Vicinal Surfaces

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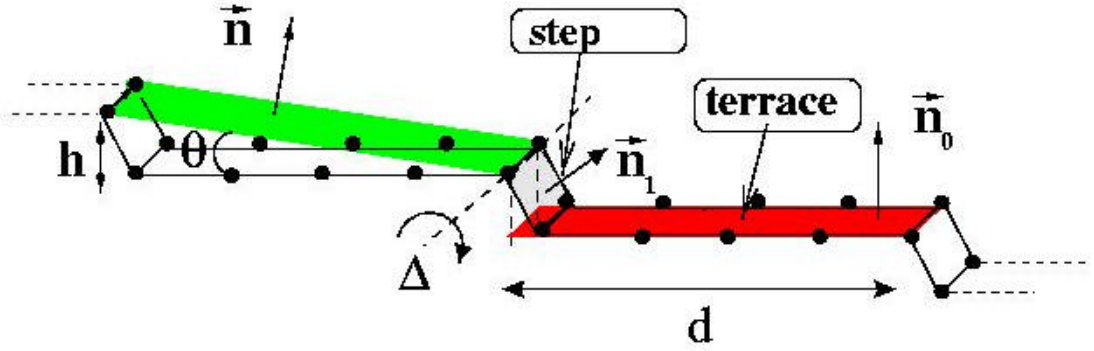

Overview

1) Introduction

2) Calculation Methods

Tight-Binding Empirical potential

3) Geometry and calculation details

4) Energetics of vicinal surfaces

Step and kink energy Step-step interaction

Effective Pair Potential Island shapes

5) Electronic Structure

6) Phonons

7) Stability of vicinal surfaces

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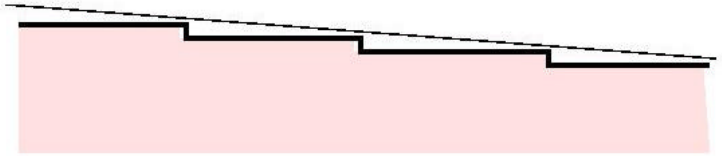
Why study vicinal surfaces?

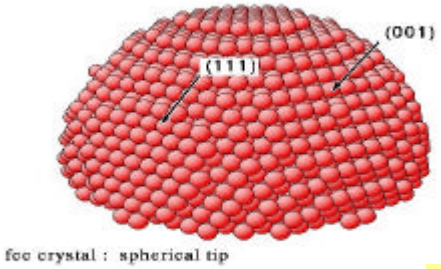
1) Any surface has steps



2) surface morphology

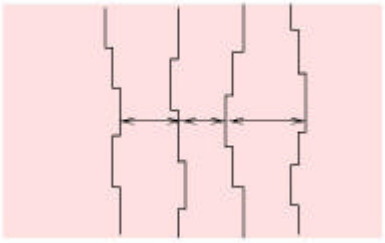
Crystal shape

from $g(j,q)$



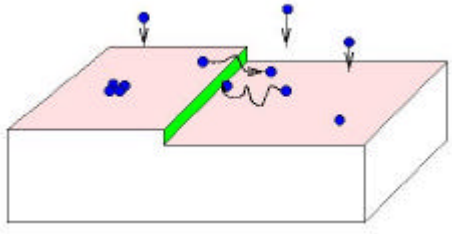
Step roughening transition

$T \uparrow \quad \Delta F_{step} \downarrow$



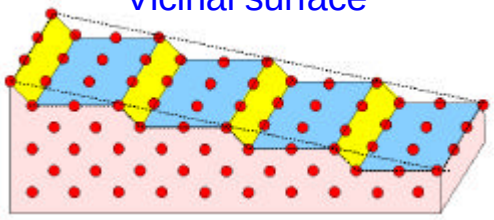
Epitaxial growth

Equilibrium shape of adislands



3) Stability with respect to faceting

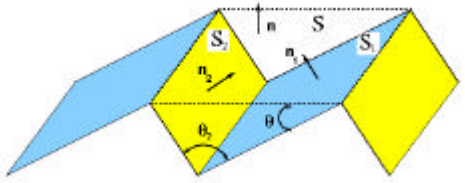
Vicinal surface



Monoatomic steps

OR

Faceted surface



« Factory roof »

Which model and what you get ?

Phenomenological description

- ★ Continuous model f(p)
- ★ Discrete Hamiltonian

→ *General behaviors*

Empirical potentials

- ★ EAM EMT
- ★ Second Moment

→ *Step energies, elastic step-step interaction, no QM*

Electronic structure methods

- ★ Ab-initio
- ★ Tight-binding

→ Step energies, step-step interaction, electronic structure

Tight-Binding Method

Hamiltonian

$$H = T + \sum_i V(r - R_i)$$

Basis

$$|il> \qquad l = s,\ p(x,y,z),\ d(xy, yz, zx, x^2 - y^2, 3z^2 - r^2)$$

- $< il \mid H \mid jm > \qquad i \neq j$

10 Hopping integrals

$$\begin{cases} sss, sps, sds, pps, ppp, dds, ddp, ddd = b_{SK} \\ b_{SK} = b_{SK}(R)\, f_c(R) \end{cases}$$

(2 center approximation) $R_{ij} // Oz$

- $< il \mid H \mid il >$

3 on-site terms

$$e_s, e_p, e_d \qquad \begin{cases} e_{il} = a_l + b_l r_i^{2/3} + c_l r_i^{4/3} + d_l r_i^2 \\ r_i = \sum_{j \neq i} r(R_{ij})\, f_c(R_{ij}) \end{cases}$$

orthogonal

$$< il \mid jm >= d_{ij} d_{lm}$$

Eigenvalue eq. $HX = eX$

Non-orthogonal

$$< il \mid jm >= S_{ij}^{lm}$$

Generalized eigenvalue eq. $HX = eSX$

Total Energy

$$E_{tot} = \sum_{nocc} \mathrm{E_n}$$

Local charge neutrality

$$e_{il} = e_{il}^0 + dV_i \quad \Rightarrow \quad E_{tot} = \sum_{nocc} \mathrm{E_n} - N \sum_i dV_i$$

Empirical Potential

Embedding potential

$$E = \sum_{i,\, ji \neq j} V(R_{ij}) f_c(R_{ij}) + \sum_i \underbrace{F(r_i)}$$

Embedding function

$$\underbrace{r_i = \sum_{j \neq i} g(R_{ij}) f_c(R_{ij})}$$

« density »

$r_i = Z_i^1 + Z_i^2 g_2$

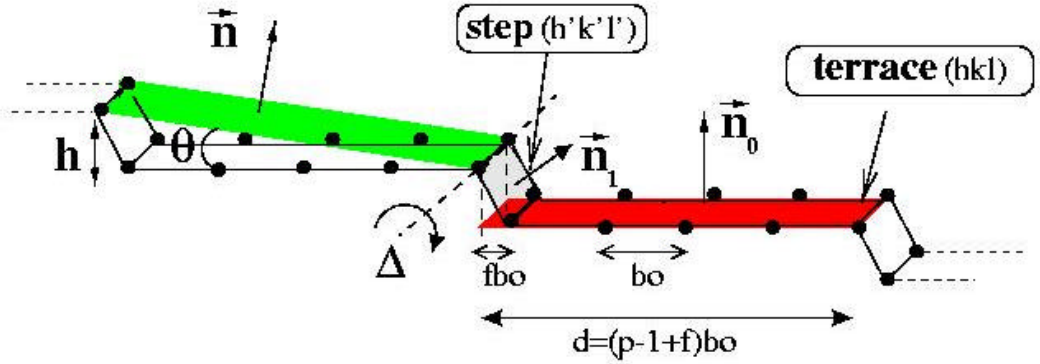
(rigid lattice) $g(R_1) = 1$

- Second Moment (SMA): $F(r) = -x\sqrt{r}$
- EAM/EMT: $F(r) = ...$
- Modified SMA: $F(r) = -xr^a$

Vicinal Surface

Geometry

$$p(hkl)\times(h'k'l')$$



energetics

$$\frac{g(\vec{n})}{\cos(q)} = g(\vec{n}_0) + \frac{\tan(q)}{h}\, b(q)$$

Surface energy per unit projected area

Step energy per unit length

Calculation procedure

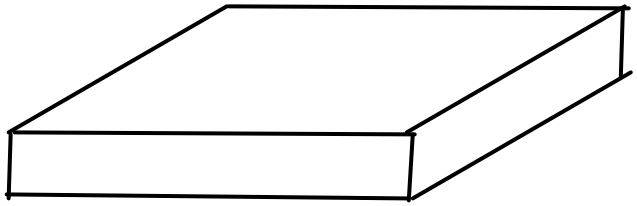
Convenient formulation

$$E_{step}(p) = E_S(p) - (p - 1 + f)E_S(\infty)$$

Step energy per step atom

Surface energy per surface atom

Slab geometry



$$E_S = \frac{E_{slab} - NE_{bulk}}{2}$$

Calculation details

Number of vicinal planes: 11xp
Fermi broadening: 0.2eV
Number of k points: 64
Energy convergence: 1meV

$$E(0) \approx E(T_{el}) - \frac{1}{2} T_{el} S(T_{el})$$

Step energies

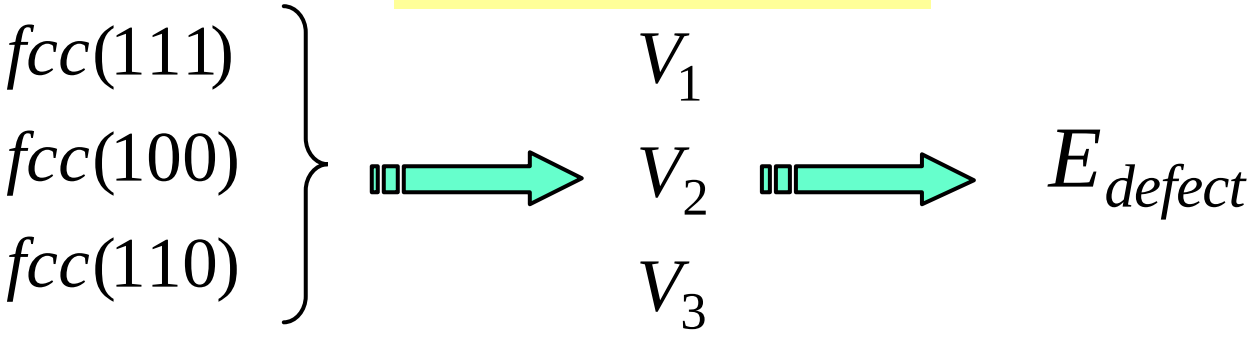
$$E^{\infty}_{step} = E_{step}(p \to \infty)$$

Vicinal surface		Step energy (eV/atom)						
	$p \to \infty$	TB		Effective Pair Potential				
				TB	Vitos	Methfessel	Eichler	Galanakis
Rh	$p(111)\times(100)$ **(A)**	**0.638**	$2V_1+4V_3$	**0.657**	**0.583**	**0.520**	**0.650**	**0.670**
	$p(111)\times(\bar{1}11)$ **(B)**	**0.645**	$2V_1+4V_3$	**0.657**	**0.583**	**0.520**	**0.650**	**0.670**
	$p(100)\times(111)$	**0.393**	V_1+2V_2	**0.407**	**0.288**	**0.265**	**0.295**	**0.285**
	$p(100)\times(010)$	**0.747**	$2V_1+2V_2$	**0.738**	**0.550**	**0.480**	**0.580**	**0.596**
	$p(110)\times(111)$	**0.056**	V_2+2V_3	**0.035**	**0.043**	**0.070**	**0.045**	**0.011**
Pd	$p(111)\times(100)$ **(A)**	**0.425**	$2V_1+4V_3$	**0.429**	**0.460**	**0.423**		**0.500**
	$p(111)\times(\bar{1}11)$ **(B)**	**0.432**	$2V_1+4V_3$	**0.429**	**0.460**	**0.423**		**0.500**
	$p(100)\times(111)$	**0.289**	V_1+2V_2	**0.295**	**0.106**	**0.222**		**0.298**
	$p(100)\times(010)$	**0.536**	$2V_1+2V_2$	**0.533**	**0.265**	**0.427**		**0.548**
	$p(110)\times(111)$	**0.027**	V_2+2V_3	**0.006**	**0.045**	**0.015**		**0.024**
Cu	$p(111)\times(100)$ **(A)**	**0.348**	$2V_1+4V_3$	**0.347**	**0.380**			**0.426**
	$p(111)\times(\bar{1}11)$ **(B)**	**0.345**	$2V_1+4V_3$	**0.347**	**0.380**			**0.426**
	$p(100)\times(111)$	**0.191**	V_1+2V_2	**0.192**	**0.200**			**0.241**
	$p(100)\times(010)$	**0.352**	$2V_1+2V_2$	**0.359**	**0.363**			**0.456**
	$p(110)\times(111)$	**0.060**	V_2+2V_3	**0.020**	**0.046**			**0.011**

Effective Pair Potential

$$E_{defect} = \sum_{i=1}^{N} n_i^{eff} V_i$$

(Vitos et al.)



- ★ EPP works suprisingly well
- ★ Large discrepancy between different calculations
- ★ Good agreement for (111) surfaces
- ★ Very small step energy for (110)

BUT

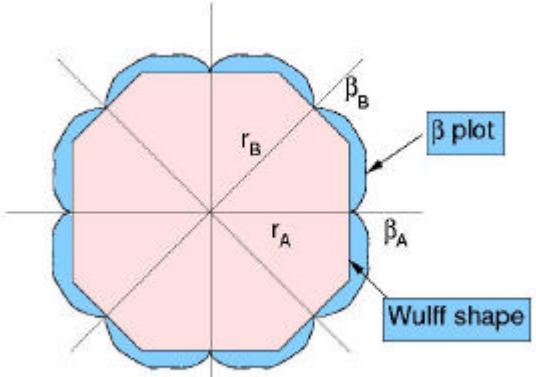
- ★ No distinction between A and B steps
- ★ No step-step interaction

Pair interactions

	Surface energies (ev/atom)							
	(111)	(100)	(110)	V_1	V_2	V_3	Reference	V_1^0
Rh	1.091	1.379	2.112	0.332	0.038	-0.001	This work	0.352
	1.002	1.310	1.919	0.262	0.013	0.015	Vitos et al	0.324
	0.99	1.27	1.84	0.215	0.025	0.023	Methfessel et al	0.313
	1.11	1.47	2.13	0.285	0.005	0.020	Eichler et al	0.360
	1.034	1.404	2.047	0.311	-0.013	0.012	Galanakis et al	0.344
Pd	0.655	0.828	1.317	0.238	0.029	-0.011	This work	0.217
	0.824	1.152	1.559	0.159	-0.027	0.036	Vitos et al	0.269
	0.68	0.89	1.33	0.205	0.008	0.003	Methfessel et al	0.223
	0.822	1.049	1.596	0.250	0.014	0.000	Galanakis et al	0.269
Cu	0.581	0.748	1.121	0.166	0.013	0.004	This work	0.188
	0.707	0.906	1.323	0.163	0.018	0.014	Vitos et al	0.224
	0.675	0.874	1.327	0.215	0.013	-0.001	Galanakis et al	0.221

Island Shapes

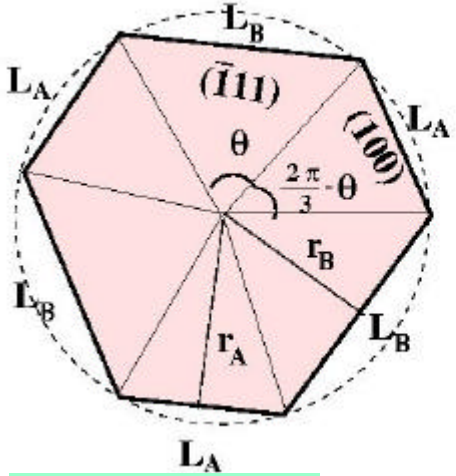
β-plot



$$\frac{r_A}{r_B} = \frac{b_A}{b_B}$$

Island shape

Fcc(111)

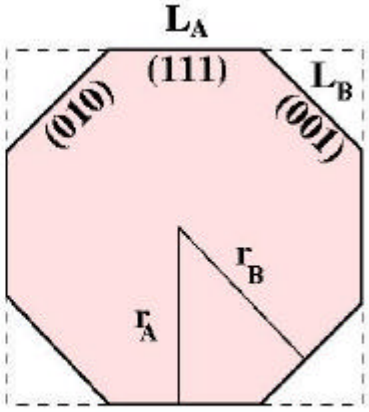


$b_A = b_B$

Regular hexagon

$$\frac{L_A}{L_B} = \frac{2 - b_A / b_B}{2 b_A / b_B - 1}$$

$$L_A > L_B \Rightarrow b_A < b_B$$



$$\frac{L_A}{L_B} = \frac{\sqrt{2} - b_A / b_B}{\sqrt{2} b_A / b_B - 1}$$

Fcc(100)

$\sqrt{2} b_A / b_B < 1$

square

$\sqrt{2} b_A / b_B > 1$

broken corners square

Comparison with experiment

Only available data for Copper

Fcc(111)

Experiment

$\overline{E_{step}^{111}} = 0.27$ **eV/step atom**

$\frac{E_{step}^{A}}{E_{step}^{B}} = 1.1\% + 1$

Tight-binding

$\overline{E_{step}^{111}} = 0.\mathbf{346}$ **eV/step atom**

$\frac{E_{step}^{A}}{E_{step}^{B}} = 0.9\% + 1$

Fcc(100)

Experiment

$E_{step}^{A} = 0.22\ eV/step\ atom$

$\frac{r_B}{r_A} = \frac{E_{step}^{B}}{\sqrt{2}E_{step}^{A}} = 1.24$

Tight-binding

$E_{step}^{A} = 0.191\ eV/step\ atom$

$\frac{r_B}{r_A} = \frac{E_{step}^{B}}{\sqrt{2}E_{step}^{A}} = 1.30$

Step-step interaction

Different types of interactions

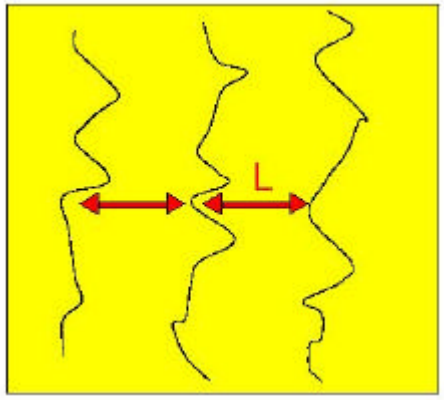
entropic

Non-crossing of steps

$1/L^2$

elastic $1/L^2$

Atomic relaxation



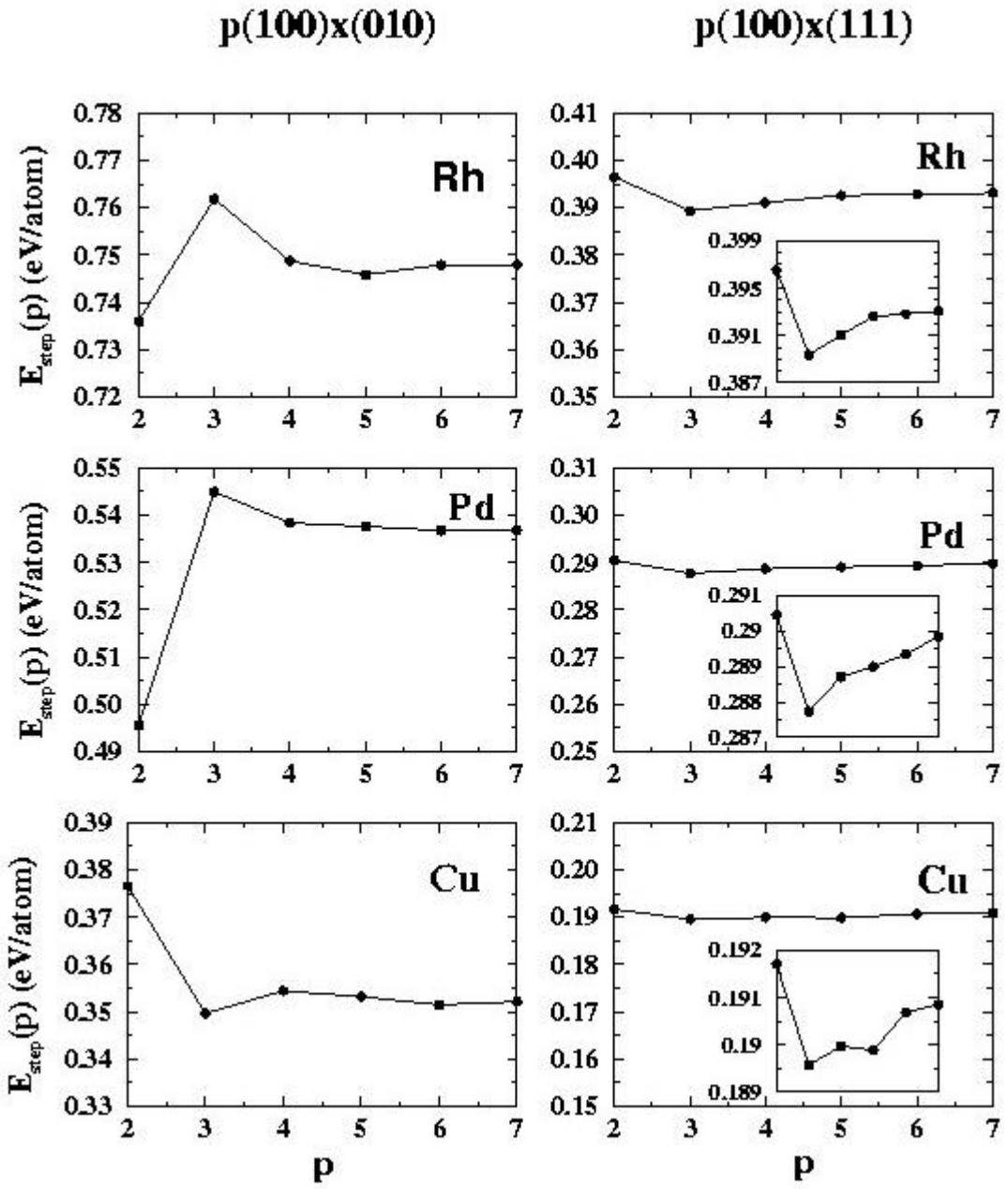
$1/L^2$ **dipole-dipole**

Electric dipole at step edges

$$\frac{\cos(2k_F L + d)}{L^n}$$

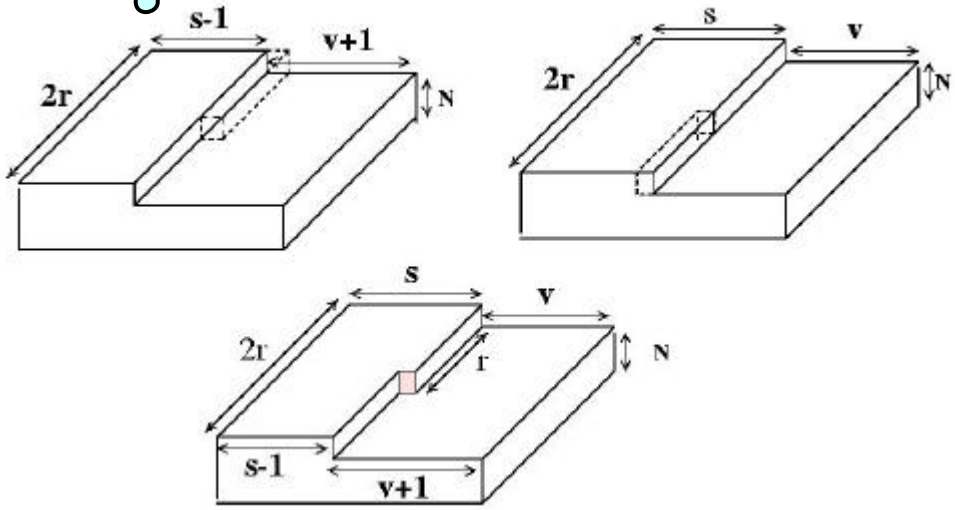
electronic

Friedel oscillation


p(100)x(010)
p(100)x(111)
Rh
Pd
Cu
$E_{step}(p)$ (eV/atom)
p

kink energies

Supercell geometry



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

(terrace)x(ledge)	Rh	Pd	Cu		
			TB	Other Calc.	Experiments
$(111)\times(100)$	0.339	0.249	0.143	0.092	0.113±0.007
$(111)\times(\bar{1}11)$	0.329	0.242	0.148	0.117	0.121±0.007
$(100)\times(111)$	0.349	0.247	0.146	0.139	0.123 ; 0.129
V_1	0.332	0.238	0.166		

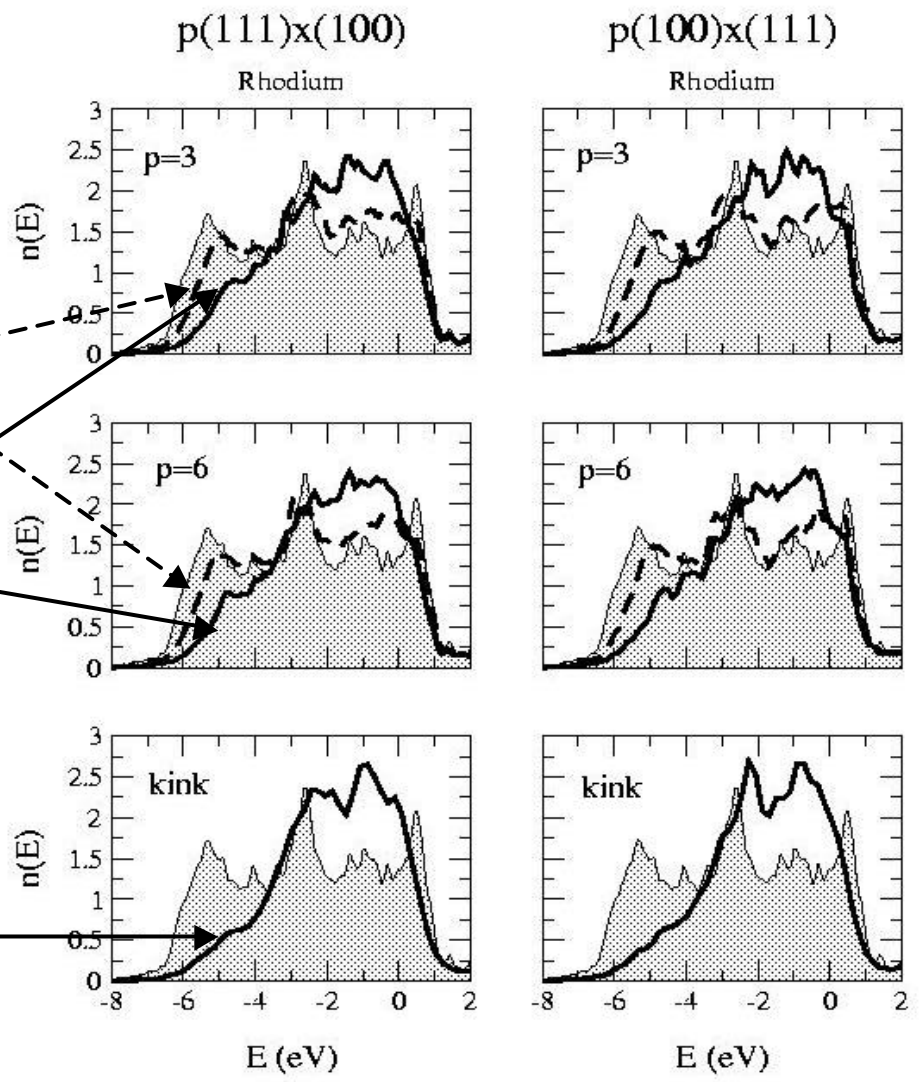
Electronic structure

Local density of states

surface sites

step sites

kink sites

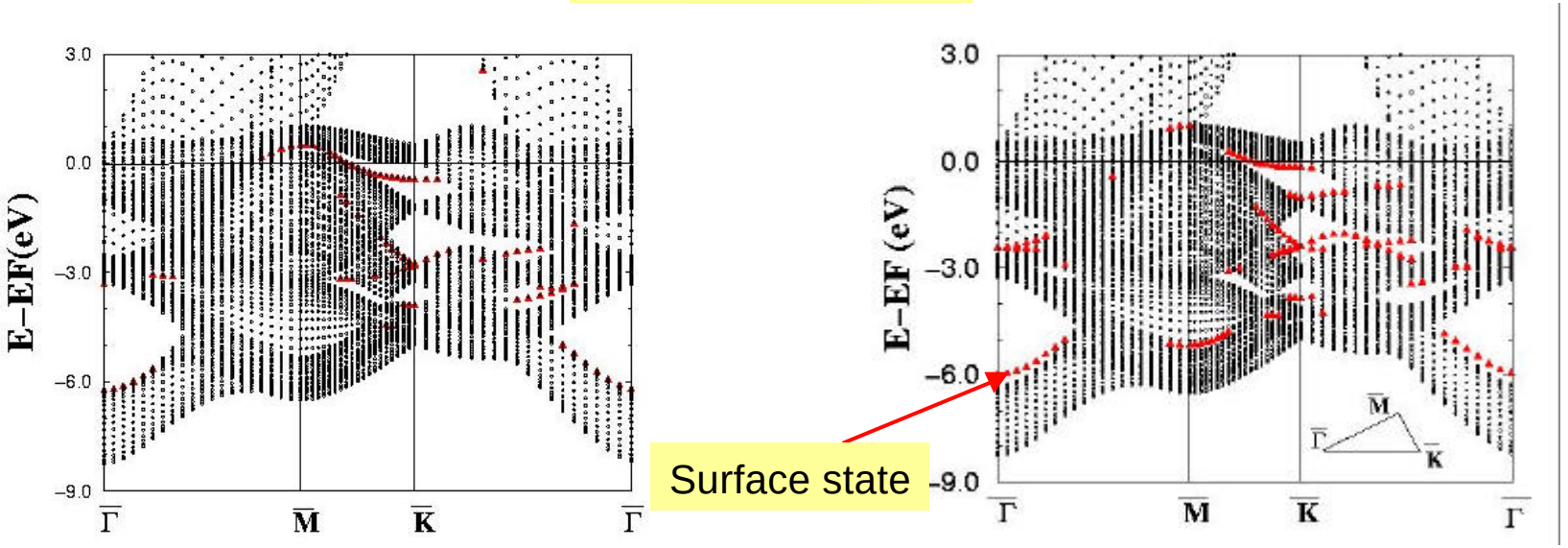


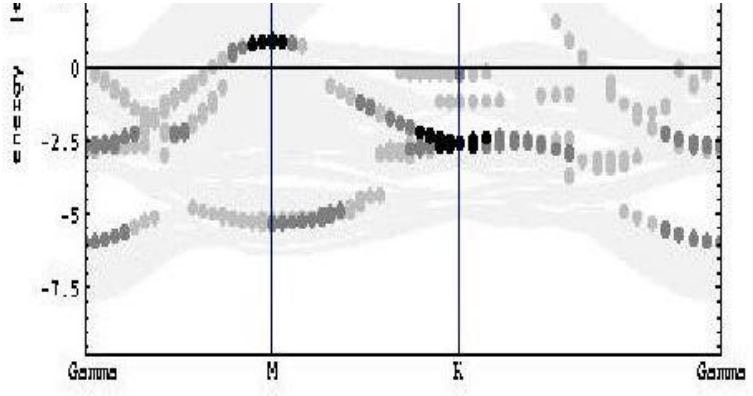
Electronic structure

No LCN

Rh(111) surface

LCN

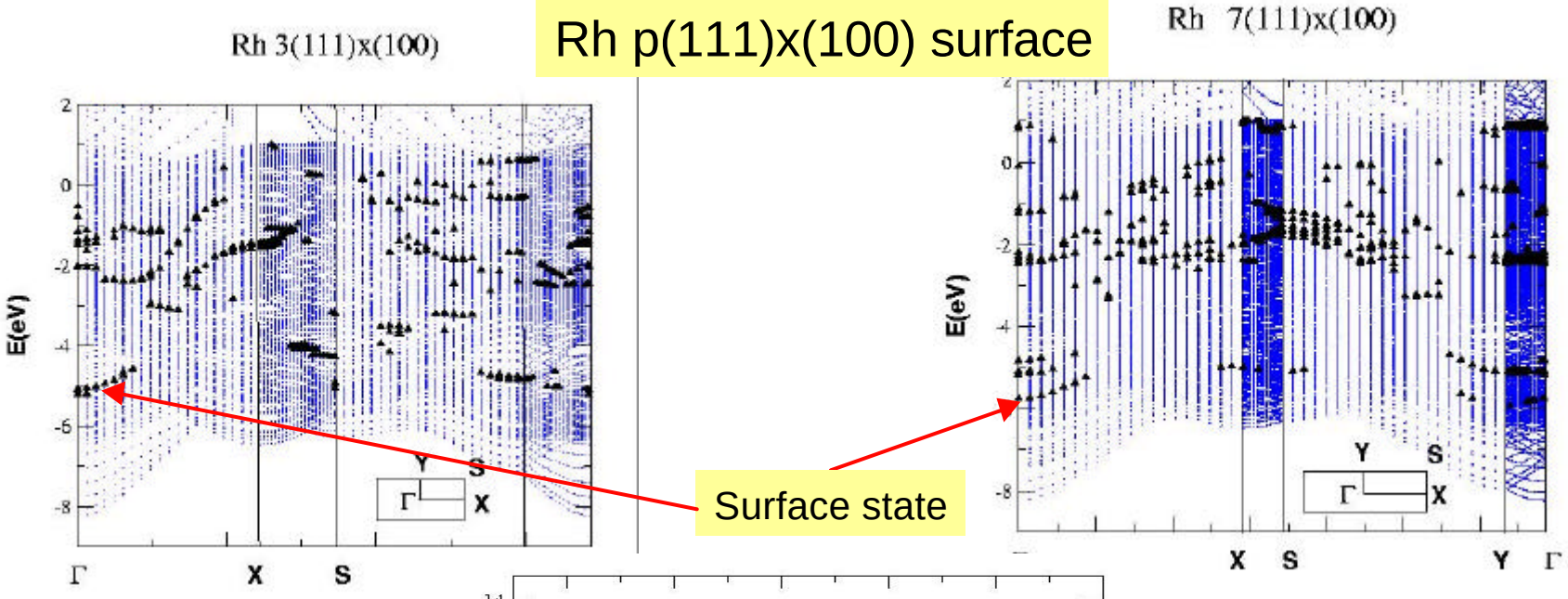




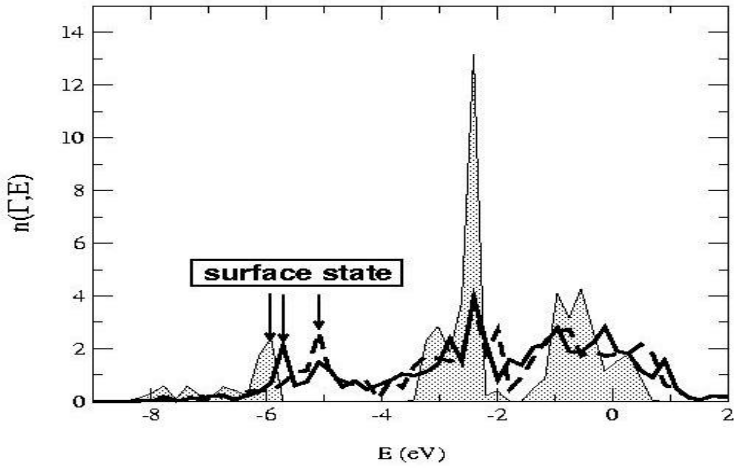
Ab-initio (Eichler)

Electronic structure

Rh p(111)x(100) surface



Spectral density of states at Γ



Phonons

Generalized Second Moment Potential

$$E = A \sum_{i,\, ji \neq j} (R_0 / R_{ij})^{p} f_c(R_{ij}) - x \sum_i \left(\sum_{j \neq i} \exp(-2q(R_{ij} / R_0)) f_c(R_{ij}) \right)^{2/3}$$

Fit on
- cohesive energy E_c
- bulk Modulus B
- shear moduli C, C'

$R_c = 4\ \text{Å}$ *(2nd neighbours)*

Copper

$A = 0.206\,eV$

$x = 1.102\,eV$

$p = 7.206$

$q = 2.220$

Harmonic approximation

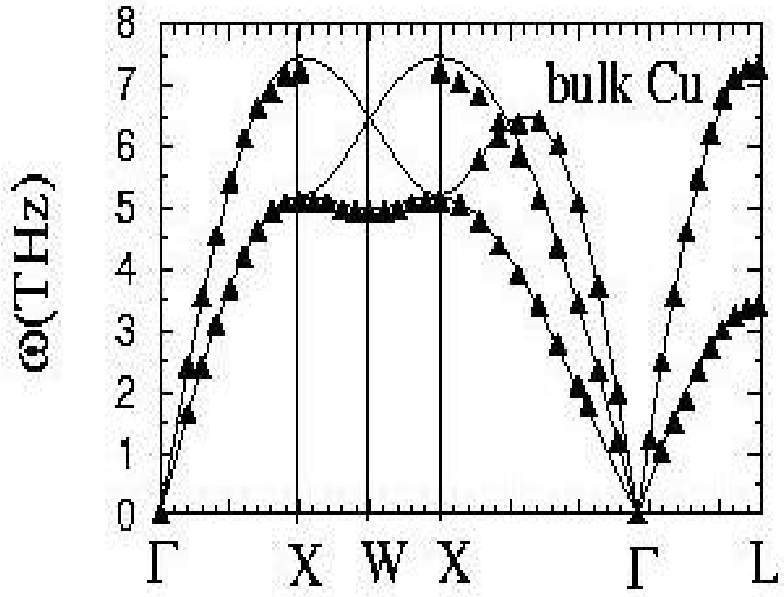
Energy minimization: conugate gradient algorithm

Dynamical Matrix

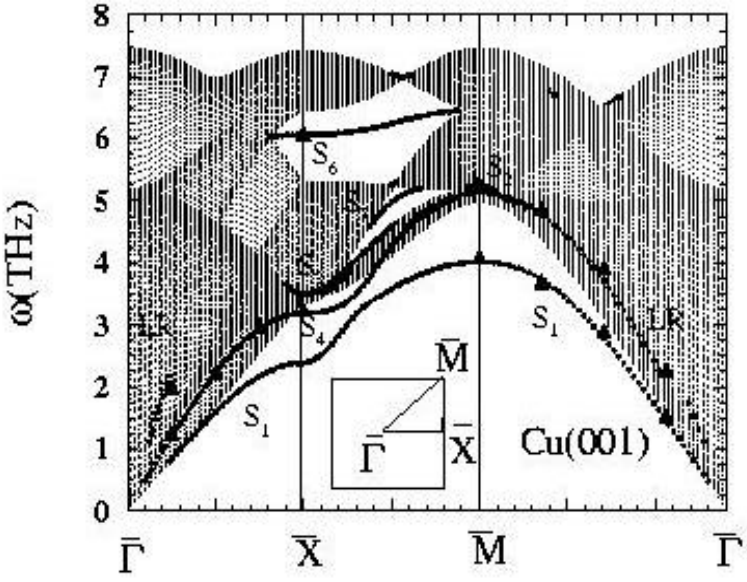
$$D_{ij}^{a\,b} = \frac{1}{M} \frac{\partial^2 E}{\partial r_i^a \, \partial r_j^b}$$

Vibrational spectra

Bulk Cu

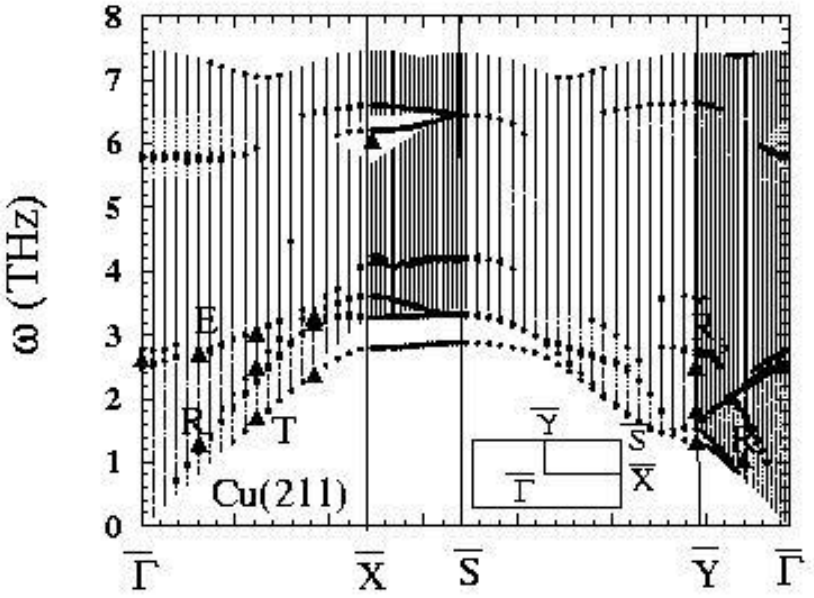


Cu(001)



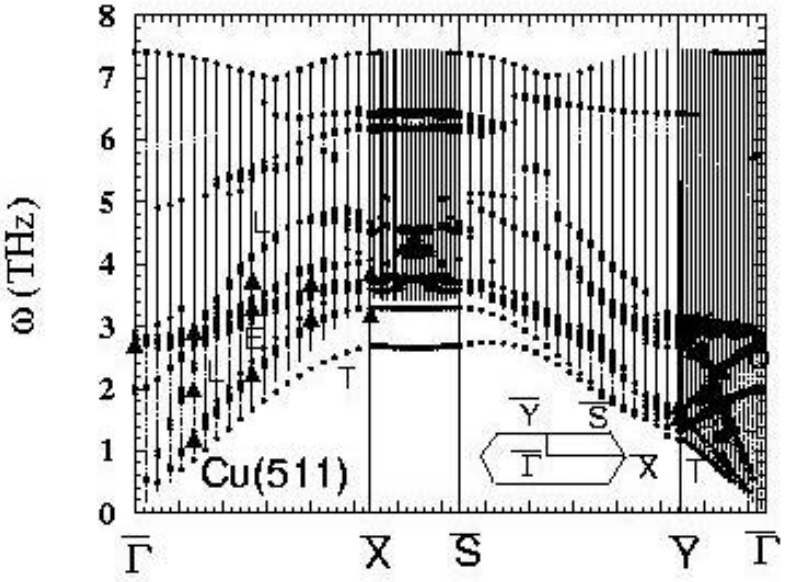
Vibrational spectra

Cu (211)



3(111)×(100)

Cu (511)



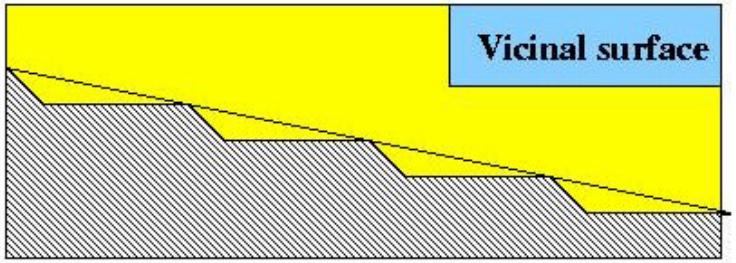
3(100)×(111)

Stability of vicinal surfaces

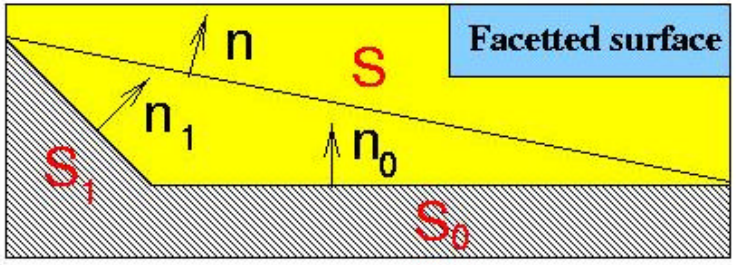
Faceting or not faceting?

(that is the question)

$$gS < g_0 S_0 + g_1 S_1$$



$$gS > g_0 S_0 + g_1 S_1$$



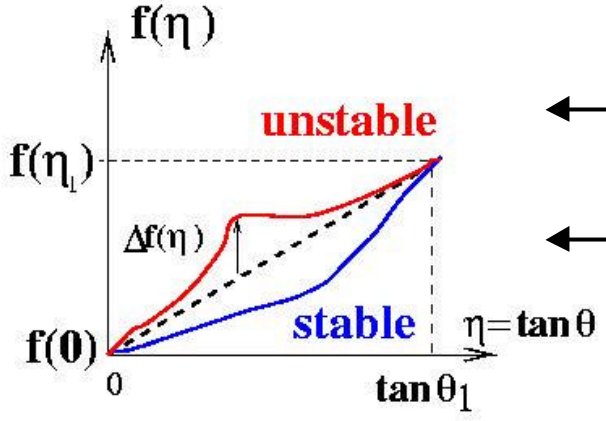
Same average orientation

$$\left(h = \tan(q) \;,\quad f(h) = \frac{g(q)}{\cos(q)} \right)$$

Position of $f(h)$ wrt straight-line

$$f(h) \gtrless (1 - h/h_1) f(0) + h/h_1 f(h_1)$$

$$q = (\vec{n}, \vec{n}_0), q_1 = (\vec{n}_1, \vec{n}_0)$$



$\Delta f(?) > 0$

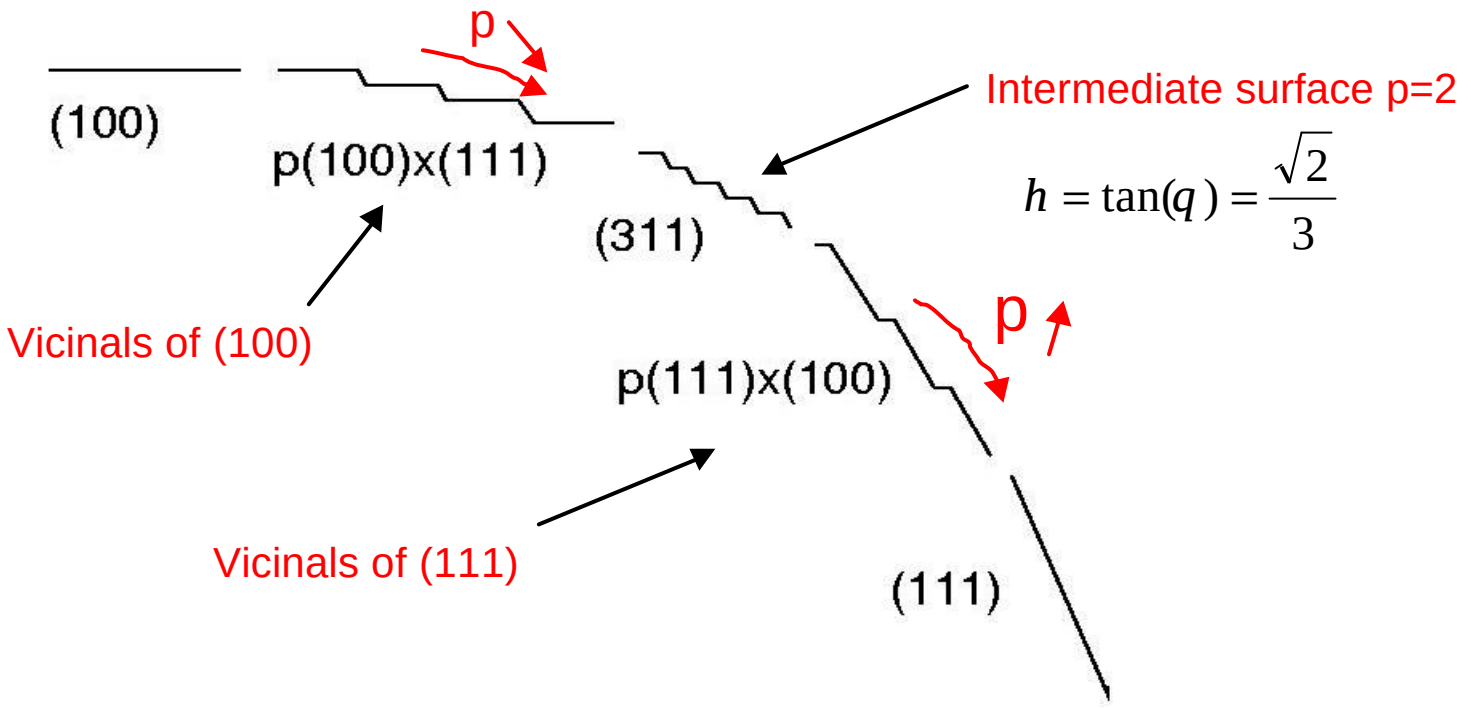
$\Delta f(?) < 0$

Stability of vicinal surfaces

p(100)x(111) and p(111)x(100)

(2p-1,1,1) (p+1,p-1,p-1)

$h = \tan(q) = 0$



$h = \tan(q) = \sqrt{2}$

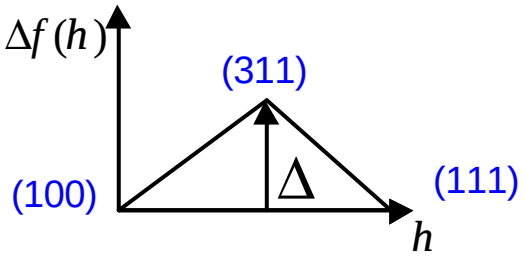
Stability of vicinal surfaces

Rigid lattice

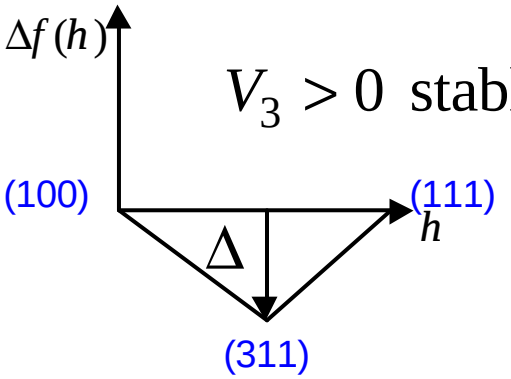
Pair potential

$R_c < R_5$ No step interaction

$\Delta \propto -V_3$



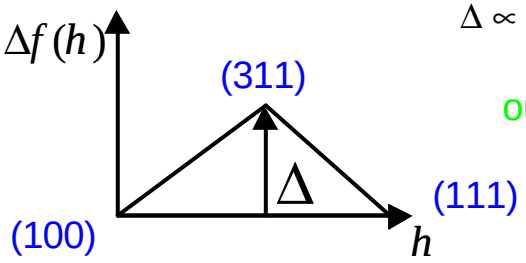
$V_3 < 0$ unstable



Embedding potential

$R_c < R_3$ No step interaction

$\frac{d^2F}{dr^2} > 0$



$\Delta \propto [F(7+g_2) - F(9+3g_2)] - [F(8+5g_2) - F(10+5g_2)]$

outer edge (111) (100) inner edge

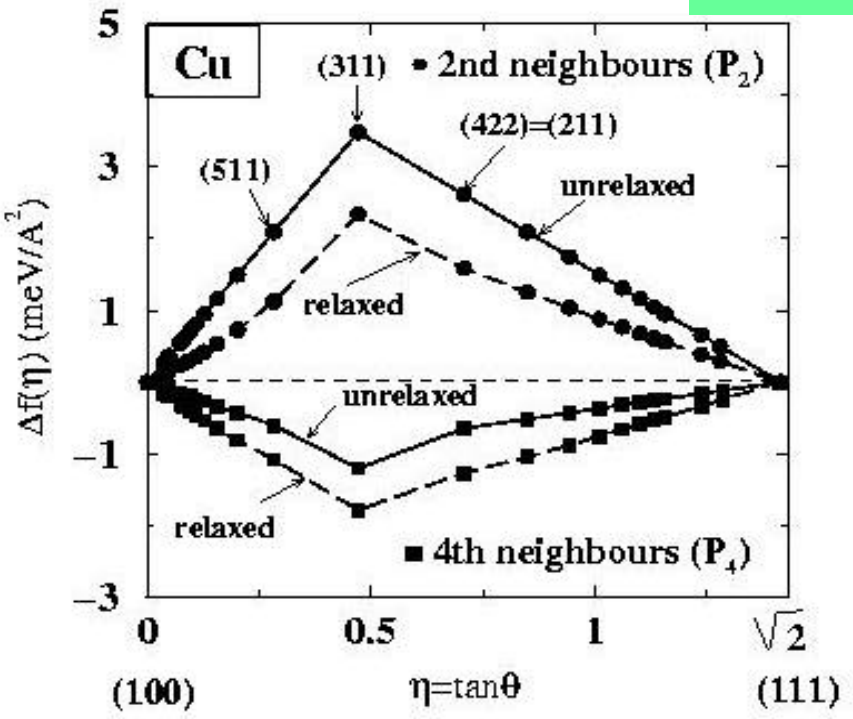
Always unstable

Stability of vicinal surfaces

Embedding potential

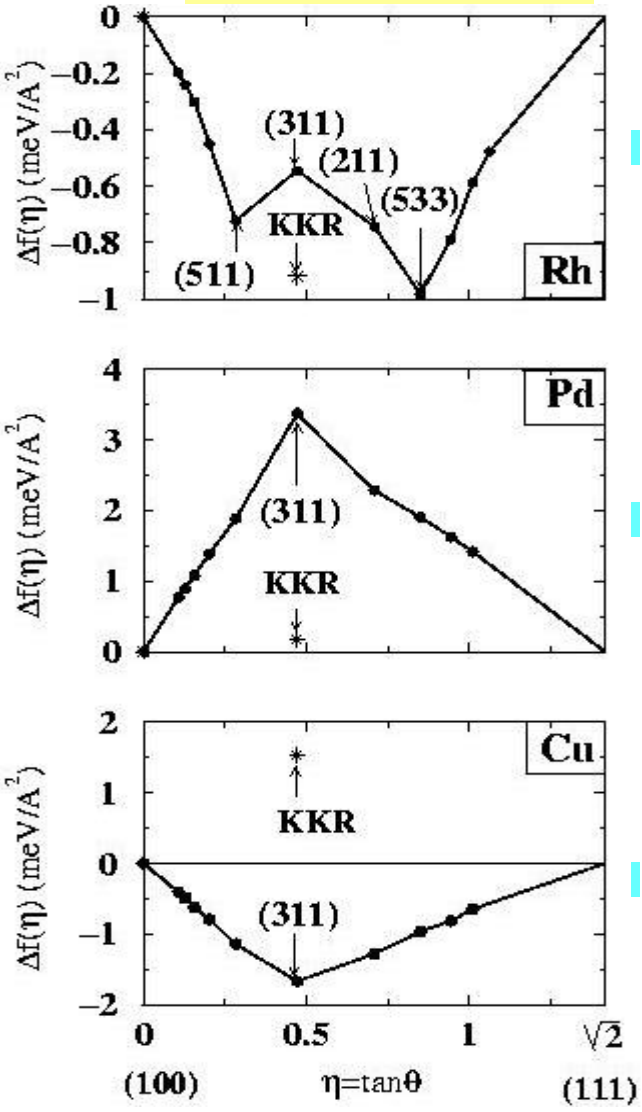
Effect of

- further neighbours → ★ Short range Interaction ★ influence on the stability
- atomic relaxation → ★ Repulsive elastic interaction ★ positive curvature ★ small influence on stablity



Stability of vicinal surfaces

Tight-binding



Great variety of scenarii

Faceting between 2 vicinals

Faceting between (100) and (111)

Vicinal surface stable

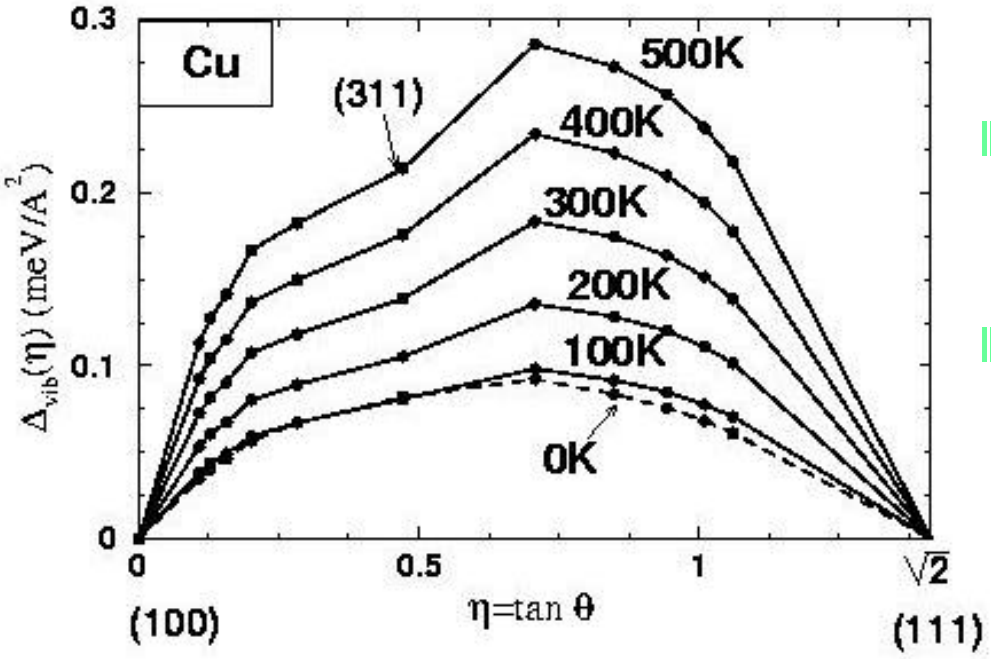
Stability of vicinal surfaces

What about Phonons?

From Frenken and Stoltze: stabilization
but Einstein model, S only, and one term missing

Vibrational Free energy

$$F_{vib} = 3k_B T \int_0^{+\infty} \ln[2sh(\frac{\hbar w}{2k_B T})]n(w)dw$$



Very small effect

destabilization effect

Conclusions

Vicinal surfaces have a rich and subtle behavior

Empirical potentials lead to a too schematical behavior

Only calculations based on the determination of the electronic states allow to account for the diversity of experimental possibilities.