Systematics of Adsorption near a Step

Peter J. Feibelman
Sandia National Laboratories, Albuquerque, New Mexico 87185

(Received 8 June 1992)

Local-density-functional (LDF) calculations show that on Al(331), a surface whose narrow (111)-like terraces are separated by (110)-like steps, a trivalent Al adatom is strongly attracted to step bottoms, while a monovalent H adatom prefers step edges. H-adatom potential energies in the threefold terrace sites on Al(331) and Al(111) differ by only about 0.1 eV. This is because H atoms are small and must sit close to substrate atoms, where step effects are rapidly screened. Al adatoms, being larger, prefer the terrace sites of Al(331) by more than 0.25 eV.

PACS numbers: 68.35.Bs, 68.35.Dv, 71.45.Nt

The behavior of adatoms near surface steps plays a key role in materials synthesis, and is expected to be important in understanding surface chemical reactions. For these reasons it is essential to know what basic parameters determine where and how strongly adspecies bind to steps, and what governs their motion across them. Ordered vicinal surfaces provide an excellent laboratory for studying adatom-step interactions because they can be well characterized experimentally, and because their periodicity reduces the size of the computational challenge they pose to theoretical analysis. In this Letter, I report first-principles calculations of the energetics of single-atom adsorption on Al(331). The results show how an adatom's valence and radius affect the nature of its interaction with a step. Differences in these basic parameters imply very different behaviors for H and Al adsorbed on Al(331).

The driving force that determines adatom-step interactions is the saturation of valence, or equivalently, the elimination of "dangling bonds." This is achieved if an adatom can bind to outer-layer surface atoms without forming bonds that lie too close to each other, and without contributing new dangling valence electrons of its own. A H atom will typically bind in a high-coordination site on a smooth metal crystal face, reducing the unsaturated valence at the surface by one electron. High coordination is preferred because a more diffuse electron distribution between the H and the surface corresponds to a reduction of electron-electron repulsion. However, in general, on optimal adsorption geometry involves a compromise between satisfaction of the bonding needs of the adatom *and* of the surface, and on Al(331), Al atoms at step edges have only seven neighbors, compared to terrace atoms with nine and step-bottom atoms with eleven. The LDF calculations I report here predict that H's will bind more strongly (by 0.33 eV) at step edges, where they are coordinated to a single Al, than on terraces where they have three Al neighbors. This means that passivation of step-edge atoms is more important, in H adsorption, than forming a diffuse bond-charge density.

An Al adatom, possessing three valence electrons cannot passivate step-edge Al's. Too many bonding electrons would have to be squeezed into too small a region of space. Consequently, in Al adsorption on Al(331) the driving consideration is that the ad-Al have the maximum number of substrate neighbors. This permits all three of its valence electrons to participate in bonds, while the bond charge is as diffuse as possible. Thus, an ad-Al on Al(331) prefers the fivefold coordination site at the base of a step, the site for continued growth of the Al crystal.

One can easily imagine reasons why an adatom's radius should be important to the nature of its interaction with a step. For example, because the occupied state wave functions of small atoms are compact, a small adatom's orbitals cannot simultaneously overlap those belonging to the atoms at the top of a step *and* at the bottom. This means that a step does not offer high-coordination sites to a small adatom. The bridge geometry adopted by H on W(001) provides evidence that this is a reasonable way to think. H binds in a twofold geometry on W(001) because the separation of nearest W's on this surface is so large, 5.97 bohrs, that in the fourfold hollows, the H(1*s*) orbital has little overlap with *any* of its nearest surface neighbors' valence wave functions [1]. Analogously, in H adsorption on Al(331), the binding energy at site *C* in Fig. 1 is 0.52 eV less than at the step-edge bridge site *B* (where in both cases, a "site" is a location where the force on the H vanishes), because the H is effectively bonded only to the step-bottom Al, which is the surface atom least in need of an additional bond.

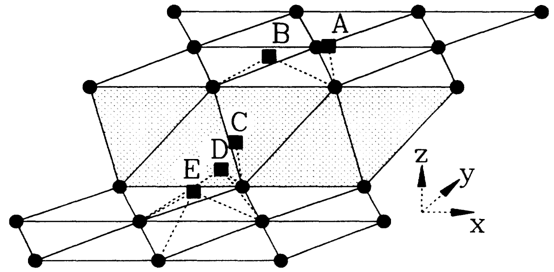

FIG. 1. Schematic illustration of the Al(331) surface, showing four locations, *A*–*D*, where a H adatom experiences a force close to zero. The filled circles and squares represent Al and H nuclear positions, respectively.

Screening is another reason that an adatom's radius influences its interaction with a step. A small adatom sits close to the plane defined by its nearest-neighbor substrate nuclei, where the substrate electron density is relatively large, and therefore screening is quite effective. This suggests that the potential due to a step will only be "felt" by a H adatom if the step is *very* close by. Thus step-edge atoms should contribute little to the binding of a H atom in site *D* (cf. Fig. 1) which is close to the plane of the terrace at the step bottom, and the energy difference between site *D* and site *E*, which lies farther out on the terrace, should be rather small. This picture is verified by the results in Table I. They show that the energies of H in sites *D* and *E* are virtually the same, and are no more than 0.10 eV greater than for H in a threefold hollow on Al(111). In contrast, an Al adatom, which is considerably larger than a H, and therefore lies higher above the (111) terrace, is bound more strongly by 0.26 eV in the threefold, hcp hollow at the top of the Al(331) step than in the hcp hollow on Al(111).

Results reported here were obtained via the matrix Green's function scattering theory method [2] (MGF-STM), which makes it possible to compute the electronic structure of a spatially compact adsorbate on an infinitely extended, otherwise perfect, metal crystal. In the MGF-STM one first solves for the Bloch-wave wave functions of the perfectly periodic host, here a "fifteen-layer [3]" Al(331) slab. Then one computes the occupied state wave functions in which Bloch waves incident on the defect region scatter into outgoing Bloch waves. Although the size of the Al(331) slab's unit cell does drive up the cost of computing its Bloch waves, that extra cost is the *only* significant one when comparing to adsorption calculations for a low-Miller-index crystal plane. The size of the scattering theory component of the problem is governed by the number of substrate centers whose orbitals overlap the adsorbate-induced potential. This is not much larger than on a flat surface.

TABLE I. Calculated potential energy vs position of H and Al adatoms on Al(331) and Al(111). Columns give the locations of sites of various descriptions, the corresponding potential energies E_P (in eV), and the magnitude of the force on the adatom at each location (in eV/bohr). The position vectors (in bohrs) are given in the coordinate system of an ideal (111) terrace, as explained in the text. E_P's are referenced to the experimental valence electron energies of the isolated-atom species, 13.6 eV for H and 53.25 eV for Al. The labels *A*, *B*, etc., correspond to Fig. 1.

Site description	Location	Residual force	E_P
	H/Al(331)		
Onefold edge (*A*)	(2.65,9.11,6.64)	0.018	−2.00
Twofold edge (*B*)	(0.0,9.57,5.99)	0.023	−1.87
Over-edge barrier (*C*)	(0.0,7.22,2.83)	0.065	−1.37
fcc step-bottom (*D*)	(0.0,6.00,1.94)	0.045	−1.63
hcp step-top (*E*)	(0.0,3.01,1.99)	0.027	−1.67
	H/Al(111)		
Threefold hcp hollow	(0.0,3.06,1.98)	0.000	−1.57
Threefold fcc hollow	(0.0,6.12,1.95)	0.032	−1.69
	Al/Al(331)		
Fivefold step-bottom	(0.0,6.37,4.15)	0.080	−3.68
Twofold long-bridge	(2.65,6.13,4,43)	0.021	−3.11
Twofold over edge	(0.0,8.69,7.48)	0.064	−2.47
Threefold fcc step-top	(2.65,1.49,3.74)	0.041	−3.00
Threefold hcp step-top	(0.0,3.07,3.89)	0.019	−2.95
	Al/Al(111)		
Threefold fcc hollow	(2.65,1.49,3.93)	0.007	−2.66
Threefold hcp hollow	(0.0,3.07,3.92)	0.025	−2.69

MGF-STM calculations project electronic structure problems into bases of localized (contracted Gaussian) orbitals [2]. To obtain an adequate basis set for Al(331), I first compare results of linear combination of atomic orbitals (LCAO) and of highly converged, plane-wave pseudopotential (PWPP) calculations, for an ideal seven-layer Al(111) slab [4]. The energy bands in the final LCAO calculation differ by no more than 87 meV from those of the PWPP electronic structure, with a basis including an *s* function, two radial *p* orbitals, and a radial *d* function on each Al nucleus, two *s* functions at each octahedral site, a *p* function 3.5 bohrs atop each surface nucleus, and an *s* function in each threefold hollow, 4.5 bohrs above the outermost plane of Al nuclei. In addition, the LCAO forces on the atoms in the first two layers turn out to equal 50 and −137 meV/bohr, close to the values, 31 and −120 meV/bohr, which emerge from the PWPP calculation.

These results suggest using a similar basis for Al(331). The main necessary modification is to supplement the floating orbitals in the vacuum above and below the (331) slab, to allow more freedom for electron spillout and for Smoluchowski smoothing [5] of the charge density near step edges. The floating orbitals I use for Al(331) are, in addition to atop-site *p* functions as for Al(111), two *s* functions roughly 4.5 bohrs above the threefold hollows of the (111) terraces and another two at a height of ∼6.5 bohrs [6]. [The height of a step on ideal Al(331) is 4.3 bohrs.] I use the same *s* functions in the hollows as at the octahedral sites interior to the slab. Table II provides details concerning the basis.

The geometry of the clean Al(331) slab is fixed by reducing the forces on Al atoms, in a PWPP calculation, to less than 2 mRy/bohr, using eight special *k* points for the surface Brillouin zone (SBZ) sample [7]. In the corresponding LCAO calculation, using the basis just described, the forces are also less than 2 mRy/bohr. At the same time, the energy levels in the LCAO and PWPP calculations agree to better than 85 meV for all eight *k* points in the SBZ sample, while the work functions are

TABLE II. c_a's and a's (in bohr^{-2}) for the four radial functions, $R_l(r) = r^l \sum_a c_a \exp(-ar^2)$, centered at Al nuclei. The basis for Al(331) also includes Gaussians with $a=0.2$ and 0.4, centered at film-interior octahedral sites, and ~4.5 and ~6.5 bohrs above the surface layer in each threefold hollow. In addition, there are $l=1$ radial functions, $r\exp(-0.19r^2)$, centered 3.5 bohrs above each surface atom.

$l=0$		$l=1$		$l=2$	
a	c_a	a	c_a	a	c_a
0.18	1.9353152	0.19	1.1241311	0.36	0.43657490
0.25	−2.0554491	0.25	−1.5396089		
0.44	1.0812525	0.40	1.11172654		
1.05	−1.8909852	0.60	−0.45103173		
1.40	1.1166946				
		$l=1$			
		0.19	0.36595391		

4.03 and 4.14 eV, respectively. Thus, the LCAO basis, with 248 orbitals in the surface unit cell, provides an excellent representation of the electron density of Al(331). In the subsequent adsorption calculations, an Al adatom was represented by the same nucleus-centered twelve functions as were used for the Al's of the substrate. The basis for an H adatom is that reported in Ref. [8].

In Table I, I report potential energies [9] for H and Al on Al(331) at a variety of sites where the force on these adatoms is near zero. For convenience, sites are given with respect to the coordinates of an ideal (111) terrace. Thus, on relaxed Al(331), a step-edge atom is found at (0.0,0.12,−0.18), midterrace atoms are at (±2.65,4.61, 0.01), there is a step-bottom atom at (0.0,9.04,0.04), and, in accordance with the periodicity of the surface, there are atoms at the next higher step edge at (±2.65, 10.82,4.15) [7]. [Here and below, position vectors are given in bohrs.] For unrelaxed Al(331), these atoms would reside respectively at (0.0,0.0,0.0), (±2.65,4.59, 0.0), (0.0,9.18,0.0), and (±2.65,10.71,4.33) bohrs.

The table shows that an Al adatom binds to the step most strongly at the epitaxial growth site (0.0,6.37,4.15) where it is approximately fivefold coordinated [cf. Fig. 2(a), which shows charge sharing between the ad-Al and its neighbors at the step top, at the step bottom, and at midterrace]. To move it to either of the inequivalent threefold hollows at the step edge requires about 0.7 eV. To move along the step the Al must pass through the long bridge at (2.65,6.13,4.43), where its binding energy is reduced by 0.57 eV. To move up to the next higher terrace it must pass through the bridge site (0.0,8.69,7.48) at a cost of 1.21 eV. These results strongly suggest that diffusion across steps will not occur. Even if a concerted replacement process [10] lowered the barrier to hopping from a step-top site to the step bottom (or the reverse) the poor binding of the Al at the step top makes it unlikely that this process would be attempted often enough ever to succeed.

These results agree qualitatively with Tung's observations of single Al atom diffusion on Al(331) [11]. Tung reports diffusion along steps only, and estimates a barrier of 0.46 eV from the diffusion onset temperature. The

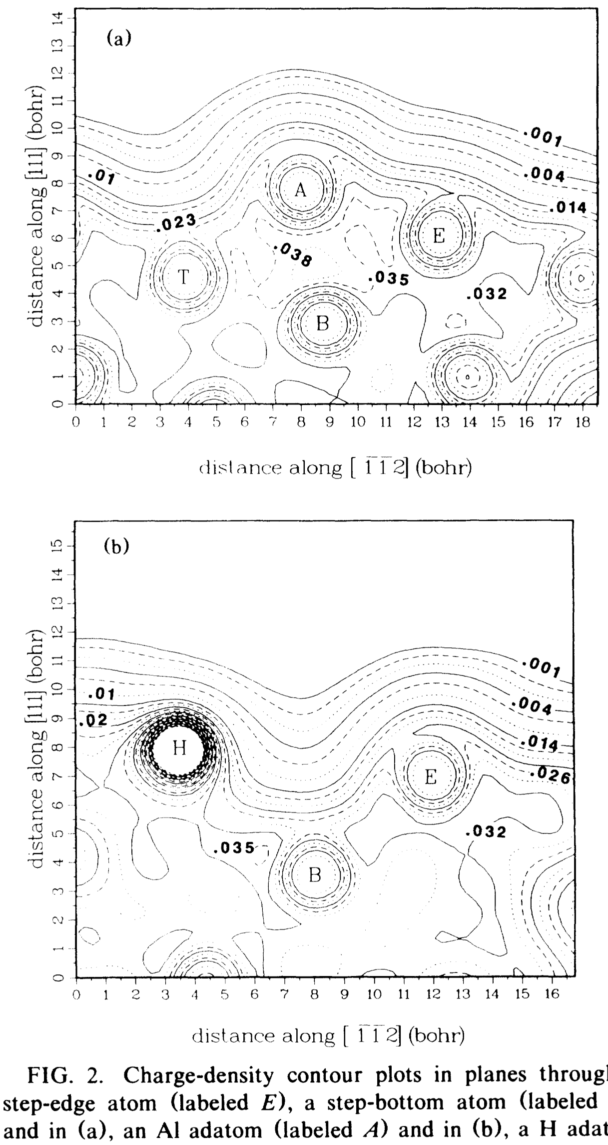

FIG. 2. Charge-density contour plots in planes through a step-edge atom (labeled E), a step-bottom atom (labeled B), and in (a), an Al adatom (labeled A) and in (b), a H adatom (labeled H). In (a) the plotting plane passes close to a midterrace atom (labeled T). The contours differ by factors of 1.58, between 0.001 and 0.01, and by increments of 0.03 for charge densities greater than or equal to 0.014. Units of the charge density are e/bohr^3.

difference between this estimate and the calculated 0.57 eV is small enough that it is hard to judge whether the discrepancy should be attributed to the inaccuracy of the experimental estimate or to a failure to include all the physics in the calculation, i.e., motion of the substrate Al atoms accompanying displacement of the adatom.

The results for H adsorption on Al(331) contrast dramatically with those for Al, and indicate that passivation of the Al step-edge atoms' unsaturated valence is the dominant aspect of the H-Al(331) interaction. H prefers the onefold step-edge site (2.65,9.11,6.64) by 0.33 eV relative to any site on a terrace [12], while the binding energy is only 0.13 eV lower at the twofold step-edge bridge site, (0.0,9.57,5.99). These results imply that migration along step edges will be facile.

To move in the y-z plane, from the step-edge bridge to the terrace below, the H must pass near to what for Al was the favored fivefold coordination site. For H diffusion, however, the y-z plane presents a *barrier* near (0.0,7.22,2.83), where the H is essentially only coordinated to the step-bottom Al. Because this barrier is so high, H diffusion in the y-z plane is suppressed.

The implication of the small difference in H binding energies, just 0.04 eV, between the step-bottom fcc threefold site (0.0,6.00,1.94) and the hcp threefold site (0.0,3.01,1.99) adjacent to the step edge is that the H at the step bottom does not profit from proximity to the Al's at the top of the step. Figure 2(b) confirms that this is the case. Notice that while there is charge buildup between the H and the midterrace atom, in Fig. 2(b), there is none between the H and the atom at the step edge. This result, compared to Fig. 2(a) for Al, illustrates the important role of atomic radius in the adatom-step interaction.

Further evidence for the significance of the H atom's small radius is that its binding energy in the threefold terrace sites is found to be only 0.1 eV greater than in the hcp threefold hollow on Al(111). For the large Al adatom, which must sit higher above a terrace, where screening is less effective, the binding energy in the step-top threefold hollows on Al(331) is about 0.24 eV greater than in the threefold hollows of Al(111).

In the present work, the focus has been on the role of adatom size and valence in determining interactions with a step. An additional question is the role of step geometry. In the fcc crystal system, for example, the steps on a (211) surface rise at a lower angle from the (111) terraces than is the case for the (331). This means that an adatom large enough to benefit from being adjacent to a (331)-type step might not find a (211)-type step as attractive. Pursuing this and related ideas will be the focus of calculations in the near future. One would hope that a "demystification" of steps, and their role in surface chemical phenomena, will result from this work.

This work supported by the U.S. Department of Energy, under Contract No. DE-AC04-76DP00789.

---

[1] See P. J. Feibelman and D. R. Hamann, Surf. Sci. **186**, 460 (1987), and references therein.

[2] A. R. Williams, P. J. Feibelman, and N. D. Lang, Phys. Rev. B **26**, 5433 (1982); P. J. Feibelman, Phys. Rev. B **35**, 2626 (1987).

[3] Using a fifteen-layer slab to represent Al(331) is like using a five-layer slab to model Al(111). Terraces on opposite sides of a fifteen-layer (331) slab are separated by 4 times the Al(111) layer separation.

[4] J. S. Nelson and P. J. Feibelman (unpublished). These and the adsorption calculations were performed using the norm-conserving pseudopotentials of D. R. Hamann, Phys. Rev. B **40**, 2980 (1989), and the exchange-correlation potential of D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980), as parametrized by J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981). The PWPP basis-set cutoff was 14 Ry to insure good convergence. However, only ten special k points were used in the irreducible portion of the surface Brillouin zone, since the calculations were only aimed at developing a localized orbital basis. The in-plane Al-Al distance used was 5.298 bohrs, the PWPP optimal value for bulk fcc Al.

[5] R. Smoluchowski, Phys. Rev. **60**, 661 (1941).

[6] The Al's of the outer layer of the relaxed (331) surface do not lie exactly in a plane. The chosen positions of the hollow-site orbitals were 4.5 and 6.5 bohrs above the hollows of the *ideal* (331) surface. They were not moved when the outer-layer atoms' positions were relaxed. This is the meaning of "roughly" 4.5 bohrs and ~6.5 bohrs, in the text.

[7] J. S. Nelson and P. J. Feibelman, Phys. Rev. Lett. **68**, 2188 (1992). The relaxed geometry obtained in this calculation is in excellent agreement with the low-energy-electron-diffraction analysis of D. L. Adams and C. S. Sørenson, Surf. Sci. **166**, 495 (1986).

[8] P. J. Feibelman, Phys. Rev. B **43**, 9452 (1991), Table II.

[9] Zero-point motion of the H is not included in the calculations, nor is any adsorption-induced local lattice relaxation.

[10] P. J. Feibelman, Phys. Rev. Lett. **65**, 729 (1990).

[11] R. Tung, thesis, University of Pennsylvania, 1980 (unpublished).

[12] A similar result, that onefold atop bonding is preferred for (1×1)H/Al(110), is reported by B. Hammer, K. W. Jacobsen, and J. K. Nørskov (unpublished). However, these authors' assertion that Al surfaces generally prefer atop-bonded H is contradicted by present calculations, implying that on Al(111), H in the fcc threefold hollow is favored relative to the atop site by 0.17 eV.

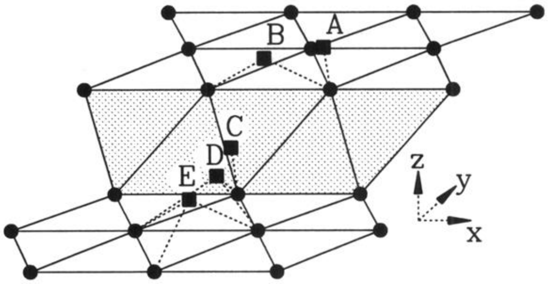

FIG. 1. Schematic illustration of the Al(331) surface, showing four locations, *A–D*, where a H adatom experiences a force close to zero. The filled circles and squares represent Al and H nuclear positions, respectively.