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1st-principles step- and kink-formation energies on Cu(111)

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In rough agreement with experimental values derived from Cu island shapes vs. temperature, ab-initio calculations yield formation energies of 0.27 and 0.26 eV/ step-edge-atom for (100)- and (111)-microfacet steps on Cu(111), and 0.09 and 0.12 eV per kink in those steps. Comparison to ab-initio results for Al and Pt shows that as a rule, the average formation energy of straight steps on a close-packed metal surface equals ~7% of the metal's cohesive energy.

Introduction - Though scanning-probe microscopies have revolutionized surface science by offering atomic-resolution views of surface structure, extracting fundamental energetic parameters from micrographs is generally a challenging problem. The statistical models,[1] rate equations[2] and numerical simulations[3] one uses typically require assumptions or approximations whose validity is not a given. In addition, because undercoordinated surface atoms, at surface steps for example, are particularly attractive to low-valence impurities, the energies one wishes to extract are susceptible to significant distortion by seemingly negligible concentrations of contaminants.[4,5]

Given these difficulties, validation of experimental analysis by comparison to theory is desirable. Numerous recent publications argue, in effect, that development of the Generalized Gradient Approximation (GGA)[6] to Density Functional Theory

(DFT),[7] and enormous advances in computer speed and algorithmic power make that possible.

Experimental determination of absolute step- and kink-formation energies on Cu(111) is the timely example at which the present work is aimed. Three recent measurements[8-10] and two semi-empirical calculations[11,12] of these basic surface energies are in serious disagreement:

In the first, Icking-Konert, et al. derived a Cu(111) step-formation energy by analyzing the time-dependence of island ripening.[8] The result, however, 0.45 eV/ step-edge-atom, seemed unrealistically large compared to Stoltze's[11] and Karimi, et al.'s[12] semi-empirical values, 0.21 and 0.26 eV/step-edge-atom, and also to Bonzel's extrapolation[13] from near-melting-point surface free-energy data, which yields ~0.30 eV/step-edge-atom.

Deriving the Cu(111) step-formation energy instead by analyzing the thermodynamic shape-fluctuations of vacancy islands, Schlößer, et al.[9] find it to equal 0.22±0.02 eV. This, they note, is roughly half the value obtained in Ref. 8 and is in very good agreement with Stoltze's Effective Medium Theory result.[11]

Most recently, Icking-Konert, et al., report extracting formation energies for (100)- and (111)-microfacet or "A-" and "B-type" straight steps on Cu(111) (which need not be the same) from the temperature-dependent rounding of hexagonal vacancy and adatom islands.[10] They obtain 0.31±0.04 eV/step-edge-atom for both step-types, noting, however, that the value for the A-type step is measurably 1.1±0.5 % smaller than for the B-type. A kink-formation energy of 0.110±0.005 eV also emerges from their analysis as a fit-parameter, although generally one would expect different kink energies for steps whose formation energies are not identical.[14]

These new results of Icking-Konert, et al.[10] are in much better agreement with the published semi-empirical formation energies, 0.21 and 0.26 eV,[11,12] but are 40% higher than the values obtained by Schlößer, et al..[9] The difference, Icking-Konert, et al. suggest, is the result of unwarranted assumptions in Ref. 9 concerning the isotropy of step free-energies.

In the best of worlds, the present *ab initio* calculations would settle the matter of which experimental analysis method yields step- and kink-formation energies most reliably. Unfortunately, the theoretical results, 0.27 and 0.26 eV/step-edge-atom for A- and B-type steps on Cu(111) (which differ little from the semi-empirical values of Ref. 12) sit squarely between the energies reported in Ref.'s 9 and 10, and thus do not yield the desired firm conclusion. Beyond that, they disagree with both Refs. 9 and 10 in predicting that A- rather than B-type steps will have a (slightly) larger formation energy.

In the paragraphs that follow, I describe the method used to produce *ab initio* step and kink-formation energies, then present the results and review their comparison to experiment. Since assessing the reliability of experimental step-formation energies would be easier, in general, if they were known to scale according to a dependable "rule of thumb," I conclude this note with a mention of other published *ab-initio* formation energies for straight steps on fcc(111) surfaces. Like those for Cu(111), they equal ~7% of the metallic cohesive energy.

Method - The results reported here were obtained using the efficient and accurate total-energy and molecular-dynamics package, VASP (Vienna *ab-initio* simulation package),[15-17] its corresponding ultrasoft-pseudopotential data-base,[18] and the

Perdew-Wang '91 Generalized Gradient Approximation (GGA).[6] Though plane-wave calculations for Cu typically require unwieldy basis sets, use of an ultrasoft pseudopotential assures total-energy convergence with the modest basis-cutoff of 17.2 Ry. This feature of VASP is vital to making the present calculations tractable despite their involving large unit cells. To accelerate electronic relaxation, I use the Fermi-level smearing approach of Methfessel and Paxton, with a width = 0.3 eV.[19]

I compute straight-step formation energies via the approach proposed, and used for Al surfaces, by Stumpf and Scheffler (SS).[20] Because it only requires comparing the energies of surfaces whose normal is (111), this approach minimizes quantum-size-effect (QSE) errors introduced in representing semi-infinite surfaces by thin model slabs, and it maximizes error cancellation in Brillouin Zone sampling.

In principle, step-formation energies could be computed more efficiently in terms of the energetics of periodic vicinals,[21] because their unit cells are smaller than those of the island-covered (111) surfaces of the SS method. But this apparent advantage in efficiency is overwhelmed by a need for increased accuracy in the face of worse error cancellation.

In all the calculations reported here, only the atoms of the upper two layers of each model slab and the islands on them are allowed to optimize their positions. I relax till forces are less than 0.03 eV/Å, fixing the remaining atoms in their bulk Cu geometry. In all cases, I set the slab lattice parameter to the bulk GGA value for a 60 k-point sample of the irreducible 1/48th of the Brillouin Zone, namely 3.64 Å (experiment = 3.61 Å).

Computing the average step-formation energy - The arrangement of atoms on a close-packed surface dictates (see Fig. 1) that if one edge of a monolayer-high stripe island is an A-type step, then the other must be B-type. Thus, one may evaluate the average of the A- and B-step formation energies via a *gedanken* experiment in which perfect (111) slabs, N and N+1 layers thick, are reconstructed to form slabs supporting a periodic arrangement of stripe-islands.[20]

The striped surfaces are N+1 layers thick in cross-sections through the stripe islands and N-layers thick through the inter-island valleys. To form a stripe-island slab from perfect slabs, with stripes and valleys *s* and *v* atomic rows across, requires energy,

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

Here E(*s*,*v*) is the energy of the striped slab and E(N) is that of a perfect N-layer slab. $\bar{E}_{form}$ is the desired result, the average formation energy per atom of the A- and B-type steps.

The energies required on the right-hand side of Eq. 1 can be obtained in computations involving the same Brillouin Zone sample, minimizing sampling error in the difference. QSE's on the striped slab are a blend of those which occur on the two perfect thin slabs, again minimizing error.

Computing the A- vs. B-step formation-energy difference -To obtain the *difference* between the formation energies of the two step types on Cu(111), I again follow SS's approach, computing energies of periodic slabs supporting triangular islands whose edges are either A- or B-type steps, as in Fig. 2. As the islands become larger, more perimeter atoms are distant enough from a corner that they are effectively step-edge atoms. Moreover, islands containing [J (J + 1) / 2] atoms have 3 (J - 1) Cu's on their perimeters. Thus, as J increases, the energy difference between A- and B-edged triangular islands approaches three times the formation-energy difference per step-edge atom of the two kinds of step. As in computing

$\bar{E}_{form}$, use of the same Brillouin Zone sample for differently oriented triangular islands minimizes sampling error, while similar slab geometries minimize QSE contributions.

Computing kink-formation energies - To arrive at a formula for kink-formation energies consider the following *gedanken* experiment: Start from 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. On each, imagine a supercell $2r$ atoms long in the direction parallel to the stripes and valleys. Now remove a block of r atoms from either the A- or the B-type stripe-island edge of the first slab and attach it to the step of the same character on the second. One has thereby formed four kinks, two per supercell on each of two slabs with identical kinked-stripe islands.

Accordingly, assuming that r is big enough that kink-kink interaction can be neglected, the kink-formation energy, $E_{form}(kink)$, is obtained from the formula,

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

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 factor $2r$, on the right-hand side of Eq. 2, accounts for the supercell length.

A key element in this argument is that the pair of kinks created on removing blocks of atoms from an edge, or on adding them, are of the same character (see Fig. 3). That is, if the block is removed from or added to an A-edge, then the kinks formed are both B-type microfacets, and vice-versa. This means that no analogue of the triangle-island calculation is needed to isolate kink-formation energies for A- and B-type steps.

Computed step and kink formation energies - Results from stripe and triangle-island evaluations of step-formation energies are summarized in Tables 1 and 2.

I present calculated energies for kink formation in Table 3. Convergence and accuracy of the results may be assessed by noting how they vary with unit-cell and island sizes, slab thicknesses and number of Surface Brillouin Zone sampling vectors.The general conclusion is that sampling error and QSE's distort the computed formation energies results by a few meV

Average step-formation energy on Cu(111) - Results in Table 1 for the average step-formation energy on Cu(111) are spread over a range of 8 meV. In the first two rows, I compare 4- and 5-layer slabs with stripe islands and valleys on them both 4 atomic rows wide. To assure convergence of the SBZ sample, I use a rather fine rectangular mesh of **k**'s, 18 in the $[1\bar{1}0]$- by 3 in the $[11\bar{2}]$-direction. The effect of adding a layer to the bottom of the 4-layer slab is a 5 meV or ~2% decrease in $\overline{E}_{form}$.

The lower three rows of Table 1 show the effect of varying stripe and valley widths on a 4 layer slab. I now use a 50% larger surface unit cell, and for consistency, a SBZ mesh of 18 **k**'s in the $[1\bar{1}0]$- by 2 in the $[11\bar{2}]$-direction. Again the differences for the different test cases are within a few meV.

Step-formation-energy difference in Cu(111) - Calculations of triangular-island energies require large unit cells to minimize island-island interactions. (For example the 28-atom-island calculations reported in Table 2 correspond to a unit cell containing 388 Cu atoms!) Since it is therefore desirable to sample the SBZ as efficiently as possible, I first check whether a single k-point, namely $\bar{\Gamma}$, yields an accurate value of E_A-E_B for a representative island size. (Here and henceforth E_A and E_B represent the formation energies per step-edge-atom of A- and B-type steps.) Comparing the first two rows of Table 2 implies that it is. The third row of the table implies that using a 4-layer slab is also adequate.

Comparison of rows 5 and 6 of Table 2 indicates that island-island interaction has only a small bearing on the calculated results. Finally, the small variation in the rightmost column of the Table indicates that 10 meV/atom is a good estimate of the formation energy difference between A- and B-type steps on Cu(111), with a systematic error in the neighborhood of 1 meV or 10%, due to QSE's.

Combining the results of Tables 1 and 2, the GGA formation energies of A- and B-type steps on Cu(111) are found to equal 0.27 and 0.26 eV. Simple thermodynamics then implies that a zero-temperature equilibrium island on this surface should be a hexagon with its B-edges about 14% longer than its A edges.[22]

This result is somewhat at variance with the room temperature experimental observations of Refs. 9 and 10, according to which the A edges are slightly longer than the B's. The island aspect ratio, however, is a rather sensitive test of the formation energy difference. It varies 3 times faster than the energy ratio when the latter is nearly 1.[22]

Kink energies - A simple estimate of the energy needed to form two kinks in an A-type step is $2E_B$-E_A. The reason is apparent in Fig. 3. Forming a kink pair amounts to creating two B-type microfacets each one Cu-Cu distance long, and eliminating a portion of A-type step which is also one Cu-Cu distance long. Similarly, twice the kink formation energy on a B-type step should $\approx 2E_A$-E_B, and thus, the kink formation energy difference should $\approx 3(E_B$-$E_A)/2$.

Calculated results based on Eq. 2, displayed in Table 3, roughly agree with these estimates. The computed kink-formation energies are about half a step-formation energy per step-edge-atom, and the energy to form a kink on a B-type step is larger, reflecting the higher formation of A- as against B-type steps. Numerical differences between the calculated and estimated kink-formation energies are attributable to the fact that the microfacets created are short, i.e. just one Cu-Cu spacing long.

Comparison to experiment - As noted above, the GGA yields step-formation energies, E_A=0.27eV and E_B=0.26eV, whose average lies equidistant from the experimental value of 0.22 eV/atom found by Schlößer, et al.,[9] and that reported by Icking-Konert, et al., 0.31 eV.[10] In addition, the GGA result that $E_A>E_B$ conflicts with *both* Refs. 9 and 10, which say, respectively, that $E_A/E_B=0.98\pm0.02$ or 0.989±0.005. Thus, unfortunately, the *ab-initio* calculations offer no support for the validity of the one experimental analysis as against the other, and are themselves open to questions of reliability.

The GGA values of the energies needed to form kinks in A- and B-type steps, 92 and 117 meV, average to an energy close to what is reported in Ref. 10, $E_{kink}(A)\approx E_{kink}(B)=0.110\pm0.005$ eV. On the other hand, the individual GGA kink energies evidently disagree with those of Ref. 10 by several percent.

Some of the disagreement found here may stem from comparing 300K experiments to a theory appropriate to absolute zero. Some may be the result of systematic error in the GGA itself, which is hard to quantify or predict from system to system. This said, the degree to which theory and experiment *do* agree supports the idea that Cu surface phenomena are reasonably well described by current first-principles electronic structure theory, and one may hope that in future, experimental step- and kink-formation energies will converge toward the GGA values.

Discussion: Systematics of *ab-initio* step-formation energies - When systematic error is a concern it is generally helpful to try to identify patterns in results from several systems.[23] If most but not all of the results appear to obey a "law," then the exceptions signal special physics or systematic problems. With this in mind it is interesting to ask whether step-formation energies on close-packed metal surfaces obey a simple scaling law. For example, do they scale with cohesive energy?

Table 4 shows that although not much information is yet available, this is an apt question. *Ab-initio* results for the (111) surfaces of Cu, Pt and Al suggest that the average of A- and B-type step-formation energies scales as ~7% of the cohesive energy of the corresponding metal.

The exception among the tabulated results is the GGA value for Pt(111). Though the LDA result fits the trend, the GGA step-formation energy for Pt(111) is no larger than that for Cu, a metal only 60% as cohesive. Boisvert, et al.,[25] who published the GGA number for Pt, discount it, saying that the GGA is known not to work as well for Pt as the LDA. The Pt lattice parameter, for example, is much closer to experiment within the LDA than in the GGA.

Without disputing this remark, it seems clear that the failure of the PW '91 GGA to produce a sensible Pt(111) step-formation energy is a sign of a systematic problem with the approximation. Efforts to see whether the problem correlates with the lattice parameter error, whether the same problem occurs for other 5d metals, whether different scaling obtains for simple and noble as against transition metals, etc., may provide insight useful in improving the GGA.

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22. Let R_E equal the ratio of A- to B-type step-formation energies and R_L equal the ratio of the lengths of the A- and B-type steps that bound a hexagonal island in equilibrium at T=0K. Then $R_L = \infty$, if $R_E<1/2$; $R_L = (1-R_E/2)/(R_E-1/2)$, if $1/2<R_E<2$; and $R_L = 0$ if $R_E>2$.

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Figure captions -

1. Stripe islands on an *fcc*(111) surface. The stripes and the valleys between them are both 4 atomic rows wide. The island are necessarily bounded by an A- and a B-type step. The surface unit cell is indicated by the dotted rectangle.

2. The two types of triangular island on an *fcc*(111) surface.

3. A stripe island with kinks on its A-type edge. Notice that all the kinks correspond to B-type microfacets. The surface unit cell for the corresponding calculation is indicated by the dotted rectangle.

Table Captions -

1. Average step-formation energies for various model slabs. **N** is the number of slab layers below the stripes, *s* is the stripe width, in atomic rows, *v* is the valley width in atomic rows, and $\overline{\mathbf{E}}_{\mathbf{form}}$ is the average of the A- and B-step formation energies per edge atom.

2. Computed step-formation energy differences versus model parameters for periodic arrangements of triangular Cu islands on Cu(111) slabs. The first column gives the dimensions of the periodic supercell, the second, the number of k-vectors in the full Surface Brillouin Zone sample. N is the thickness of the model slab beneath the islands, in layers. For each triangular island, J(J+1)/2 is the number of atoms it contains, of which 3(J-1) is the number on its edges. The formation energy difference in eV between two islands of the same size bounded by A- and by B-type steps is E_A-E_B. The last column gives this difference per edge atom.

3. Calculated kink formation energies on stripe islands. *s* and *v* are stripe and valley widths on the 4-layer slabs used in the calculations. ***r*** is the length of blocks bounded by kinks in the calculations, as well as the spaces between them. $\mathbf{E}_{\mathbf{form}}$ is the kink-formation energy computed via Eq. 2. $\mathbf{E}_{\mathbf{form}}$**(est.)** is the kink-formation energy estimate based on formation energies of straight steps (see main text).

4. Comparison of *ab-initio* step-formation and cohesive energies for *fcc*(111) surfaces, with step-formation energies in eV/step-edge-atom and cohesive energies in eV/atom.

Table 1: Stripe-island results for average step-formation energies

unit cell	N	*s*	*v*	$\overline{E}_{form}$(eV)
$1\times4\sqrt{3}$	4	4	4	0.265
$1\times4\sqrt{3}$	5	4	4	0.260
$1\times6\sqrt{3}$	4	4	8	0.266
$1\times6\sqrt{3}$	4	6	6	0.268
$1\times6\sqrt{3}$	4	8	4	0.261

Table 2: Triangle-island results for step-formation energy differences

unit cell	k's	N	J(J+1)/2	3(J-1)	E_A-E_B (in eV)	(E_A-E_B)/ 3(J-1)
$8\times4\sqrt{3}$	1	4	10	9	0.08	0.009
$8\times4\sqrt{3}$	4	4	10	9	0.08	0.009
$8\times4\sqrt{3}$	1	5	10	9	0.08	0.009
$8\times4\sqrt{3}$	1	4	15	12	0.13	0.011
$8\times4\sqrt{3}$	1	4	21	15	0.14	0.009
$9\times5\sqrt{3}$	1	4	21	15	0.17	0.012
$9\times5\sqrt{3}$	1	4	28	18	0.20	0.011

Table 3: Energetics of kink formation on stripe islands

s	*v*	r	step type	E_{form}	E_{form}(est.)
6	6	4	A	92 meV	125 meV
6	6	4	B	117 meV	140 meV

Table 4: Comparison of DFT step-formation and cohesive energies for *fcc*(111) surfaces

Surface	E_{form}(A)	E_{form}(B)	E_{coh}(exp't)[d]	$\bar{E}_{form}/E_{coh}$
Cu(111) - GGA[a]	0.27	0.26	3.49	7.6%
Pt(111) - LDA[b]	0.43	0.38	5.84	6.9%
Pt(111) - GGA[b]	0.29	0.25	5.84	4.6%
Al(111) - LDA[c]	0.24	0.23	3.39	7.0%

[a] present calculation

[b] Ref. 24

[c] Ref. 20

[d] Ref. 25

Fig. 1

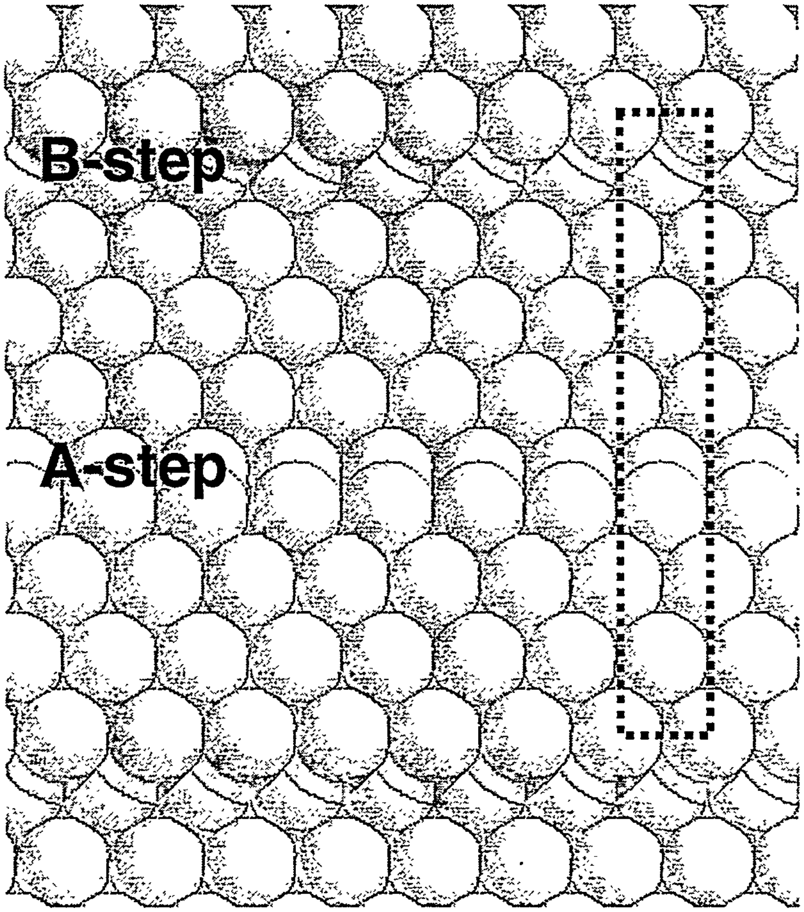
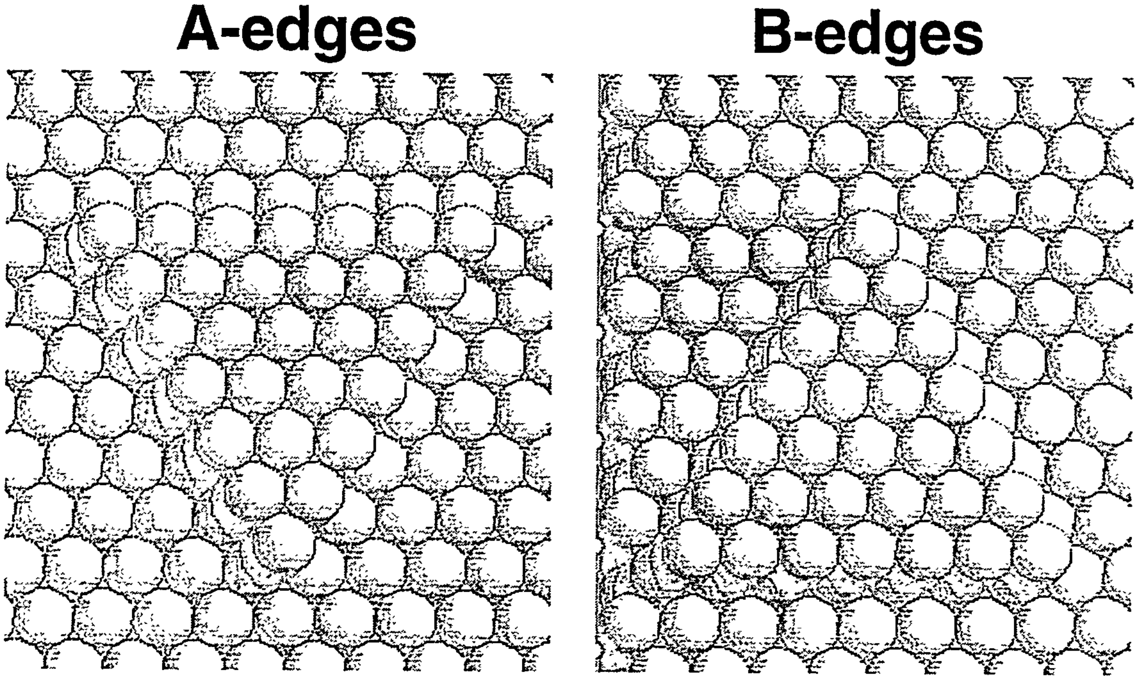


Fig. 2



A-edges

B-edges

Fig. 3