

# Crystal Growth: Physics, Technology and Modeling

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## Lecture 4. Properties of crystal surfaces

<http://www.unipress.waw.pl/~stach/cg-2021-22>

# Bonding in crystals

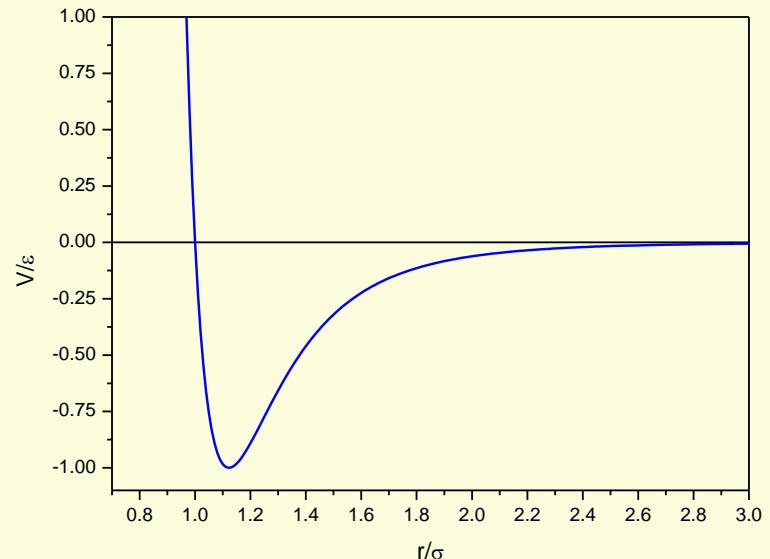
Condensed phases (solid, liquid) – enthalpy of the system is negative

Interaction potential – e.g. Lennard-Jones potential (noble gases)

$$V(r) = \epsilon \left[ \left( \frac{r}{\sigma} \right)^{-12} - \left( \frac{r}{\sigma} \right)^{-6} \right]$$

$\epsilon$  – Interaction potential strength

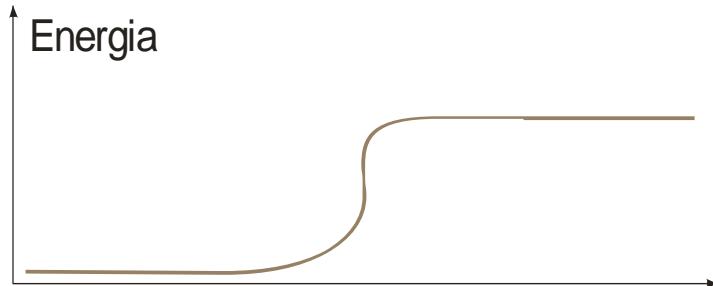
$\sigma$  – Interaction potential range



Interactions – strength and range may be different.

In ionic crystal – range is essentially Infinite (Coulomb force)

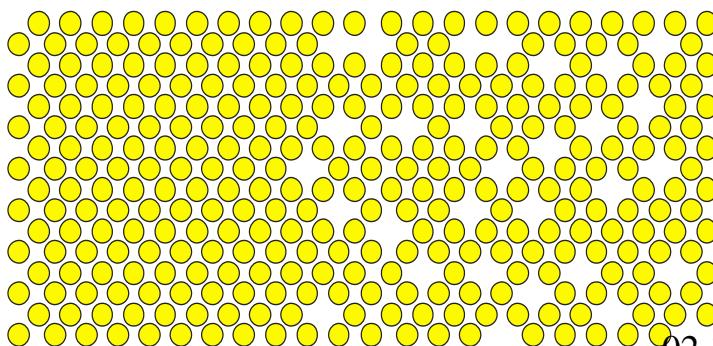
# Surface layers – energetic properties



- **Large size crystals (above 20 nm in size)** – crystal body can be divided into interior and surface layer

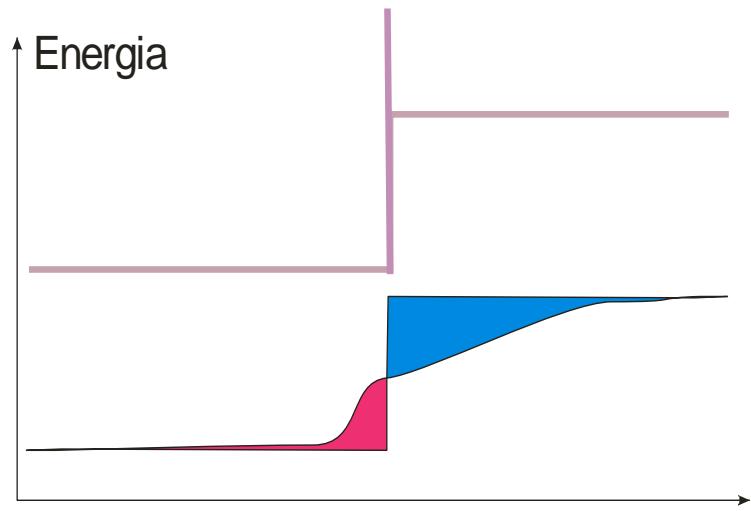


- **Interior** – is uniform
- **Surface layer** – energy, density are changed, different from uniform properties
- **Gibbs description** – uniform bulk & additional surface contribution



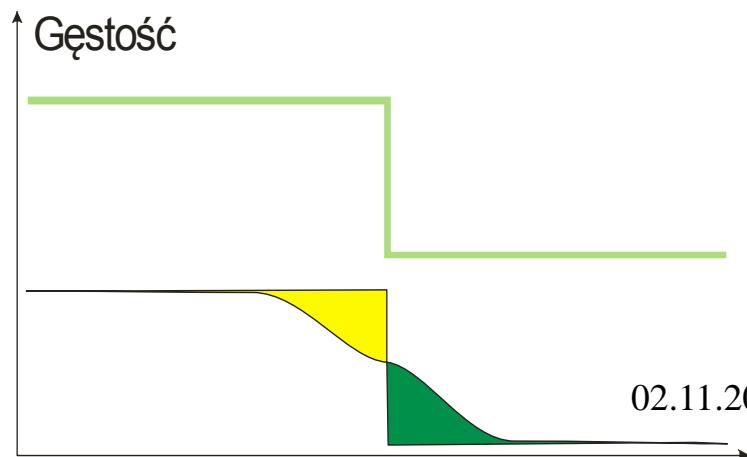
## Gibbs surface model

- **Gibbs model** – uniform properties of the bulk and additional surface density associated with the surface



*Selection of the position of Gibbs surface :*

- *Surface energy density disappears*
- *Surface mass density disappears*



## Standard Gibbs selection of the surface – single component system

- Mass –contribution from the volume terms only

$$M = \int_{V_\alpha} \rho(r) d^3r + \int_{V_\beta} \rho(r) d^3r$$

No contribution from surface term.

- Free energy – contribution from the volume and the surface terms

$$F = \int_{V_\alpha} f_\alpha(r) d^3r + \int_{V_\beta} f_\beta(r) d^3r + \int_S \gamma(r) d^2r$$

- Free energy – Gibbs model

$$F = f_\alpha V_\alpha + f_\beta V_\beta + \gamma A$$

$V_\alpha, V_\beta$  - phase volume  
 $A$  – interface area

For multi-component system the unique selection of the mass surface free position for all components is not possible.

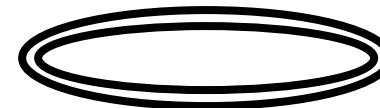
## Surface tension and surface free energy density (liquids)

- Surface free energy density – energy for unit of the surface



$$F = \int_A \gamma(r) d^2r \approx \gamma A$$

- Surface tension – the force acting on the unit of circumference



The work used by external force to increase surface area ( $A \rightarrow A + \delta A$ )

$$\Delta W = \oint_L \sigma \delta x dr = \sigma \delta A$$

The surface energy change ( $A \rightarrow A + \delta A$ )

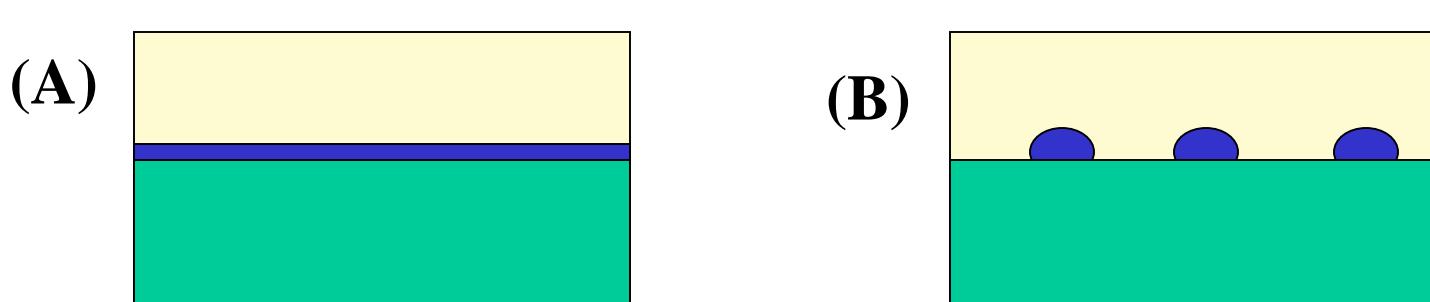
$$\Delta F = \gamma \delta A$$

$$\Delta W = \Delta F \quad \longrightarrow$$

$$\sigma = \gamma$$

## Surface wetting

- Consider three uniform, isotropic systems: **gas(1)**, **solid(2)** and **liquid(3)**
- Interface energy is described by three parameters:  $\gamma_{12}$ ,  $\gamma_{13}$ ,  $\gamma_{23}$ .

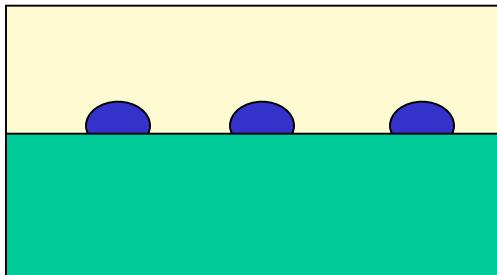


- The condition for full wetting of the surface by liquid is

$$\gamma_{13} > \gamma_{12} + \gamma_{23}$$

## Partial surface wetting –wetting angle

- **Partial surface (A) wetting occurs when**

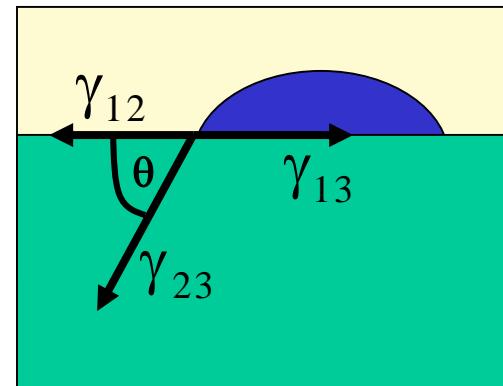


$$\gamma_{13} < \gamma_{12} + \gamma_{23}$$

$$\gamma_{23} > \gamma_{12} + \gamma_{13} \rightarrow \gamma_{13} > \gamma_{12} - \gamma_{23}$$

- **Wetting angle is defined as**

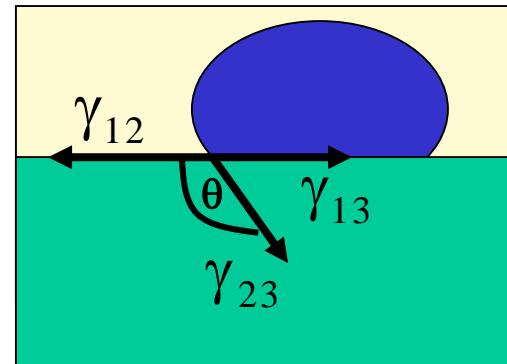
$$\gamma_{13} = \gamma_{12} + \gamma_{23} \cos(\theta)$$



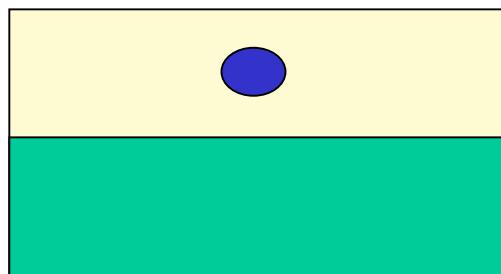
## Absence of wetting

- Wetting angle is defined by the relation

$$\gamma_{13} = \gamma_{12} + \gamma_{23} \cos(\theta)$$



- Absence of wetting occurs when



$$\gamma_{12} < \gamma_{23} + \gamma_{13}$$

## Isothermal, isochoric stability conditions

- Stability condition – minimal Helmholtz free energy F

$$\delta F \geq 0 \quad \delta F = -p_\alpha \delta V_\alpha - p_\beta \delta V_\beta + \gamma \delta A + \mu_\alpha \delta N_\alpha + \mu_\beta \delta N_\beta$$

The constraints

$$N_\alpha + N_\beta = \text{const}$$

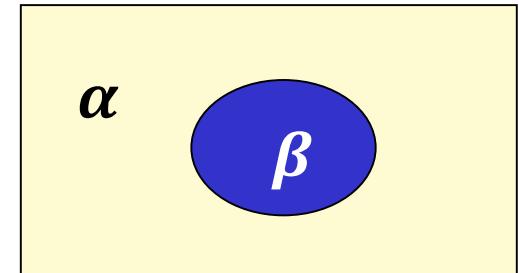
$$\delta N_\alpha = -\delta N_\beta$$

$$V_\alpha + V_\beta = \text{const}$$

$$\delta V_\alpha = -\delta V_\beta$$

$$T = \text{const}$$

$$\delta T = 0$$



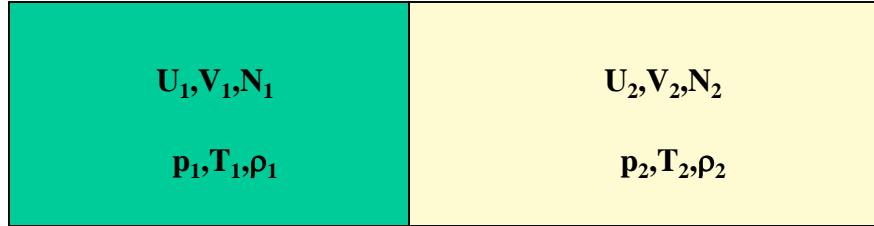
- Stability equations (equilibrium conditions)

$$p_\alpha = p_\beta + \gamma \frac{\delta A}{\delta V_\alpha}$$

$$\mu_\alpha(p_\alpha, T) = \mu_\beta(p_\beta, T)$$

*Equilibrium state depends on the shape*

## Flat surface



- **Equilibrium conditions**

$$p_\alpha = p_\beta + \gamma \frac{\delta A}{\delta V_\alpha} \quad \mu_\alpha(p_\alpha, T) = \mu_\beta(p_\beta, T)$$

- Flat surface – its area could be kept constant under volume change of the phases

$$\frac{\delta A}{\delta V_\alpha} = \frac{\delta A}{\delta V_\beta} = 0$$

*The equilibrium conditions do not depend on the size – these conditions are tabulated in phase diagrams*

$$p_\alpha = p_\beta = p \quad T_\alpha = T_\beta = T$$

## Curved surface – isotropic case

- Equilibrium conditions

$$p_\alpha = p_\beta + \gamma \frac{\delta A}{\delta V_\alpha} \quad \mu_\alpha(p_\alpha, T) = \mu_\beta(p_\beta, T)$$

- Isotropic case - sphere

$$V = \frac{4\pi R^3}{3}$$

$$A = 4\pi R^2$$

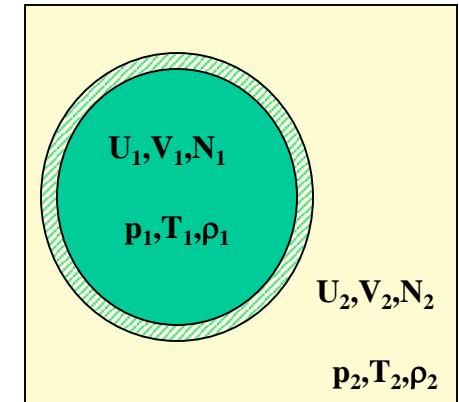
$$\frac{\delta A}{\delta V} = \frac{2}{R} = \frac{1}{\kappa_\alpha} + \frac{1}{\kappa_\beta}$$

$\kappa_\alpha, \kappa_\beta$  - surface curvatures

The equilibrium conditions do depend on the size

$$p_\alpha = p_\beta + \frac{2\gamma}{R}$$

$$T_\alpha = T_\beta \neq T_{PT}$$

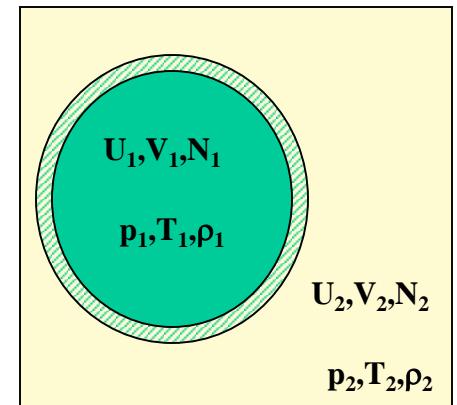


## Curved surface – Gibbs-Thompson effect

- Equilibrium condition

$$p_\alpha = p_\beta + \frac{2\gamma}{R}$$

- Pressure change – chemical equilibrium condition is changed



$$\mu_\alpha(p + dp, T + dT) = \mu_\beta(p, T + dT)$$

Gibbs - Thompson effect – change of equilibrium temperature of the curved surface

## Gibbs – Thompson effect

- Flat surface

$$\mu_\alpha(p, T) = \mu_\beta(p, T)$$

- Linear expansion

$$vdp - s_\alpha dT = -s_\beta dT$$



- Curved surface

$$\mu_\alpha(p + dp, T + dT) = \mu_\beta(p, T + dT)$$

$$dT = \frac{vdp}{s_\alpha - s_\beta} = \frac{T_{PT}dp}{L}$$

$$dp = \frac{2\gamma}{R}$$



$$dT = \frac{2T_{PT}\gamma}{LR} = \frac{2T_{PT}d_o}{R}$$

Gibbs – Thompson effect – curvature caused equilibrium temperature change

$$T(R) = T_{PT} \left( 1 - \frac{2d_o}{R} \right)$$

$$d_o = \frac{\gamma}{L_{PT}} = \frac{\gamma}{T_{PT}(s_\alpha - s_\beta)}$$

L – Latent heat of phase transition for volume unit

$d_o$  - Capillary length

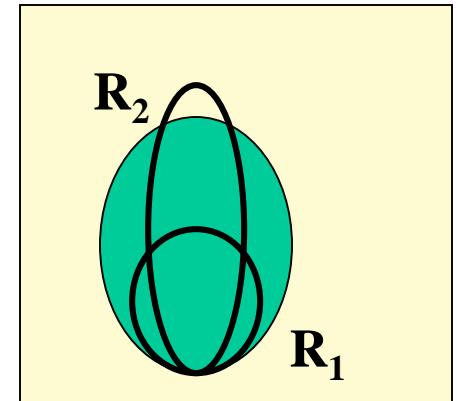
## Curved surface – anisotropic case

- Equilibrium condition

$$p_\alpha = p_\beta + \gamma(\theta, \varphi) \left[ \frac{1}{R_1} + \frac{1}{R_2} \right] = p_\beta + \gamma(\theta, \varphi)[\kappa_1 + \kappa_2]$$

- Two curvatures causes the chemical potential difference

$$\mu_\alpha(p + dp, T + dT) = \mu_\beta(p, T + dT)$$



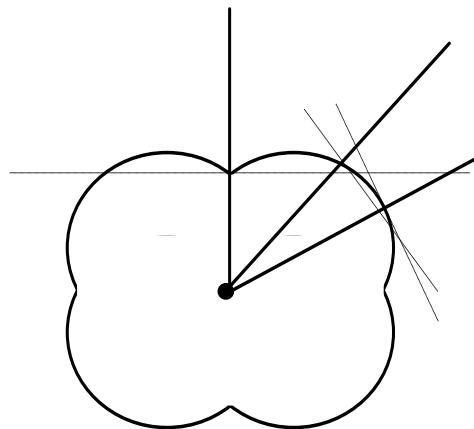
Gibbs – Thompson effect – curvature caused equilibrium temperature change

$$T(R) = T_{PT} \left( 1 - \left[ \frac{d_1(\theta, \varphi)}{R_1} + \frac{d_2(\theta, \varphi)}{R_2} \right] \right)$$

$$d_{1,2}(\theta, \varphi) = \frac{\gamma(\theta, \varphi)}{L_{PT}} = \frac{\gamma(\theta, \varphi)}{T_{PT}(s_\alpha - s_\beta)}$$

## Anisotropic surfaces – the surfaces of real crystals

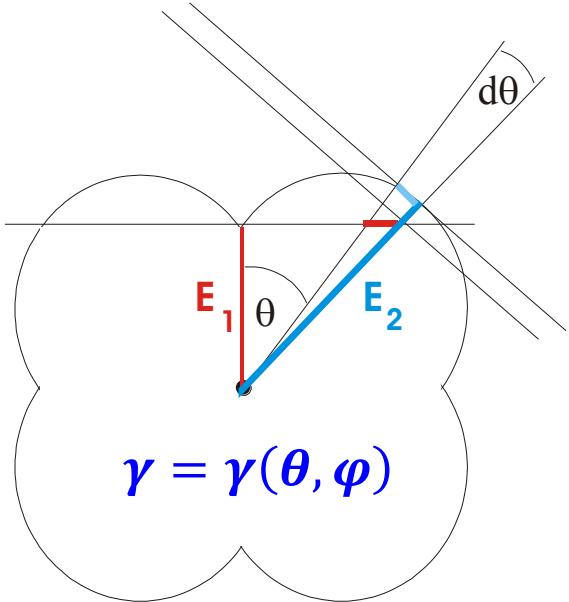
- Crystal surfaces have orientation dependent surface energy density
- The angular diagram of this dependence is known as  $\gamma$ -plot.



$\gamma$ -plot and Wulf construction

### Wulf construction

Crystal equilibrium shape is equal to the minimal volume contained within the surfaces, perpendicular to the lines from the  $\gamma$ -plot origin, drawn at their intersections with the  $\gamma$ -plot .



## Wulf construction

- The angular diagram of this dependence is given as  $\gamma$  - plot.
- Calculate the energy  $\Delta E$  contained with the minimal angle interval  $d\theta$

- Case 1

$$\Delta E_1 = E_1 dl_1 = \frac{E_1 dl_{\perp}}{\cos(\theta)} = \frac{E_1}{\cos(\theta)} dl_{\perp}$$

- Case 1

$$\Delta E_2 = E_2 dl_{\perp}$$

$$\Delta E_2 > \Delta E_1$$



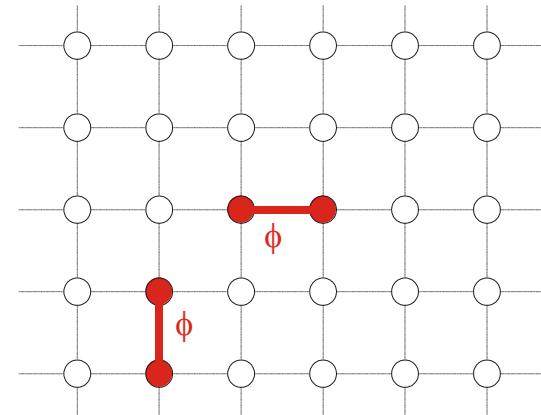
$$\Delta E_2 < \Delta E_1$$

- Case 1
- Case 2

## Wulf construction

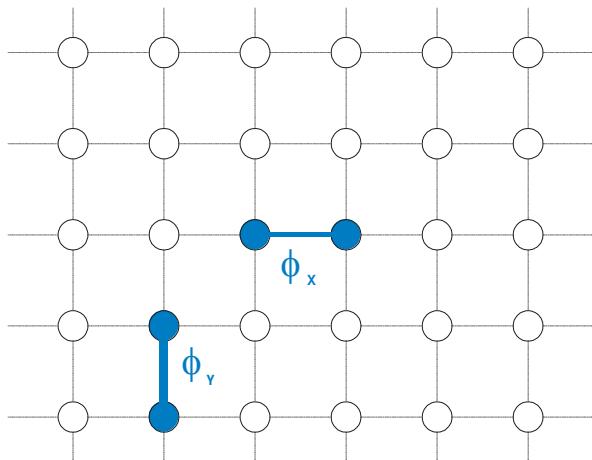
# Kossel crystal – the simplest case

- Square lattice
- Nearest neighbor (nn) interaction
- Interaction energy is isotropic ( $\phi$  - nn interaction energy (bond energy))
- Z – number of nn ( $d = 2$   $Z = 4$ ,  $d=3$   $Z = 6$ )

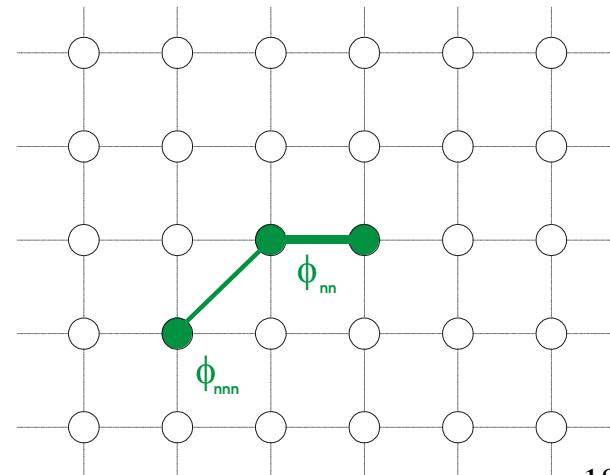


- Extensions

- Anisotropic interactions

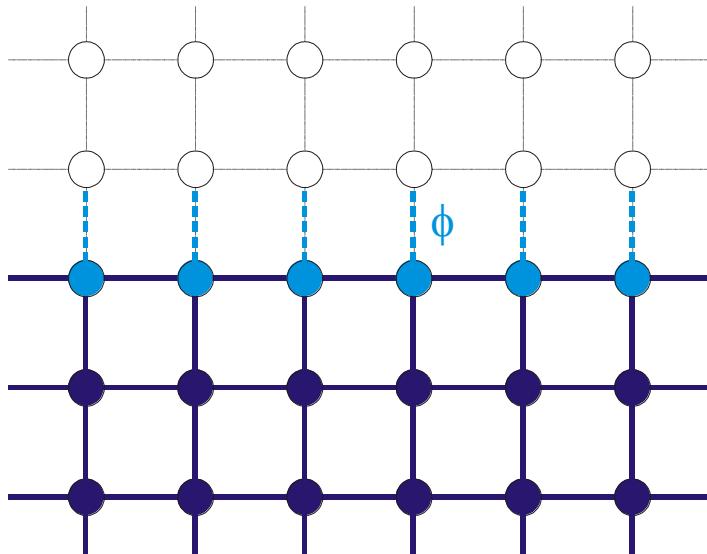


- Next nearest neighbors (nnn) interaction



## Kossel crystal surfaces

- Surface – layer of atoms with broken (not saturated) bonds



$$E_s = -\frac{ZN_s \phi}{2} = -N_{\text{bond-S}} \phi$$

- Bulk crystal energy

$$E_{cr} = -\frac{ZN\phi}{2}$$

- Surface energy

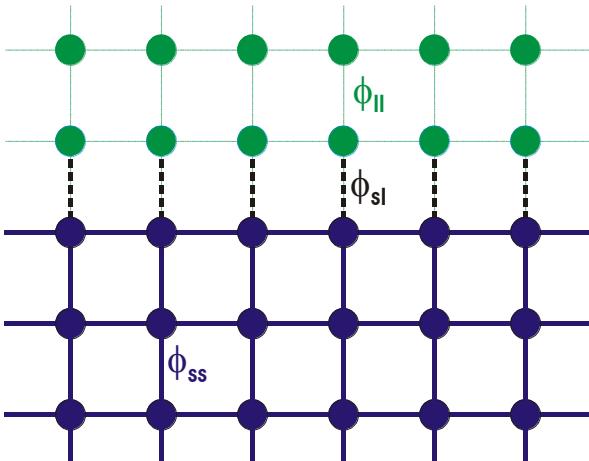
$$E_{sur} = N_{sur} \phi$$

- Total energy

$$E_{tot} = E_{cr} + E_{sur} = -\frac{ZN\phi}{2} + N_{sur} \phi$$

The simplest coherent model of the bulk and the surface.

## Liquid-crystal interfaces in Kossel model



- Bond energy in crystal-  $\phi_{cr}$ , in liquid -  $\phi_{ll}$  and crystal-liquid interface -  $\phi_{cl}$
- Number of atoms in crystal  $N_{cr}$ , liquid  $N_l$
- Number of bonds in crystal  $N_{cr}^{bond}$ , liquid , in crystal-liquid interface

- Crystal energy

$$E_{cr} = -N_{cr}^{bond} \phi_{cr} = -\frac{N_{cr} Z \phi_{cr}}{2}$$

- Liquid energy

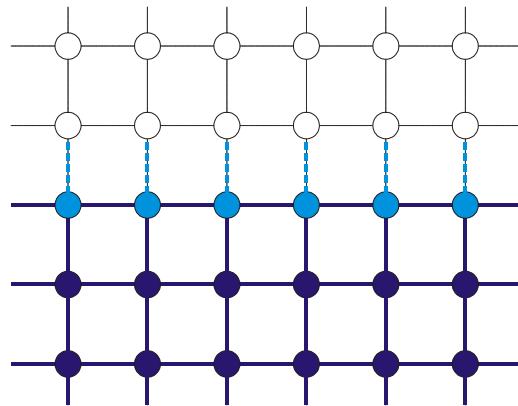
$$E_{cr} = -N_l^{bond} \phi_{cr} = -\frac{N_l Z \phi_{ll}}{2}$$

- Crystal-liquid interface energy

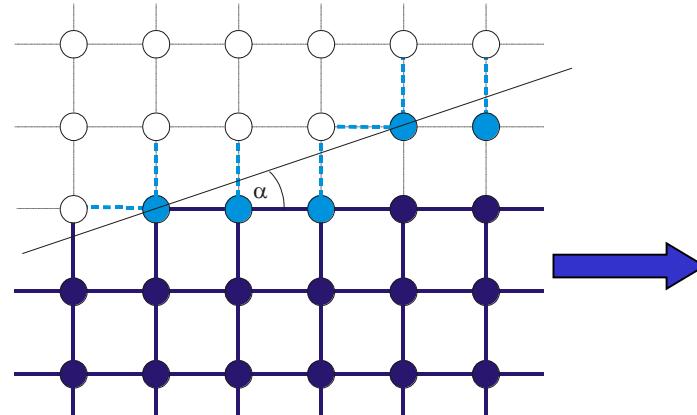
$$E_{cr-l} = -N_{cr-l}^{bond} \left[ \phi_{cr-l} - \frac{\phi_{cr} + \phi_{ll}}{2} \right]$$

## Example in 2d – crystallographic (01) and vicinal surfaces

- Crystallographic flat surface (01)



- Vicinal surface

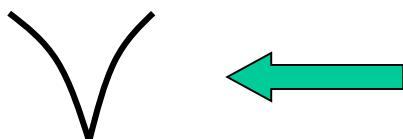


- $n$  - step width
- $\alpha$  - step angle

$$|tg(\alpha)| = \frac{1}{n}$$

- Vicinal surface energy

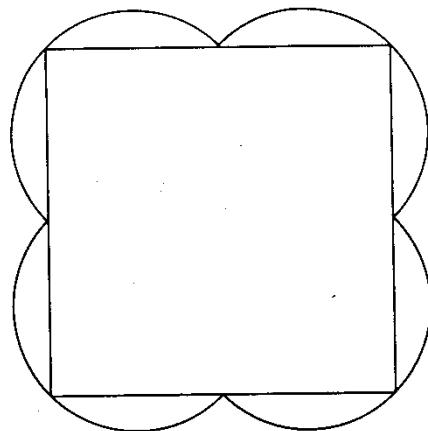
$$\gamma(\alpha) = \frac{1+n}{n |\cos(\alpha)|} = \gamma(|\cos(\alpha)| + |\sin(\alpha)|)$$



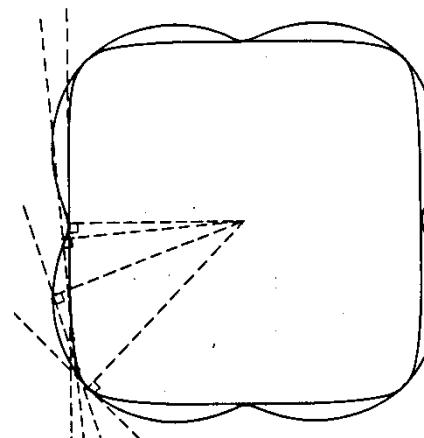
$\gamma$  - plot – cusp for low Miller index surfaces

## 2-d Kossel crystal – equilibrium shape at $T > 0$

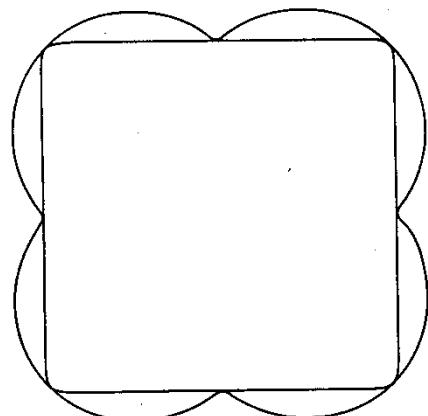
$kT/\phi = 0$



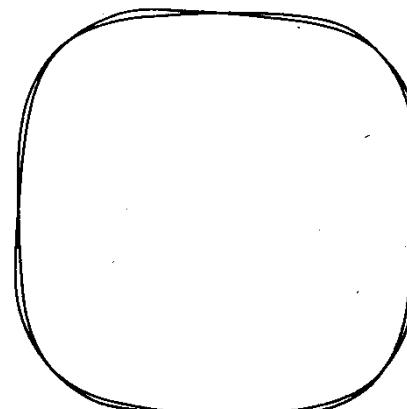
$kT/\phi = 0.3$



$kT/\phi = 0.1$

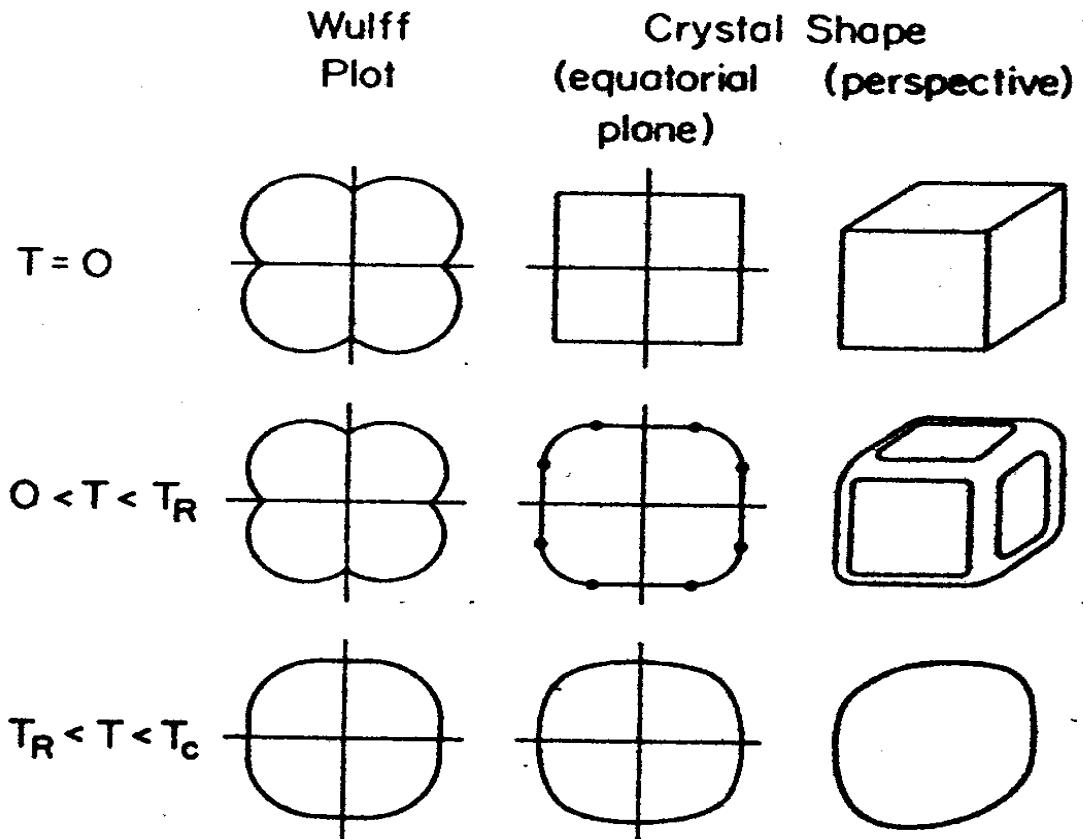


$kT/\phi = 0.6$

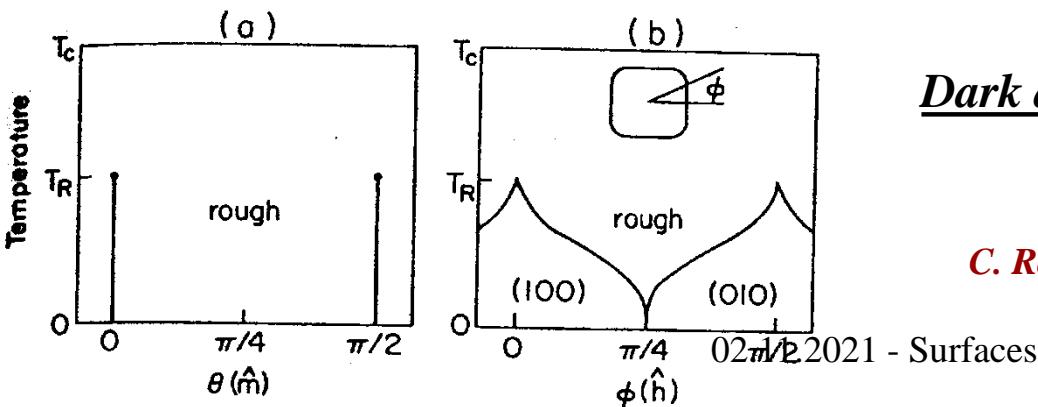


*C. Rottman & M. Wortis Phys. Rev. B 24 (1981) 6274*

## 3-d Kossel crystal – equilibrium shapes



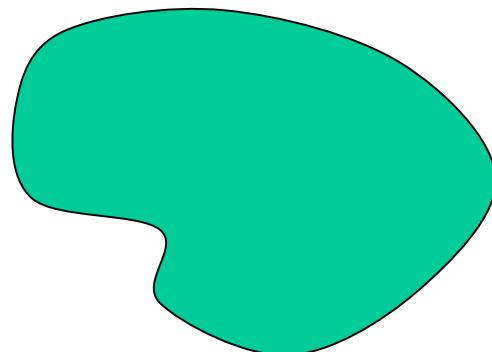
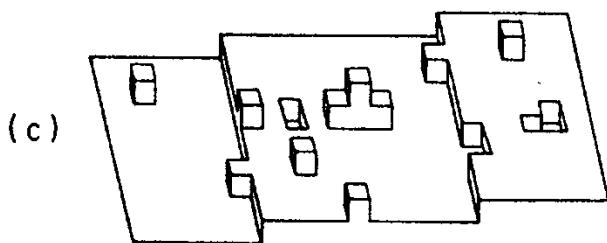
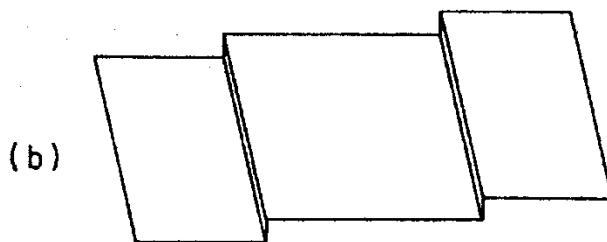
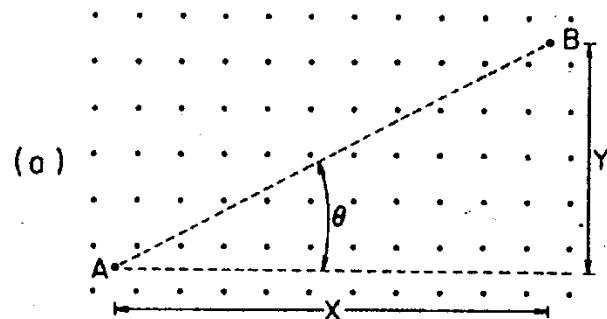
Phase diagram



Dark dots – transition from flat to vicinal surface

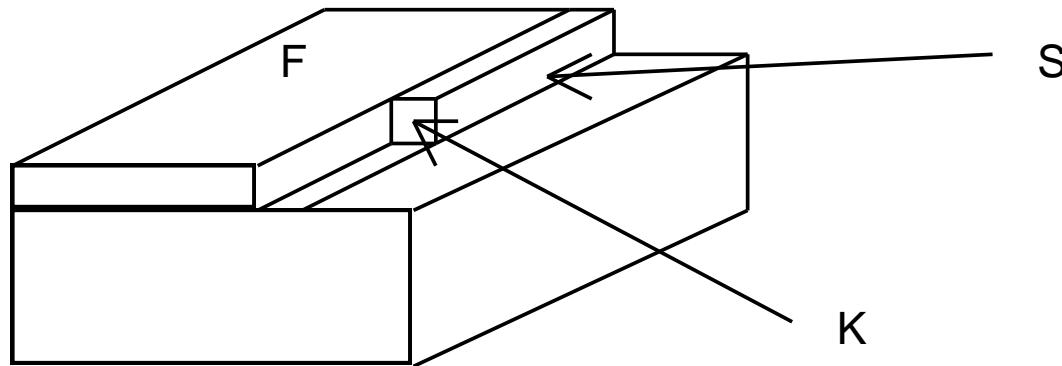
C. Rottman & M. Wortis Phys. Rep. 103 (1984) 59

## 2-d oraz 3-d surfaces



- step is one-dimensional object (line)

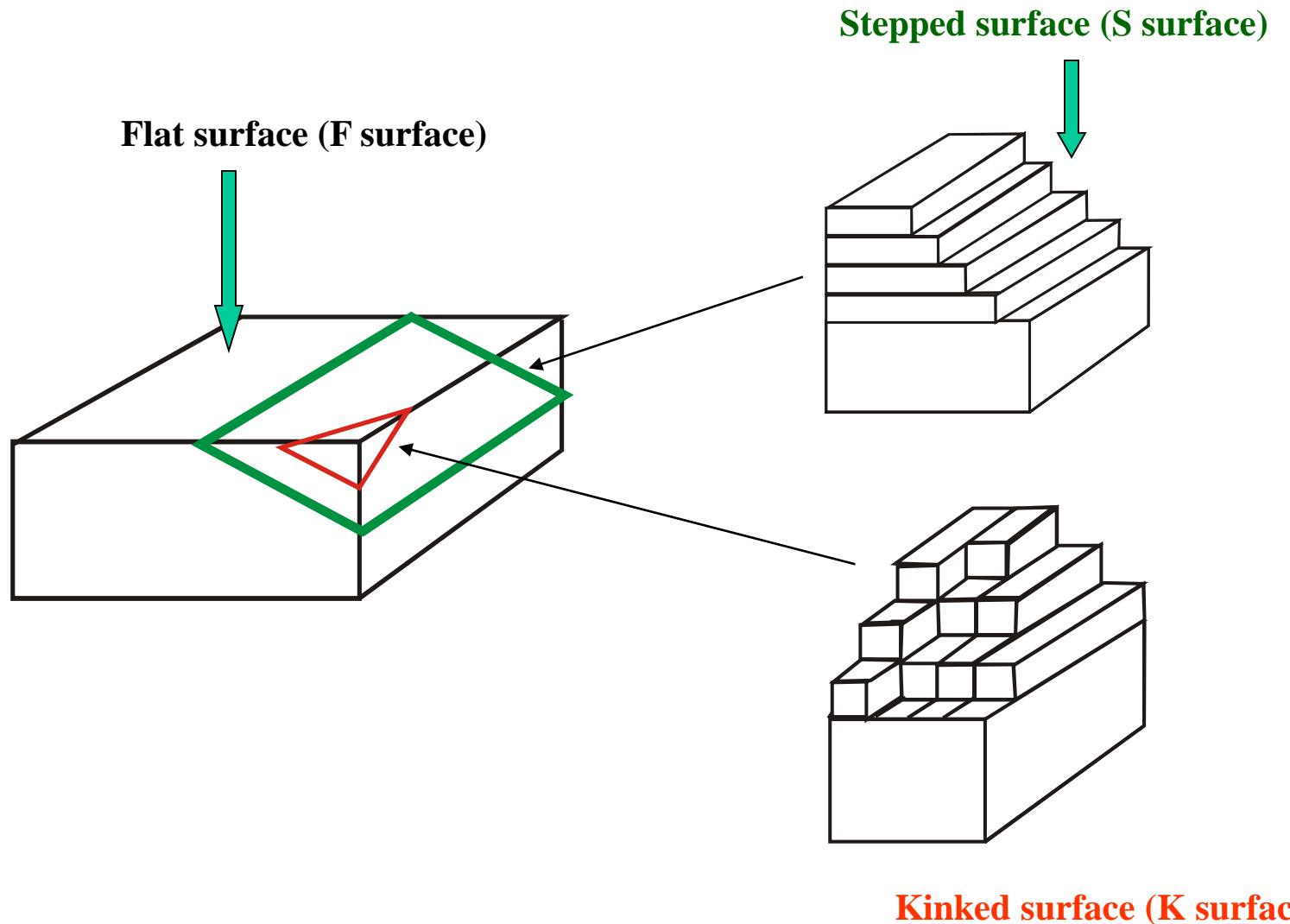
## Atomic structure of three-dimensional surfaces



- Low Miller index surfaces are denoted as F surfaces (F – flat)
- Atomic layers are terminated by edge. Atomic layer edges are called steps (S).
- Termination of the atoms row at the adge is called kink (K)

*Traditionally the model is called TLK – terrace – ledge – kink model.*

## 3-d surface types

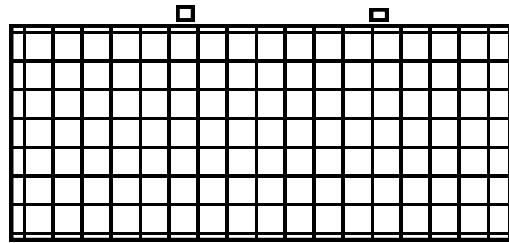


## Flat and rough surfaces

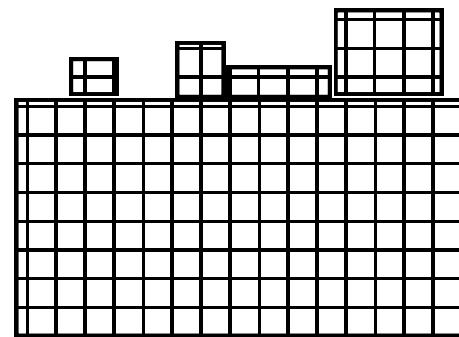
- Surface roughness  $R$  is defined as:

$$R \equiv \frac{N - N_o}{N_o}$$

*N – number of broken bonds*  
*N<sub>o</sub> – minimal number of broken bonds*



gladka



szorstka

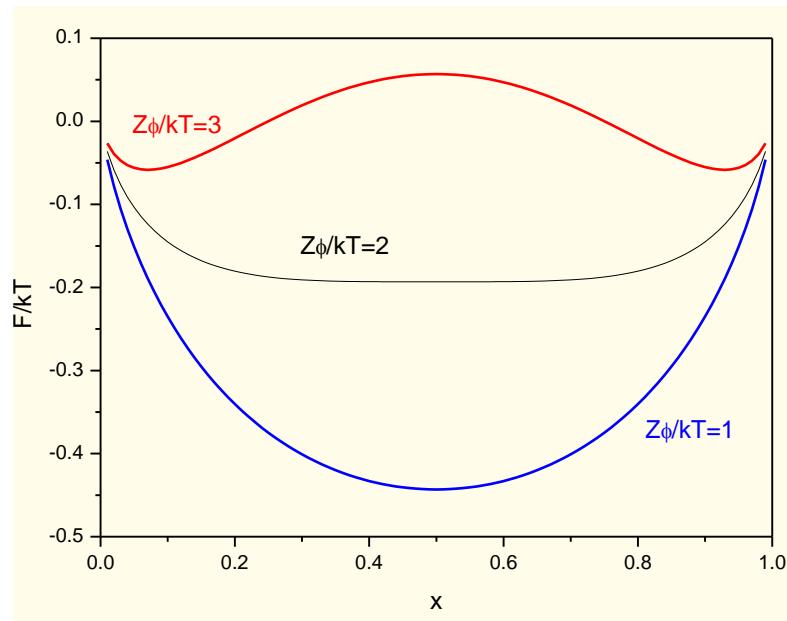
**Mathematical roughness is different from Atomic Force Microscope roughness.**

## Surface phase transition rough-flat

- Single layer model:
- Mean field theory (Bragg – Williams approximation)

Surface free energy

$$F = kT[x \ln(x) + (1-x) \ln(1-x)] + Z\phi x(1-x)$$



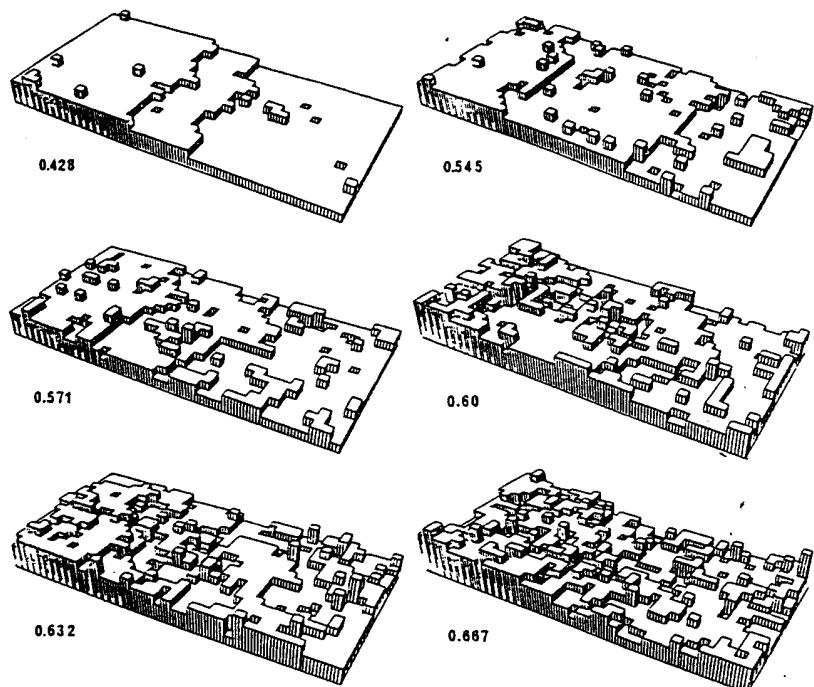
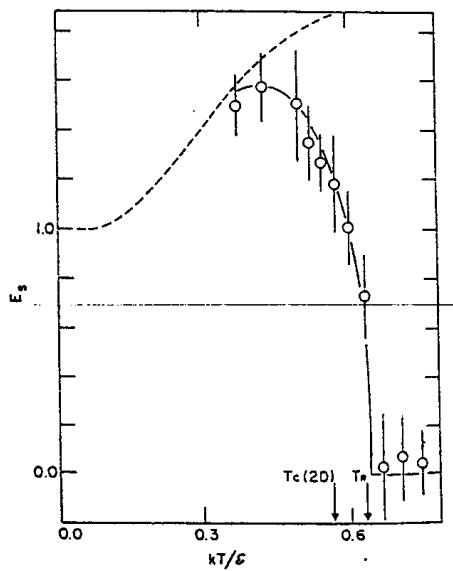
$$x = \frac{N_{at}}{N_o}$$

*Phase transition at  $Z\phi=2kT$*

## Surface phase transition rough-flat: numerical simulations

- Stepped surface with quasi-periodic boundary conditions
- Solid-on-Solid (SOS) approximation
- Stepped and step-free surfaces energy difference
- Microscopic configurations at different temperatures

$$\alpha = \frac{kT}{\phi} = \frac{kT}{\varepsilon}$$



Phase transition at  $kT = 0.61\phi$

H.J. Leamy & G.H. Gilmer J. Cryst. Growth 24 (1974) 499

## Equilibrium step properties

- Step – 1-d object (line)
- No phase transitions
- Step – rough object
- Step – solid – surface exchange of atoms

$$\mathbf{T}_R = \mathbf{0}$$

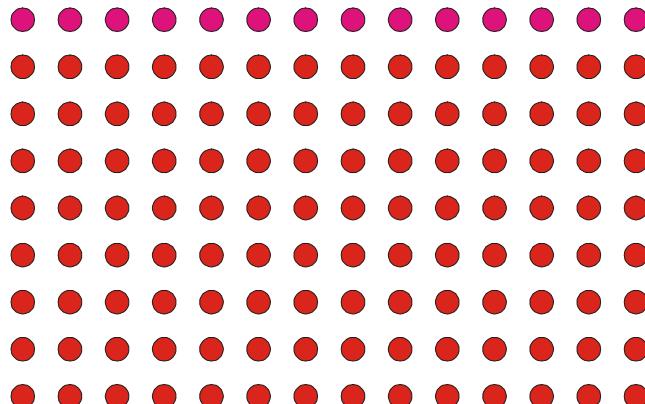
## **Surfaces of real crystals – clean (no foreign atoms)**

- **Jahn-Teller effect – lattice symmetry breaking to lower system energy**
- **Two basic effects: relaxation and reconstruction**
- **Surface relaxation: modification of atom positions preserving translational lattice symmetry (parallel to the surface)**
- **Surface reconstruction: modification of atom positions breaking translational lattice symmetry**

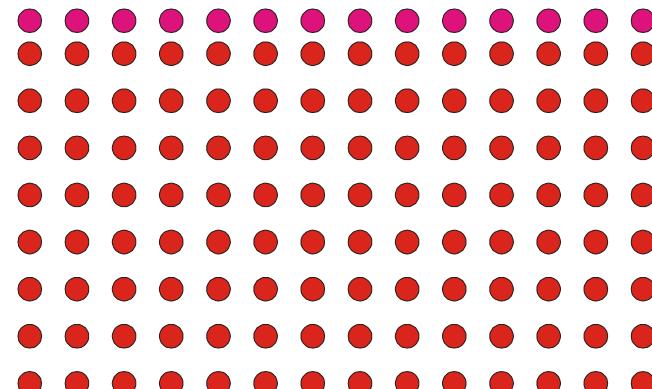
## Surface relaxation

- Observed at metal surfaces
- Electric properties of the surface are not changed

Termination surface

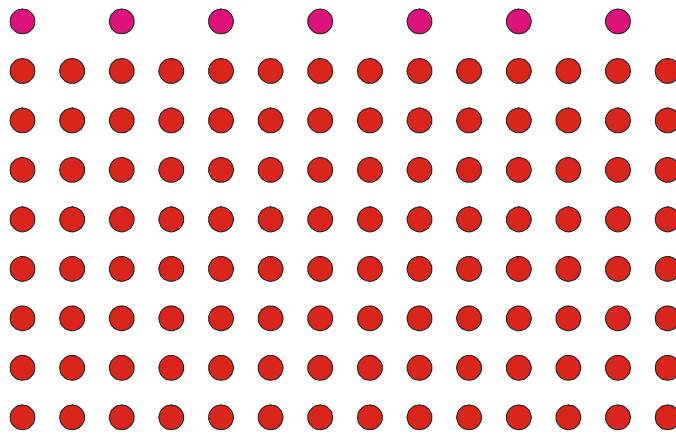


Relaxed surface

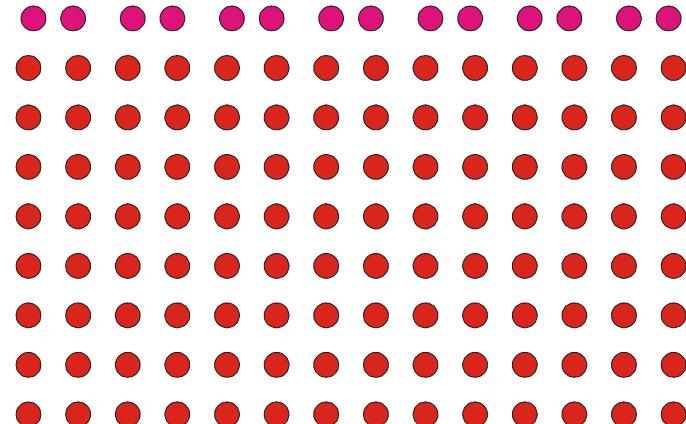


## Reconstructed surfaces - examples

2x1 – missing row reconstruction

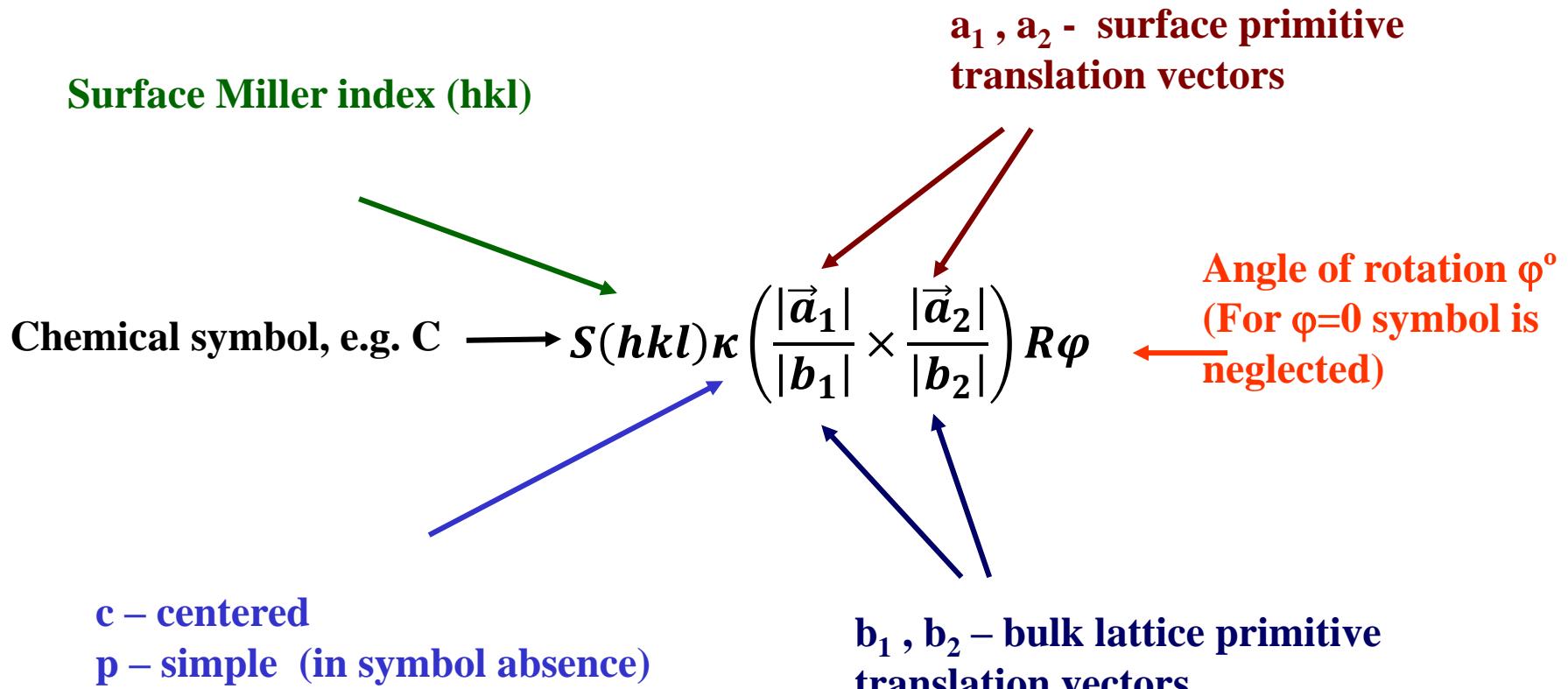


2x1 – pairing reconstruction



Wood notation – description of reconstructed surfaces

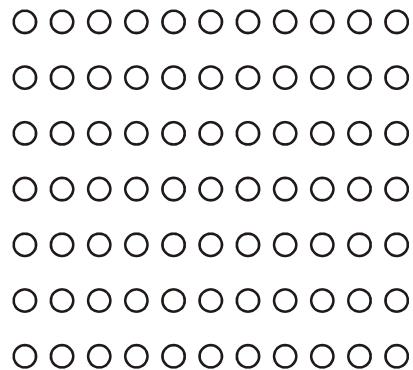
## Wood notation (Wood Symbol)



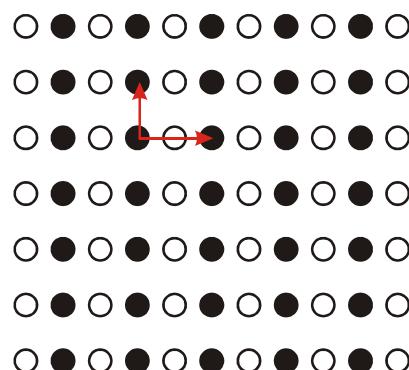
Wood notation is not unique

## Wood symbols - examples

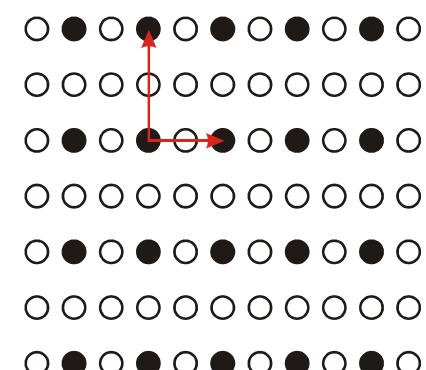
(1x1)



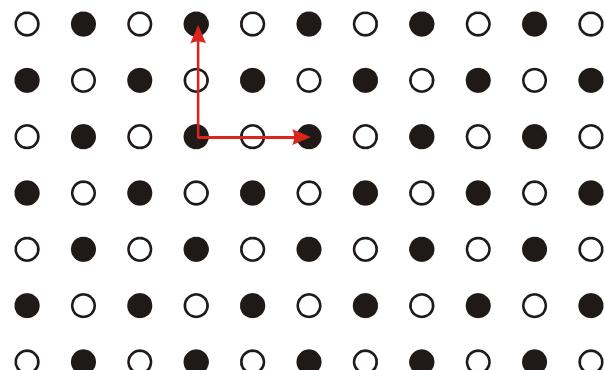
(2x1)



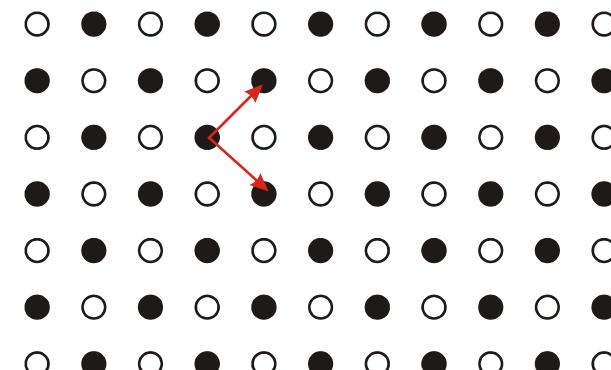
(2x2)



(2x2)



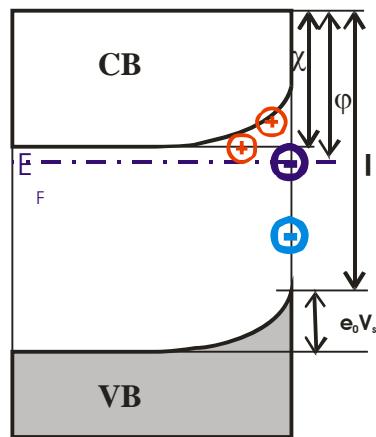
$(\sqrt{2} \times \sqrt{2})$



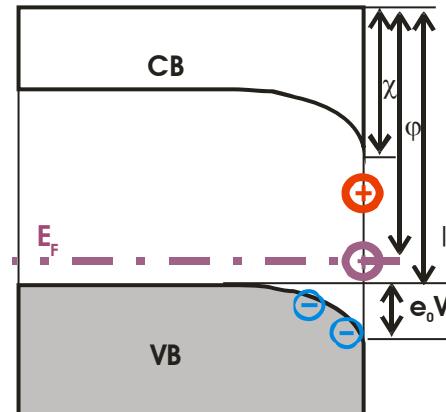
# Semiconductor surfaces – reconstruction, charges and fields

- Strong, directional bonds, saturation by creation of new bonds
- Strong tendency to saturation by attachment of foreign atoms
- Reconstruction – may include several atomic layers
- Charged surface states induce fields that penetrate into deep interior

- **Surface acceptor**



- **Surface donor**



I – ionization energy

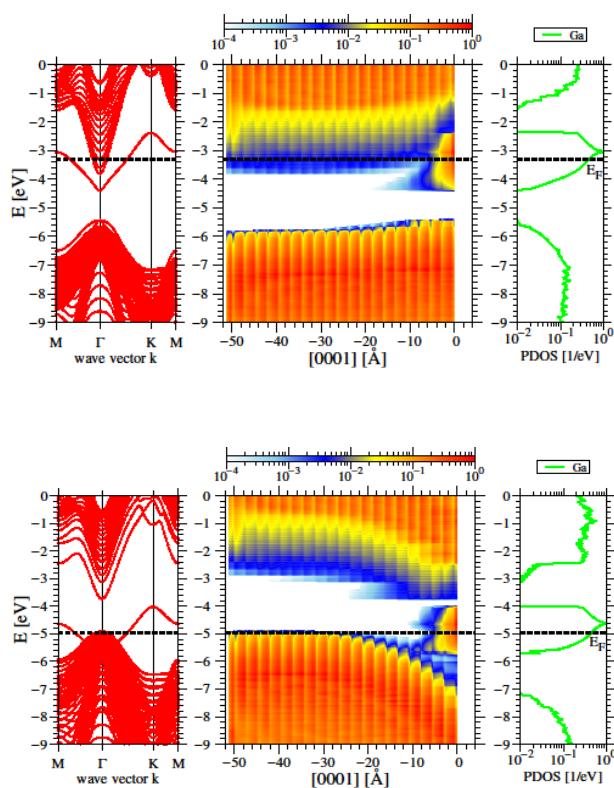
$\phi$  – work function

$\chi$  – electron affinity

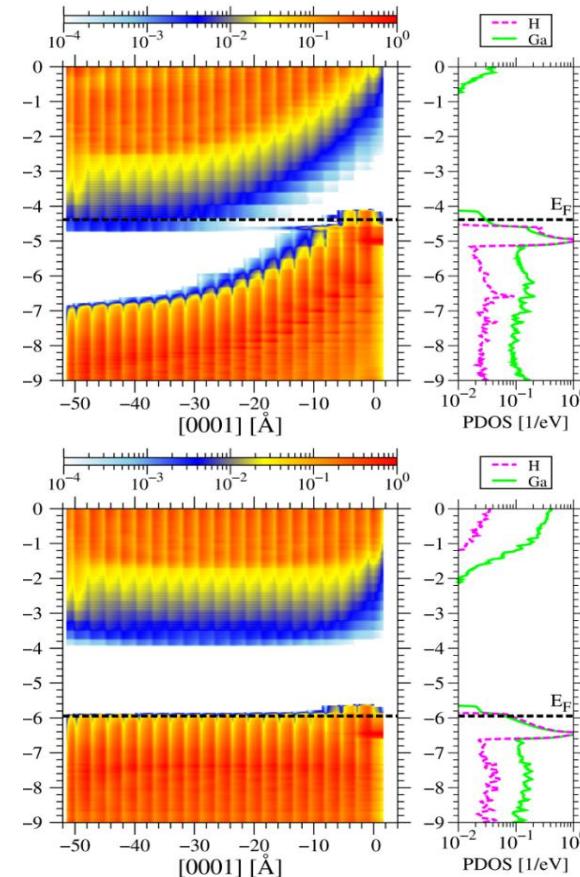
In metal all values are identical

# Electronic properties of semiconductor surfaces – GaN(0001) surface

Clean surface



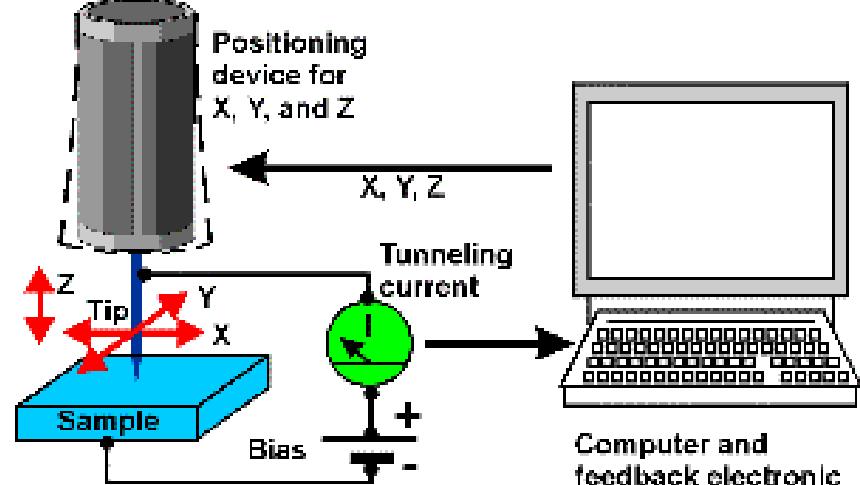
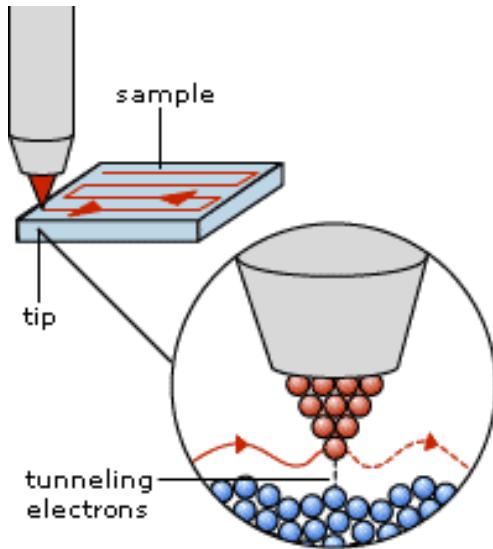
1 ML coverage



n type

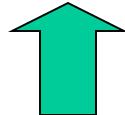
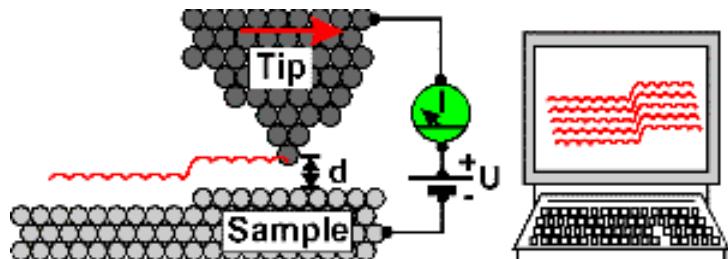
p type

## Scanning Tunneling Microscope – STM

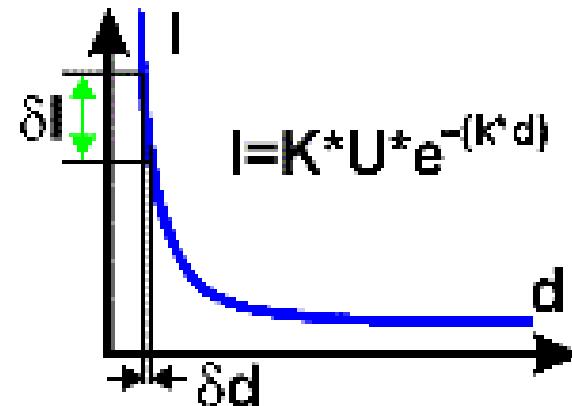


Nobel Laureates:  
Heinrich Rohrer and Gerd Binnig 1986

## STM work mode



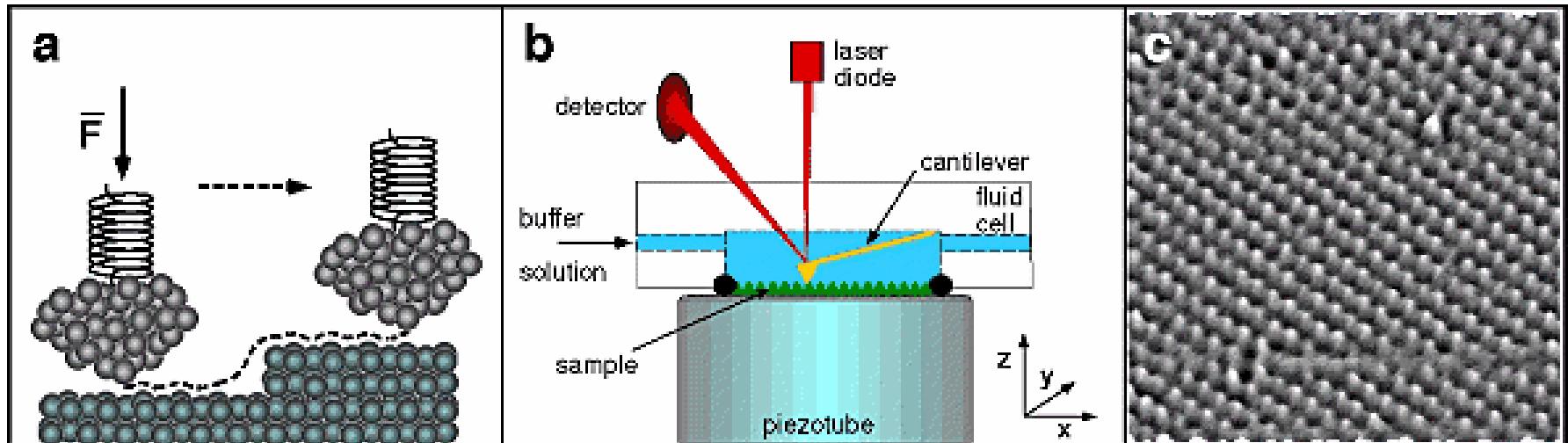
The tip interacts with  
the surface



Tunneling current vs distance  
K and k – constants

**STM can achieve atomic resolution!**

# AFM – measurement technique



↑  
AFM tip – surface  
interaction

↑  
Laser detection of tip  
motion

↑  
Atomic resolution – mica  
surface ( $d = 5.4 \text{ \AA}$ ).

# AFM – Atomic Force Microscope

Atomic Force Microscope - NovaScan

**ESPM II**

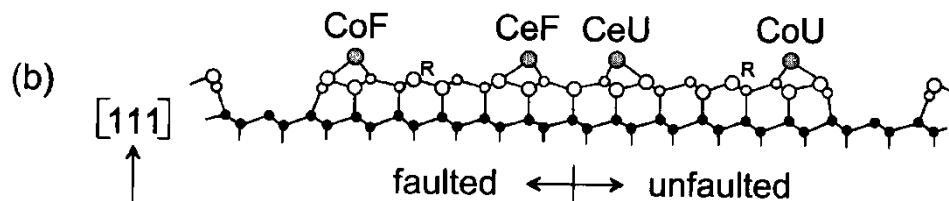
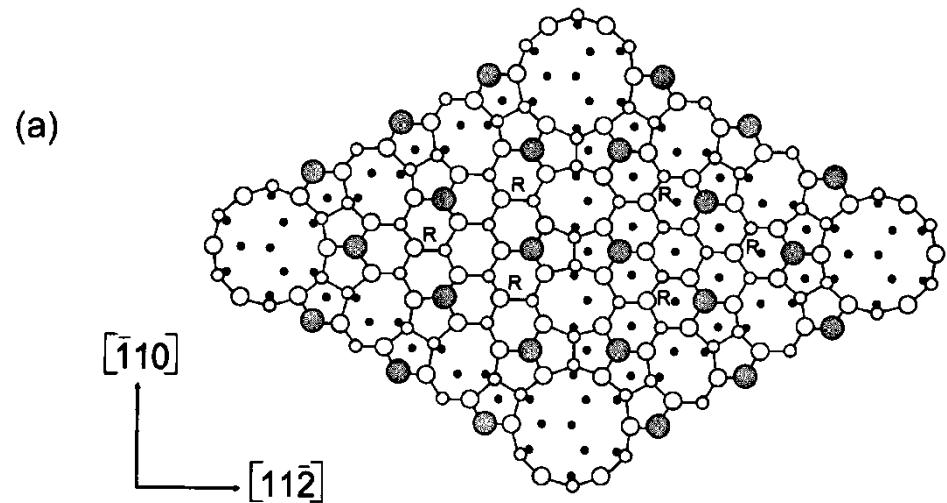


**OSPM II**

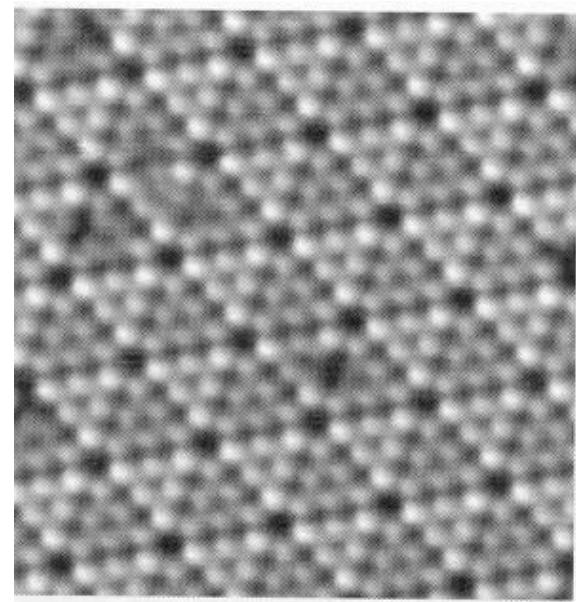


## Si (111) 7x7 surface (dimer – adatom – stacking fault)

Si (111) (7 x 7) surface - model

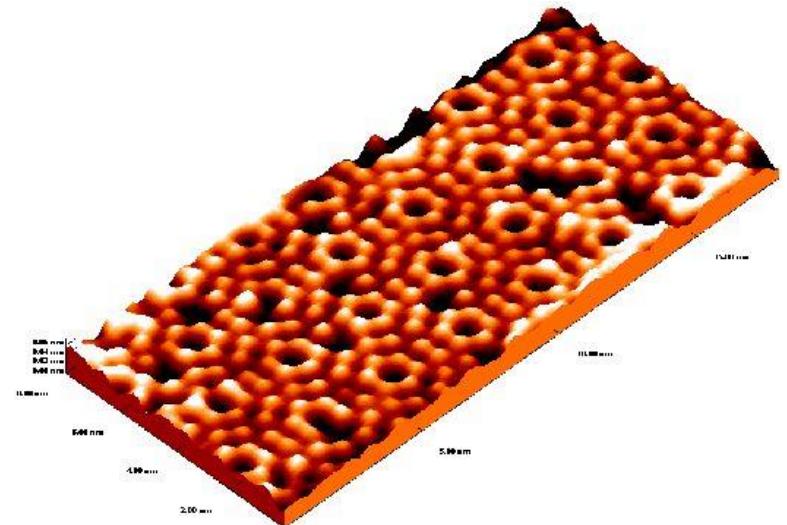
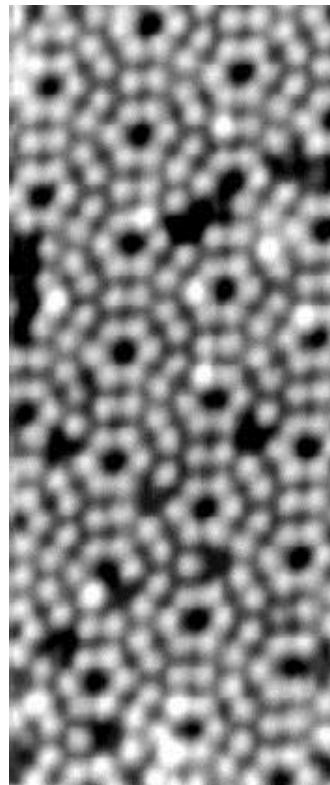
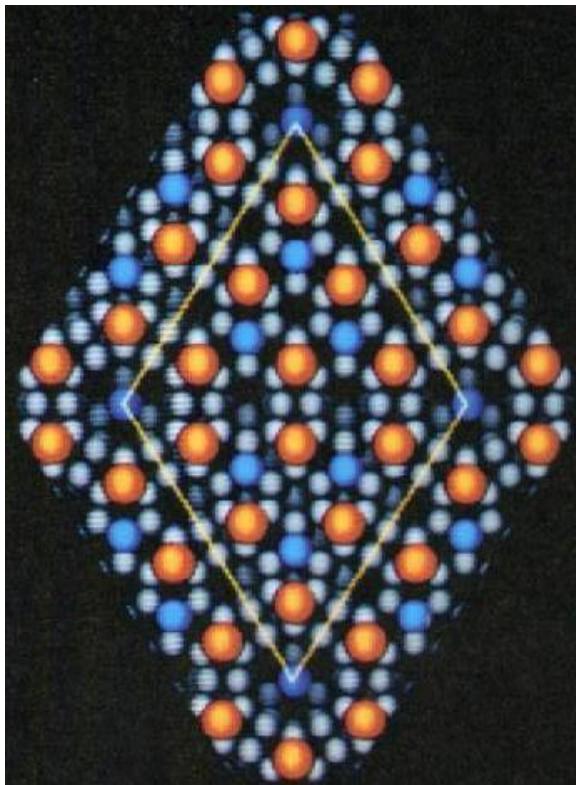


STM picture



*K. Takanayagi et al. Surf. Sci. 164 (1985) 367*

## Si(111) (7x7) reconstruction – STM picture



**3-d model**

**Model -  
R.M. Tromp (IBM)**

**STM picture**

## Literature

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- W. Schommers, P. Von Blanckenhagen, *Structure and Dynamics of Surfaces II*, Ch. 3.2, Springer 1987.
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- H. Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer 2010
- A. Zangwill, *Physics at Surfaces*, Cambridge Univ. Press. 1996