PHYSICAL REVIEW B VOLUME 52, NUMBER 23 15 DECEMBER 1995-I

Energetics of steps on Pt(111)

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(Received 30 June 1995)

First-principles local-density approximation optimizations for Pt(331), Pt(221), Pt(211), and Pt(533) slabs, the surfaces of which are vicinal to Pt(111), are used to extract approximate theoretical energies per unit length for the two varieties of unkinked step on Pt(111). As expected on the basis of bond counting, the calculated energies of the (111)-type and (100)-type steps are nearly equal, about 0.46–0.47 eV per step-edge atom. Near equality of the step-formation energies does not agree with Michely and Comsa's finding that (111)-type edges are about 50% longer than (100) edges for islands on Pt(111) equilibrated at 700 K, corresponding to a formation free energy that is 13% lower.

I. INTRODUCTION

The energetics of atoms in and near surface-defect structures, particularly monoatomic steps, are basic to an understanding of both crystal growth and surface chemistry. First-principles calculations of a surface-defect electronic structure have, nevertheless, been long in coming, because the low symmetry of defects complicates their analysis. With a few exceptions,[1] such calculations have only been done for *s*-*p* bonded materials.[2,3] It is timely to proceed further: Adsorption at transition-metal steps is the focus of numerous experimental studies, with goals ranging from the fundamental, e.g., the measurement of surface diffusion barriers,[4] to the practical, e.g., improved automotive catalysts.[5] The burgeoning scanning tunneling microscopy (STM) literature of *d*-band-metal growth morphologies begs for interpretation. A notable example is the study of equilibrium island shapes on Pt(111), by Michely and Comsa (MC).[6] It directly yields a fundamental parameter, the ratio of the energies per unit length of the two close-packed step types (see Fig. 1) that can exist on this surface.

Until now, most simulations of surface defects have been based on semiempirical interatomic-force models.[7] The reason is that the semiempirical schemes are computationally very fast. They are, therefore, well adapted to the study of systems with many inequivalent atoms. But the speed of the semiempirical methods comes at a cost, the *a priori* simplification of the interatom force laws. In the popular embedded atom method (EAM),[8] for example, directional bonding and charge-transfer contributions are dropped at the outset. The reliability of the concepts drawn from semiempirical simulations rests on the assumption that the database used to construct the force laws is suitable for the surface geometries of interest. This questionable assumption can be avoided, or at least tested, by applying first-principles methods, specifically, local-density approximation (LDA) calculations.[9] The cost is, of course, much lengthier computations.

Here, I apply the first-principles approach to the energetics of monolayer-high (111)- and (100)-type steps on the Pt(111) surface [see Figs. 1(a) and 1(b)]. I report LDA-optimized geometries and corresponding surface energies for Pt(331), (211), (221), and (533) thin slabs, whose surfaces are vicinal to Pt(111). These surfaces have relatively narrow (111) terraces. Those of the (331) and (211) crystal slabs are three atom rows wide, while those of the (221) and (533) films are four rows across.

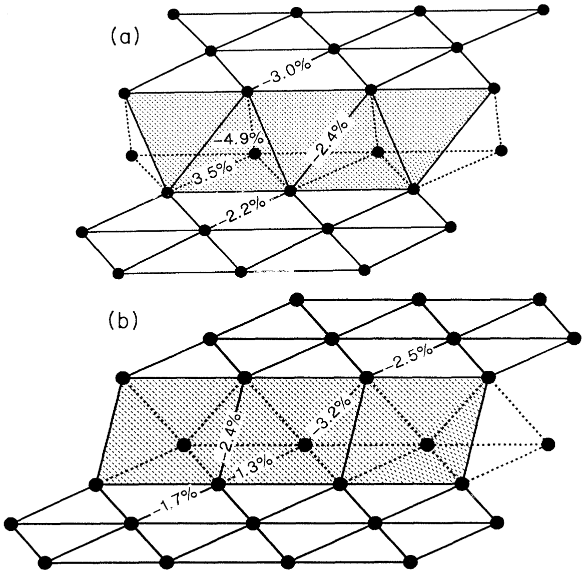

FIG. 1. (a) Schematic of a monolayer high, (111)-type step on a fcc(111) terrace. Notice that the step-edge atoms have seven-nearest neighbors, two along the edge, two on the upper terrace, one inside the solid and two at the step bottom. The percentage changes shown, of the bond lengths relative to ideal, LDA Pt, are those calculated for a 36 atom/unit cell, Pt(221) slab, i.e., one that is nine (111) layers across. (b) Schematic of a monolayer high, (100)-type step on a fcc(111) terrace. Again the step-edge atoms have seven-nearest neighbors, two along the edge, two on the upper terrace, but now two inside the solid and only one at the step bottom. The percentage changes shown, of these bond lengths relative to ideal, LDA Pt, are those calculated for a Pt(533) slab, nine (111) layers across.

0163-1829/95/52(23)/16845(10)/$06.00

The (331) and (221) surfaces have (111)-type steps. The steps on the (211) and (533) surfaces are (100) type. To extract isolated-step formation energies, I extrapolate the surface energies obtained for these relatively narrow-terraced films to the arbitrarily wide-terrace limit.

The result of the extrapolation is a ratio of step energies, close to 1:1, that disagrees with MC's experiment. Similarly to the EAM results of Nelson *et al.*,[7] I find formation energies of 0.46 and 0.47 eV per edge atom for (111)- and (100)-type steps on Pt(111). This conflicts with the STM data, which implies that to form a (111)-type step costs 13±2% less energy per unit length than to create a (100)-type step. The LDA thus fails to account for a small but significant energy difference; using 0.47 eV/edge atom for the formation energy, the difference should be about 0.06 eV per step-edge atom. Much of the discussion presented below is aimed at determining the source of this discrepancy. I consider numerical accuracy, use of the LDA itself, the importance of the relatively high temperature at which the MC's islands were equilibrated and then frozen in, and the possibility of atomic scale step reconstruction.

That the step-formation energy difference is small is *not* a surprise. In the only published first-principles comparison of step energies on a metal, Al(111), Stumpf and Scheffler (SS)[2(d)–2(f)] explain that it should be, because at both (111)- and (100)-type steps, the step-edge atoms are sevenfold coordinated.[10] The fact that step-bottom atoms have 11 nearest neighbors for (111) steps and only 10 for the (100) steps is barely significant—the curve of binding energy vs number of neighbors is expected to saturate when the number of neighbors is large.[11]

For (111)- as against (100)-type steps on Al(111), SS predict a formation-energy difference of only −17 meV/atom. To compute such a small difference accurately, it is essential to minimize numerical error. For this reason, SS do not use vicinal surface calculations to obtain step energies. Concerned that different sampling of the surface Brillouin zone (SBZ) for different vicinal surfaces might lead to unacceptably large errors, they restrict their focus to (111)-oriented slabs on which they either carve grooves or add islands. Using such slab geometries, they find it necessary to perform calculations involving as many as 245 Al atoms per unit cell.

This is the reason that SS confine their attention to Al, even though the available measurements (MC's) concern steps on Pt. Al's soft pseudopotential and relatively low valence corresponds to minimal computational cost. Application of the same methods to Pt would be inconvenient, if not unfeasible. On the other hand, although studying steps and other surface features of Al is certainly instructive, even highly accurate calculations of Al step energies are not a substitute for reasonably accurate calculations of Pt, if one wants to compare to Pt data, and ultimately to simulate the growth of a Pt crystal.

SS emphasize the qualitative agreement of their Al(111) step-energy ratio with MC's for Pt(111). Their calculation yields a 7.1% smaller formation energy for (111)-type steps than for (100) type; for Pt(111), MC find that the (111)-step-formation energy is 13±2% smaller. MC analyze STM images of hexagonal islands equilibrated at about 700 K, and deduce the Pt(111) step-energy ratio from the fact that (111)-type island edges of the equilibrated islands are 1.5 times as long as (100) edges. SS predict that an Al(111) the ratio would be 1.2

More recently, Tsong reported that equilibrated islands on Ir(111) are perfectly regular hexagons.[12] On Ir(111), then, experiment implies equal formation energies for (111)- and (100)-type steps. Does this result mean that the Al calculations fail qualitatively to describe step energies on Ir? Not at all. The zeroth-order result, with which theory agrees, is that the step energies are close. As SS note, the small formation-energy difference for the two step types is likely a covalent effect. Calculating it for a representative sample of materials is important to obtain a basis for understanding its source. The analysis, however, is likely to be as challenging as explaining differences in the heats of adsorption at fcc and hcp threefold hollow sites on (111) surfaces.

It is worth noting, finally, that the present surface energy computations for vicinal surfaces, although they do not involve a hundred-atom unit cells, still require a rather large-scale calculational effort: For terraces that are λ atomic rows wide, the two dimensionally repeated cell contains λ atoms per (111) layer of slab thickness. To eliminate interference between the two sides of a slab, as well as to have an internal region that is bulklike to a good approximation, one wants to consider slabs that are several (111) layers thick. I study slabs that are seven or nine (111) layers across, corresponding to 21 or 27 Pt atoms per cell for the (331) and (211) cases, and 28 or 36 atoms per cell for the (221) and (533) surfaces. Calculations for unit cells of this size are facilitated by massively parallel computation. The work reported here is based on the use of the parallel implementation of a first-principles, localized basis, LDA computer code (called "QUEST") by Sears, Schultz, and Feibelman,[13] and was done on an 1824-processor Intel Paragon.

The remainder of this paper is organized as follows: In Sec. II, I provide details of the computational approach. In Sec. III, I present the results of the various vicinal-surface calculations, i.e., geometries, work functions and surface energies, as well as the extrapolation to isolated-step formation energies. Finally, in Sec. IV, I discuss the results, and particular, the possible sources of the outstanding disagreement with experiment.

II. COMPUTATIONAL APPROACH

The step energies and geometries that I report here emerge from self-consistent, local-density approximation calculations,[9] in a basis of contracted Gaussian orbitals. The only physical and systematic approximations in the method are the assumptions that the effects of electron exchange and correlation (XC) are faithfully represented by the Ceperley-Alder local XC potential,[14] and that electron-nuclear interactions are adequately described via Hamann's semirelativistic, generalized norm-conserving pseudopotential.[15]

Since the focus of the present study is a *small* observed energy difference between Pt(111)- and (100)-type steps, numerical accuracy is a key issue. Considerable care must be taken to choose an adequate set of basis orbitals and to assure convergence of the various necessary real- and momentum-space integrals. One must maximize error cancellation in extracting surface energies for vicinal surfaces from thin vicinal slab calculations. Finally, one needs an accurate way to obtain isolated step formation energies from vicinal surface results. I address these various issues in the following subsections.

A. Choice of basis orbitals

Although plane-wave-based electronic structure calculations have the enormous advantage that they can be systematically improved by increasing the plane-wave cutoff, for systems of strong-pseudopotential atoms, the number of plane waves required per atom can be large. This is a serious drawback when one wants to study unit cells containing many atoms, and it is the reason I adopt a basis of localized orbitals, no more than 15 per Pt atom, to compute the energetics of vicinal slabs.

The disadvantage of a localized orbital basis is that it is hard to establish how well converged it may be. My approach is to assure that for a representative slab with a relatively small unit cell, the energy bands using the localized orbital set (contracted Gaussians) are in excellent agreement with the bands that emerge from a well-converged linearized augmented plane-wave (LAPW) calculations.[16] Since the LAPW method is systematically improvable, this is an incisive comparison.

In the present case, I begin with the basis set developed in Ref. 17 for a Pt(111) slab. It includes two *s* functions, as well as the *p*- and one *d*-like radial function centered on each Pt nucleus, and in addition, a *p*-like "floating" (i.e., not nucleus-centered) orbital atop each surface-layer Pt nucleus and an *s* function above each surface hollow. With this basis, a total-energy optimization yields a Pt lattice parameter of 7.36 bohr, in agreement with the LAPW result, and for a five-layer ideal Pt(111) slab, the occupied linear combination of atomic orbitals (LCAO) energy bands disagree with the LAPW bands by no more than 0.11 eV across the surface Brillouin zone (SBZ).

Of course there are no steps on a Pt(111) slab. So success in comparing LCAO and LAPW results for (111) slabs is not a guarantee that a similar comparison would succeed for vicinal ones. On the other hand, previous Al(111) and Al(331) calculations have shown that if an atom-centered orbital set is adequate to describe the (111) surface, then adding more floating Gaussian orbitals in the neighborhood of step edges provides the additional variational flexibility needed to describe the steps.[2(a)] To describe vicinal Pt surfaces, I follow the recipe that worked well for Al(331), adding a second layer of *s* functions above the (111) terraces' hollows, and making no distinction between the centers of floating orbitals and Pt nuclear positions when it comes to moving orbital centers to optimize vicinal slab geometry. In the (111) case, I place the first layer of hollow site orbitals 4 bohr above the outer plane of Pt nuclei. For the vicinal surfaces, I start the second layer of hollow orbitals 6 bohr above the outer Pt(111) terraces. This permits considerable electron polarization to occur near the step edges. [The ideal inter-(111)-layer spacing is 4.25 bohr.]

As a rule one finds that relaxed steps are flatter than ideal. This is a simple bond-order bond-length correlation: the few bonds of low-coordination surface atoms are shorter than the many bonds of better-coordinated atoms. Since the bonds between step-edge Pt's and their nearest neighbors are expected to be considerably shorter than the bond length in bulk Pt, it is important to choose an orbital basis flexible enough to permit near-step bond compression. With this in mind, I add an extra ("2nd ζ") *d*-like Gaussian orbital centered on each Pt atom that is exposed to the vacuum, and also on the step-edge nearest neighbor that does not contact the vacuum. I choose the attenuation constant of this orbital to equal 0.15 bohr^{-2}. A recalculation of bulk Pt with the extra *d* orbital yields a Pt bulk modulus only 1% larger than the value of 3.09 Mbar that one obtains in the LAPW approach. Leaving it out results in cohesion for compressed bulk Pt that is too weak, and thus a bulk modulus that is 9% higher than the LAPW value.

B. Surface energy calculations

To compute the energies of the (111)- and (100)-type steps on Pt(111), as explained in detail in Sec. II C and Appendix A, I extrapolate surface energy results for vicinal surfaces with rather narrow terraces. A surface energy, E^s, is typically extracted from an N-layer slab calculation, by applying the formula

$$E^s=[E_{\text{slab}}(N)-NE_{\text{bulk}}]/2 \ . \tag{1}$$

In Eq. (1), $E_{\text{slab}}(N)$ is the slab total energy per two dimensionally repeated unit cell and E_{bulk} is the energy per cell for a "bulk" layer in the interior. N is assumed to be sufficiently large that quantum size effects are negligible. The factor 2 accounts for the fact that a slab has two symmetry-equivalent surfaces.

There are several ways that one might choose to compute E_{bulk}. In the case of vicinal surface calculations this choice can make an important difference, because N is a rather large number. For example, for a slab whose terraces are four-atom rows wide by seven (111) layers thick, $N=28$. Thus, a difference of 0.01 eV in the value used for E_{bulk} corresponds to a difference of 0.14 eV in the resulting surface energy. Since the formation-energy difference observed for Pt(111)- and (100)-type steps is on the order of only 0.06 eV, care is obviously required in deciding what to use. The main idea, as emphasized by Stumpf and Scheffler,[2(d)–2(f)] is to minimize errors associated with finite slab thickness and with sampling the Brillouin zone via a finite number of k vectors.

A straightforward way to avoid a finite-thickness error in computing E_{bulk} is to evaluate it directly for a three dimensionally periodic bulk crystal. This is in contrast to the usual approach, comparing total energies of slabs of a different number of layers. It also differs from single slab methods in which each layer's contribution to the total energy of a slab is evaluated separately.[18] Small, finite-thickness errors are unavoidable in a value of E_{bulk} calculated by these methods, because the effect of the surfaces is not completely screened out in the center of a reasonable thickness slab. Small errors, to reiterate, are dangerous when they are multiplied by a substantial $N/2$ to obtain the desired result.

The advantage of computing $E_{\rm bulk}$ directly from slab total energies is the cancellation of errors associated with the use of a finite k-vector sample in evaluating Brillouin-zone integrals numerically. Since losing this cancellation is undesirable, it is clear that evaluating $E_{\rm bulk}$ directly for a three dimensionally periodic bulk crystal only make sense if this is done *differently for each slab orientation,* so that the same BZ sample can be used for slab and bulk in each case.

The bulk energy results quoted in Table I, which differ by as much as 0.001 Ry for different vicinal planes, show that this is important, though less so if one uses a finer k-vector sample. For each orientation listed, I compute $E_{\rm bulk}$ by repeating a several-layer supercell of that orientation to form bulk fcc Pt. For simplicity, I choose the number of layers in the repeated cell, so that the translation vector corresponding to the repeat is perpendicular to the plane in question. For example, I use a 19-layer supercell in the (331) orientation, because if there is an atom at $(x,y)=(0,0)$ in the νth (331) plane, then the next (331) plane with an atom at $(x,y)=(0,0)$ is plane number $\nu+19$. With this supercell, I sample the k_x-k_y plane identically in the (331) surface and bulk total-energy calculations; similar supercell constructions work for the other slab orientations.

I illustrate the convergence of k_x-k_y sampling, in Table I, by comparing the surface energies I obtain in (221)-slab calculations, using 3 as against 12 k_x-k_y points in the irreducible quarter of the SBZ. The effect of halving the spacing of the k_x-k_y sample points is less than 1 meV/Å^2. Using formulas derived in the next subsection to extrapolate from the computed surface energy to an isolated (111)-type step energy, I find that halving the k_x-k_y spacing changes the predicted (111)-step energy by only 1 meV, or about 1.1% of the total step-formation energy per edge atom. The excellent convergence of surface and step energies, using only a 3 k-vector ISBZ sample, is a consequence of the flatness of Pt's d bands.

C. Extrapolation to infinitely wide terraces

In this subsection, I set forth the asymptotic expressions I use to extrapolate to the formation energies of isolated, unkinked steps, from surface energies computed for periodic vicinal surfaces with relatively narrow (111) terraces. I provide a detailed derivation of these expressions in Appendix A (see also, Ref. 7).

Suppose that the terraces on a periodic vicinal surface are λ atom rows wide. [By definition, I count the step-bottom row as a terrace row.[19]] If the energy to create a step were zero, then the surface energy per vicinal surface unit cell would be $\lambda E^{2}_{\rm terr}$, corresponding to λ exposed atoms and a surface energy per surface atom, $E^{s}_{\rm terr}$, for the infinitely wide terrace. Since the step-formation energy is not zero, let the energy per unit cell of the vicinal surface by $\lambda E^{s}_{\rm terr}+C_{\rm step}(\lambda)$.

With this definition, one can prove (see Appendix A), for surfaces with wide (111) terraces, that the formation energies per step-edge atom are

$$E_{111\text{-step}}\rightarrow[C_{111\text{-step}}(\infty)+2E^{s}_{111}/3]/d_{111}\ , \tag{2}$$

and

TABLE I. Pt vicinal slab energetics. Summary of calculated vicinal slab energetics. In the first column, the orientation of the slab surface, and λ, the number of rows across a terrace. Second column: Thickness of the slab in (111) layers. Third column: Number of equally spaced k vectors used to sample $\frac{1}{4}$ of the surface Brillouin zone. Fourth column: Total slab energy, in Ry. Fifth column: Energy per layer of a bulk Pt, calculated using a supercell of this orientation [e.g., of (331) layers in the row corresponding to a (331) slab]. Sixth column: Surface energy of the vicinal slab per surface area. Seventh column: The excess energy $C(\lambda)$, as defined in Sec. II C. Eighth column: the energy of an isolated step of this type, as obtained from Eq. (2) or (3) for (111)-type or (100)-type steps.

Surface plane, λ	No. of (111) layers	No. of (k_x,k_y)'s	Slab energy (Ry/unit cell)	Bulk atom energy (Ry)	$E_{\rm surf}$ (eV/Å^2)	$C_{\rm step}(\lambda)$ (eV)	$E_{\rm step}$ (eV/atom)
(331),3	9	8	−1428.3408	−52.914 89	0.149	−0.084	0.481
(331),3	7	8	−1110.8484	−52.914 89	0.150	−0.064	0.501
(221),4	7	12	−1481.1310	−52.914 82	0.145	−0.096	0.469
(221),4	9	12	−1904.4503	−52.914 82	0.144	−0.102	0.463
(221),4	9	3	−1904.4029	−52.913 48	0.144	−0.107	0.458
(211),3	9	10	−1428.3030	−52.914 99	0.147	0.192	0.474
(211),3	7	10	−1110.8103	−52.914 99	0.148	0.210	0.492
(533),4	7	3	−1481.0538	−52.913 55	0.144	0.188	0.470
(533),4	9	3	−1904.3619	−52.913 55	0.144	0.188	0.470
(111),1	9	19	−476.110 99	−52.915 06	0.129		

$$E_{100\text{-step}} \rightarrow [C_{100\text{-step}}(\infty) + E^{s}_{111}/3]/d_{111} \ , \qquad (3)$$

for the two kinds of unkinked steps. In these equations, d_{111} is the nearest-neighbor distance of the fcc crystal, E^{s}_{111} is the value of E^{s}_{terr} appropriate to a (111) terrace. The terms involving E^{s}_{111}, in these formulas, represent the fact that step-edge atoms overlap the underlying terraces, reducing the total area exposed to the vacuum per surface atom. The reason that the area-correction terms are different in Eqs. (2) and (3) is that the (111)-type step rises at a steeper angle from the (111)-type step rises at a steeper angle from the (111) terrace than does the (100)-type step.

III. RESULTS OF THE VICINAL-SURFACE CALCULATIONS

Here, I present the results of optimizing the geometries of the Pt(331), (221), (211), and (533) slabs, including step geometries, work functions, and surface energies. I extrapolate the surface energy results to vicinal surfaces with infinitely wide terraces, via Eqs. (2) and (3), obtaining formation energies for (111)- and (100)-type steps on Pt(111).

A. Step geometries

I relax the various films to their optimal unit-cell geometries via a modified Broyden iteration-relaxation method,[20] fixing the atomic positions of the central (111) layer in each case. Thus, for the (331) and (211) films, I hold the unit-cell's central three atoms fixed in relative position, while for the (221) and (533) slabs I fix the central four Pt nuclei. I relax the remaining atomic positions until no orbital center is subject to a force greater than 2 mRy/bohr. For the thinner slabs [seven (111) layers across], this procedure leaves the central (111) layer under some stress. Allowing it to relax as well, for the (331) slab, reduces the calculated surface energy by only 4 meV/atom. For the thicker slabs [nine (111) layers across], the forces on the central-layer atoms are less than 2 mRy/bohr, even though they have not been allowed to relax. Thus, the surface energies obtained for the slabs that are nine (111) layers across the representative of what one would find for still thicker ones.

In general, relaxed steps are expected to be flatter than ideal. Step-edge atoms share their valence electrons with fewer neighbors and, therefore, have shorter, stronger bonds than atoms that are more highly coordinated. These effects have been documented for close-packed steps on Al vicinal surfaces, and, as seen in Tables II and III, also occur on the vicinal surfaces of Pt(111). In Table II, for the various vicinal slabs, I show how the lengths of step-edge atoms' bonds to their neighbors compared to the bulk Pt nearest-neighbor spacing. In Table III, I do the same for the bonds of the step-bottom atoms to their nearest neighbors. Systematically, one sees that the step-edge atoms are pulled toward the remainder of the solid. The bonds that are shortened most are the ones between step-edge atoms and their nearest neighbors inside the metal. Table III shows that at the same time, the step-bottom atoms move outward and away from the step edge. The bonds between these atoms and their neighbors on the step side become longer, those to their neighbors away from the step shorten, and finally, their bonds to the layer below are lengthened. The LDA nearest-neighbor distance in bulk Pt is 5.21 bohr. Thus, the relaxations in Tables II and III correspond to changes in Pt-Pt bond lengths of the order of as much as 0.26 bohr.

TABLE II. Changes in distances to nearest-neighbors of step-edge atoms. Summary of step-relaxation results for the edge atoms of the various vicinal slabs. [In all cases, the slabs are the ones that are nine (111)-layers thick.] Percentages given represent changes in nearest-neighbor bond lengths of the step-edge atoms relative to the nearest-neighbor separation, 5.21 bohr, in bulk, LDA Pt. Note that the step-edge atoms move toward the solid and toward the step, so that the step flattens.

Neighbor	Distance on (331)	Distance on (221)	Distance on (211)	Distance on (533)
Along step	0.0%	0.0%	0.0%	0.0%
Step bottom	−2.5%	−2.4%	−2.5%	−2.4%
Upper terrace	−3.7%	−3.0%	−2.9%	−2.5%
Interior	−4.4%	−4.9%	−3.1%	−3.2%

B. Work functions and step dipole moments

The work function, Φ, of a vicinal surface is often[21] lower than Φ for the terrace to which it is vicinal.[22,23] This phenomenon is generally attributed to the Smoluchowski effect,[24] the smoothing of the electron-density corrugations at a surface driven by electron kinetic-energy reduction. Smoothing corresponds to a displacement of surface electron density toward the solid and thus (recalling that this is the same electron displacement direction as when alkali-metal atoms are adsorbed on a surface) a negative $\Delta\Phi$. In Table IV, I give values of $\Delta\Phi$ calculated for the various vicinal surfaces studied here. They are negative, as expected. In what follows I extrapolate these results to surfaces with wider terraces, both for the sake of comparison to experiment (Ref. 22), and to obtain values of the dipole associated with each step type.

As the terrace width of a periodic vicinal surface narrows, the dipole moment associated with each of its steps changes, for two reasons. One is that the dipoles of the neighboring steps interact more strongly with each other. This can increase or decrease the step dipole moments depending on the dipole orientation. The other reason is that for narrower terraced surfaces, the normal to the vicinal surface tilts farther away from the normal to the terraces. This tilt reduces the contribution of each step to the vicinal-surface work function, by a factor of the cosine of the angle between the normals, even if the charge-density distribution near each step is unaffected by the electric fields associated with neighboring steps.

For terraces three and four rows wide, the effect of the relative orientation of vicinal surface and terrace normals is no more than a few percent. For example, the cosine of the angle between the (331) and (111) directions is 0.93, while between (221) and (111) it is 0.96. If interactions

TABLE III. Changes in distances to nearest neighbors of step-bottom atoms. Summary of step relaxation results for the step-bottom atoms of the various vicinal slabs. [In all cases, the slabs are the ones that are nine (111) layers thick.] Percentages given represent changes in nearest-neighbor bond lengths of the bottom-edge atoms relative to the nearest-neighbor separation, 5.21 bohr, in the bulk, LDA Pt. Note that the step bottom atoms move out of the solid and away from the step, so as to allow the step to flatten.

Neighbor	Distance on (331)	Distance on (221)	Distance on (211)	Distance on (533)
Along step	0.0%	0.0%	0.0%	0.0%
Step edge	−2.5%	−2.4%	−2.5%	−2.4%
Exposed on terrace	−2.9%	−2.2%	−2.7%	−1.7%
Under step on terrace	+2.6%	+3.5%	+0.8%	+1.3%
Subterrace away from step	+0.4%	+0.3%	+2.4%	+1.5%
Subterrace toward step	+3.7%	+4.6%	+3.0%	+3.6%

between neighboring step dipoles is also small, then the work-function change for vicinal surfaces of a given step type should be proportional to the dipole moment per step and inversely to the step-step separation. Table IV, shows that this is roughly the case. Thus, one can easily extract approximate values of the step dipole moment for each step type.

The dipole associated with the (100)-type step is calculated to be about 33% smaller in magnitude than that of the (111) steps. This result is consistent with the Smoluchowski smoothing picture.[24] (100)-type steps rise less steeply from the (111) terraces than (111) steps do. The electron-gas corrugation associated with (100)-type steps is, thus, weaker than with (111) type. Consequently, one would expect less electron-density smoothing and a smaller work-function reduction relative to Pt(111) for vicinal surfaces with (100)-type steps. Interestingly, the measurement of Pt vicinal-surface work functions by Besocke, Krahl-Urban, and Wagner (BKW) (Ref. 22) yields the opposite result. By observing the low-energy cutoff of the secondary electrons emitted when a 200-eV electron beam strikes an appropriately oriented, cylindrical Pt crystal, BKW find that $\Delta\Phi$ does indeed vary inversely with terrace width. Thus, they extract step dipole moments of −0.52 and −0.63 D/edge atom for (111)- and (100)-type steps, from their data. The corresponding calculated values, −0.21 and −0.14 D/edge atom are evidently considerably smaller and oppositely ordered.

In attempting to understand the source of this discrepancy, bear in mind that BKW did not measure work functions for terraces any narrower than three times the width of the four-row-wide, (221) and (533) terraces studied here. Extrapolating to the step densities corresponding to Pt(221) and Pt(533), which amounts to assuming that coupling among the step dipoles can be neglected even for terraces four atoms wide, one obtains $\Delta\Phi(221) = -0.86$ eV and $\Delta\Phi(533) = -0.96$ eV from BKW's results. The values calculated here are −0.35 and −0.21 eV. It seems unlikely that a work-function discrepancy as large as 0.75 eV could be the result of a systematic LDA error.

One possibility worth considering is that the extrapolation is invalid. That is, when there is a step every third or fourth row of atoms, neighboring dipoles depolarize each other, analogously to what happens when alkali-metal coverage is increased on metals. This seems unlike-

TABLE IV. Pt vicinal surface work functions. Calculated work functions Φ and step-related dipole moments μ. Note that the work-function change, $\delta\Phi$, times the width, w, of the unit cell is roughly a constant for each step type. The dipole moments are computed in units of D/step-edge atom, using the Helmholtz formula (cf. Ref. 21).

Surface plane	Number of layers	Φ (eV)	$\delta\Phi$ (eV)	width, w (Å) of unit cell	w (Å)$\delta\Phi$ (eV)	μ (D)/step
(331)	9	5.62	−0.49	6.00	−2.94	−0.21
(331)	7	5.69	−0.42	6.00	−2.52	−0.18
(221)	7	5.76	−0.35	8.26	−2.90	−0.21
(221)	9	5.74	−0.37	8.26	−3.03	−0.22
(211)	9	5.84	−0.27	6.75	−1.82	−0.13
(211)	7	5.88	−0.23	6.75	−1.58	−0.11
(533)	7	5.90	−0.21	9.03	−1.90	−0.14
(533)	9	5.93	−0.18	9.03	−1.63	−0.12
(111)	9	6.11				

ly, however, given that the calculated values of μ_{step} are almost equal for terraces three and four rows wide, that have the same type of step (cf. Table IV).

A stronger possibility is that BKW's results might have been influenced by undetected contamination of the Pt crystal surface,[25] and/or by a miscut leading to the presence of kinks.[26] As a first test of the idea that the BKW's surfaces were contaminated, I optimized the geometries of Pt(331) and Pt(211) slabs, on which rows of H atoms are adsorbed at every step-edge twofold site. The work functions for these "H-contaminated" slabs, relative to clean Pt(111), are −0.31 and −0.21 eV. For clean Pt(331) and Pt(211), the shifts are instead −0.49 and −0.27 eV. Thus, adsorbed H *reduces* the magnitude of the work function changes associated with steps. This means that had "adventitious H" affected the BKW results, then on an uncontaminated Pt sample the observed work-function changes should have been still bigger. The disagreement with the present calculations would then have been worse rather than better.

Of course, H is far from the only potential contaminant. Mundschau and Vanselow[25] point out that S, P, and Si contamination of Pt surfaces are easy to miss, because of overlap of Auger lines. In their review of the literature concerning reconstruction of the "clean" Pt(100) surface, "not one Auger spectrum could be found providing unequivocal evidence of surface cleanliness." This problem was not widely appreciated prior to 1981.[27,28]

In view of the cleanliness question, an experimental attempt to reproduce the results of Ref. 22 would be welcome. Such a study should not only involve close attention to surface impurities, but also to crystal orientation. A slight miscut might lead to a significant kink density.[26] Kinks in themselves can be expected to affect work functions. In addition, kinks are excellent nucleation sites for the buildup of surface impurities.

C. Surface energies

To compute surface energies for the various vicinal slabs, I use Eq. (1). As discussed above (see Sec. II B), to maximize error cancellation associated with BZ sampling, I compute a slightly different value of E_{bulk} for each slab orientation by repeating a several-layer supercell of the same orientation to form bulk fcc Pt. The resulting surface energies are listed in Table I. As expected, reflecting the fact that the energy to form a step is greater than zero, the surface energies of the vicinal slabs, are greater than that of Pt(111).

The convergence of the computed surface energies with regard to slab thickness is very good, by the standards of usual LDA calculations. They differ by only a few meV/Å^2, i.e., less than 1%, between the calculations for slabs that are seven and nine (111) layers in cross section. Convergence with respect to BZ sample is indicated by the excellent agreement of the surface energies computed for Pt(221), using 3 or 12 k-vector samples of the irreducible $\frac{1}{4}$ of the zone. Rapid convergence of the BZ sampling is expected for a d-band metal, because the bands are relatively flat.

Comparing slabs with the same number of atom rows/terrace, one sees that the surface energies of the slabs with (111)- and (100)-type steps are very close to each other. This suggests the result to come for isolated-step energies; they are virtually identical for the two-step types.

D. Formation energies for (111)- and (100)-type steps on Pt(111)

To estimate formation energies of isolated (111)- and (100)-type steps on Pt(111), I use the extrapolation formulas Eqs. (2) and (3). The weak dependence of the excess surface energies $C_{111\text{-step}}(\lambda)$ and $C_{100\text{-step}}(\lambda)$ between $\lambda=3$ and 4 is an expected manifestation of step-step interaction. This effect amounts to a difference in the excess surface energy per vicinal-surface unit cell, or equivalently, per step of roughly 20 meV. Importantly, however, the step-step interaction effect is repulsive for both the (111)- and (100)-type steps. That is, in both cases, the excess surface energy per step drops as one goes from terraces that are three-atom rows wide to four rows wide. Thus, the error in the calculated step-energy difference associated with step-step interaction tends to cancel.

The calculated formation energies for (111)- and (100)-type steps are given in the last column of Table I. The best values for isolated steps on a semi-infinite Pt crystal are 0.46 eV/atom for the (111) step and 0.47 eV for the (100) step, corresponding to the widest (four-atom row wide) terraced and thickest [nine-(111) layer thick] slabs. In contrast to the conclusion that is apparent from MC's STM images of islands on Pt(111), these energies are equal to within 10 meV/edge atom. In the concluding section of this paper, I discuss possible reasons for the discrepancy.

IV. DISCUSSION

It is not hard to conceive of explanations for the discrepancy between the relative energies of (111)- and (100)-type steps extracted from the Michely-Comsa STM images, and those found here. To begin, it is worth remembering that the experimental energy difference is only 13% of the average of the step-formation energies. Thus, the formation-energy difference that must be accounted for is only 60 meV/per step-edge atom.

The possible explanations for the discrepancy between the calculated formation energy ratio and the MC data are as follows.

(1) It stems from a failure of the LDA. Since there exists no systematic scheme for improving on LDA, it is hard to refute this idea. There is plenty of evidence that LDA calculations predict condensed matter structures accurately. Nevertheless, for two atomic geometries that are close in energy, the reliability of the local-density approximation is open to question.

The results of EAM calculations by Nelson *et al.* do stand as something of a counter argument. The EAM, whose parameters are fit to an experimental database, is not the LDA and generally yields different lattice parameters, surface energies, etc. It is, therefore, of interest that the EAM formation energies for the two step types[7] are virtually equal (though somewhat smaller, 0.36 eV/atom rather than 0.47), just as the LDA's are.

(2) The discrepancy is a matter of basis-set convergence or some other convergence issue. The fact that the near equality of step-formation energies holds for both three-row-wide and four-row-wide terraces of two different thicknesses represent a strong argument that the terraces I used were wide enough, and that the slabs were thick enough. In a LCAO calculation, one can never prove that the basis set is converged. I have, however, conducted numerous tests involving adding floating orbitals, longer-tailed Gaussians on the surface Pt's, etc. As is necessary in a variational calculation, adding extra functions does yield somewhat improved cohesion. The step-formation-energy results quoted in Table I are thus all perhaps 30 meV/atom higher than they would be for the best basis set. But what is at stake in the comparison to the MC data is the *relative* energy of the two-step types. I have found no basis improvement that affects the energy difference to within an order of magnitude of the 60 meV necessary to account for MC's island shapes.

(3) The steps in the experiment are locally reconstructed. In the calculations reported here, I start from an "ideal" vicinal slab geometry, i.e., Pt positions at the surface that correspond to whichever crystal plane of bulk, fcc Pt. These positions are allowed to relax, but not to adopt a lower-symmetry configuration. Nor do I add or subtract atoms in the unit cell. Under ordinary circumstances, and certainly in the images of Michely and Comsa,[6] resolution is not adequate to reveal individual Pt atom positions. Thus, step reconstruction cannot be ruled out. On the other hand, under certain STM tip conditions, presumably when there is an atom or cluster on the tip that is easily deformed,[29] atomically resolved STM images can be obtained even for as weakly corrugated metal surface as Pt(111). By this means (with a Xe atom on the STM tip), Eigler has obtained atomically resolved images of unkinked steps on Pt(111) that show no sign of any local reconstruction.[30]

(4) The experimental step-energy difference is a finite-temperature effect. LDA energy and geometry optimization is a zero-temperature calculation. The MC islands were equilibrated and quenched at a temperature T above 700 K.[6] This temperature, expressed as an energy, is roughly 60 meV. Thus, kT is of the same order of magnitude as the energy difference that needs to be explained. Nelson *et al.* show, in the course of their EAM study, that one can ignore step-wandering ("configurational entropy") contributions to the free-energy difference of the two-step types.[7] They do not consider the effects of vibrational entropy, however.

Qualitatively, one would not expect a large vibrational entropy contribution to the ratio of the step free energies. Associating small entropy with stiff springs and large entropy with soft ones, the fact that the zero-temperature formation energies are about the same for the two step types suggests that their free energies will also be. Nevertheless, if one is interested in formation free-energy difference of only 60 meV, a calculation is certainly warranted. Such a calculation, based on the EAM, is in progress.[31]

V. CONCLUSION

The regularity of the hexagonal islands equilibrated at over 700 K and observed via STM by Michely and Comsa on Pt(111),[6] offers an appealing experimental test of our ability to simulate the energetics of defects on transition-metal surfaces. Nevertheless, MC's island shapes are the result of a *small* difference in the free energies per unit length of the two kinds of step, (111) and (100) type, that form the island edges, that may, in fact, be dominated by the entropy contributions. Accounting for the island shapes accordingly remains a problem, one that lies at the limits of present-day computation.

ACKNOWLEDGMENTS

I have profited from numerous conversations with Roland Stumpf. I am also grateful to T. L. Einstein, T. Rahman, R. Vanselow, and J. C. Hamilton for helpful discussions. This work was supported by the U.S. Department of Energy under Contract No. DE-AC04-94AL85000.

APPENDIX: DERIVATION OF FORMATION-ENERGY FORMULAS FOR WIDELY SPACED STEPS

To obtain the asymptotic expressions for the formation energy of an isolated, unkinked step, Eqs. (1) and (2) of Sec. II C, I compare the surface energies per unit area of wide-terraced vicinal and perfectly flat surfaces. In order to extrapolate to *arbitrarily* wide terraces in the vicinal case, it is convenient to consider the area per surface atom and the energy per surface atom separately.

First consider the areas. Suppose that the terraces on a periodic vicinal surface are λ atom rows wide.[19] Let d_{terr} be the lattice repeat distance along a step edge and let w_{terr} be the width of one terrace unit cell. Then within a single vicinal-surface unit cell, the *terrace area* exposed between each step edge and the next step bottom is $(\lambda-1)d_{\mathrm{terr}}w_{\mathrm{terr}}$, corresponding to $\lambda-1$ terrace unit cells, each of area $A_{\mathrm{terr}}=d_{\mathrm{terr}}w_{\mathrm{terr}}$. On a fcc(533) surface, for example, the (111) terraces are four $(01\bar{1})$ rows wide and the (111)-terrace area exposed between each step edge and the next step bottom, in each (533) unit cell, is $3A_{111}$, where $A_{111}=d_{111}^2\sqrt{3}/2$ is the area of the (111) surface unit cell. d_{111} is the nearest-neighbor distance in the fcc crystal, and $w_{111}=d_{111}\sqrt{3}/2$.

To establish a comparison between the areas of flat and vicinal surfaces, I define $\delta w_{\mathrm{step}}(\lambda)$ via the requirement that $[(\lambda-1)w_{\mathrm{terr}}+\delta w_{\mathrm{step}}(\lambda)]d_{\mathrm{terr}}$, be the area of the vicinal-surface unit cell. $\delta w_{\mathrm{step}}(\lambda)$ is generally greater than 0. It equals zero only if the steps rise at right angles from the terraces. $\delta w_{\mathrm{step}}(\lambda)$ is also less than w_{terr}. It would equal w_{terr} for a step that lies flat on the terrace, i.e., a step that does not rise at all.

Now consider the surface energy of the vicinal-surface unit cell. If the energy to create a step were zero, this quantity would be $\lambda E^s_{\rm terr}$, corresponding to λ exposed atoms and a surface energy per surface atom, $E^s_{\rm terr}$, on the infinitely wide terrace. The step-formation energy is not zero, of course, because atoms are coordinated differently at steps and on terraces. Therefore, let the energy per unit cell of the vicinal surface be $\lambda E^s_{\rm terr}+C_{\rm step}(\lambda)$, where $C_{\rm step}(\lambda)$ represents the correction to the surface energy per unit cell, due to the existence of the step.

One can now write the expression for the surface energy *per unit area,* $A(\lambda)$, of the vicinal surface,

$$E^s/A(\lambda)=[\lambda E^s_{\rm terr}+C_{\rm step}(\lambda)]/[(\lambda-1)w_{\rm terr}+\delta w_{\rm step}(\lambda)]d_{\rm terr}\ . \quad \text{(A1)}$$

In the limit of wide terraces, i.e., large λ, Eq. (A1) can be expanded in powers of λ^{-1}. Assuming that $C_{\rm step}(\lambda)$ and $\delta w_{\rm step}$ approach the constants $C_{\rm step}(\infty)$ and $\delta w_{\rm step}(\infty)$ in this limit, one has

$$E^s/A(\lambda)\rightarrow E_{\rm terr}/A_{\rm terr}+(\{C_{\rm step}(\infty)+E_{\rm terr}[1-\delta w_{\rm step}(\infty)/w_{\rm terr}]\}/d_{\rm terr})/\lambda w_{\rm terr}+O(\lambda^{-2})\ . \quad \text{(A2)}$$

The first term in Eq. (A2) is the surface energy per unit area of the terraces. In the next, the coefficient of the inverse terrace width,

$$E_{\rm step}\rightarrow\{C_{\rm step}(\infty)+E_{\rm terr}[1-\delta w_{\rm step}(\infty)/w_{\rm terr}]\}/d_{\rm terr}\ , \quad \text{(A3)}$$

equals the extra energy per unit step length associated with isolated steps. Notice that $E_{\rm step}$ is the sum of two contributions. That involving $C_{\rm step}(\infty)$ is associated with the altered coordination of the atoms that reside near the step edges. The other, represents the fact that step-edge atoms overlap the underlying terraces, reducing the total area exposed to the vacuum per surface atom.

The first contribution can only be estimated by computing $C_{\rm step}(\lambda)$, for small values of λ, and extrapolating the results to $\lambda=\infty$. If step-step interactions rapidly approach zero as a function of λ, then the extrapolation is trivial. The second term is a geometrical factor. It can be calculated simply and exactly, as follows.

In the case of (111)-type steps on a surface vicinal to fcc(111), the area of the unit cell is $d^2[3\lambda^2/4-\lambda+1]^{1/2}$, where d is the nearest-neighbor distance in the crystal. $\lambda=3$ for the (331) surface, 4 for the (221), etc. The width of the (111)-terrace unit cells is $w_{111}=d\sqrt{3}/2$. Thus, for vicinal surfaces with (111)-type steps,

$$\delta w_{111}(\lambda)=d\{[3\lambda^2/4-\lambda+1]^{1/2}-(\lambda-1)\sqrt{3}/2\}\ . \quad \text{(A4)}$$

In the limit of wide terraces, i.e., large λ, Eq. (A4) yields

$$\delta w_{111}(\lambda\rightarrow\infty)\rightarrow w_{111}/3+O(\lambda^{-1})\ . \quad \text{(A5)}$$

Equation (A5) says that since the step-edge atom of a (111)-type step lies above the midpoint of an equilateral triangle, whose base is at the step bottom, only $\frac{1}{3}$ of the step bottom atoms' (111) unit cell is exposed to the vacuum.

In the case of (100)-type steps, the area of the unit cell is $d^2[3\lambda^2/4-\lambda/2+3/4]^{1/2}$. Here, $\lambda=3$ for the (211) surface, 4 for the (533), etc. Thus, for vicinal surfaces with (100)-type steps,

$$\delta w_{100}(\lambda)=d\{[3\lambda^2/4-\lambda/2+3/4]^{1/2}-(\lambda-1)\sqrt{3}/2\}\ . \quad \text{(A6)}$$

In the limit of large λ, Eq. (A6) yields

$$\delta w_{100}(\lambda\rightarrow\infty)\rightarrow 2w_{111}/3+O(\lambda^{-1})\ . \quad \text{(A7)}$$

According to Eq. (A7), since the step-edge atom of a (100)-type step lies above the midpoint of an equilateral triangle, whose *apex* is at the step bottom, now $\frac{2}{3}$ of the (111) unit cell corresponding to step bottom atoms is exposed to the vacuum.

Substituting Eqs. (A5) and (A7) into the general formula, Eq. (A3), one finds the final results,

$$E_{\text{111-step}}\rightarrow[C_{\text{111-step}}(\infty)+2E^s_{111}/3]/d_{111} \quad \text{(A8)}$$

and

$$E_{\text{100-step}}\rightarrow[C_{\text{100-step}}(\infty)+E^s_{111}/3]/d_{111}\ . \quad \text{(A9)}$$

The difference between the area-correction terms in these formulas reflects the fact that the (111)-type step rises at a steeper angle from the (111) terrace than does the (100)-type step.

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[10] See Fig. 1. Note that the two step types differ in that a (111)-step-edge atom lies above the midpoint of a triangle of nuclei, the *base* of which is along the step bottom, while a (100) step-edge atom lies above the midpoint of a triangle, the *apex* of which is at the step bottom.

[11] It is easy to prove that if the energy per nearest-neighbor bond were constant for monoatomic-layer-height islands, then the (111)- and (100)-type step-formation energies would be identical. The argument proceeds by considering the number of bonds formed in attachment of equilateral triangular islands to the (111) surface. Such islands have either all (111)-type or all (100)-type edges.

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