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Density functional calculations of the influence of hydrogen adsorption on the surface relaxation of Ti (0001)

M. N. Huda and Leonard Kleinman

Department of Physics, University of Texas at Austin, Austin, Texas 78712-0264, USA

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We have calculated the effect of hydrogen adsorption on the work function and surface relaxation of Ti (0001). Calculations were performed for 100% and 25% coverage of the fcc and hcp adsorption sites as well as 100% coverage of both sites. The average of the relaxations obtained with 100% occupation of the fcc or hcp sites is in excellent agreement with experimental full coverage. With fractional hydrogen coverage, we find considerable difference in the relaxation of the surface Ti atoms, depending on their distances from the hydrogen atom.

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There has been a long-standing disagreement between the measured and calculated multilayer relaxation of several transition metal surfaces.[1,2] In particular a 1976 low-energy electron diffraction (LEED) measurement[3] of Ti (0001) found a surface relaxation of −2%, while a full potential linearized augmented plane-wave (FPLAPW) calculation[2] using the local density approximation (LDA) for exchange and correlation obtained a −7.7% relaxation. Recently Teeter and Erskine[4] remeasured the Ti (0001) relaxation using LEED while paying particular attention to the effect of hydrogen adsorption. They found for their clean surface a relaxation of −4.9%, although in improved agreement, still some distance from the calculated value. They determined that their "clean" surface had approximately 13% of saturated hydrogen coverage, increasing to 23% during the course of the experimental run, for an average of 18%. They also found that a hydrogen-saturated surface caused the surface relaxation to be reduced to −3.7%. They could not say whether the hydrogen saturated surface consisted of 100% coverage of the hcp sites, or 100% coverage of the fcc sites, or 100% coverage of both sites, or random coverage of both sites, with occupation of both of two nearest neighbor sites unlikely.

In this paper we report the results of generalized gradient approximation (GGA) calculations (in the PW91 form[5]) of the multilayer relaxation of 15-layer clean Ti films, as well as the relaxation with 100% hydrogen coverage of the fcc and hcp sites, and 100% coverage of both sites. Using an 11-layer film we calculated the relaxation occurring when 25% of the fcc or hcp sites are occupied. The projected augmented wave (PAW) method[6,7] was used within the Vienna *ab initio* simulation package (VASP 4.6.21).[8–10] All plane waves up to 300 eV were used in the expansion and a 14×14×8 (14×14×1) sampling of the bulk (thin film) Brillouin zone (BZ) was used. BZ integrations were performed using the Methfessel-Pack method.[11] We checked the convergence on an 11-layer Ti film. Using all plane waves up to 500 eV lowered the total energy per atom by 0.0008 eV. Increasing the **k**-point sample to 20×20×1 increased the total energy per atom by 0.0001 eV.

In Table I we compare our LDA and GGA bulk Ti lattice constants, bulk moduli, and cohesive energies with experiment and with two other LDA calculations, one[2] using the FPLAPW method and the other[12] using pseudopotentials. The lattice constant discrepancies among the three LDA calculations are larger than one would like. The GGA usually, but not always, yields better lattice constants and surface relaxations than the LDA. In the present case GGA results are in much better agreement with experiment than our LDA and therefore all our surface calculations were performed using the GGA.

All surface calculations were performed using a 15-layer Ti film except when a 2×2 surface unit cell was required, when 11 layers were used. All atoms were relaxed until the forces on them were less than 10 meV/Å. In Table II we compare our calculated interplanar relaxation, surface energy, and work function with experiment and with the results of Refs. 2 and 12. The only other calculation[15] of which we are aware used a non-first-principal local volume potential, which resulted in $\Delta d_{12}/d_0 = -2.0\%$. We repeated the calculation for an 11-layer film and obtained work function $\Phi = 4.419$ eV, surface energy $E_s = 0.891$ eV/surface atom, and $\Delta d_{12}/d_0 = -7.53\%$ in near perfect agreement with the 15-layer film, demonstrating that our thin-film surface well represents the surface of a semi-infinite crystal. Cho and

TABLE I. Our LDA AND GGA calculated lattice constants, bulk modulus, and cohesive energy of bulk titanium compared with the LDA results of Refs. 2 and 12 and with experiment.

	a (Bohr)	c (Bohr)	c/a	B (GPa)	E_{coh} (eV)
Ref. 2	5.443	8.610	1.581		
Ref. 12	5.538	8.825	1.594	132	
LDA	5.397	8.527	1.580	136	6.56
GGA	5.520	8.722	1.580	119.3	5.59
Exp.[a]	5.575	8.844	1.586	105	4.85

[a] Reference 13.

TABLE II. Comparison of calculated surface relaxation, and surface energy of Ti (0001) with Refs. 2 and 12 and with experiment.

	$\Delta d_{12}/d_0$	$\Delta d_{23}/d_0$	$\Delta d_{34}/d_0$	$\Delta d_{45}/d_0$	Φ (eV)	E_s/surface atom
	−7.55%	2.86%	−0.94%	−0.27%	4.42	0.898
Ref. 2	−7.70%	2.80%			4.64	0.980
Ref. 12	−6.80%	1.20%			4.75	1.040
Exp.	−4.90%[a]	1.40%[a]	−1.10%[a]		4.45[b]	

[a] Reference 4.

[b] Reference 14.

Terakura[12] (Feibelman[2]) used an 8- (7-) layer film and relaxed only two layers.

In Table III we list the height of the adsorbed hydrogen above the relaxed surface plane of Ti, the work function, the adsorption energy, and several interplanar relaxations when all of the fcc sites are saturated, all of the hcp sites are saturated, and when both sites are saturated. The adsorption energy for one hydrogen per surface cell is,[16]

$$E_{\mathrm{ads}} = E(\mathrm{clean}) + \tfrac{1}{2}E(\mathrm{H}_2) - E(\mathrm{H\ saturated}),$$

where the calculated value of $E(\mathrm{H}_2)$ is −31.7529 eV and the H_2 bond length is 0.7495 Å in very good agreement with the experimental values of −31.7302 eV and 0.7414 Å. To compare the dissociation energy of H_2 with the experimental value of 4.519 eV we subtract −31.7529 eV from twice the −13.6035 eV we calculated for the atomic energy, to obtain 4.546 eV. The 100% occupancy of both sites case has slightly more than half of E_{ads} per hydrogen atom than the larger of the other two cases. Therefore its E_{ads} per unit cell is the largest and it would be expected to represent full coverage except for two possibilities. It is likely that the H_2 dissociation is blocked where the density of occupied sites is large. It is also likely that the entropy of H gas is sufficiently larger than that of adsorbed H that the free energy per unit cell of H on hcp sites lies below that of H on both sites.[17] That full coverage of both sites does not occur is strongly indicated by the fact that the experimental[4] full coverage $\Delta d_{12}/d_0 = -3.7\%$ compared to our calculated +2.68%. Although the hcp sites were found to yield 27 meV more adsorption energy than the fcc, for smaller coverage (see Table IV) the fcc sites appear to yield slightly more adsorption energy than the hcp. Therefore it seems likely to us that the saturated surface consists of approximately half fcc and half hcp sites.[18] If that is the case, it explains why the experimental $\Delta d_{12}/d_0$ lies midway between our fcc and hcp values.

Teeter and Erskine[4] reported that their clean surface had 23% of full hydrogen coverage at the end of their experimental run. Therefore we performed calculations with 25% occupancy of hcp and fcc sites using a (2×2) surface cell with an 11-layer film. The Δd_{ij} in Table IV are an average since there are three Ti in each unit cell that are near neighbors to the adsorbed hydrogen and one that is not. If again we assume equal occupancy of both sites, the average of the hcp and fcc $\Delta d_{12}/d_0$ is −6.40%, which gets us somewhat closer to the experimental −4.90%. The three fcc (hcp) Ti atoms neighboring the hydrogen have a calculated $\Delta d_{12}/d_0$ of -6.21% (-5.37%) while the other Ti has -8.17% (-8.31%). Thus there may be some error introduced in the interpretation of the LEED data when it is assumed that all the atoms in a plane have the same relaxation.

Our work function for the clean surface is seen to be in excellent agreement with the experimental value.[14] Undoubtedly, the experimental surface had an appreciable amount of hydrogen coverage. Therefore it is interesting to note that our calculations show only a small dependence of the work function on the hydrogen coverage. The amount and sign of the work function change is seen to depend on both the adsorption site and its fractional occupation.

In conclusion, that the H saturated surface of Ti (0001) does not consist of 100% occupancy of both fcc and hcp was shown, and if the reasonable assumption that it consists of partial occupation of both sites rather than 100% of one, we

TABLE III. Distance of the H atom in fcc and hcp sites above the Ti (0001) surface, the work function, the adsorption energy per H atom, and the Ti interplanar relaxations. The last row lists the results when both the sites are occupied.

h_{fcc} (bohr)	h_{hcp} (bohr)	Φ (eV)	E_{ads} (eV)	$\Delta d_{12}/d_0$	$\Delta d_{23}/d_0$	$\Delta d_{34}/d_0$	$\Delta d_{45}/d_0$	$\Delta d_{56}/d_0$
2.086		4.445	1.104	−4.57%	2.74%	−0.82%	−0.27%	0.17%
	1.914	4.581	1.131	−3.06%	1.22%	−0.21%	−0.33%	0.24%
1.462	1.621	4.135	0.584	2.68%	0.11%	0.41%	−0.84%	−0.33%

TABLE IV. Distance of H atoms above the Ti (0001) surface when 25% of the fcc or hcp sites are occupied, the work function, adsorption energy per H atom, and the Ti interplanar relaxations averaged over the four atoms in each plane of the unit cell.

	h (bohr)	Φ (eV)	E_{ads} (eV)	$\Delta d_{12}/d_0$	$\Delta d_{23}/d_0$	$\Delta d_{34}/d_0$	$\Delta d_{45}/d_0$	$\Delta d_{56}/d_0$
fcc	2.054	4.389	1.048	−6.70%	3.33%	−0.72%	0.08%	0.17%
hcp	2.022	4.392	1.040	−6.11%	2.97%	−0.58%	0.16%	0.21%

found excellent agreement for the surface relaxation. For a clean surface with 12.5% occupancy of both sites the discrepancy with experiment for d_{12} was reduced by 43% from the absolutely clean surface.

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[16] For two hydrogen atoms per surface unit cell the adsorption energy per H atom is, $E_{\text{ads}}=\frac{1}{2}[E(\text{clean})+E(\text{H}_2)-E(\text{H saturated})]$.

[17] L. Schlapbach and A. Züttel, Nature (London) **414**, 353 (2001) determined for a somewhat different case that the entropy cost of H adsorption is 203 meV in free energy per H atom. This can be compared with the 37-meV greater E_{ads} per unit cell we calculated for adsorption on both sites over adsorption on the hcp site.

[18] For low coverage the H atoms are randomly on hcp and fcc sites but because of the repulsion between hydrogen on near neighbor hcp and fcc sites, it seems likely that the saturated surface consists of small regions which have 100% fcc or 100% hcp coverage.