶—a contraction of the topmost interlayer

spacing by 9.0% and an expansion of the second interlayer spacing by 0.6% are obtained. The relaxation energy for a five-layer V(001) film is 6 mRy, which amounts to 4.5% of the surface energy.

To our knowledge, measurements of the surface energy of solid vanadium are not available. The only experimental results pertain to values for the liquid metal at the melting point (1.9 J/m² at 2175 K).²⁵ Based on this, semiempirical theoretical models gave a value of (Refs. 26 and 27) 2.6 J/m² for surface energy of the solid metal at 0 K. As discussed below, the difference of this value with our result (3.4 J/m²) may indicate that the semiempirical models underestimate the surface entropy.

Most experimental measurements of the tungsten surface energy are at high temperatures (greater than 1200 K), whereas our calculations are at 0 K. The one available low-temperature measurement determined the fracture surface energy of W(001) by the crack propagation method but with a large uncertainty (cf. Fig. 1). The measured value of (Ref. 28) 6.0 ± 0.9 J/m² at liquid-helium temperature appears to be in good agreement with our calculated value and very different from the result of an earlier tight-binding calculation.²⁹

Let us now examine the information contained in the high- T data for W(001). These are plotted in Fig. 1 as a function of temperature together with the theoretical results and the crack propagation value.²⁸ Here, the experimental values¹⁻⁵ at high temperature are referred to the "averaged" crystal planes, i.e., the surface anisotropy is not considered. The surface energy of (100) cleaved bcc tungsten is expected to be higher than the average owing to the presence of the sharp peak of the surface density of states near the Fermi level.²² Variations of the order of 10% from the average are characteristic of cubic metals.²⁶ As seen, the high- T values, determined using either field-emission microscopy¹⁻³ (FEM) or multiphase equilibrium techniques^{4,5} (MPE), range widely with temperature and method. The strong variation with temperature is not surprising because of the characteristics of the W(001) surface which, as we will see, lead to a rather large surface entropy.

Thus, in making comparisons with our $T=0$ K results, one needs to correct the measured high-temperature values for the entropy contribution so as to be able to extrapolate to zero temperature. Unfortunately, direct experimental

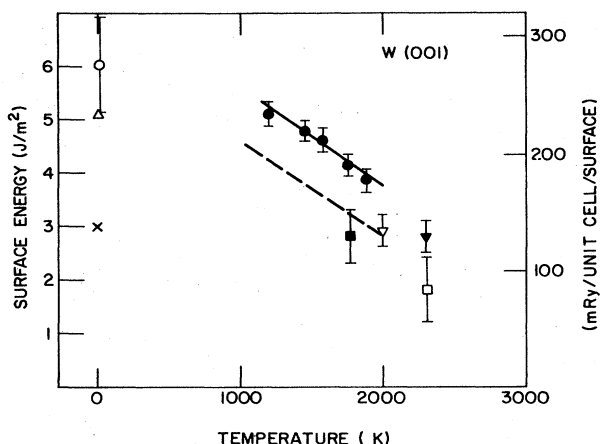


FIG. 1. Measured surface energies of W(001) as a function of temperature (symbol ∇ : Ref. 1; symbol \blacktriangledown : Ref. 2; symbol \bullet : Ref. 3; symbol \blacksquare : Ref. 4; symbol \square : Ref. 5; symbol \circ : Ref. 28) together with the theoretical values of our calculation (symbol Δ) and an earlier tight-binding result (symbol \times , Ref. 29). The broken line indicates the suggested variation of surface energy with temperature above 1000 K from an average of the surface-energy measurements (~ 2.8 J/m²) at 2000 K together with a surface entropy given by Ref. 3.

measurements of the surface entropy or surface phonon dispersions are practically nonexistent. It should be noted that a semiempirical theoretical approach^{26,27} yielded a temperature-independent additional surface entropy of about k_B (the Boltzmann constant) per mole of surface atoms for all elements (about 0.14×10^{-3} J/m² deg for tungsten). By contrast, an earlier analysis³⁰ of the experimental data on the temperature dependence of the surface energy for various solid metals gave a range of (widely scattered) values up to 3×10^{-3} J/m² deg for the surface entropy (with large uncertainties).

At high temperature, the W(001) surface is either in the $p(1 \times 1)$ phase with anomalous soft phonon modes or a disordered structure such that its free energy is minimized by gaining large lattice entropy.^{31,32} This has been verified³¹ by LEED, Debye temperature, field ion spectroscopy, and photoemission measurements. The W(001) surface undergoes a second-order phase transition to the $c(2 \times 2)$ structure for temperatures below room temperature.³¹ Since the reconstruction energy is found to be ~ 3 mRy per surface atom,³¹ the difference between our calculated result and the high- T measured values is not due to the assumed atomic

geometry in the calculation. Instead, this gives an indication that the W(001) surface tends to be soft or even disordered above the transition temperature; i.e., anomalous large surface entropy due to anharmonic effects are expected.

The large variation obtained by different investigators (even by those using the same method) is well outside their quoted errors. Since the surface energy is sensitive to the state of the surface (i.e., impurities, dislocations, etc.), it is not surprising that an absolute determination of E_s is difficult to obtain. The only systematic data as a function of temperature above 1200 K (Fig. 1) show³ an approximate linear dependence on temperature with a large surface entropy ($\sim 1.5 \times 10^{-3}$ J/m² deg or about $10k_B$ per W atom). On the other hand, Debe and King³¹ estimated that the entropy change due to surface reconstruction is about $1k_B$ per W atom at room temperature. A recent analysis of the desorption energy of hydrogen at 500 K from the W(001) surface³³ also indicates that the hydrogen-induced reconstruction reduces the entropy of the substrate surface by $1k_B$ per atom. A comparison of our calculated result with the measured surface energies at high temperatures and a crude extrapolation to low temperatures using these measured values of surface entropy in different temperature ranges shows consistency between them.

In summary, the all-electron local-density total-energy approach employing the FLAPW method for both thin films and bulk crystals yields ground-state surface energies of 5.1 J/m² and 3.4 J/m² for the W(001) and V(001) surfaces, respectively. The large values of the surface energies are related to the high density of surface states near the Fermi level. Significantly, the surface energies are found to be almost independent of the local exchange-correlation potentials employed. Because of the highly local screening at transition metal surfaces, the dominant contributions to the surface energies are from the surface and subsurface atoms. The surface relaxation (or reconstruction)³⁴ energies are small [less than 2% of the W(001) surface energy and less than 4.5% of the V(001) surface energy]. A comparison of our theoretical value at $T=0$ K with the measured surface energies at high temperatures for W(001) supports a large surface entropy above 1000 K ($\Delta S \sim 1.5 \times 10^{-3}$ J/m² deg). This implies large lattice anharmonicity and emphasizes the possible disordered nature of the W(001) surface at high temperatures.

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