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Step- vs. kink-formation energies on Pt(111)

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Ab-initio kink-formation energies are about 0.25 and 0.18 eV on the (100)- and (111)-microfacet steps of Pt(111), while the sum of the step-formation energies is 0.75 eV/atom. These results imply a specific ratio of formation energies for the two step types, namely 1.14, in excellent agreement with experiment. If kink-formation costs the same energy on the two step types, an inference recently drawn from scanning probe observations of step wandering, this ratio ought to be 1.

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Measured step- and kink-formation energies are not direct experimental output,

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in general, but emerge from theoretical analysis of scanning-probe image statistics [1-3]. Given that the analysis is model-based, consistency checks on the results are greatly to be desired. I derive such a check in what follows, and apply it to the Giesen, et al.'s inference from scanning probe observation of step wandering on Pt(111) that kink-formation energies on (100)- and (111)-microfacet (or "A-type" and "B-type") steps are equal [1].

The consistency check says this result cannot be reconciled with the ratio of A- and B-type step formation energies, 1.13:1, needed to explain the thermodynamic island shapes observed by Michely and Comsa (MC) [4]. To test this assertion, I compute theoretical kink-formation energies for A-and B-type steps on Pt(111), using the Local Density Approximation [5]. The results, 0.25 and 0.18 eV, are different for the two step types, and consistent with MC's island shapes.

The essence of the consistency check is the fact, first exploited by Swartzentruber, et al. [6], that kink- and step-formation energies are related. Here is the argument for an *fcc*(111) surface: Because the A- and B-steps of such a surface intersect at 120° angles, creating a kink in an A-type step, as in Fig. 1, *a)* adds a B-type microfacet one inter-atomic spacing long, *b)* eliminates one-half that length of the original A-type step, and *c)* adds two 120° corners, one convex, the other concave. To form a kink in an A-type step thus requires energy,

$$E_{form}(\text{A-kink; } 1) = E_{form}(\text{B-step}) - E_{form}(\text{A-step})/2 + E_C(\text{A-kink}) \quad , \qquad (1)$$

where the last term is a "corner-formation" energy. If the B-step created is extended from 1 interatomic spacing to n_k of them, then the formation-energy cost becomes

$$E_{form}(\text{A-kink; } n_k) = n_k[E_{form}(\text{B-step}) - E_{form}(\text{A-step})/2] + E_C(\text{A-kink}) \quad . \qquad (2)$$

Eq. 2 implies that E_C(A-kink) can be computed by comparing kinks of different extent. The same, of course, applies for a B-step of length n_k, whose formation-energy is,

$$E_{form}(\text{B-kink; } n_k) = n_k[E_{form}(\text{A-step}) - E_{form}(\text{B-step})/2] + E_C(\text{B-kink}) \quad , \qquad (3)$$

but a simpler, approximate approach to evaluating corner energies is to note that whether one creates a kink in an A-type or in a B-type step, one makes a convex intersection of an A- and a B-step and a concave one.

Assume that the energy needed to make a corner depends only on whether the corner is convex or concave, but not on how far the steps on either side of it extend

before coming to the *next* corner. In that case, there is only one corner energy for kinks, i.,e.,

$$E_C(\text{A-kink}) = E_C(\text{B-kink}) \equiv E_C \qquad (4)$$

With this simplification, and setting n_k=1, Eqs. 3 and 4 combine to yield an expression for E_C in terms of the average formation energies of A- and B-type steps, and of kinks in them,

$$2E_C = E_{form}(\text{A-kink};1)+E_{form}(\text{B-kink};1) - [E_{form}(\text{A-step}) + E_{form}(\text{B-step})]/2 \; . \qquad (5)$$

They also yield the step-formation energy difference directly in terms of kink-formation energies, via,

$$E_{form}(\text{A-step}) - E_{form}(\text{B-step}) = 2[E_{form}(\text{B-kink};1) - E_{form}(\text{A-kink};1)]/3 \quad . \qquad (6)$$

Eq. 6 is the desired consistency check. At a minimum it says that if the formation energies for kinks on A- and B-type steps are equal, then the same must be true of the step-formation energies. Thus, Giesen, et al.'s ratio of 1 for kink-formation energies on A- and B-type steps [1] is inconsistent with Michely and Comsa's ratio

of 1.13 for the step-formation energies [4]. The only escape from this logic is if Eq. 4 is invalid because interactions between corners on A- and B-type steps differ substantially. However, the theoretical results for Pt(111) discussed immediately below, and similar calculations for Cu(111) [7] and Pb(111) [8], imply that this is not so. They *support* the approximate validity of Eq. 4.

To compute step- and kink-formation energies for Pt(111), I use the VASP [9-11] total-energy code, its ultrasoft pseudopotentials (USP's) [12], and Local Density Approximation (LDA), as embodied in the Ceperley-Alder local exchange-correlation potential [13]. Performing only LDA calculations is warranted in light of Boisvert, et al.'s observation [14] that the Generalized Gradient Approximation [15] (GGA) yields virtually the same ratio of A- to B-step formation energies as the LDA, while, for reasons unknown, it produces less acceptable absolute Pt surface energies.

USP's yield converged total energy differences with modest basis size. For Pt, a 14.1 Ry plane-wave cutoff is sufficient. I compute step- and kink-formation energies using 5-layer slabs to represent Pt(111), removing atoms in the uppermost layer to create monolayer-high islands bounded by straight and kinked edges. In all cases I fix the atoms of lowermost two slab layers at bulk relative positions and relax the rest till forces are <0.03 eV/Å. I set the slab lattice parameter to 3.91Å, the bulk

LDA value for a 60 point sample of the irreducible 48th of the Brillouin Zone (exp't. = 3.92 Å). To accelerate electronic relaxation, I use Methfessel and Paxton's Fermi-level smearing method (width = 0.2 eV) [16].

On a close-packed surface, a stripe island is bounded by an A-type step on one side and a B-type on the other. Thus, $\overline{E}_{form}$, the average step-formation energy, is given by [7,17],

$$2\bar{E}_{form} = E(s, v) - \frac{[sE(N+1) + vE(N)]}{s+v}. \qquad (7)$$

Here E(s,v) is the energy of a striped slab N+1 layers thick in cross-sections through the stripe islands and N-layers thick through the inter-island valleys, with stripes and valleys s and v atomic rows across. E(N) is the energy of a perfect N-layer slab. To minimize quantum size effects, one must choose sufficiently large s and v.

To obtain kink-formation energies, imagine two stripe-islanded slabs. On the first, the stripes and valleys are s and v rows wide, on the other, they are $s+1$ and $v-1$ rows across. To proceed, in a supercell $2r$ atoms long, parallel to the stripes and valleys, remove a block of r atoms from either the A- or the B-type island edge of the first slab and attach it to the step of the same character on the second. This forms

four kinks, two per supercell on each of two slabs with identical kinked-stripe islands. Thus, if r is big enough that kink-kink interaction can be neglected, the kink-formation energy, $E_{form}(kink)$, is given by

$$4E_{form}(kink) = 2E_{kinked}(r, s, v) - 2r[E(s, v) + E(s-1, v+1)] , \qquad (8)$$

where $E_{kinked}(r,s,v)$ is the energy of one kinked, striped slab and $E(s,v)$ is the energy of a striped slab with unkinked stripe islands and valleys s and v rows wide. The $2r$, on the right-hand side of Eq. 2, accounts for the supercell length.

The value of $2\overline{E}_{form}$, according to Eq. 7 and calculations in a $1 \times 4\sqrt{3}$ supercell, with $(s,v)=(4,4)$, is 0.75eV. Here the Surface Brillouin Zone (SBZ) sample is 12 equally spaced k-vectors in the x-direction by 2 in the y-direction. The value $2\overline{E}_{form}$ = 0.75eV is in reasonable agreement (~8%) with Boisvert, et al.'s result, 0.81 eV, which emerges from total-energy calculations of periodic vicinal slabs [14].

I compute kink formation energies via Eq. 8, using both $(s,v,r)=(4,4,4)$ and (5,3,4) to assess sensitivity to the finite width of the stripe islands used. These calculations are performed in an $8 \times 4\sqrt{3}$ supercell (cf. Fig. 1) using a 2×2 SBZ sample. Satisfyingly, the computations for the two stripe widths yield virtually the same

kink-formation energies, 0.18 eV in both cases for the A-step, 0.25 and 0.26 eV for the B-step.

Although the computed energy for kink-formation on an A-type step is only ~7% higher than the value obtained by Giesen, et al. for both step types, (0.167±0.005)eV [1], i.e., in reasonable agreement, the theoretical result for the B-step is ~50% higher. But if Eq. 6 is valid, Giesen, et al.'s equality of the kink-formation energies is inconsistent with MC's island shapes [4], and cannot be correct. With this in mind, it is of considerable interest to ask if the two *theoretical* kink formation energies taken together correctly account for the aspect ratio of MC's hexagonal islands.

Thus, note that according to Eq. 6, if E_{form}(B-kink;1) - E_{form}(A-kink;1) = 0.07 eV, then E_{form}(A-step) - E_{form}(B-step) = 0.05 eV/atom. But we also know that $2\bar{E}_{form}$ = E_{form}(A-step) + E_{form}(B-step) = 0.75 eV/atom. Thus, via simple arithmetic, E_{form}(A-step) = 0.40 eV/atom, E_{form}(B-step) = 0.35 eV/atom, and E_{form}(A-step)/E_{form}(B-step) = 1.14. The first two of these results agree reasonably well with Boisvert, et al.'s vicinal surface calculations [14]. The last agrees perfectly with Michely and Comsa's ratio, derived from a Wulff construction.

This excellent agreement, with what amounts to a direct experimental measurement, invites the conclusion that ignoring corner-corner interactions to obtain Eqs.

4-6, is a sound approximation. Thus Eq. 6 is a meaningful consistency check on measurements of step- and kink-formation energies on surfaces with a close-packed, hexagonal arrangement of atoms, one that the equal kink formation energies of Ref. 1 appear to fail.

Beyond the value of Eq. 6 in evaluating quantitative deductions from scanning probe measurements, once methods of measuring kink-formation energies have been perfected, absolute A- and B-step formation energies will be obtainable by observing hexagonal islands in thermodynamic equilibrium to measure the A- to B-step formation energy ratio and substituting the kink results into Eq. 6 to learn the step-formation energy difference.

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Figure Caption -

1. A stripe island with kinks on its A-type edge. Note that the kinks form B-type microfacets. The $8 \times 4\sqrt{3}$ supercell used in the kink-formation energy computation is indicated by the dotted rectangle.

Fig. 1