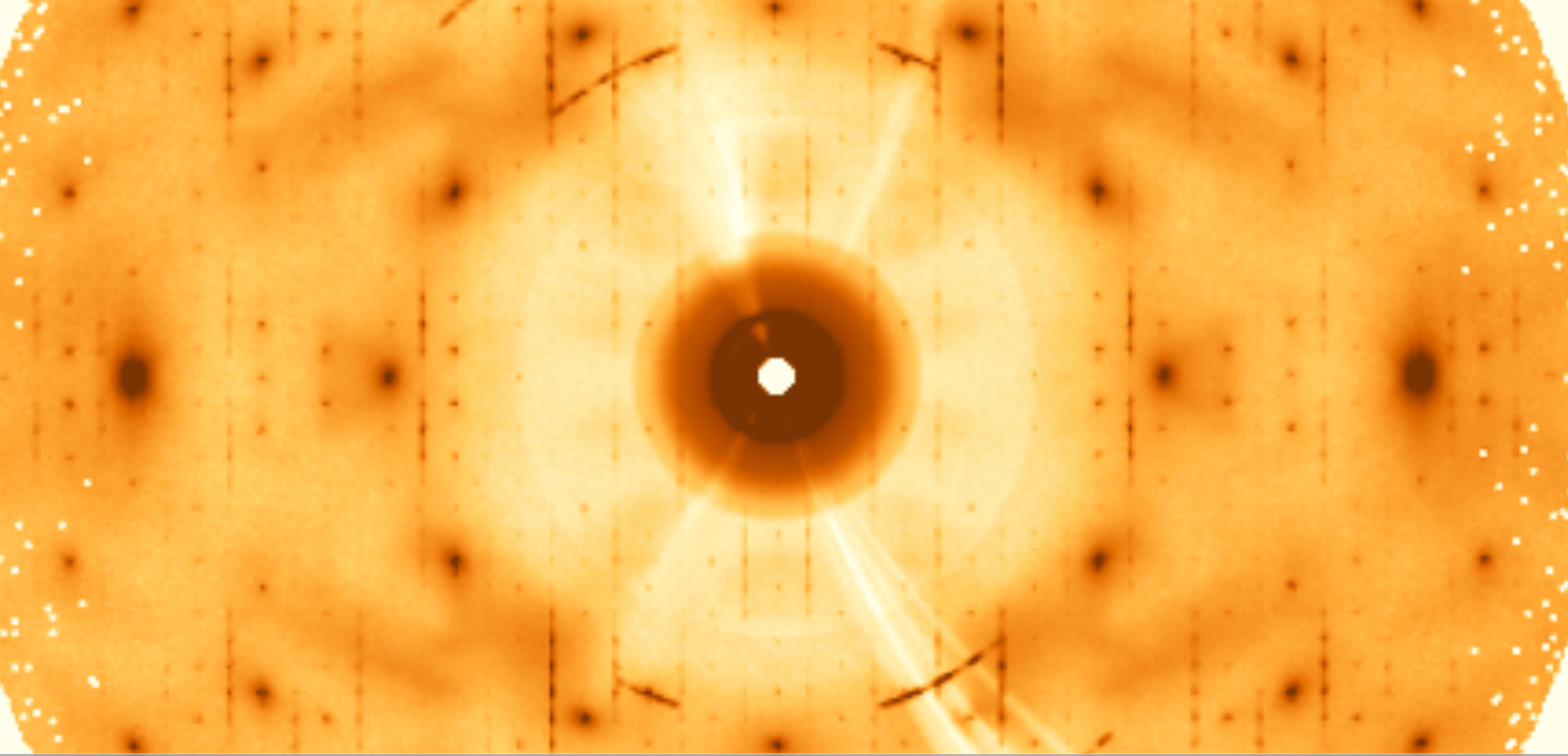


# SURFACE X-RAY SCATTERING

Alessandro Coati
SixS beamline - Synchrotron SOLEIL

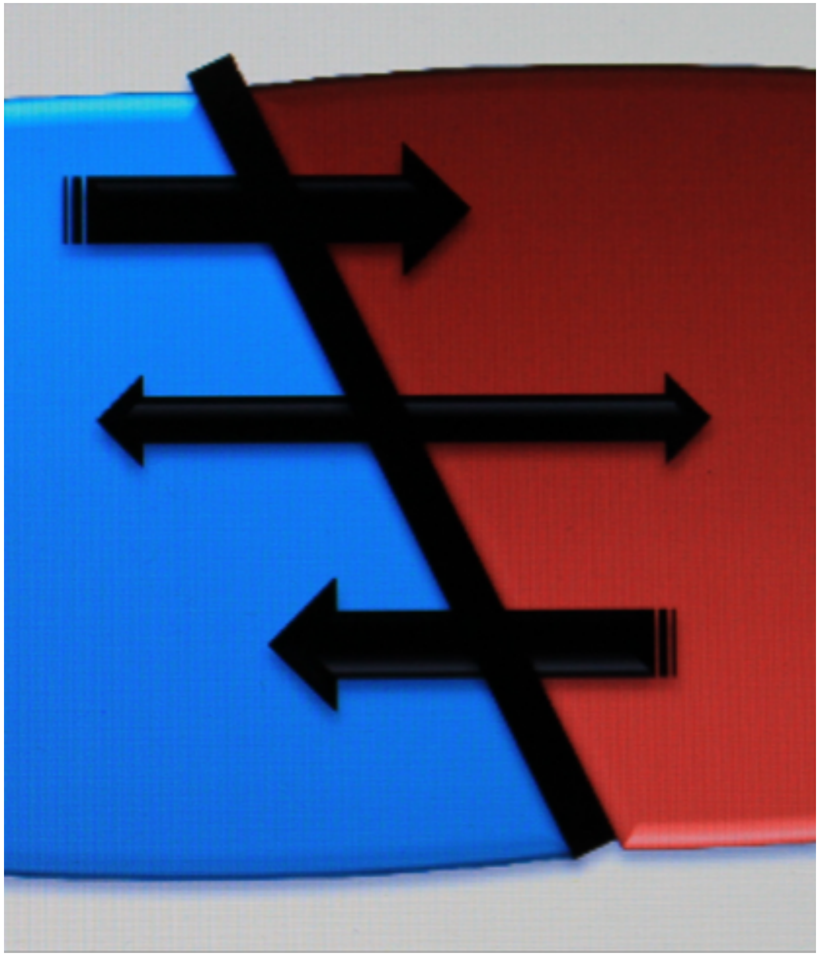
# SURFACES, INTERFACES

## Definitions

(Oxford English Dictionary)

Interface. A point where two systems, subjects, organizations, etc. meet and interact.

Surface. The outside part or uppermost layer of something.



# SURFACES, INTERFACES AND NANO-OBJECTS

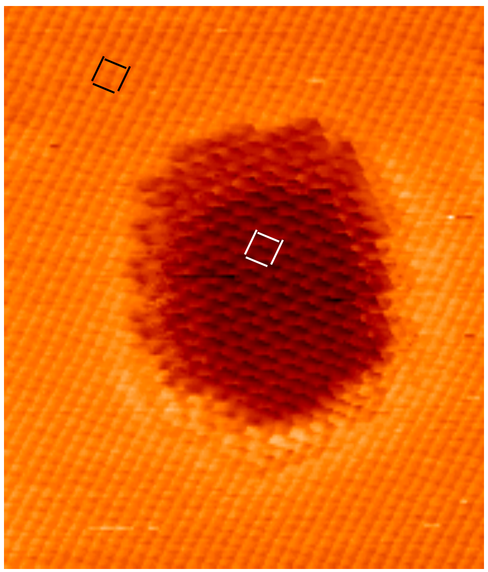
Surfaces as
- interface material vs vacuum
- support of nano-objects

Physical properties (electronic, catalytic, photonics, magnetic):
- different from the bulk
- depending on the interface nature (solid/solid, solid/liquid, solid/gaz, liquid/liquid, liquid/gaz)
- depend on the atomic structure, the size, the shape and the organisation at the nanometric scale

X-ray scattering techniques can give information on all these factors

# SURFACE SCIENCE TECHNIQUES

## Direct Space (STM)



1x1 bare Cu
c(2x2) N/Cu
Elmer et al. Surf. Sc.476, 95 (2001)

## Reciprocal space

### X-rays

$E=h\nu=hc/\lambda$(Å)=12398/E(eV)

$\lambda$=1 Å, E=12,4 keV

Abs.length > 100mm
$\sigma_a \sim Z^2$barn

n = 1-$\delta$ : GIXD

Coherence width > 1mm

### Electrons

$E=p^2/2m = (h/\lambda)^2/2m$
$\lambda$(Å)=12,265/$E^{0.5}$(eV)

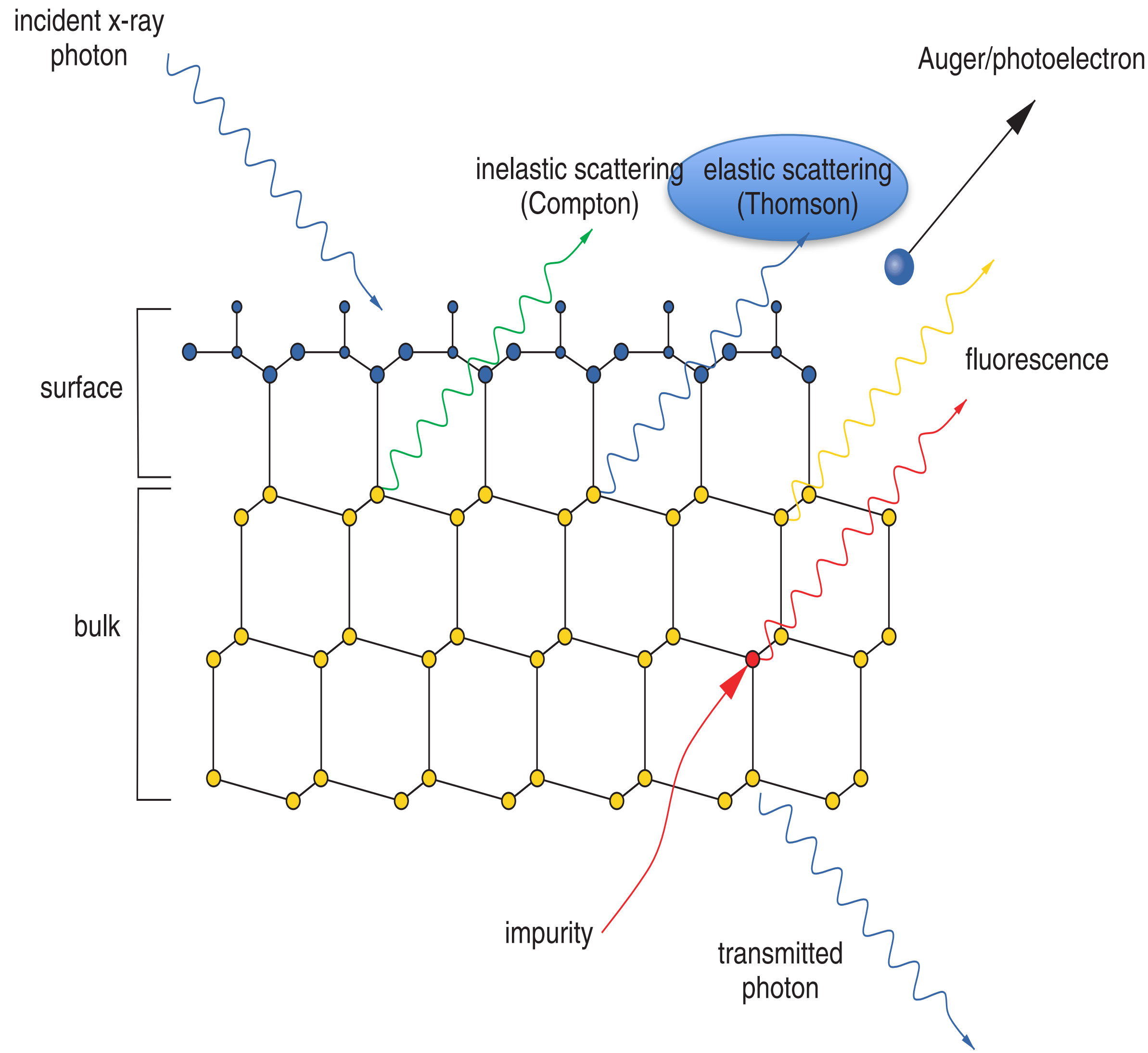
$\lambda$=1 Å, E=150 eV LEED
$\lambda$=0.1 Å, E=15 keV RHEED

Abs.length 1 nm (LEED)
$\sigma_a \sim 10^8$ barn

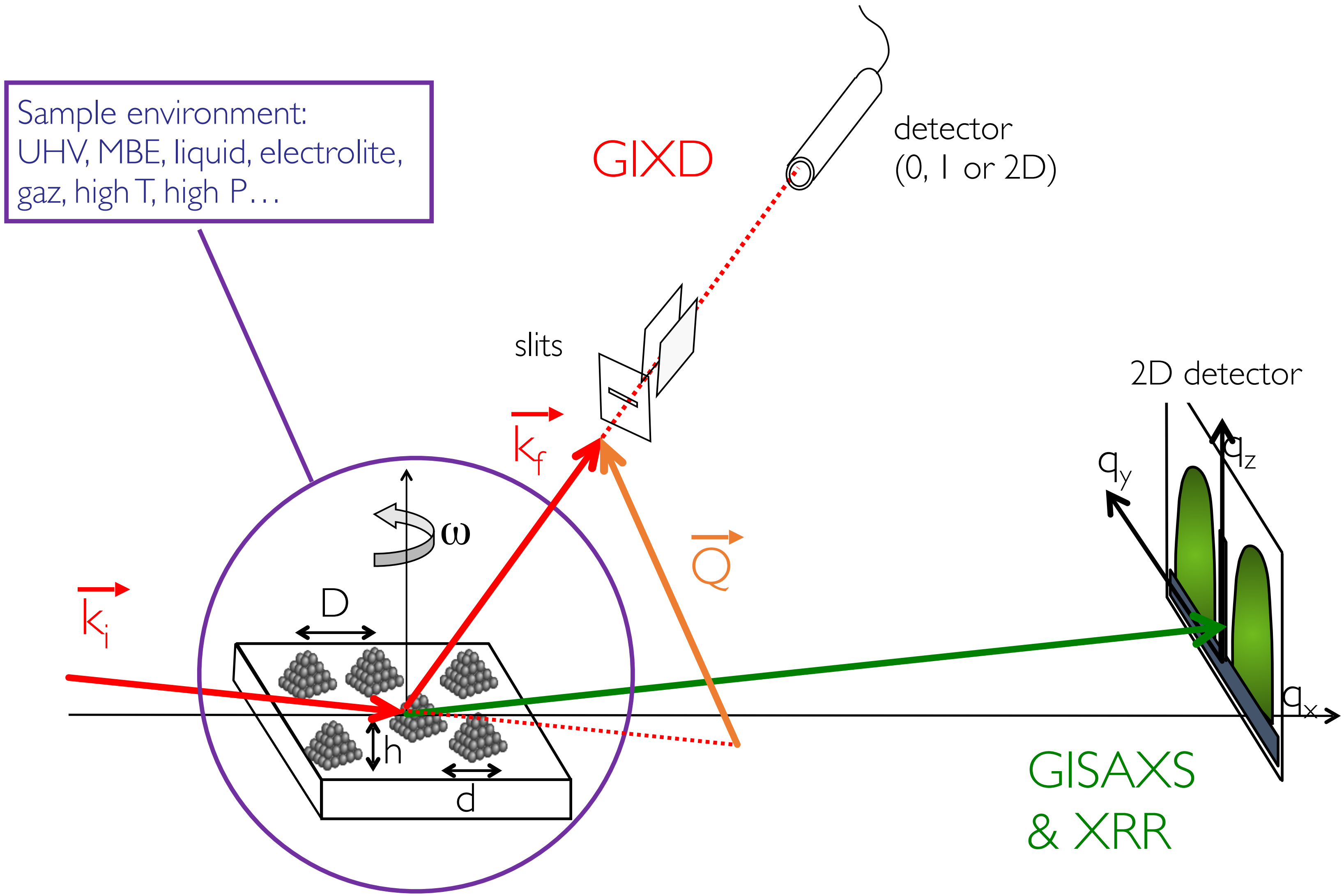
n=1+$\delta$

Coherence width < 0.1mm

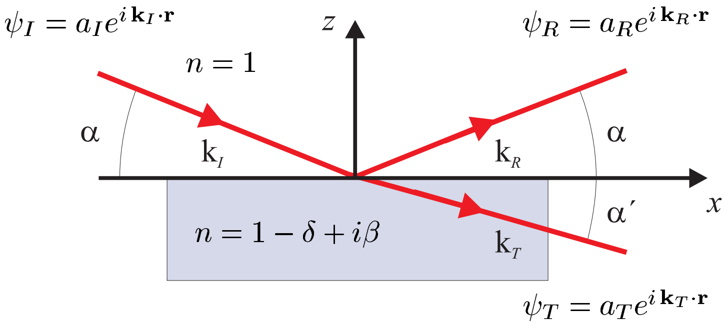
# X-RAY-MATTER INTERACTIONS



# IN-SITU MEASUREMENTS



# TOTAL REFLECTION




$$\cos(\alpha') = n\cos(\alpha_i)$$

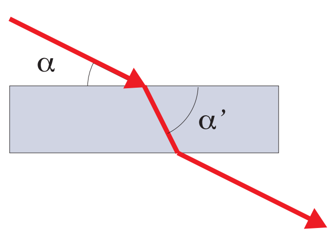
$$\boxed{n = 1 - \delta + i\beta}$$

$$\delta \approx \frac{\lambda}{2\pi}\frac{e^2}{mc^2}\rho_e \approx 10^{-5} \qquad \beta = \frac{\lambda\mu}{4\pi} \approx 10^{-6}$$

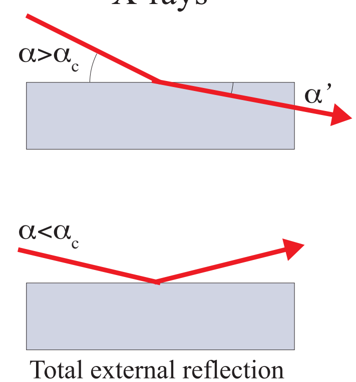
$$\cos(\alpha_c) = \mathrm{Re}(n) = 1 - \delta$$

$$\alpha_c \approx \sqrt{2\delta} \approx 10^{-3}\,rad$$

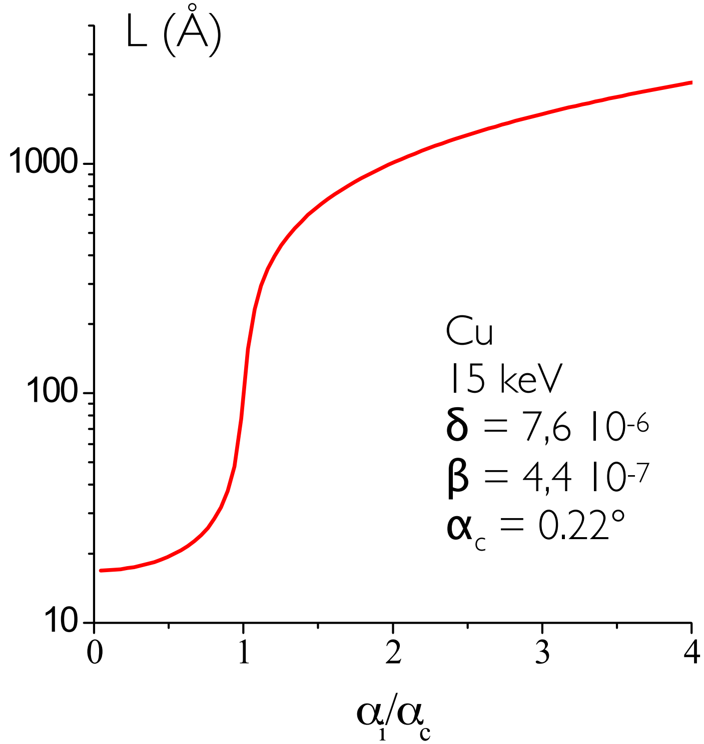
Light



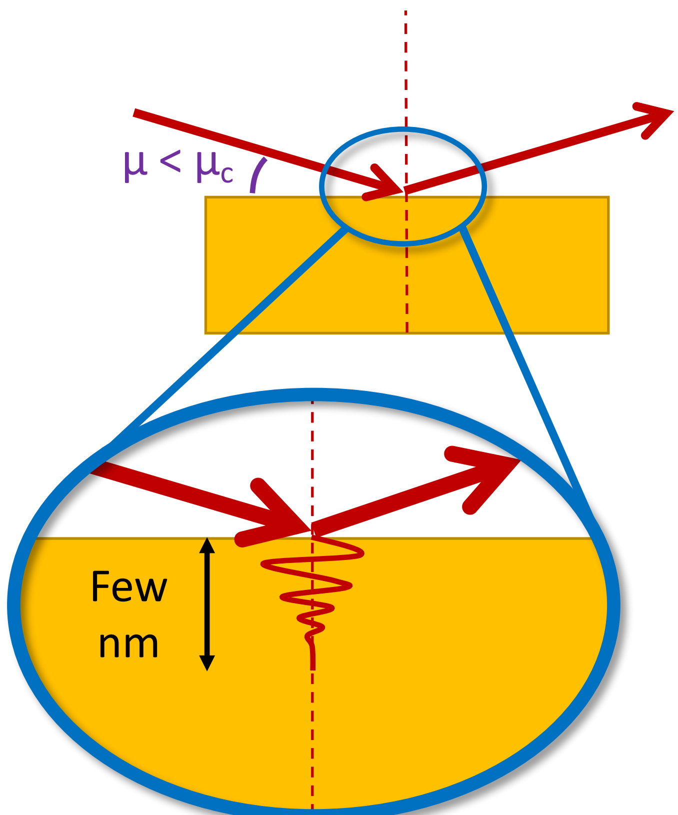

X-rays



# PENETRATION DEPTH

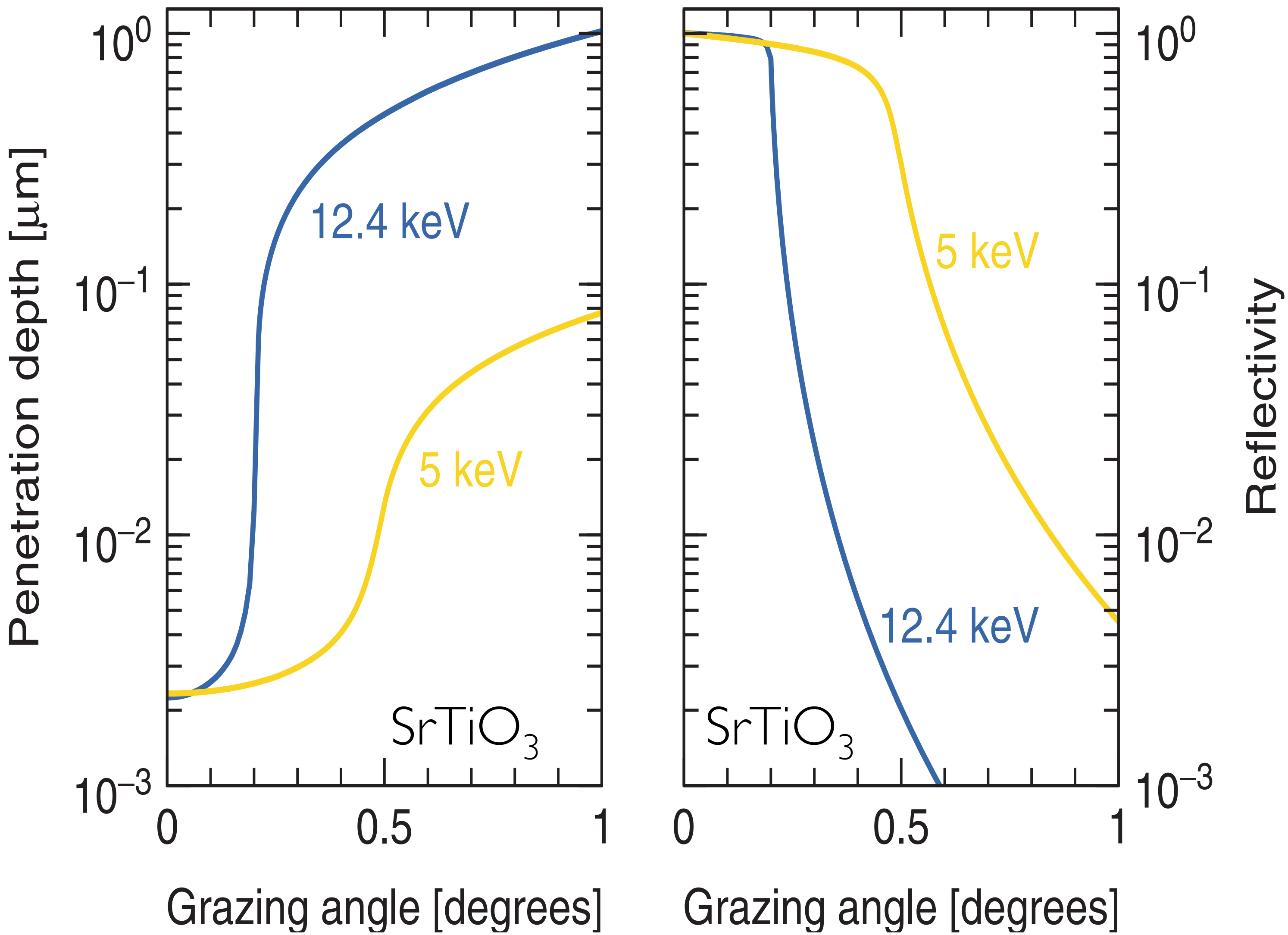



$$L \approx \frac{-\lambda}{4\pi \ \mathrm{Im}\sqrt{\alpha_i^2 - \alpha_c^2 - 2i\beta}}$$




| $\alpha_i$ | $0.1\ \alpha_c$ | $\alpha_c$ | $2\ \alpha_c$ |
|---|---|---|---|
| **L (Å)** | 15 | 100 | 1000 |

# Penetration depth



# ZnTe/GaAs

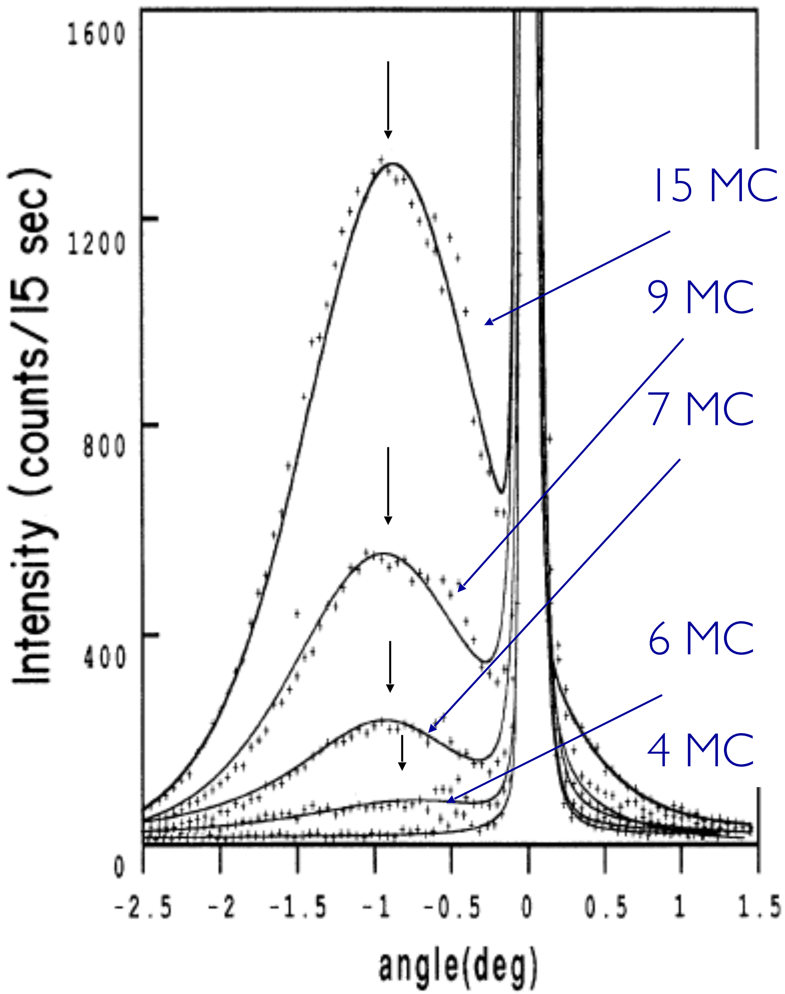



FIG. 1. $\theta$-$2\theta$ scans of the (200) reflection from ZnTe/GaAs (001) for heterostructures of increasing thicknesses (4, 6, 7, 9, and 15 ML from bottom to top curve). Profiles are aligned on the substrate Bragg peak.

$$\frac{a_{ZnTe} - a_{GaAs}}{a_{GaAs}} = 7{,}9\%$$

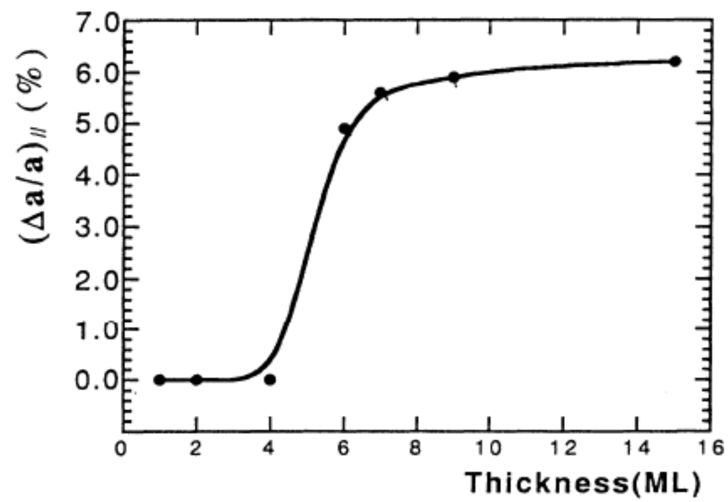



FIG. 2. Variation of $(\Delta a / a)_{\parallel}$ with the film thickness.

V. H. Etgens et al. Phys. Rev. B47, 10607 (1993)

# ZnTe/GaAs

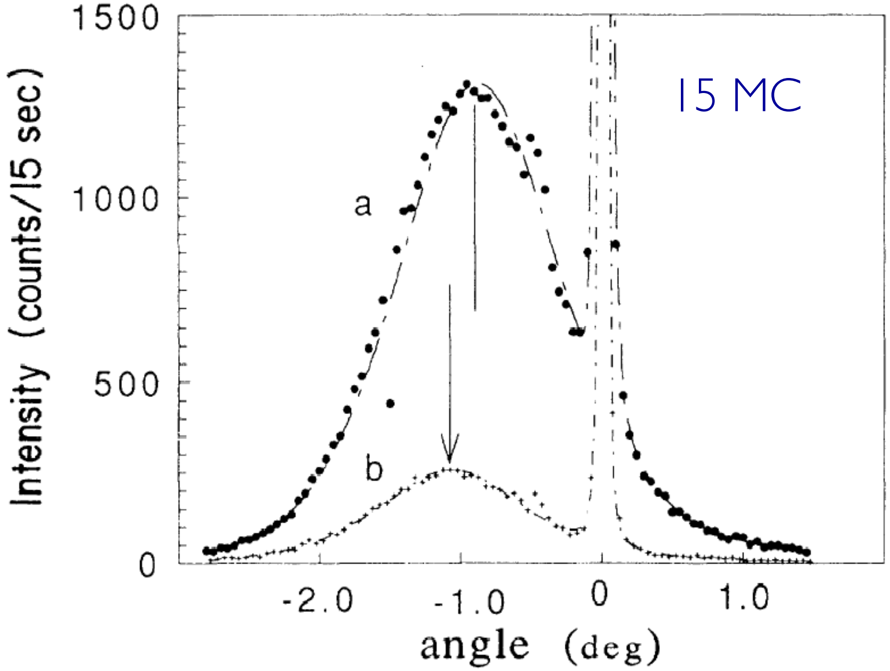
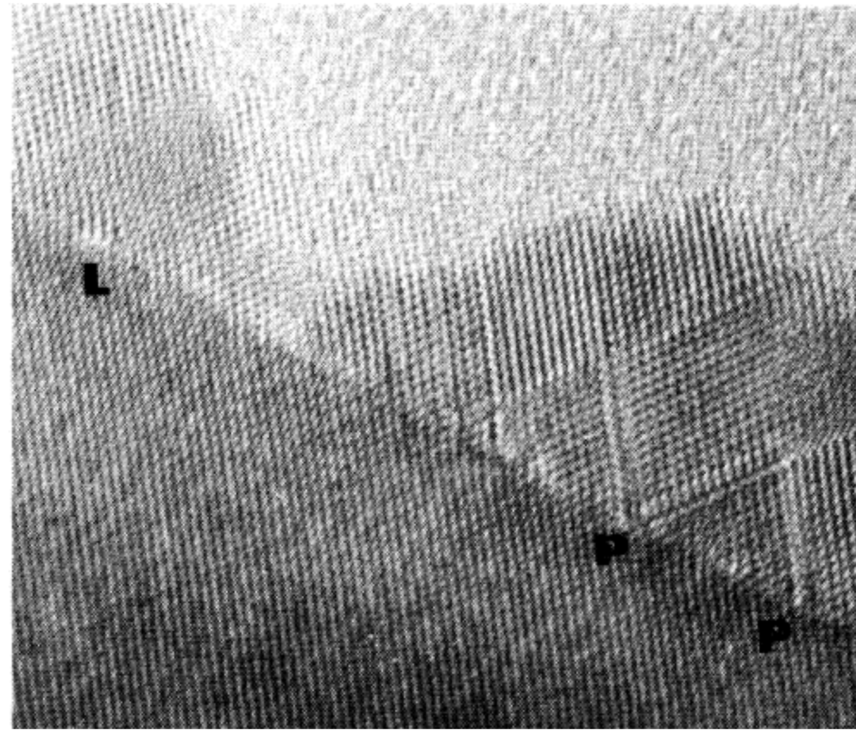
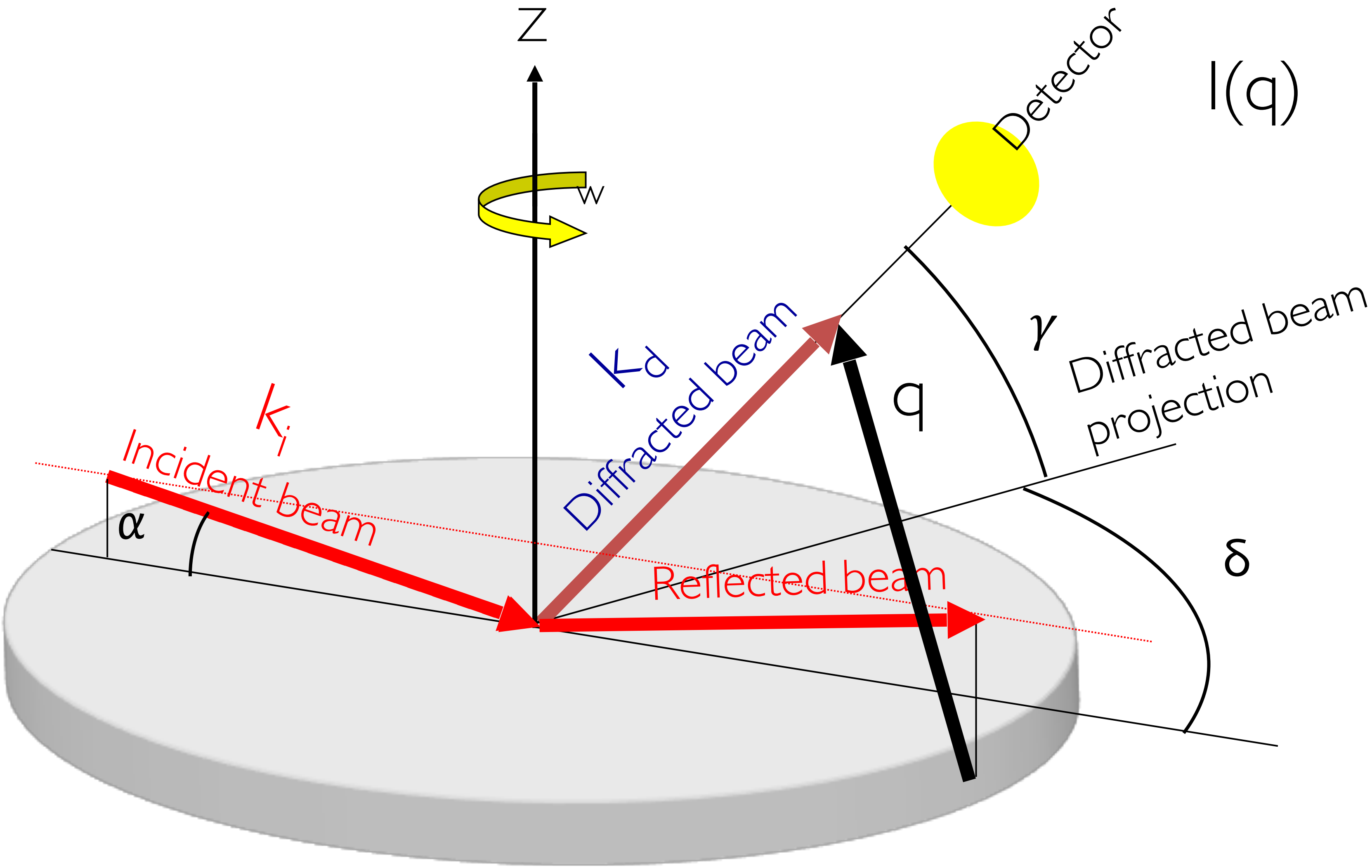



**FIG. 6.** Radial scans of the 15-ML ZnTe/GaAs at different inside angles. (curve a) $\alpha = \alpha_c$; (curve b) $\alpha = 0.3\alpha_c$.




V. H. Etgens et al. Phys. Rev. B47, 10607 (1993)

# DATA COLLECTION GEOMETRY




Scattering Vector : $q = k_d - k_i$

# Expression of the scattering intensity

$$I(\mathbf{q}) = |A(\mathbf{q})|^2 \propto \left| \int_\infty d^3r\, \rho(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) \right|^2$$

Kinematic approximation

Decomposition : crystal description

Atom $$f_{atome}(\mathbf{q}) = \int d^3r\ \rho_{atome}(\mathbf{r})\ e^{-i\mathbf{q}.\mathbf{r}}$$ Atomic scattering factor

Unit Cell $$F_n(\mathbf{q}) = \sum_j f_j\ e^{-i\mathbf{q}.\mathbf{r}_j} = TF[unit\ cell]$$ Structure Factor

Cristal $$A(\mathbf{q}) = \sum_n \sigma(\mathbf{R}_n)\ F_n(\mathbf{q})\ e^{-i\mathbf{q}.\mathbf{R}_n}$$

Lattice vector : $\mathrm{R_n}$

Crystal shape : $\sigma(\mathbf{r})$

Perfectly ordered structure : $F_n(\mathbf{q}) = F(\mathbf{q})$

The intensity diffused by the crystal is :

$$I(\mathbf{q}) = \frac{|F(\mathbf{q})|^2}{v^2}\left[ |\Sigma(\mathbf{q})|^2 \otimes \sum_{G_{hkl}} \delta(\mathbf{q}-G_{hkl}) \right]$$ where $\Sigma(\mathbf{q}) = TF[\sigma(\mathbf{r})]$

Atomic structure

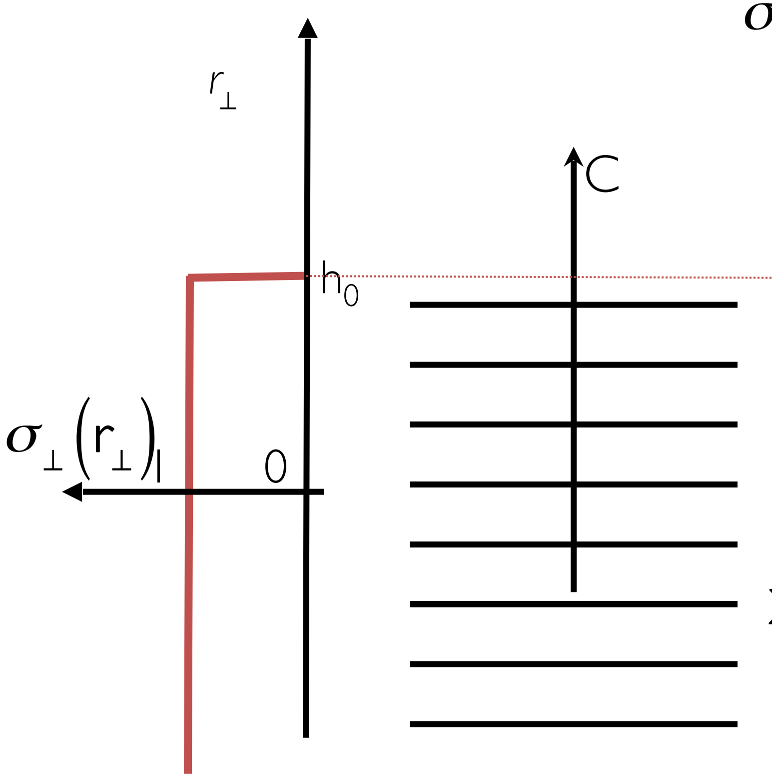
Finite size effects

periodicity

the atomic form factor is a complex quantity $f(q)=f^0(q)+f'+if''$

the terms f' et f'' are only dependent on the x-ray energy and represent the dispersion and absorption corrections, they take significant values in a close vicinity of absorption edges of the considered atom (anomalous effect)

# SEMI-INFINITE CRYSTAL




$$\sigma(r) = \sigma_{//}(r_{//})\ \sigma_\perp(r_\perp) \quad \text{where} \quad \sigma_{//}(r_{//}) = 1$$

$$\sigma_\perp(r_\perp) = 1 \quad \text{pour} \quad r_\perp < h_0$$

$$\sigma_\perp(r_\perp) = 0 \quad \text{pour} \quad r_\perp > h_0$$

Fourier transform of $\boldsymbol{\sigma}(r)$ : $\sum_{n=-\infty}^{+\infty} \frac{1}{(q_\perp - n\,c^*)^2} = \left( \frac{\pi}{c^* \sin(\pi L)} \right)^2$

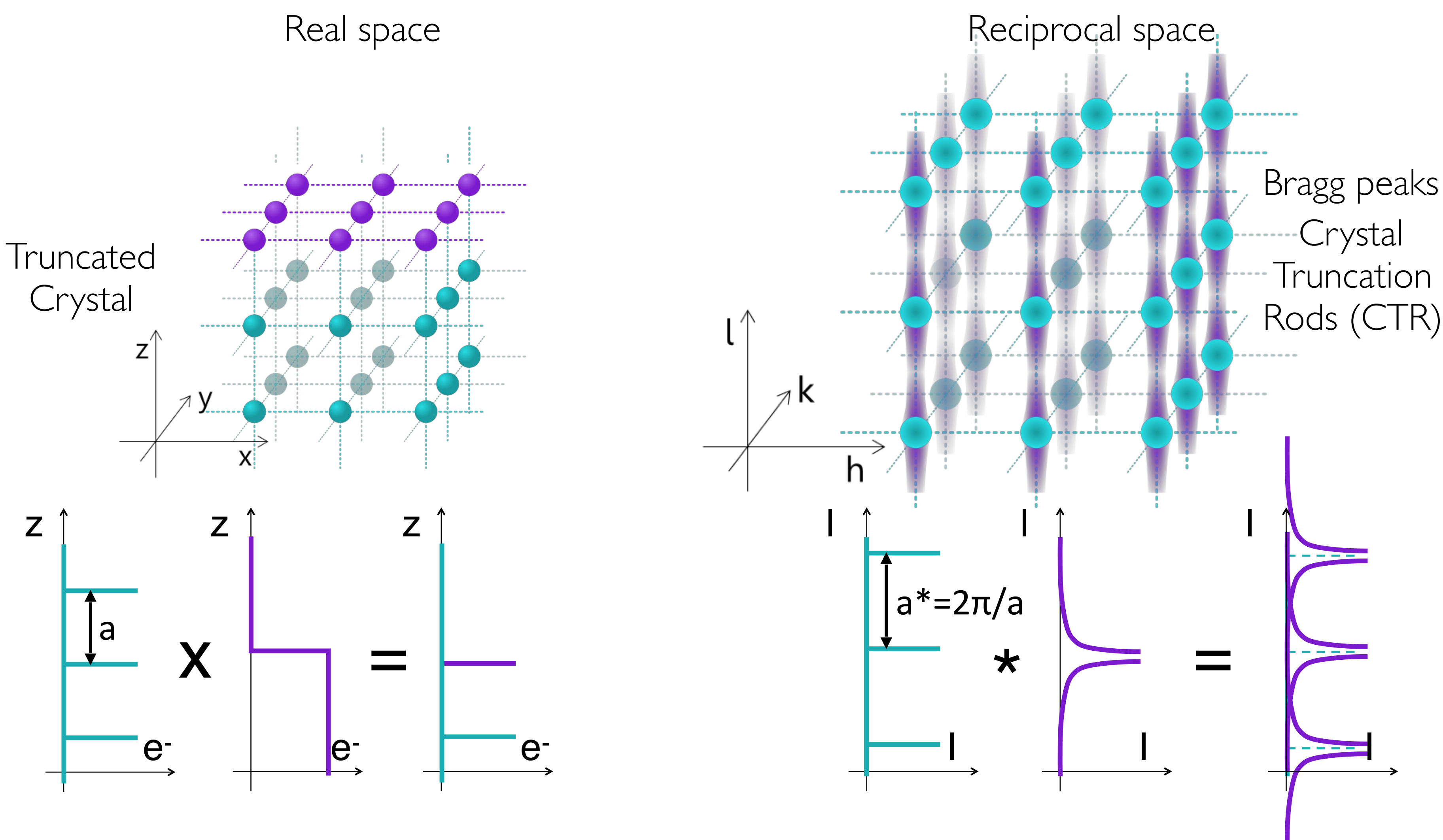
$$\Sigma(q) = \frac{e^{-iq_\perp . h_0}}{-iq_\perp}\ \delta(q_{//}) \Rightarrow \left|\Sigma(q)\right|^2 = \frac{1}{q_\perp^2}\ \delta(q_{//})$$

$$I(q) = \frac{\left|F(q)\right|^2}{s^2} \left( \frac{1}{2\sin(\pi l)} \right)^2 \left[ \sum_{G_{//}} \delta(q_{//} - G_{//}) \right]$$

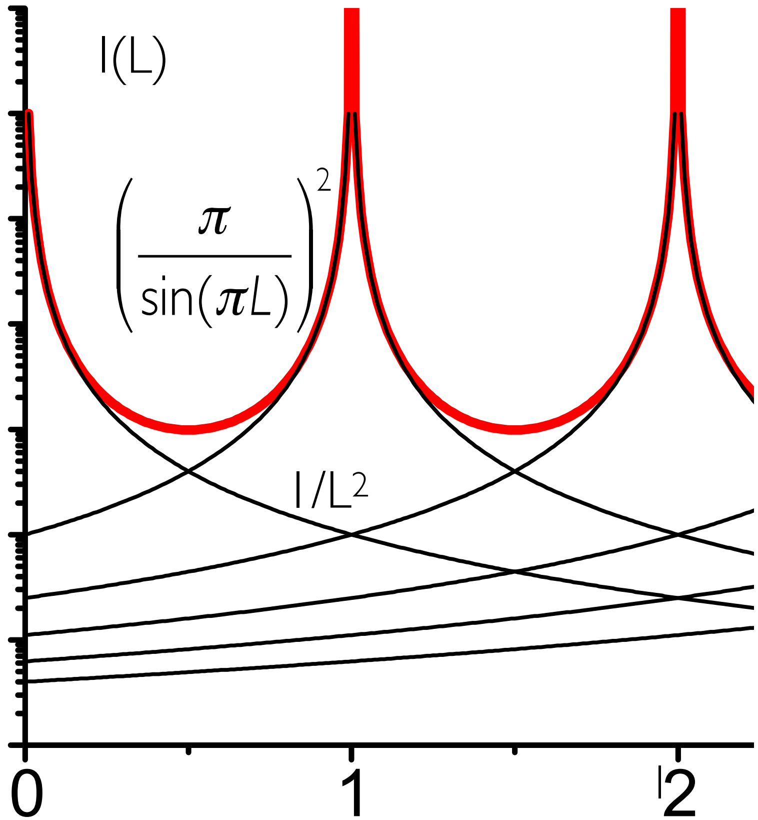
Crystal Truncation Rods (CTR):
issued from Bragg peak & perpendicular to the surface

# CRISTAL TRUNCATION ROD (CTR)

$$I(\mathbf{q}) = \frac{|F(\mathbf{q})|^2}{s^2}\left(\frac{1}{2\sin(\pi l)}\right)^2\left[\sum_{G_{//}}\delta(q_{//}-G_{//})\right]$$

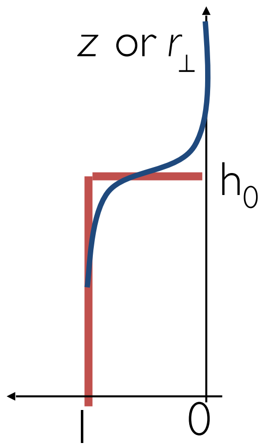


# Cristal troncation rod (CTR)




$$\sum_{n=-\infty}^{+\infty} \frac{1}{\left(q_\perp - n\, c^*\right)^2} = \left(\frac{\pi}{c^* \sin\left(\pi L\right)}\right)^2 \qquad q_\perp = Lc^*$$

# SURFACE ROUGHNESS




$$\sigma_\perp^{surf}(\mathrm{r}_\perp) = 1 \quad \text{for } r_\perp < h_0$$
$$\sigma_\perp^{surf}(\mathrm{r}_\perp) = 0 \quad \text{for } r_\perp > h_0$$

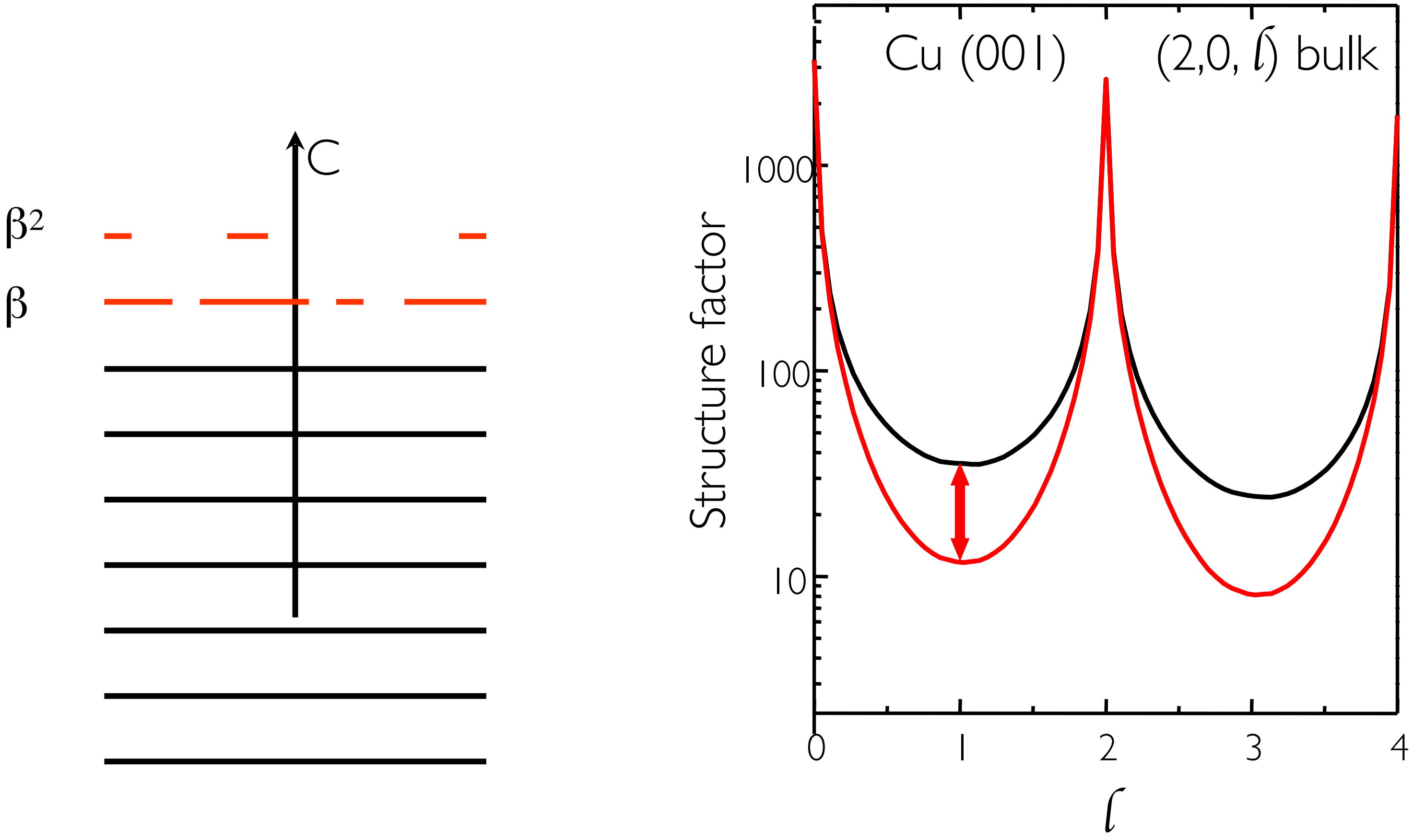
$$\sigma_\perp^{surf.\,rgh.}(\mathrm{r}_\perp) = \sigma_\perp^{surf}(\mathrm{r}_\perp) \otimes g(\mathrm{r}_\perp)$$

$$\Rightarrow \quad \left|\Sigma^{surf.rgh.}(\mathrm{q}_\perp)\right|^2 = \frac{1}{q_\perp^2}\left|TF\left[g(\mathrm{r}_\perp)\right]\right|^2$$

The Intensity decays more rapidly from the reciprocal node than for a flat surface
Roughness models:

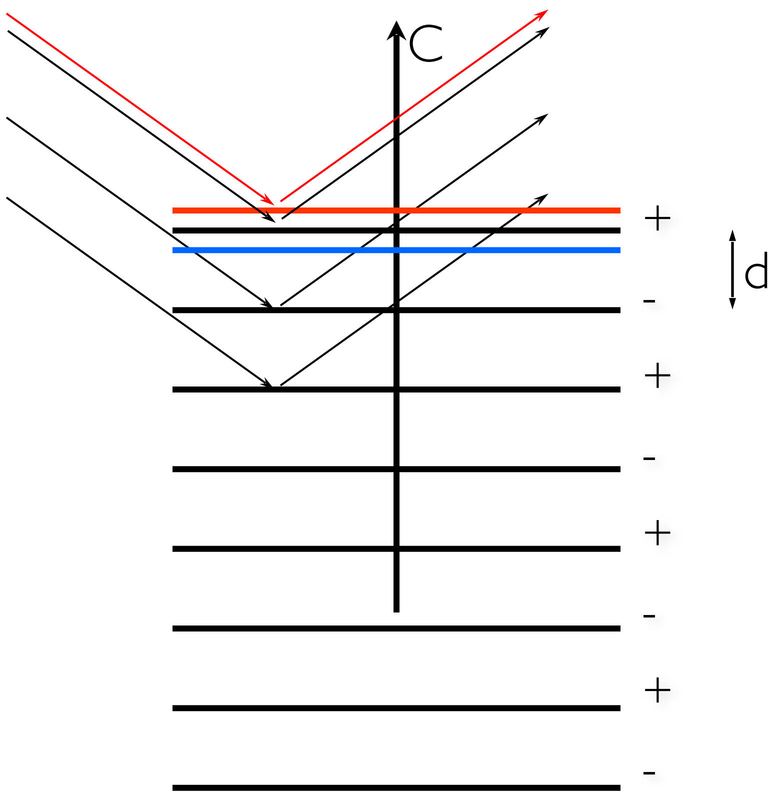
i. a simple two level model (E. Vlieg)
ii. an exponential decay (I. Robinson)
iii. a gaussian distribution of successive layers occupancy (P. Guenard)

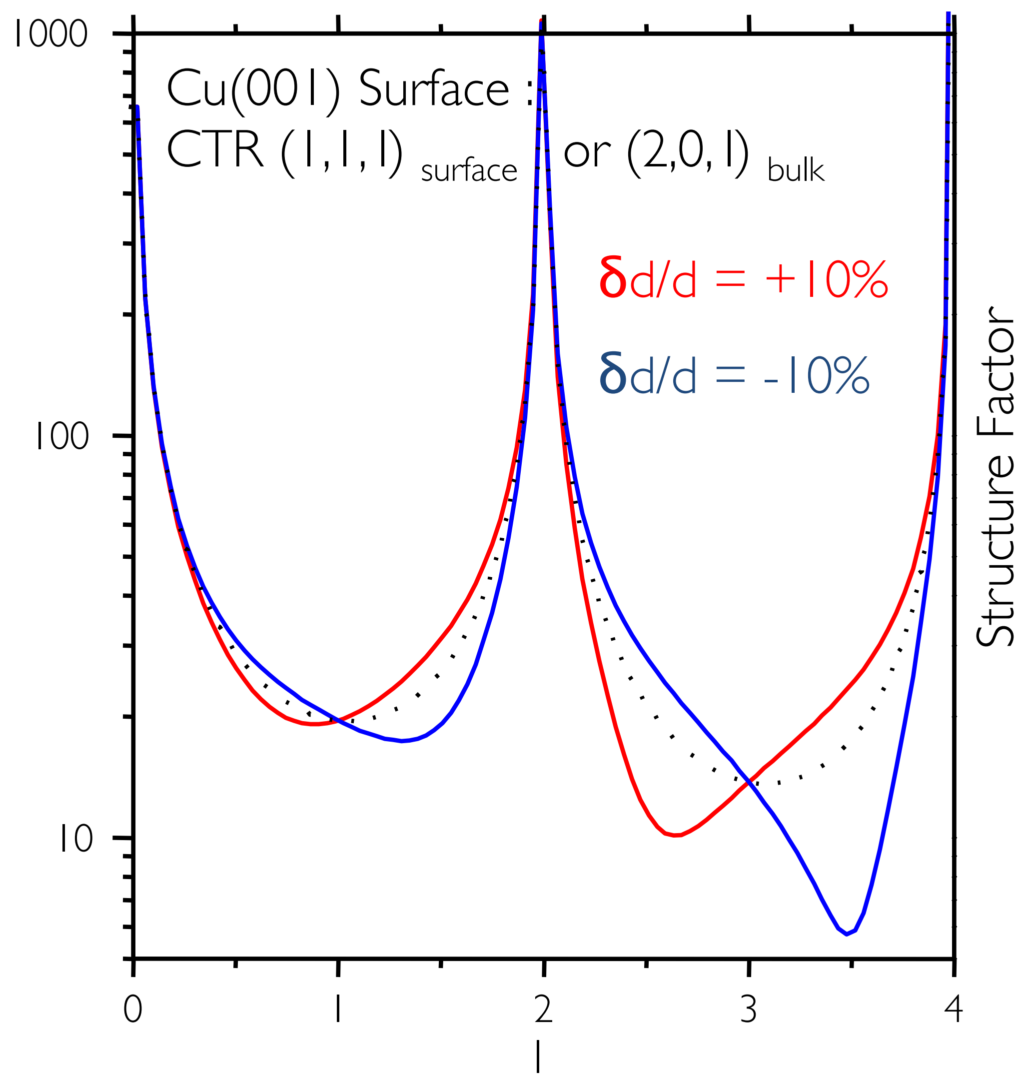
# CTR FROM A ROUGH SURFACE



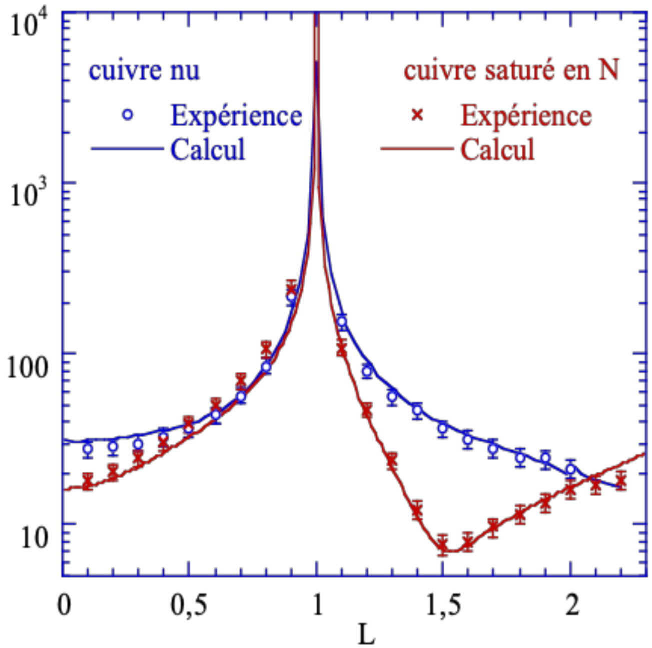

Optimal sensitivity in « anti-bragg » position, used to monitor layer by layer growth through pseudo-periodic oscillations

# CTR : Effect of the relaxation

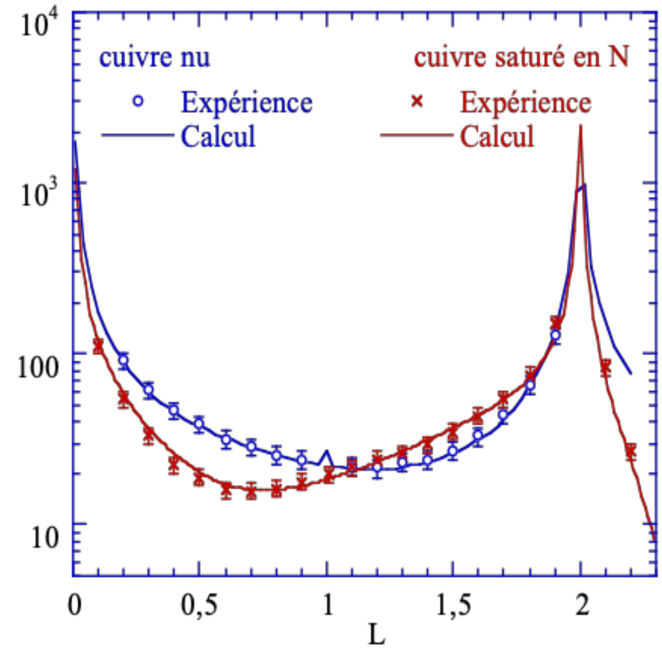


# CTR : Cu (001) et N/Cu(001)




Rod (1,1,L)




Rod (2,0,L)

| | bare Cu | saturated Cu(q =1) |
|---|---|---|
| Relaxation $d_{12}$<br>Relaxation $d_{23}$ | -3,16%<br>-0,54% | +13,54%<br>+1,46% |

B. Croset et al., Phys. Rev. Lett. 88,056103 (2002)

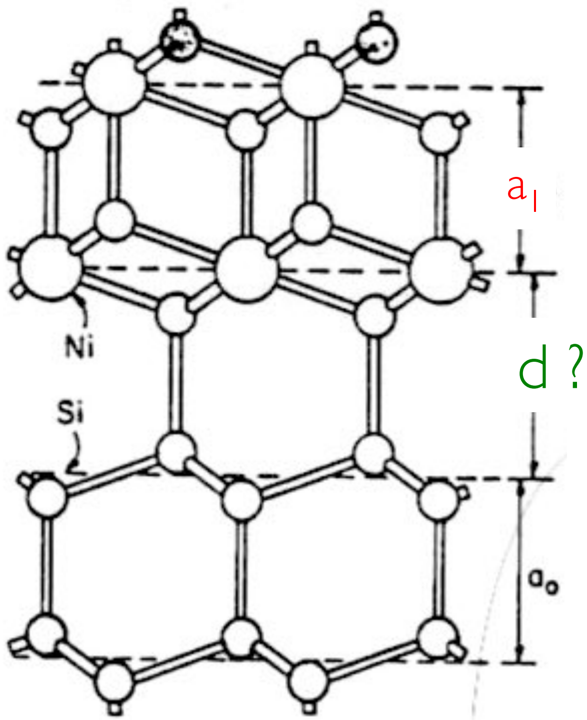
# CTR AND INTERFACES

SiNi2/Si(111) interface

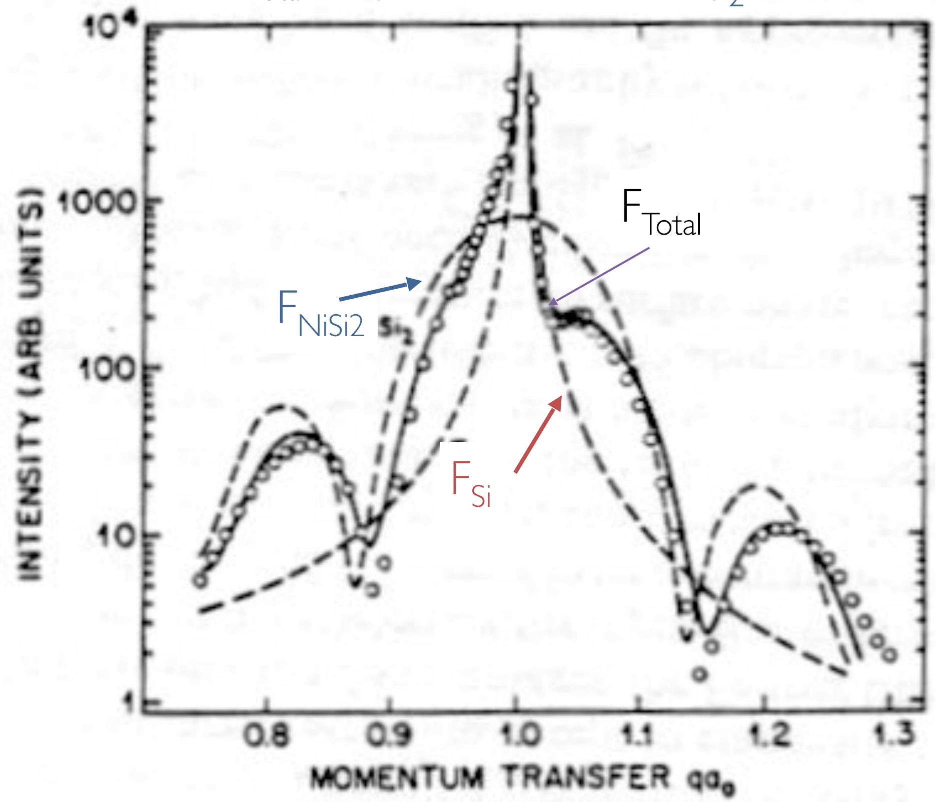
around Si(111) Bragg peak

$F_{Total} = F_{si} + \exp(2\pi l d)\, F_{NiSi2}$

NiSi2 Structure and thickness known




Si(111) structure known




Adjustment → $\frac{d}{a_o} = 1.10 \pm 0.02$ , $\frac{a_l}{a_o} = 0.996 \pm 0.003$

I. K. Robinson et al., Phys. Rev. B 38, 3632(R)

# 2D CRYSTAL

$\sigma(r) = \sigma_{//}(r_{//})\ \sigma_{\perp}(r_{\perp})$ where $\sigma_{//}(r_{//}) = 1$

$\sigma_{\perp}(r_{\perp}) = \delta(r_{\perp})$

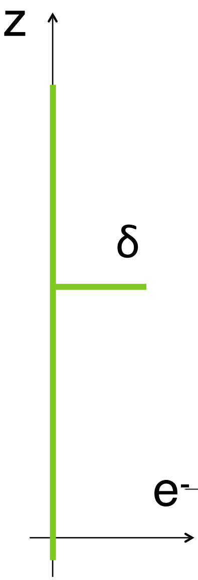
Fourier transform of $\sigma(r)$ :

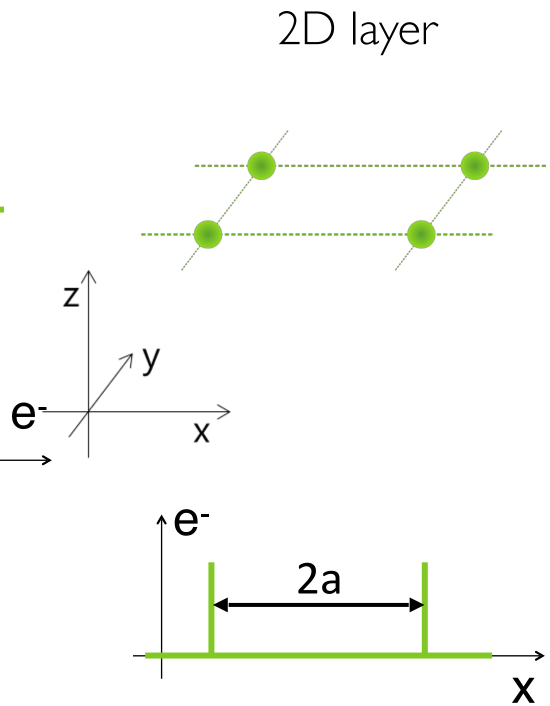
$\Sigma(q) = const\ \delta(q_{//}) \Rightarrow |\Sigma(q)|^2 = const^2\ \delta(q_{//})$

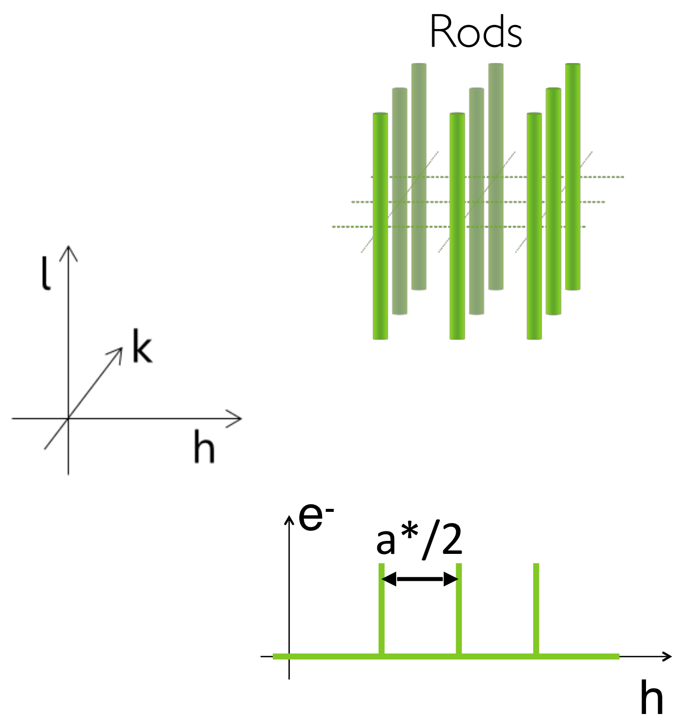
Real space

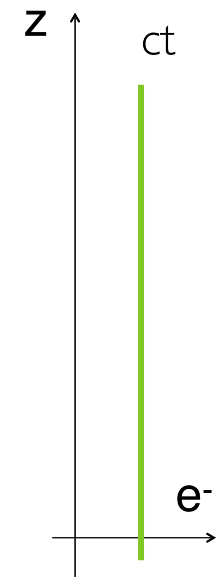
$$I(q) = \frac{|F(q)|^2}{s^2} const^2 \left[ \sum_{G_{//}} \delta(q_{//} - G_{//}) \right]$$

Reciprocal space



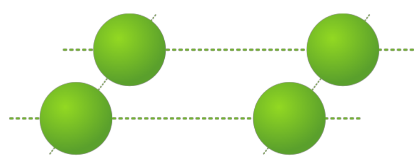



# 2D CRYSTAL

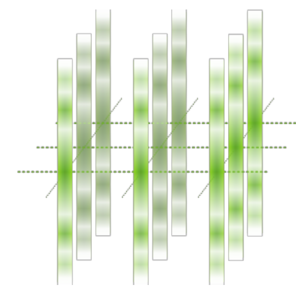
$$I(\mathrm{q}) = \frac{\left|F(\mathrm{q})\right|^2}{s^2} \, const^2 \left[\sum_{\mathrm{G}_{//}} \delta\left(\mathrm{q}_{//} - \mathrm{G}_{//}\right)\right]$$

2D layer of spheres

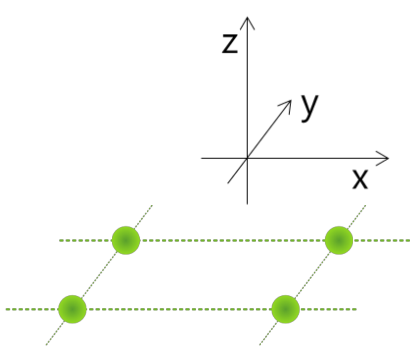
Real space



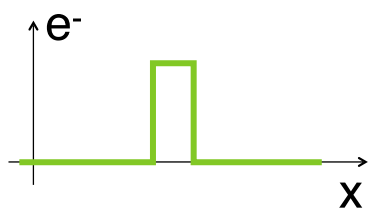
Reciprocal space

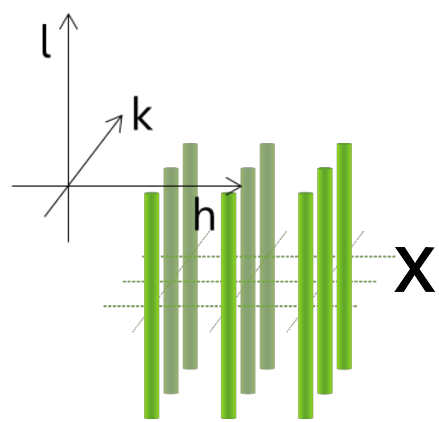


Modulated intensity

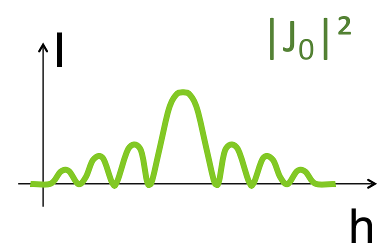



*

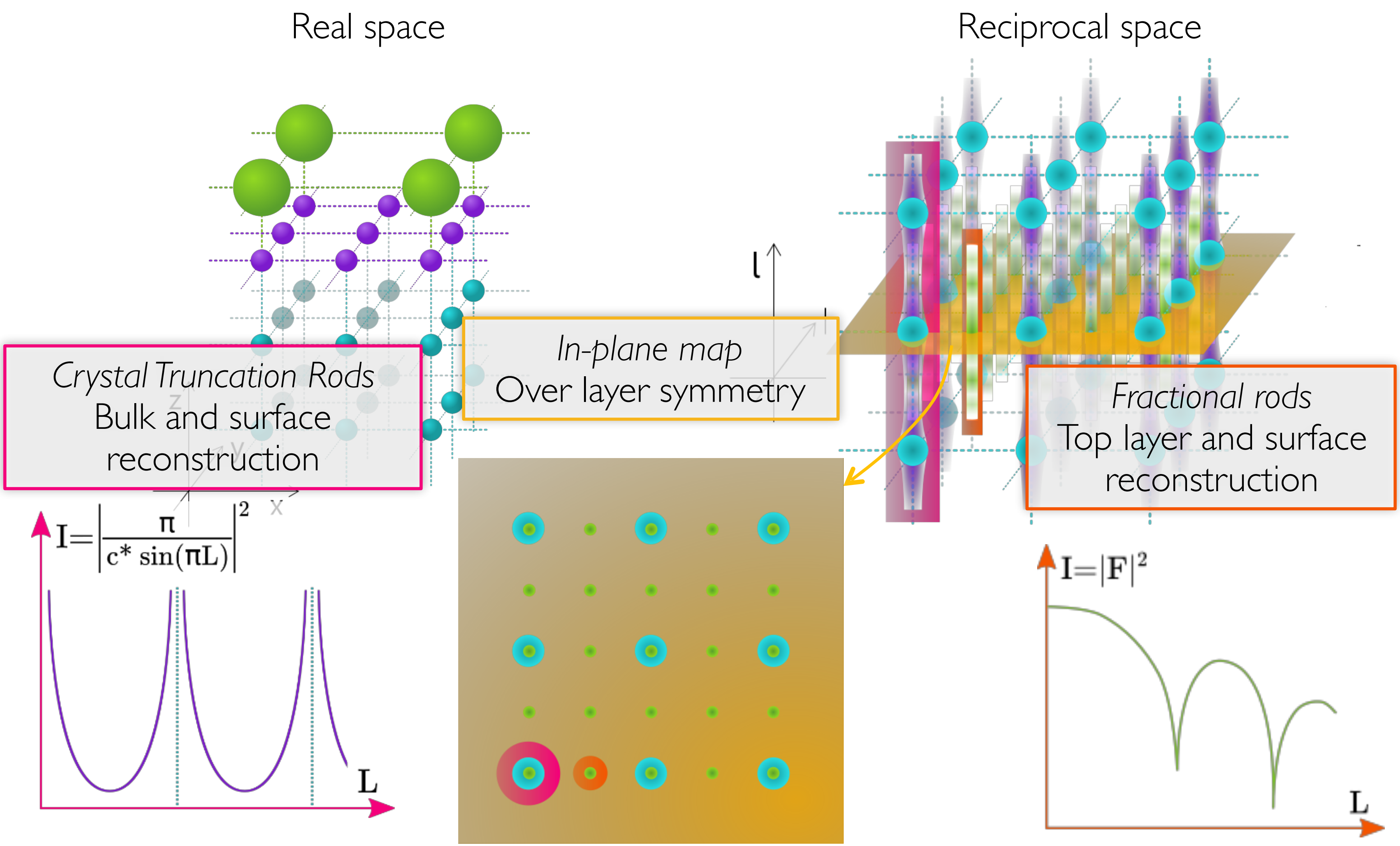



X

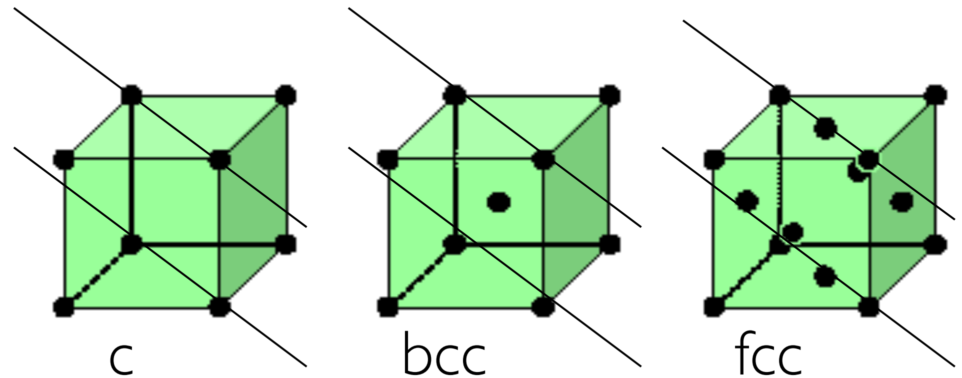


# Surface X-ray Diffraction

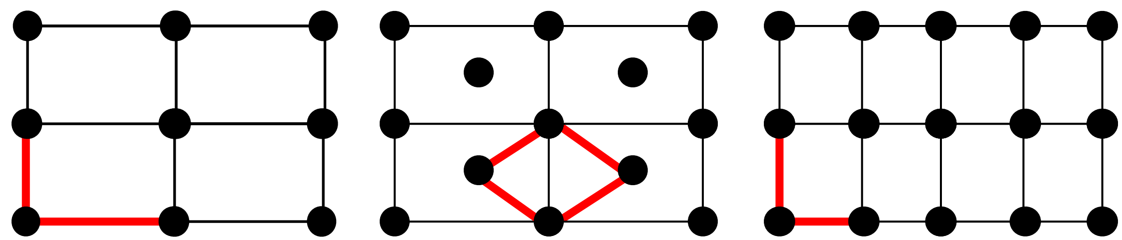


# SURFACE CRYSTALLOGRAPHY

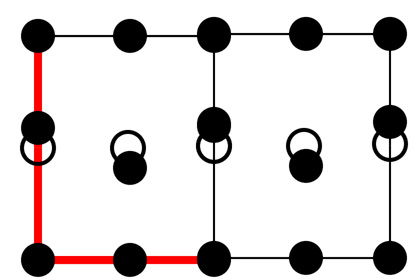
Ex: (110) cut in the 3 cubic lattices




Basis vectors $a_s$ $b_s$ of the 1x1 surface cells



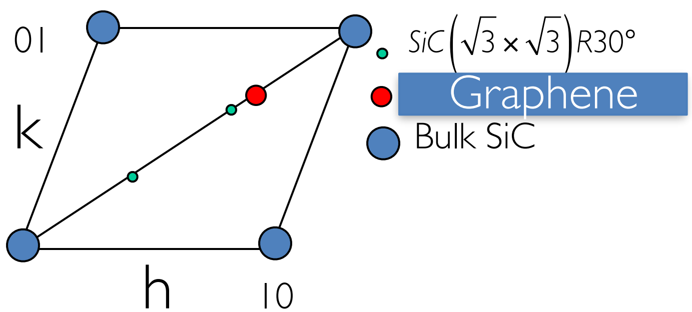
Basis vectors of a 2x2 unit cell on a reconstructed (110) surface of an fcc lattice

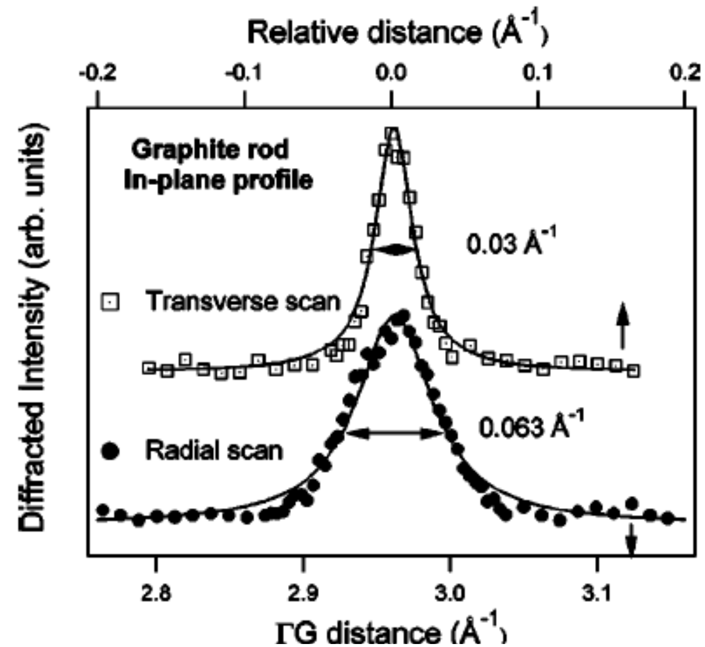


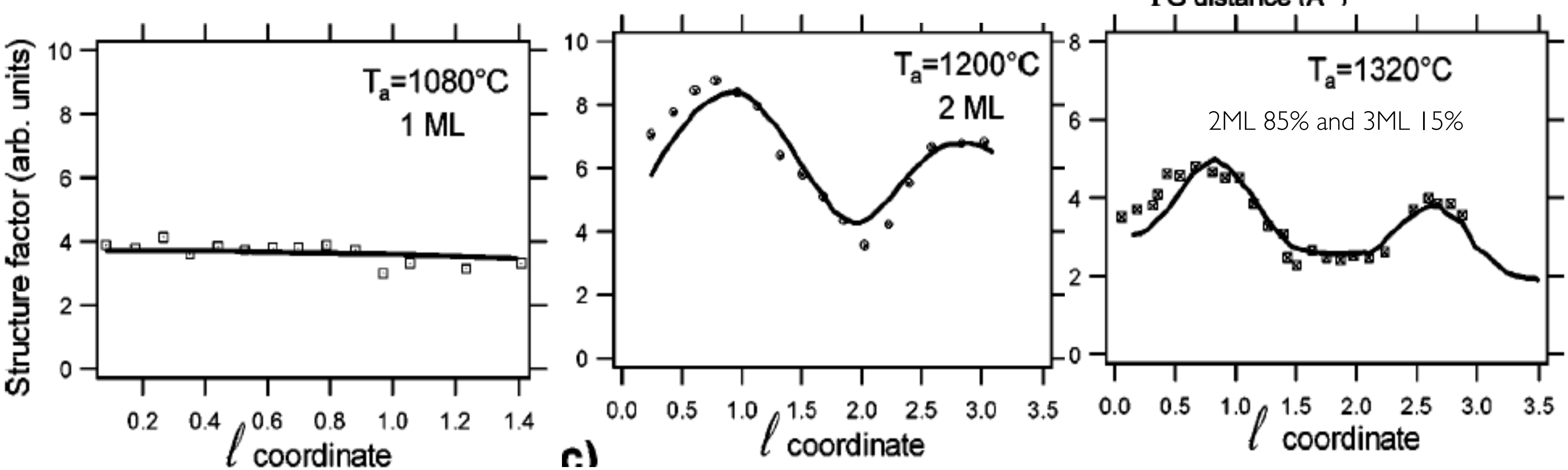
More generally mxn reconstruction

# GRAPHENE GROWTH

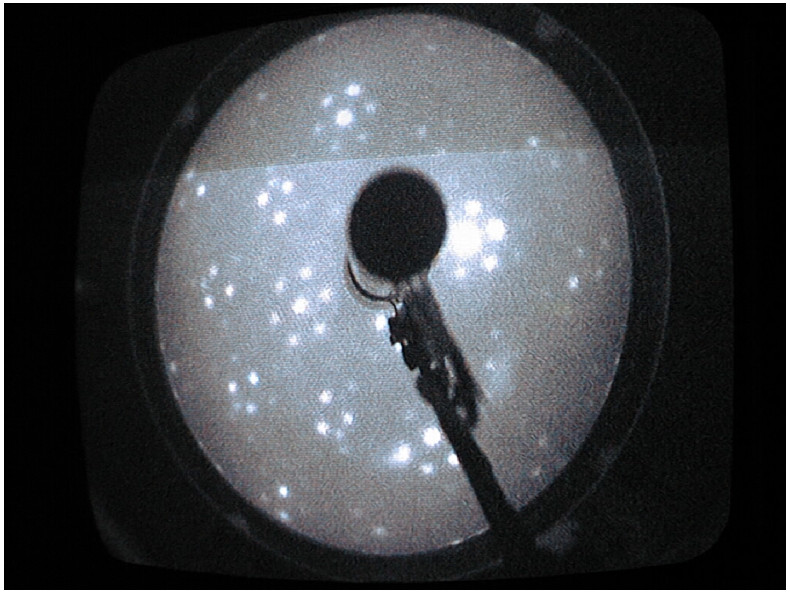
Charrier et al. J. Appl. Phys. 92, 2479(2002)

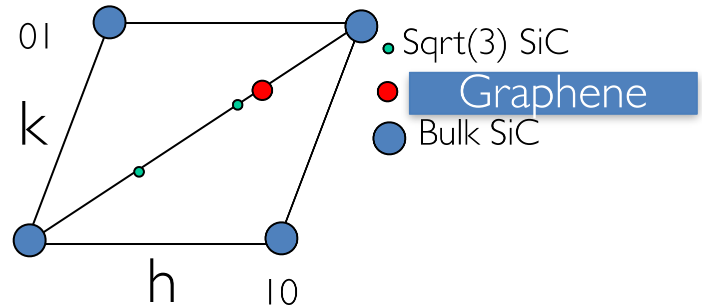


# LEED VS GIXD






$$apparent\left(6\sqrt{3}\times 6\sqrt{3}\right)$$

A fully relaxed graphene plane in registry with the SiC substrate

Multiple scattering versus single scattering

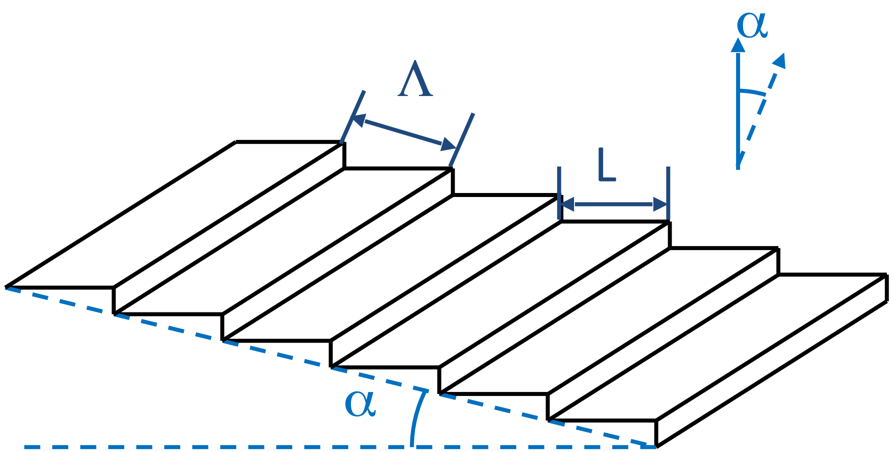
# ROD SOFTWARE

The « ROD » code

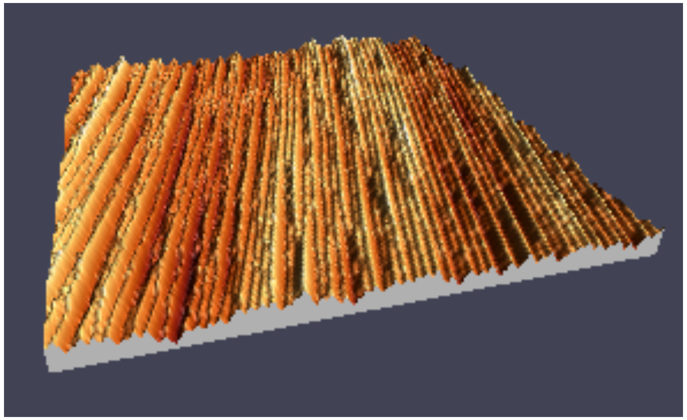
E. Vlieg, J. Appl. Cryst, 33, 401 (2000)
➔interactive webpage ANA-ROD

http://www.esrf.fr/computing/scientific/joint_projects/ANA-ROD/index.html

# Vicinal Surface

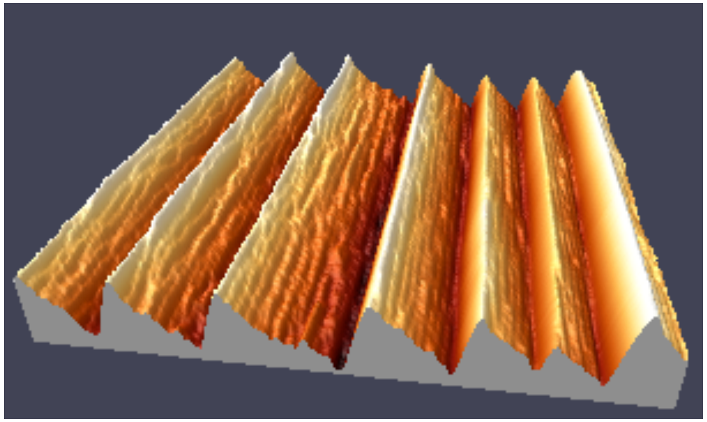



Cu(433) (100x100) nm

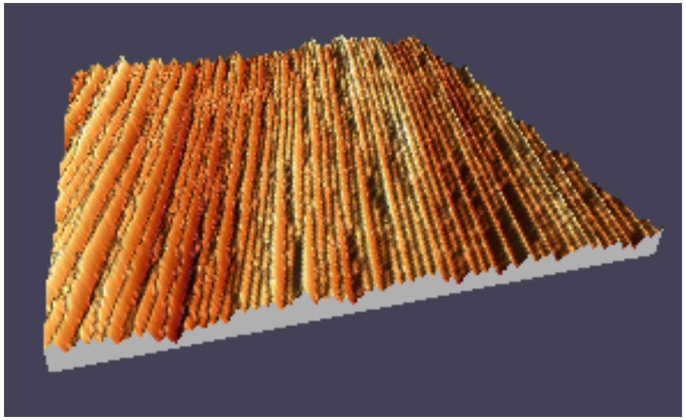


# Self Organisation: Ag/Cu

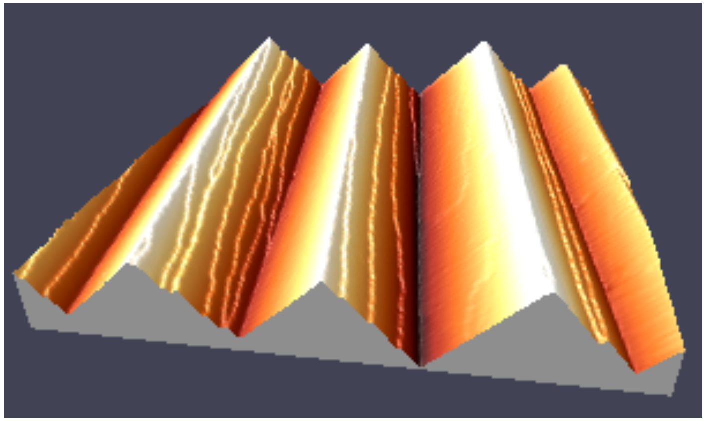
0.3 ML Ag/Cu(433) (200x200) nm



Cu (433) (100x100) nm

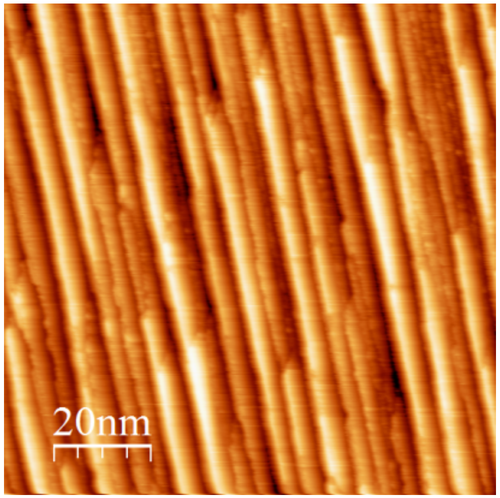


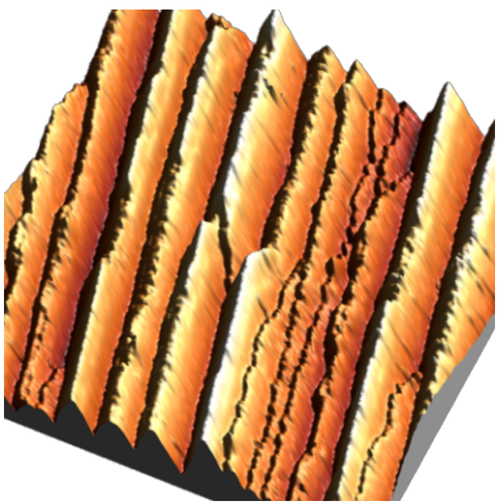
0.6 ML Ag/Cu(433) (200x200) nm



# Self Organisation: Ag/Ni

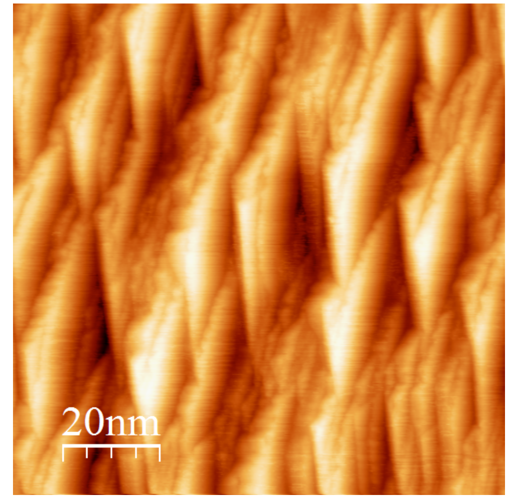
Ag/Ni(11 9 9)

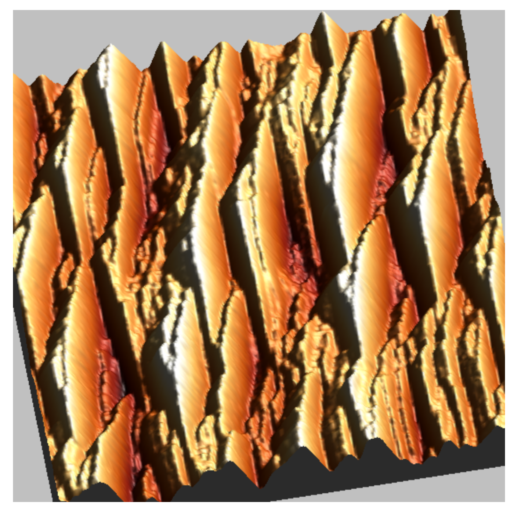


Organisation 1D

Ag/Ni(27 17 19)

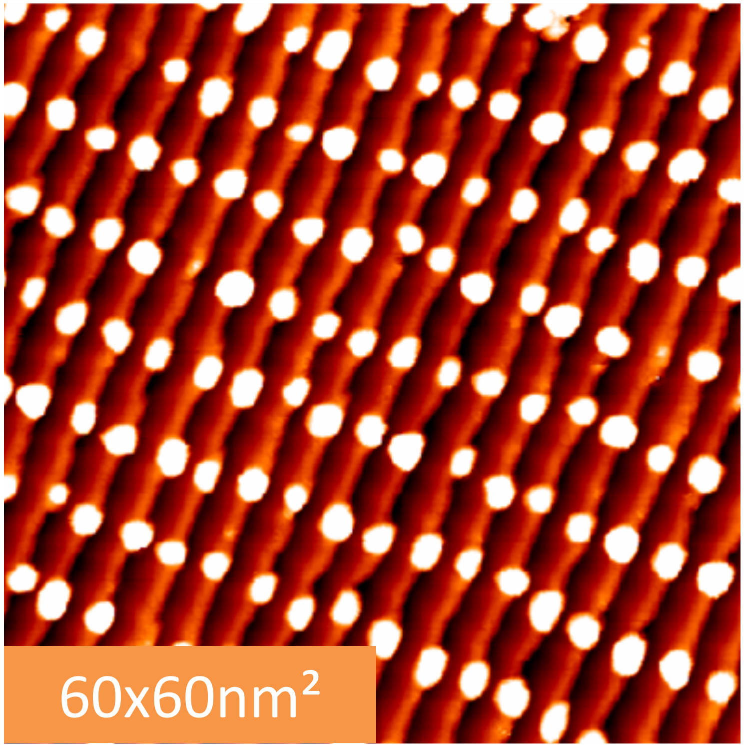


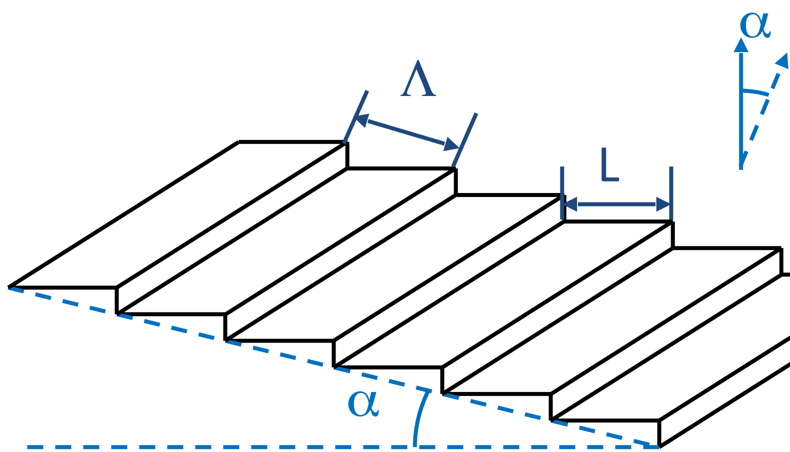
Organisation 2D

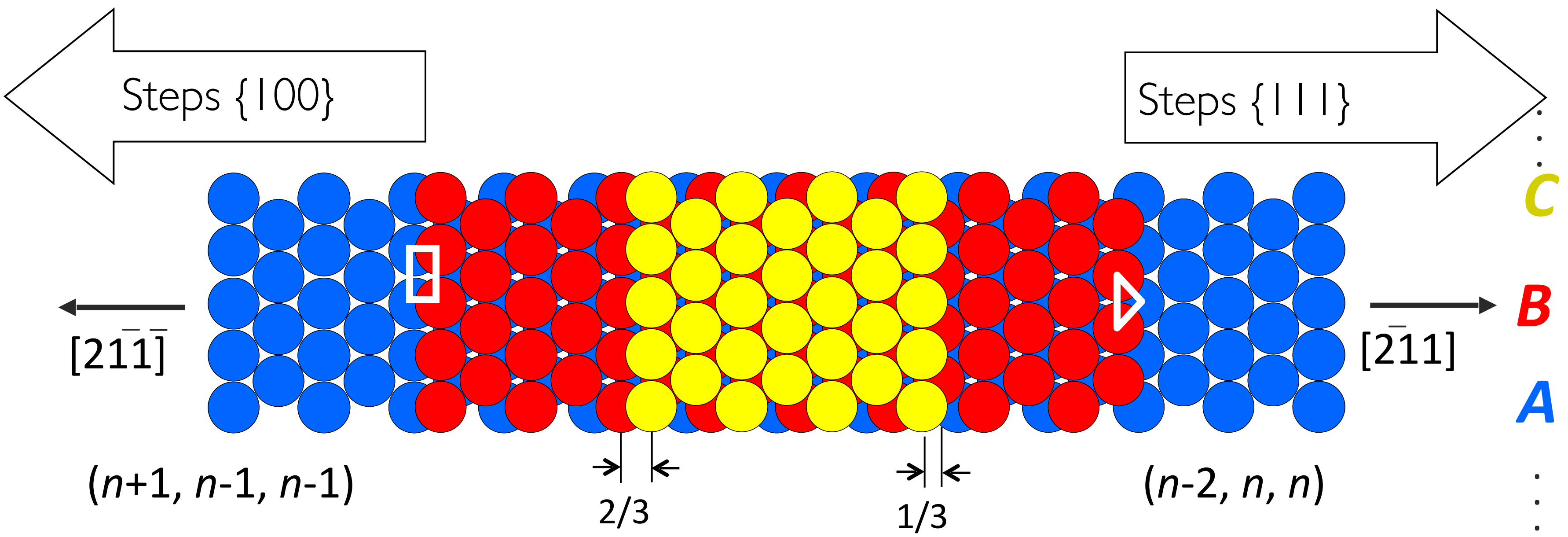
# Self Organisation: Co/Au

Co/Au(788)



# Vicinal Surfaces (111) FCC

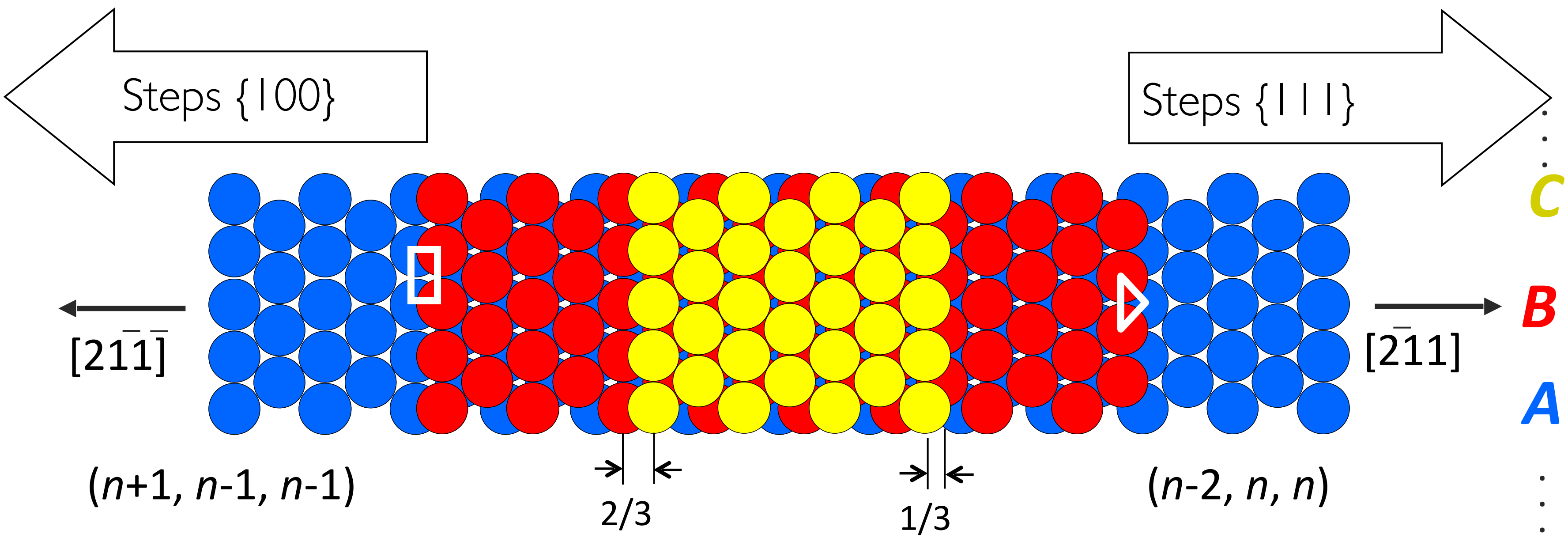


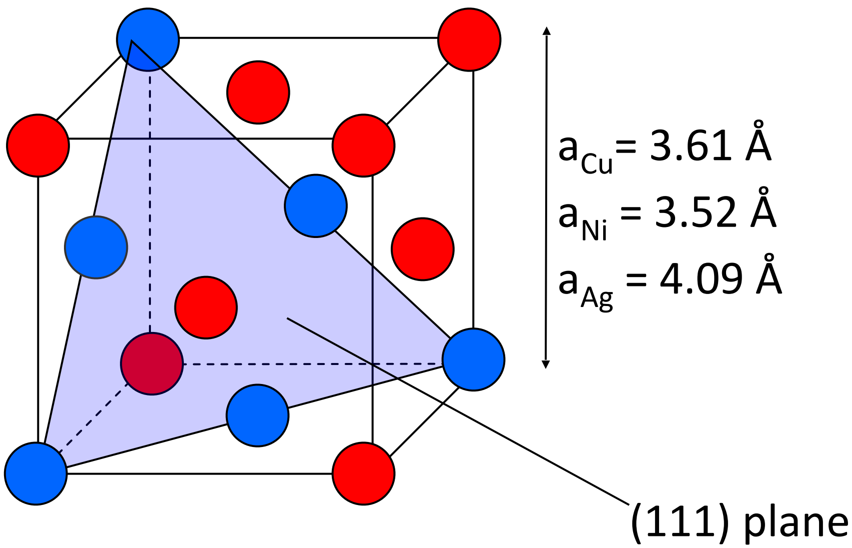
# VICINAL SURFACES (111) FCC

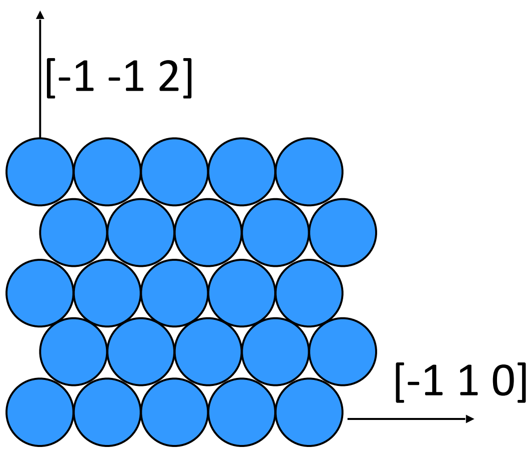
| | Angle (°) | Lines | Λ (nm) |
|---|---|---|---|
| Cu(211) | (-)19.5 | 2+2/3 | 0.626 |
| Au(322) | (-)11.4 | 4+2/3 | 1.17 |
| Ni(1199) | (-) 5.57 | 9+2/3 | 2.096 |

| | Angle (°) | Lines | Λ (nm) |
|---|---|---|---|
| Au(233) | 10.0 | 5+1/3 | 1.33 |
| Ag(133) | 22.0 | 2+1/3 | 0.629 |
| Ag(799) | 6.46 | 8+1/3 | 2.095 |



# "Model Systems": Ag/Cu, Ag/Ni



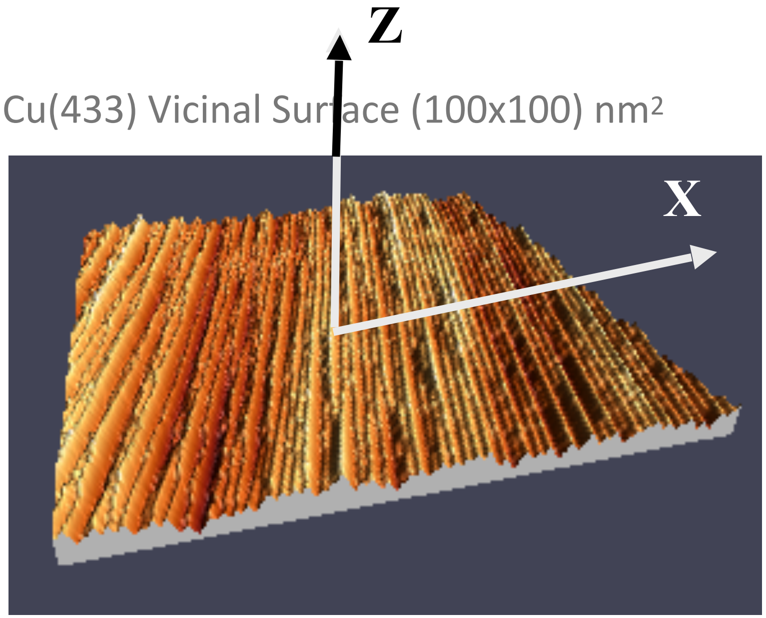




- fcc structure
- Immiscibles
- atomic radii $r_{Ag}/r_{Cu}=1,13$ $r_{Ag}/r_{Ni}=1,15$
- cohesion energies : $E_{NCu}$=-3,50 eV $E_{cNi}$=-4,44 eV $E_{cAg}$=-2,96 eV

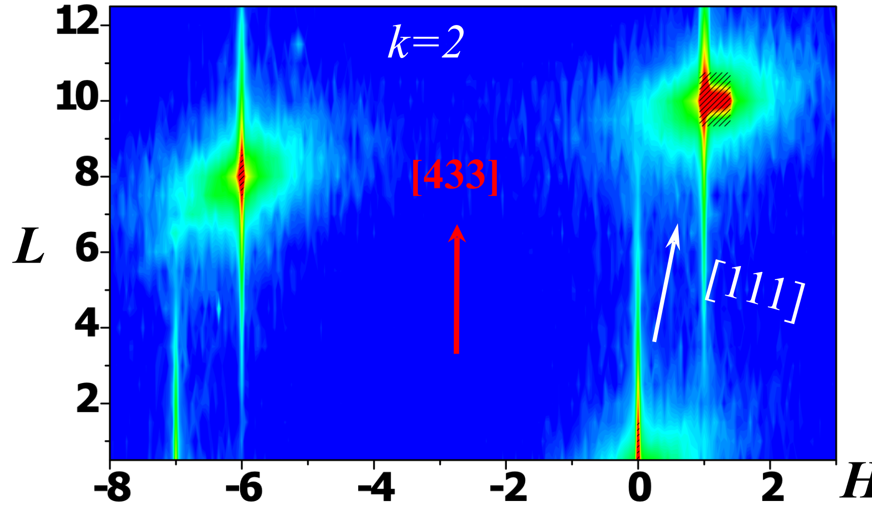
Ag segregates on Ni or Cu
Abrupt Interfaces

# ABSORBATE INDUCED FACETING : X-RAY MEASUREMENTS

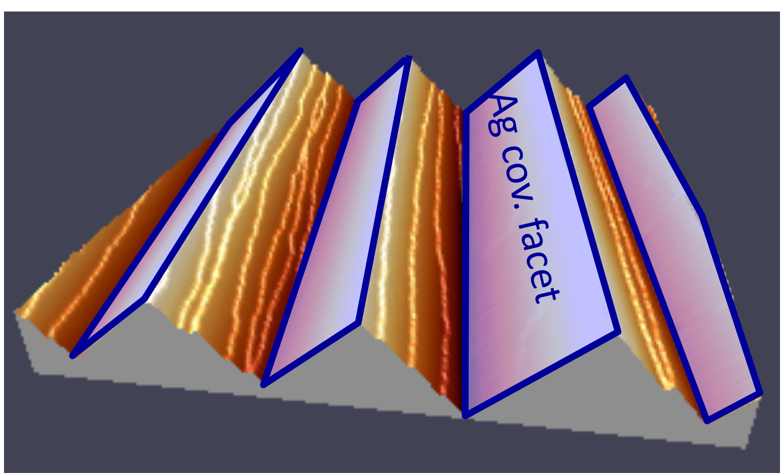
Cu(433) Vicinal Surface (100x100) nm²



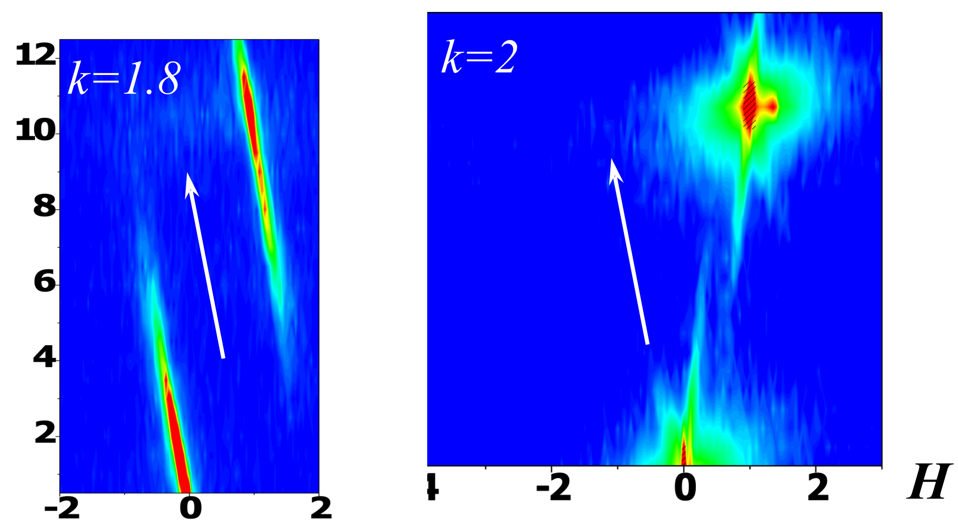

X-ray measurement : Cu(433)



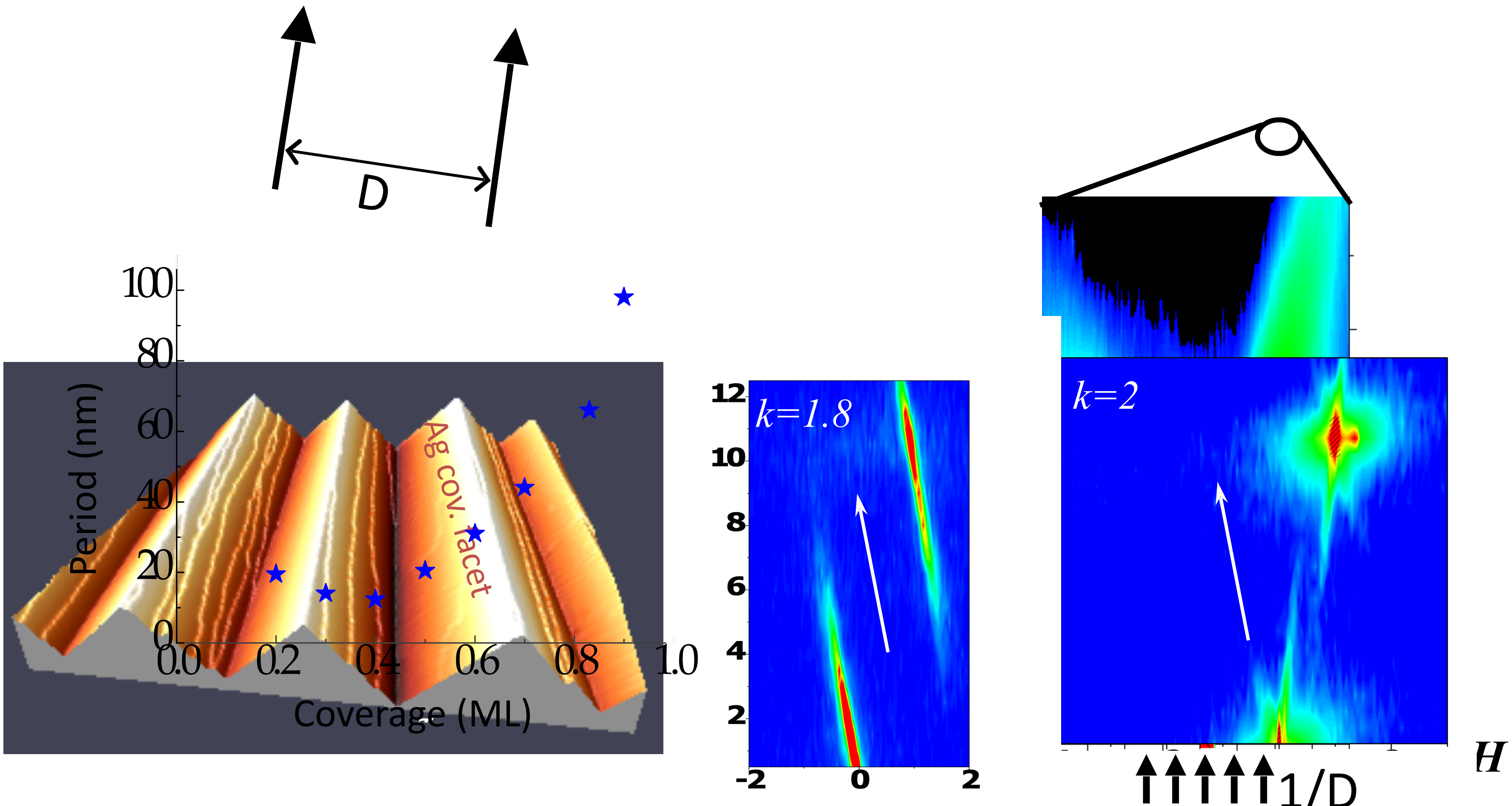

~1/3 ML Ag/Cu(433) (200x200) nm²



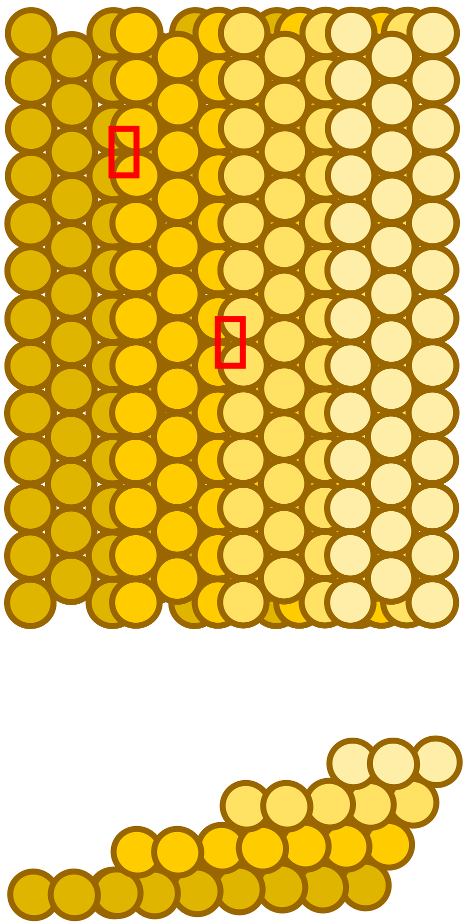

After Ag deposition and annealing

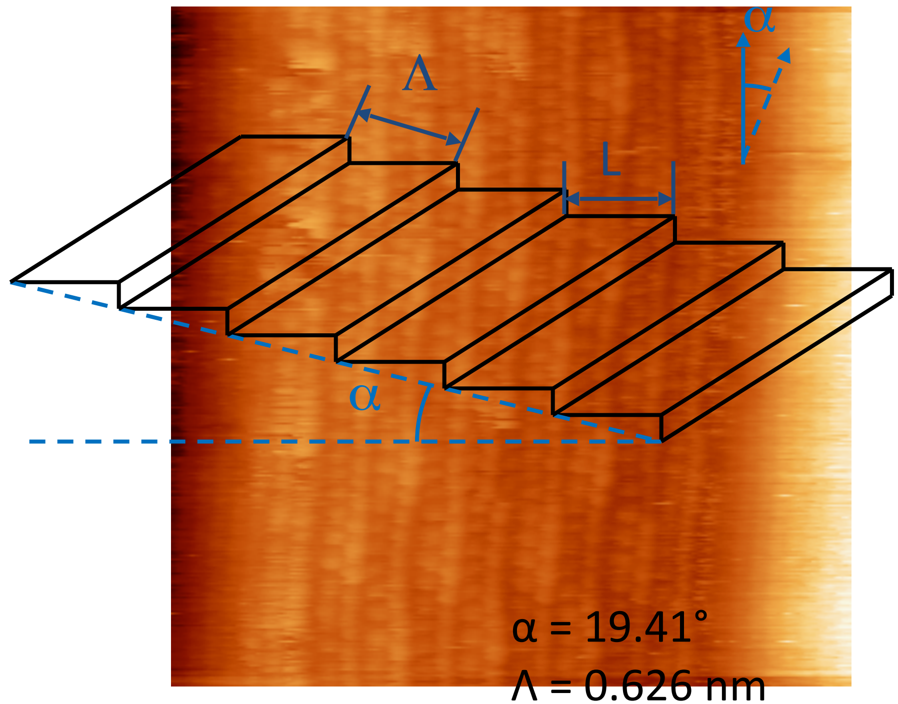


# Absorbate induced faceting : X-ray measurements

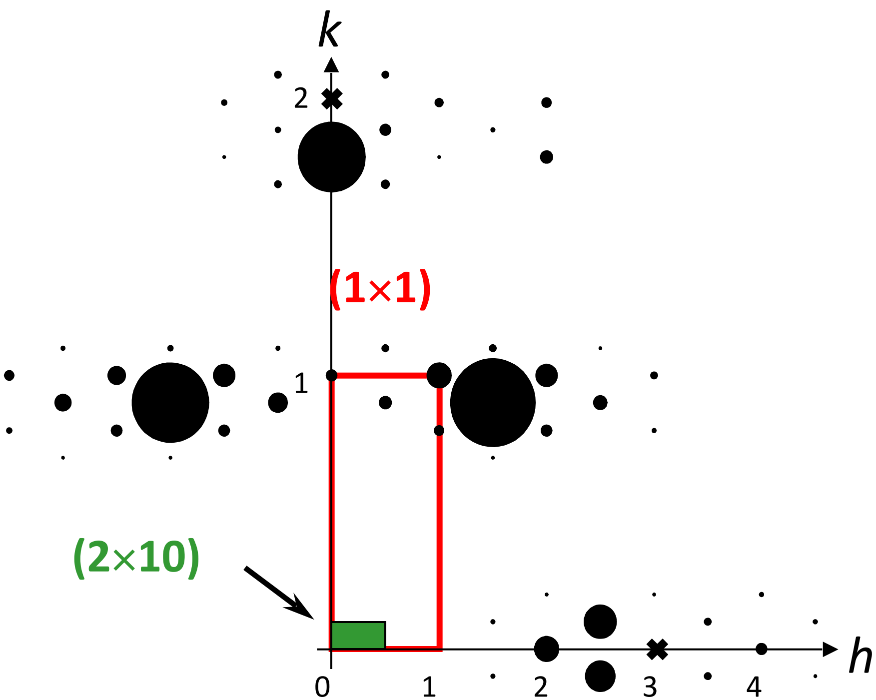


# 1 ML Ag/Cu(211)

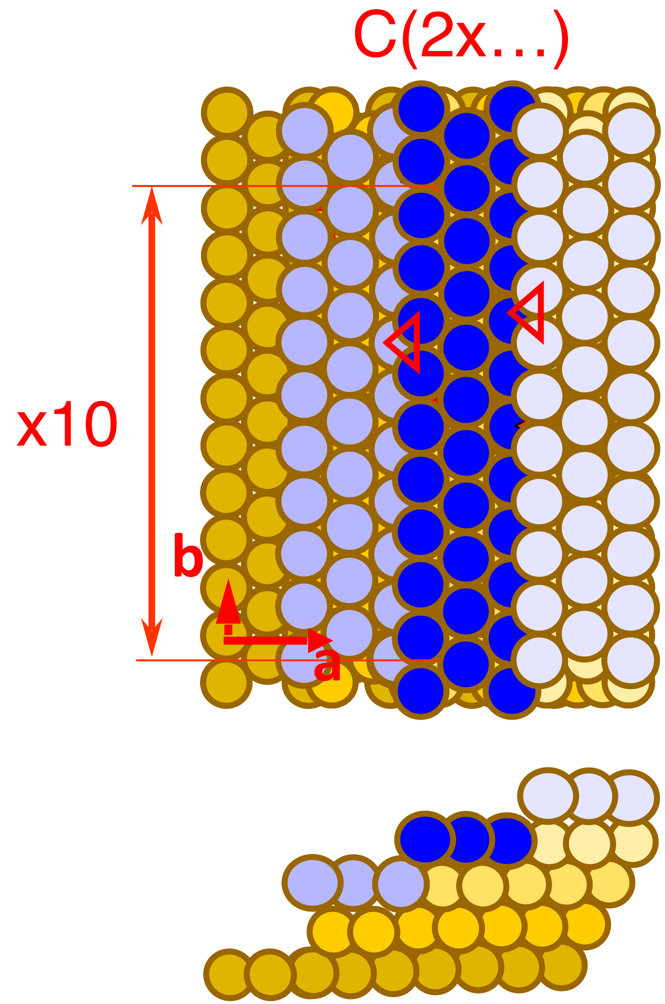




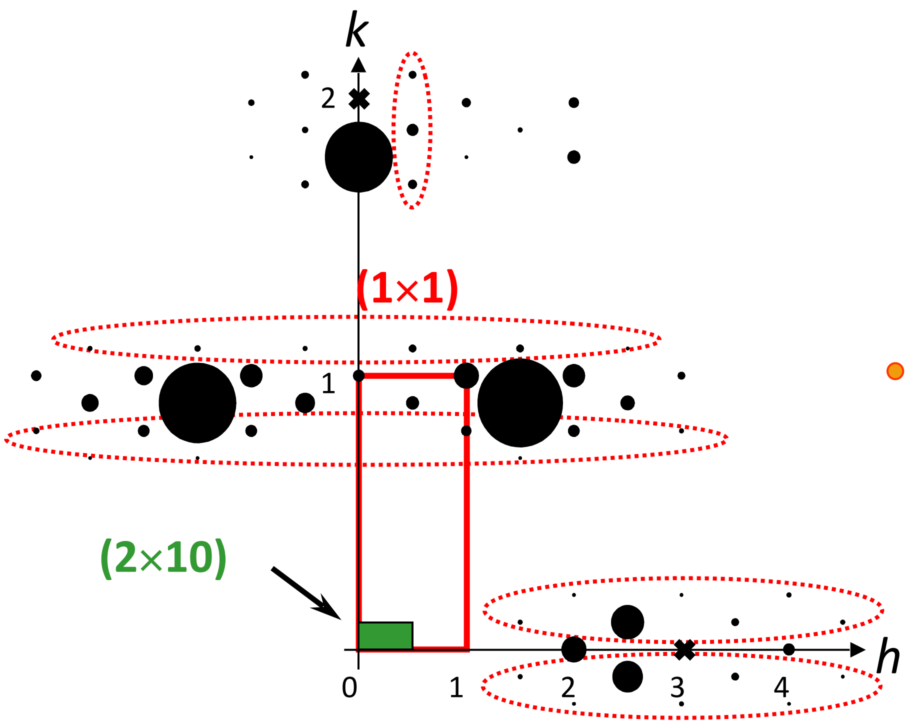
# 1 ML Ag/Cu (211) - reconstruction C(2x10)



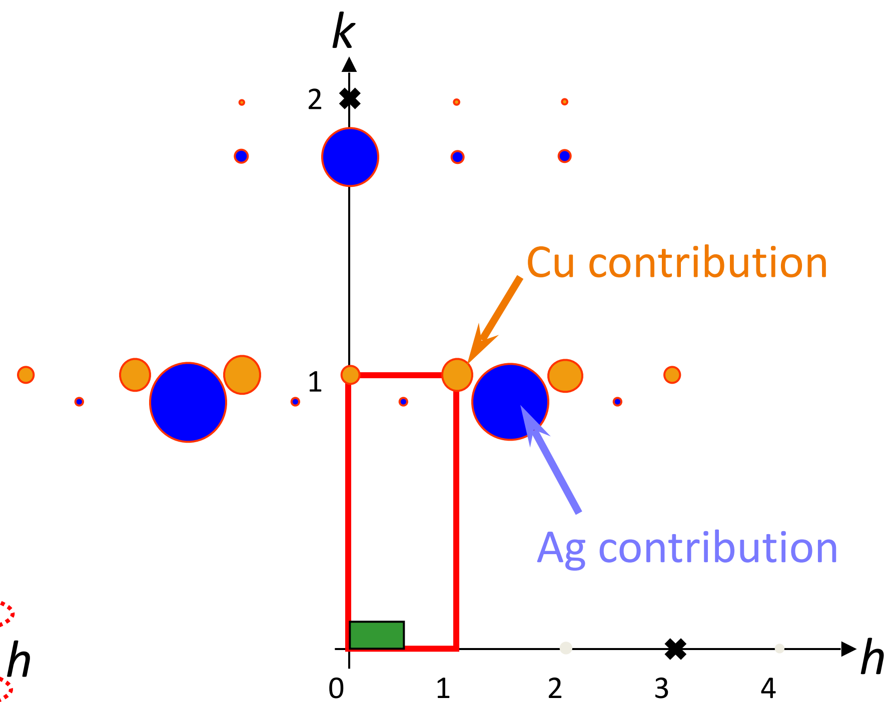

GIXD measurements



# 1 ML Ag/Cu(211) – GIXD



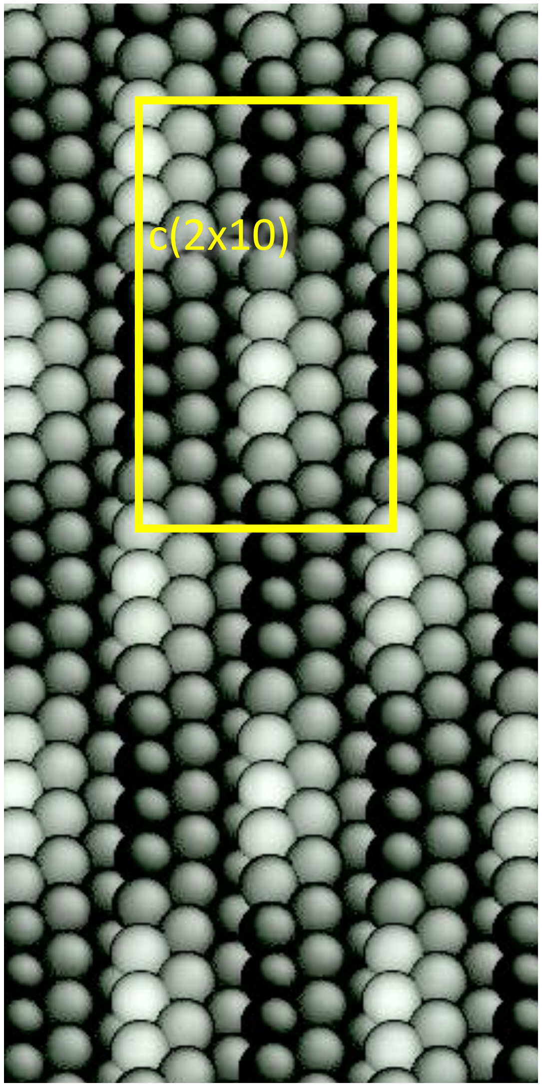

GIXD

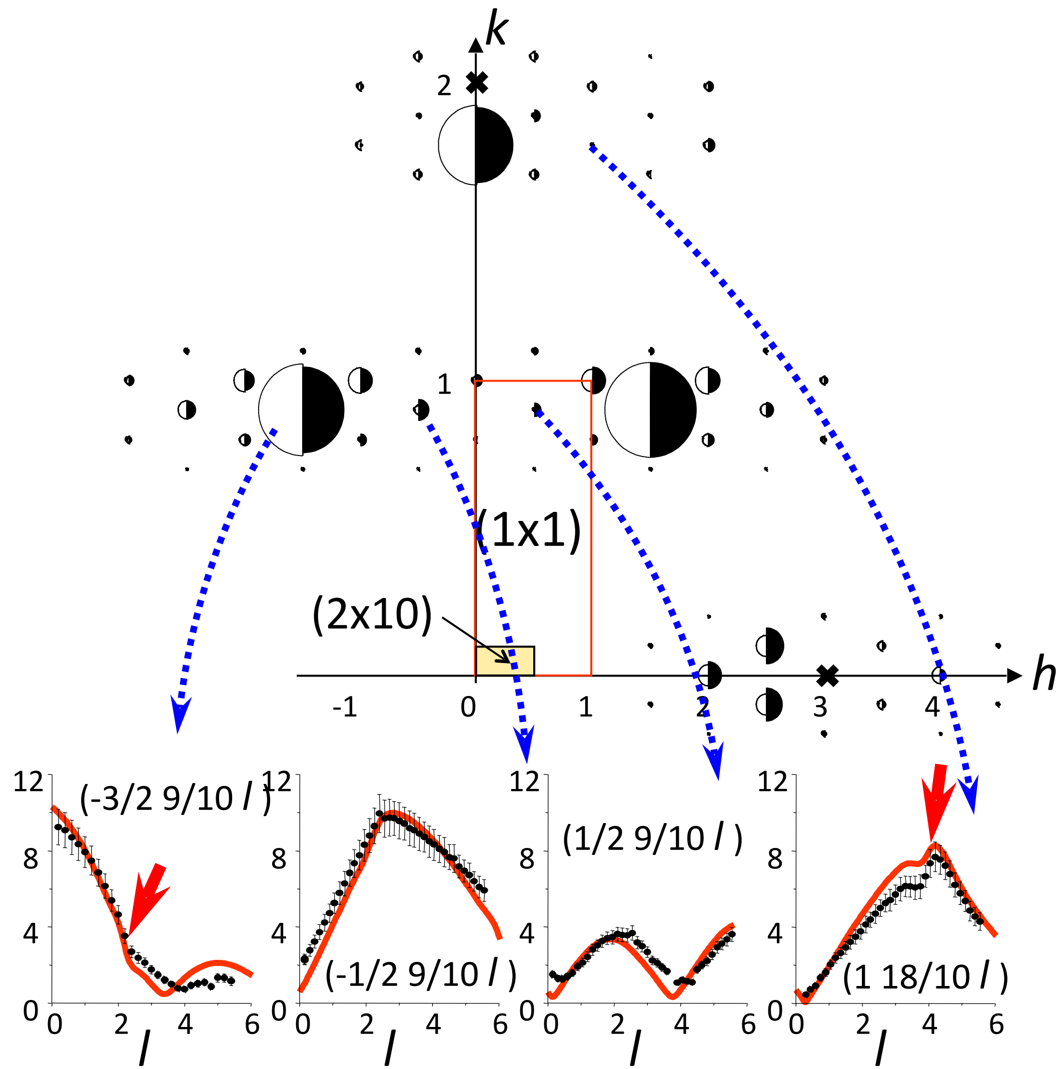



Simulation

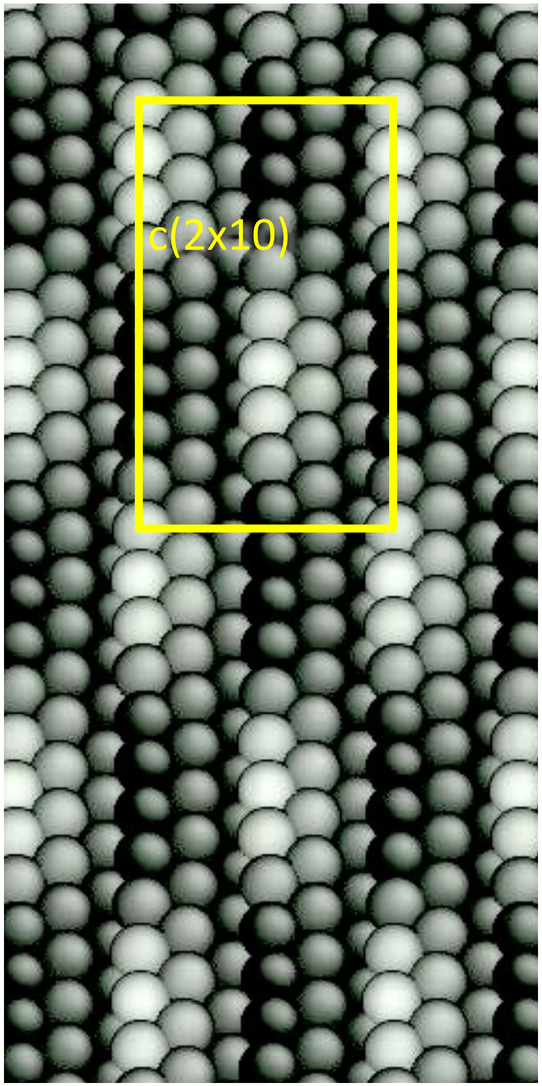
The structure is not relaxed !

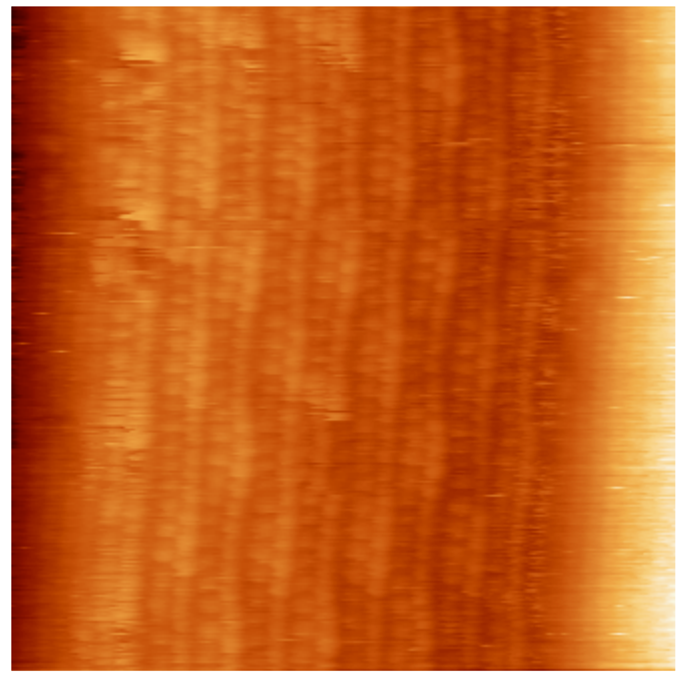
# 1 ML Ag/Cu(211) - GIXD et QMD



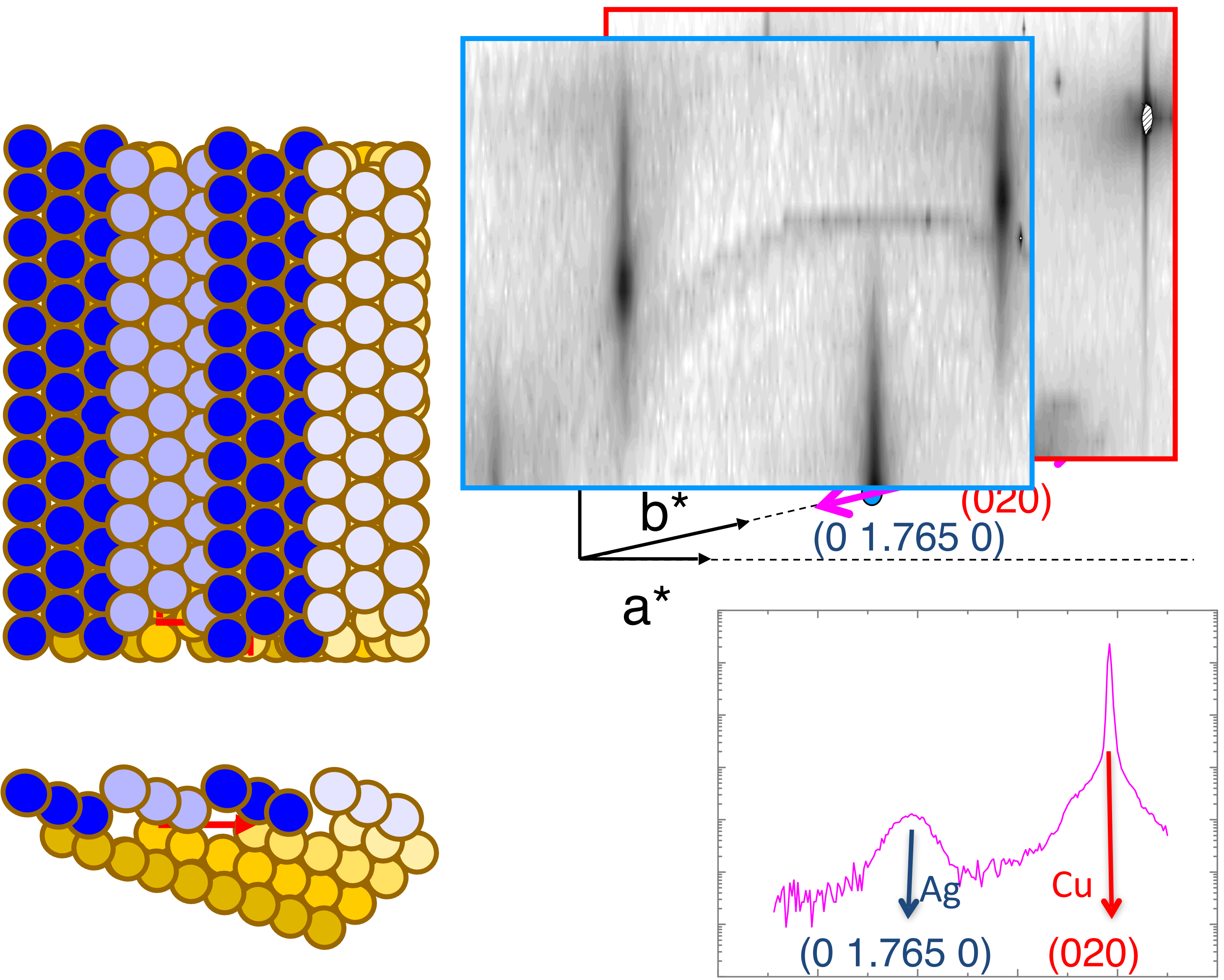
# 1 ML Ag/Cu(211) - GIXD & STM



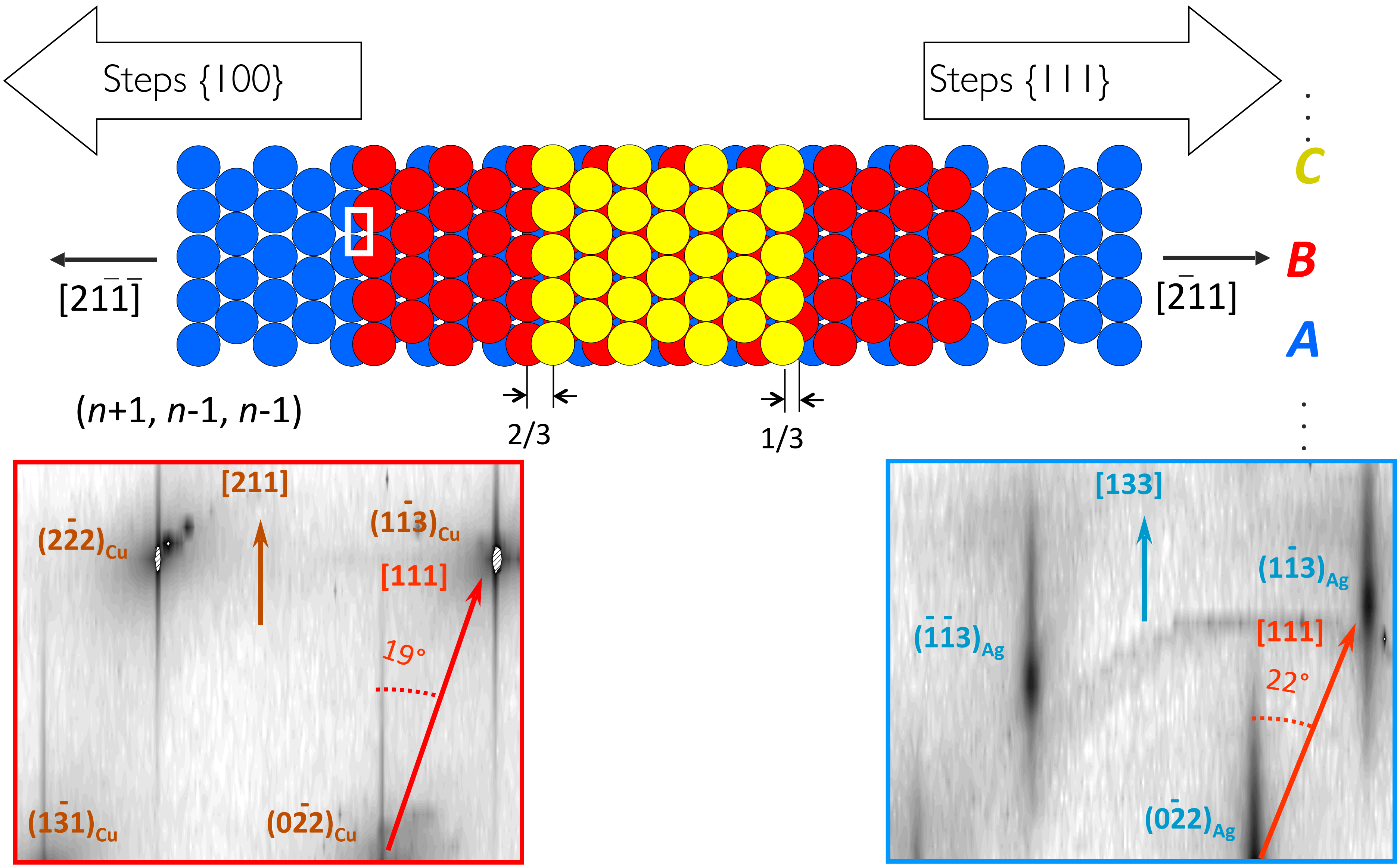



Y. Garreau, A. Coati, A. Zobelli, and J. Creuze
Phys. Rev. Lett. 91, 116101

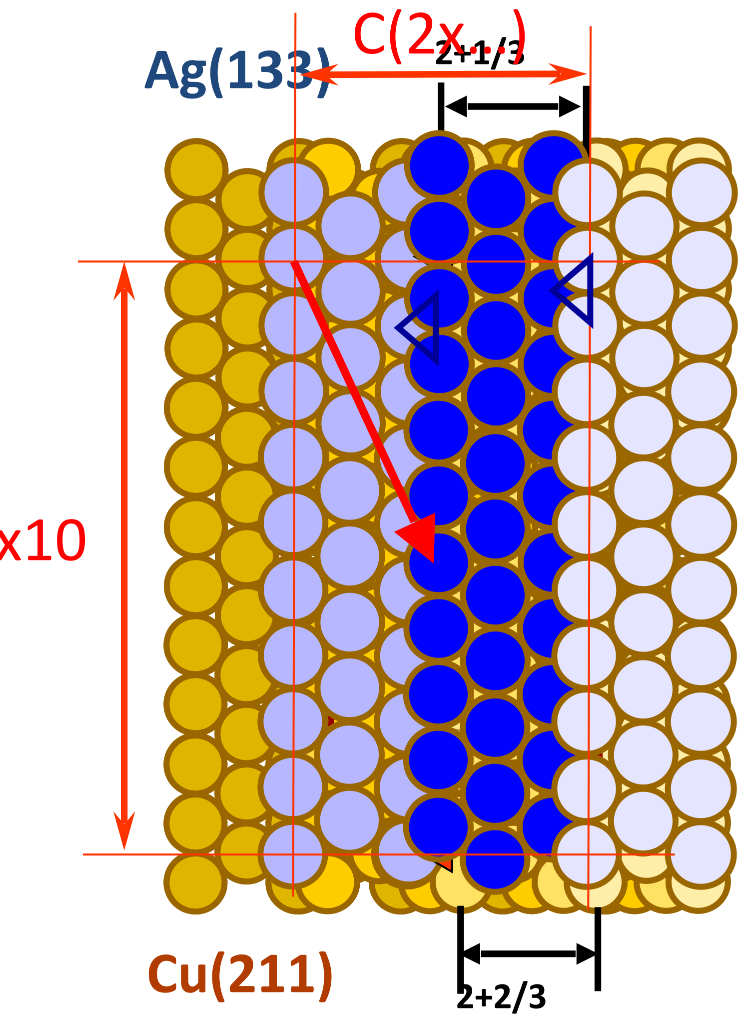
# "MAGIC" HETEROEPITAXY

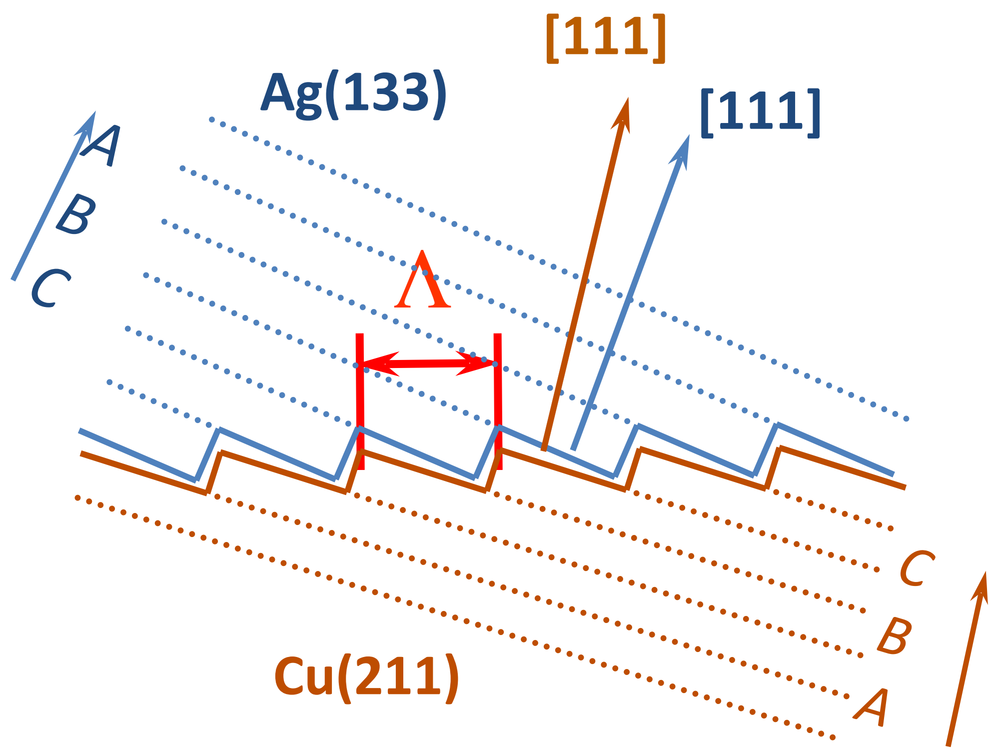


# “Magic” Heteroepitaxy



# “Magic” Heteroepitaxy

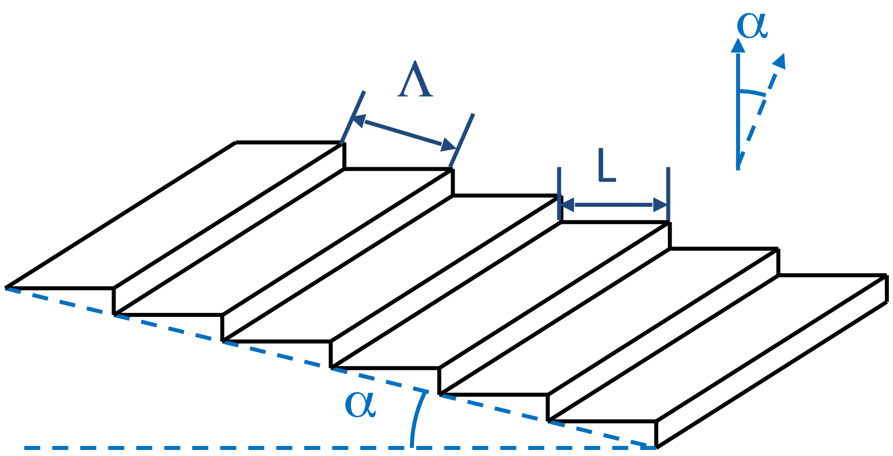


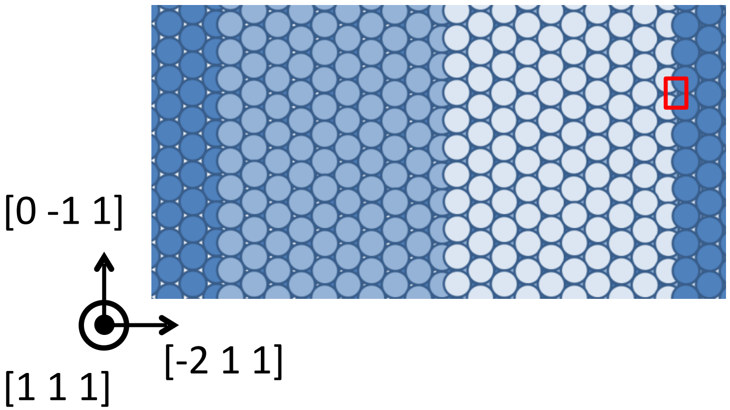

$$\frac{\Lambda_{Cu(211)}}{\Lambda_{Ag(133)}} = \frac{\left(2+\frac{2}{3}\right)}{\left(2+\frac{1}{3}\right)} = 1.14 \approx \frac{a_{Ag}}{a_{Cu}} = 0.4\%$$

Y. Garreau et al., Phys. Rev. Lett. 91, 116101 (2003)

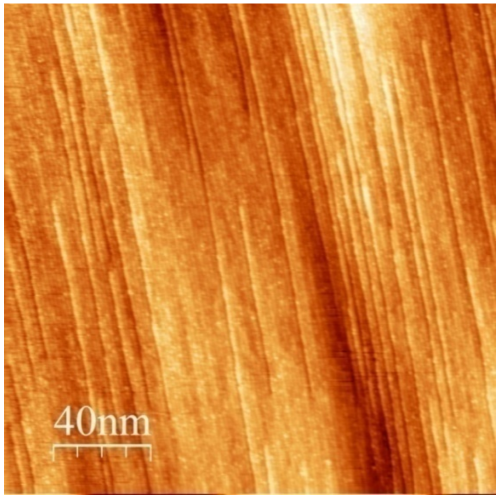
# Ni(1 1 9 9)



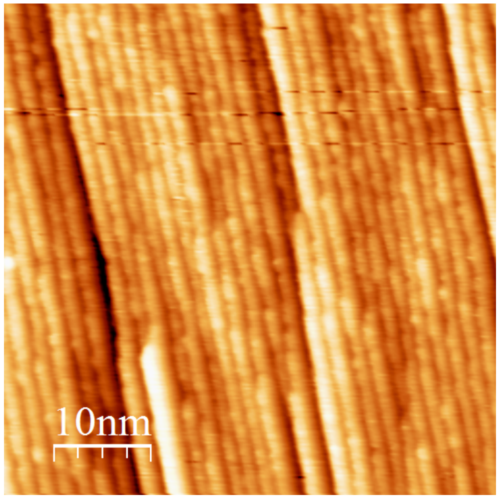

α = 5.57°
L = 2.1 nm




Terrasses : (1 1 1)
Steps: (001)




$V_s$=875mV, $I_t$=0.22nA



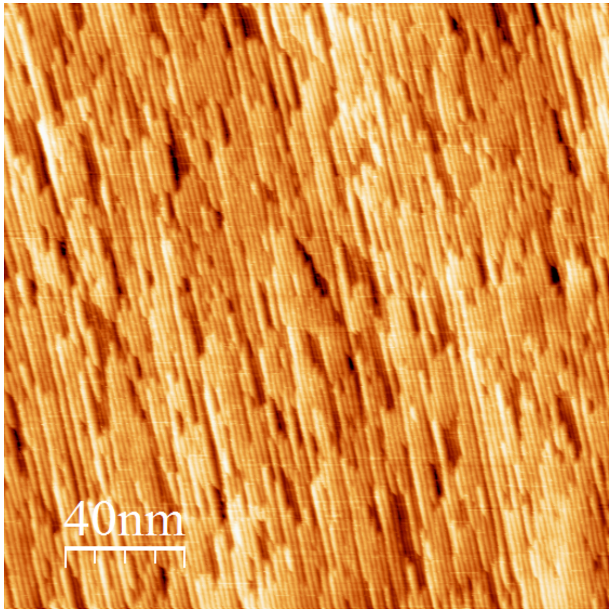

$V_s$=895mV, $I_t$=0.11nA

L = 2.09 ± 0.41 nm

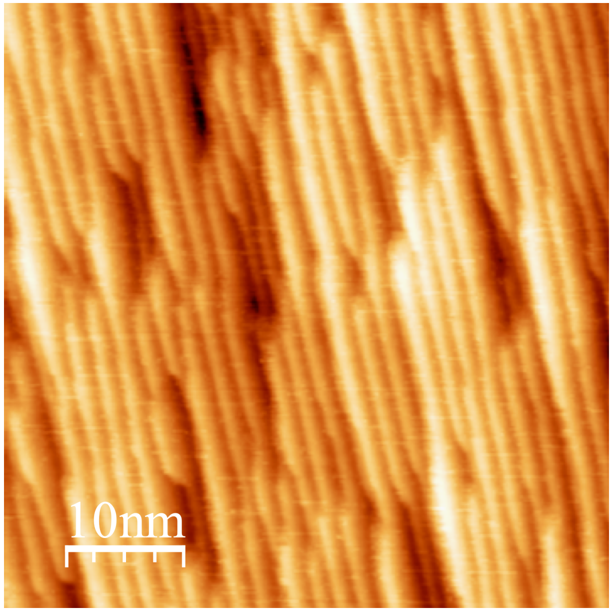
Bellec, A., et al., Physical Review B., 96(8): art.n° 085414. (2017)

# Ag(4ML)/Ni(1 1 9 9)

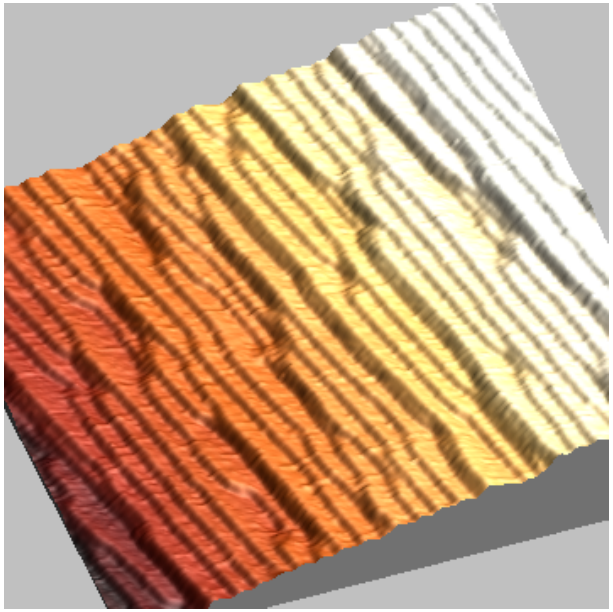
Recuit à 190°C




$200x200nm^2$ - $V_S$=0.85V - $I_t$=0.15nA

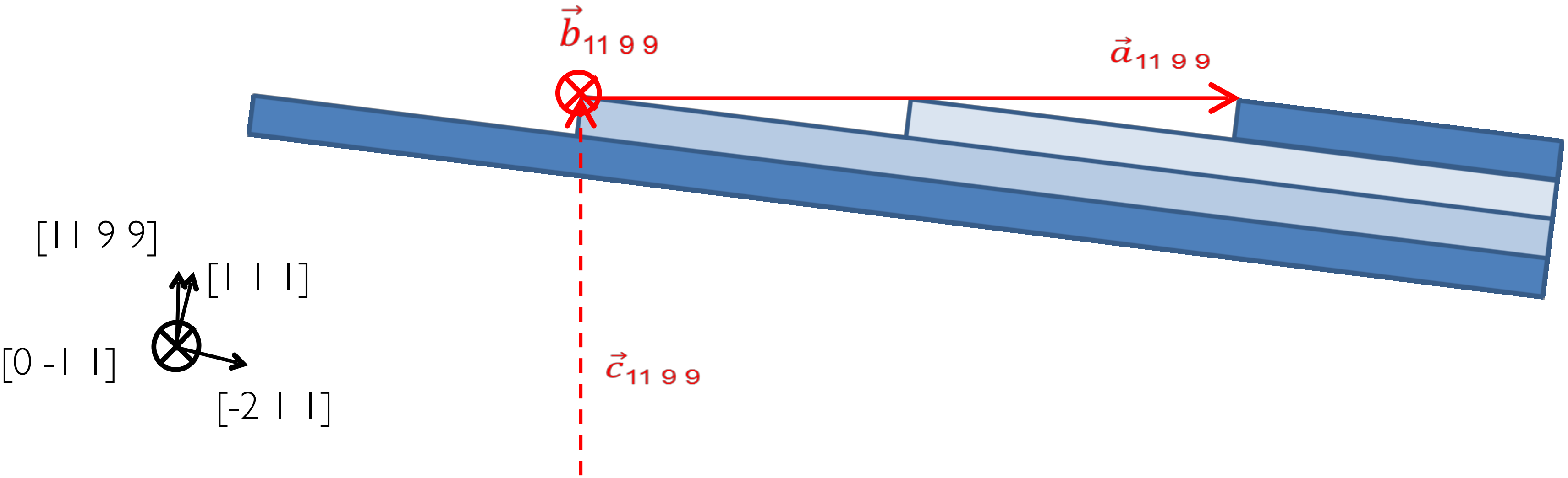


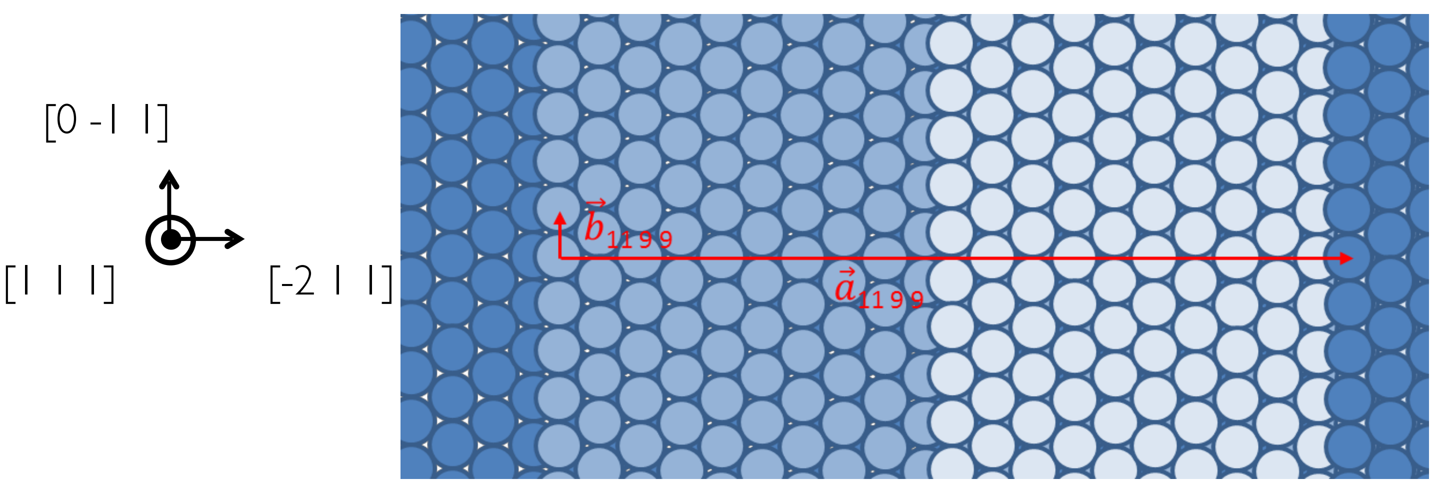

$50x50nm^2$ - $V_S$=0.85V - $I_t$=0.15nA



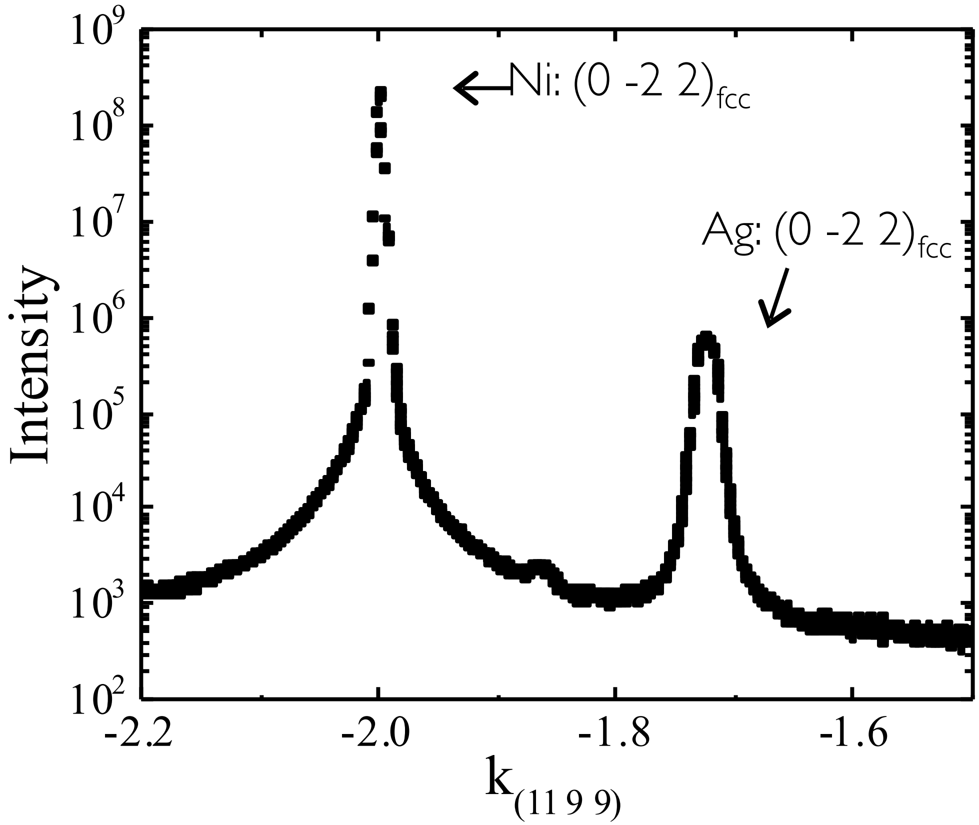
Largeur des terrasses mesurée : L =2.1± 0.3 nm

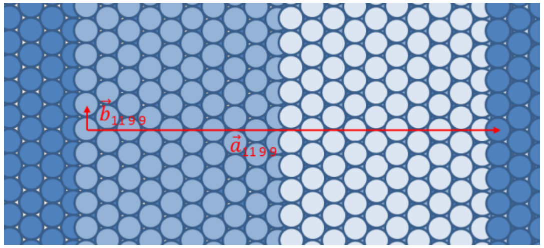
# Ag/ Ni(11 9 9): Vicinal basis



# ALONG STEP EDGES



Lattice mismatch:

$$\left|\frac{a_{Ni}^{bulk} - a_{Ag}^{bulk}}{a_{Ni}^{bulk}}\right| = 0{,}159$$

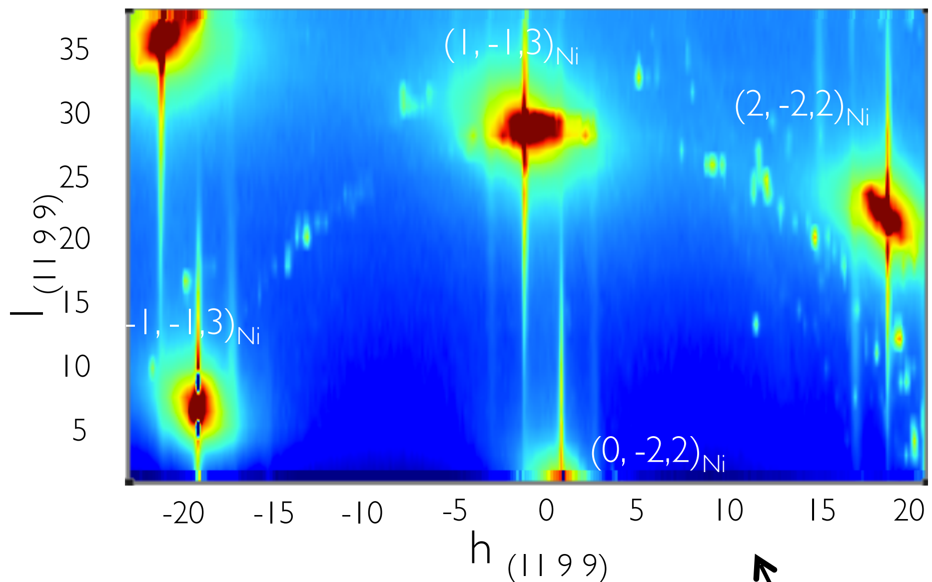
Measure:

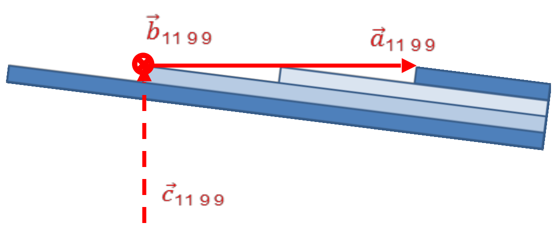
$$\left|\frac{a_{Ni}^{//} - a_{Ag}^{//}}{a_{Ni}^{//}}\right| = 0{,}161$$

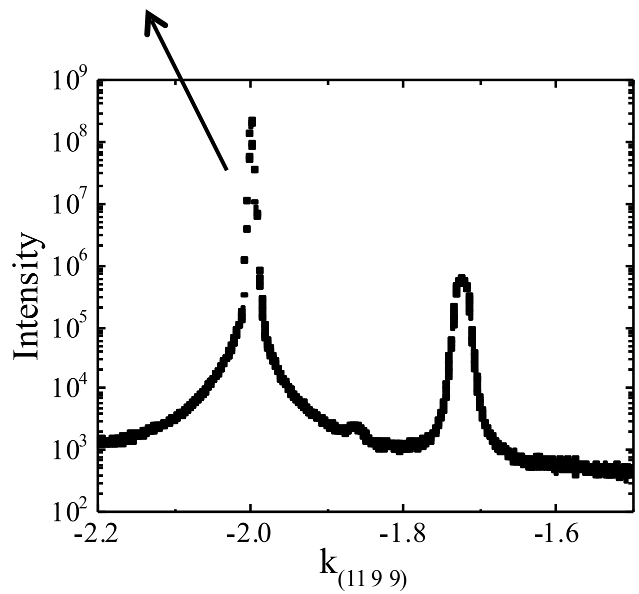
Ag is relaxed along the step edges

# RECIPROCAL SPACE MAPPING

Ni map - $k_{11\,9\,9} = -2$

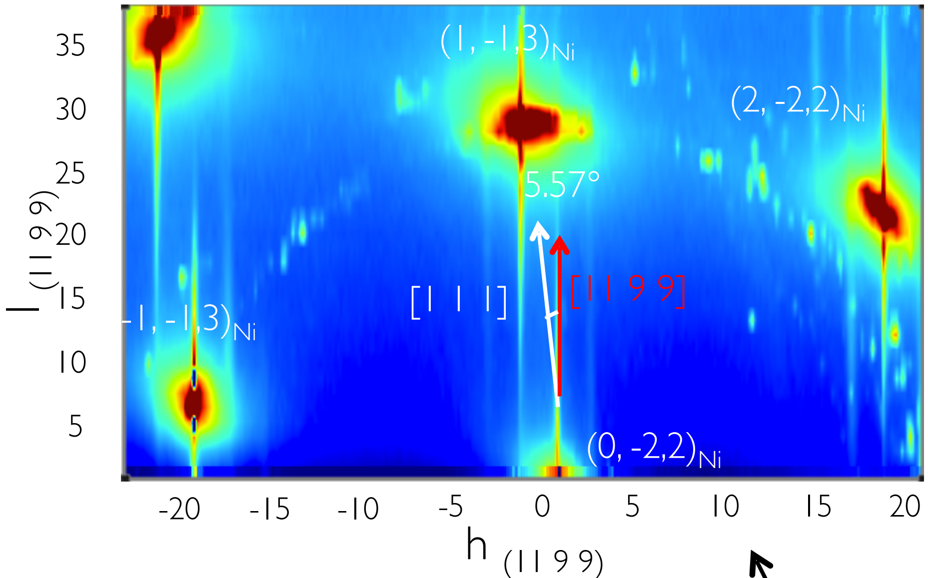


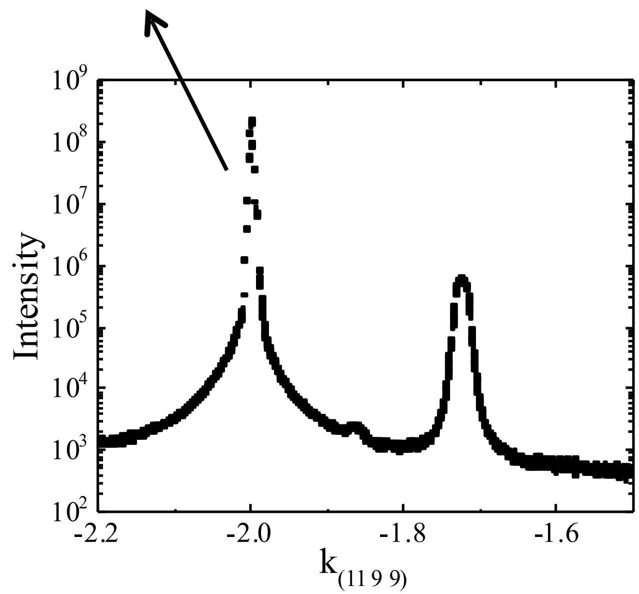



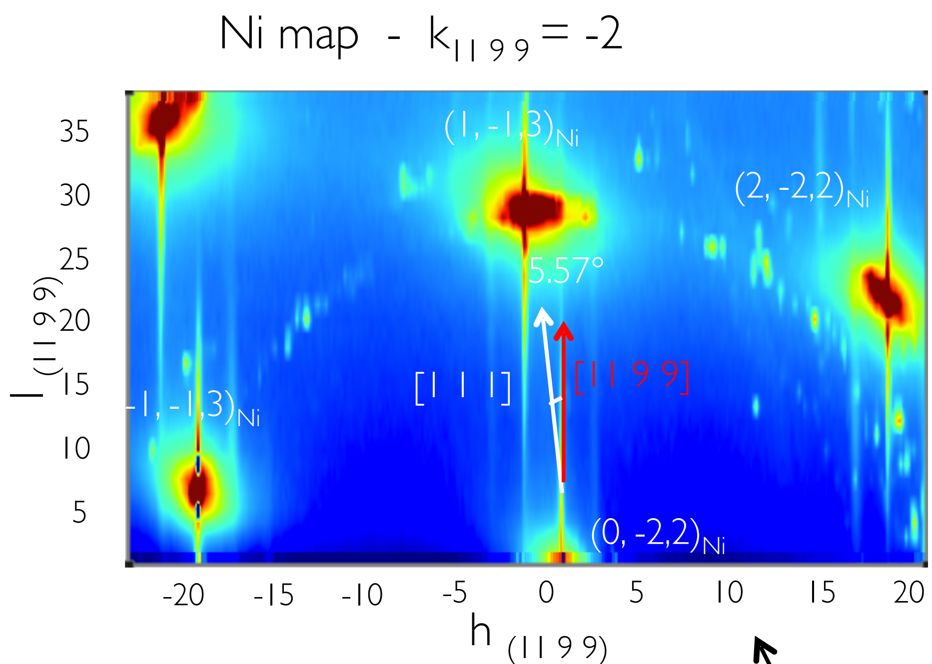
# RECIPROCAL SPACE MAPPING

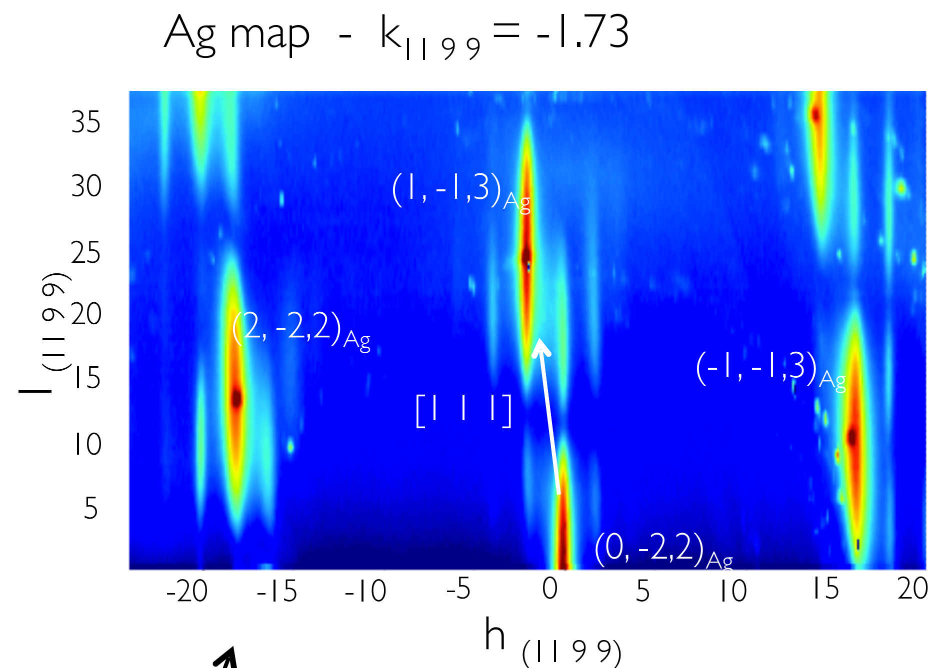
Ni map - $k_{11\ 9\ 9} = -2$

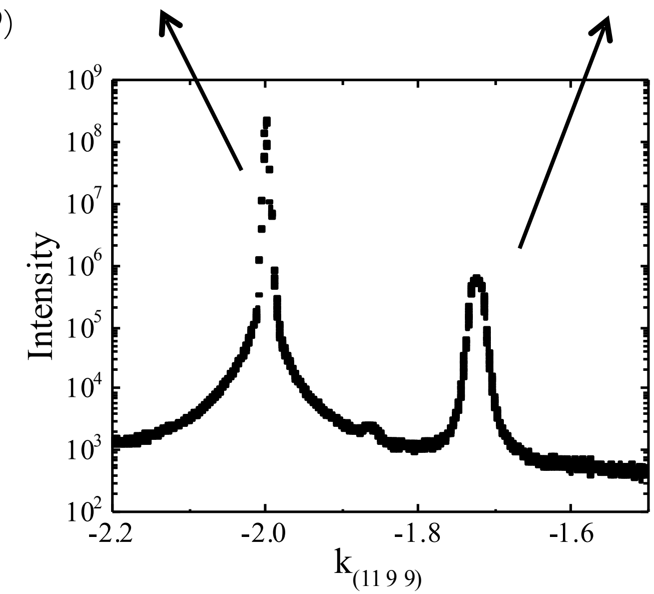


# RECIPROCAL SPACE MAPPING



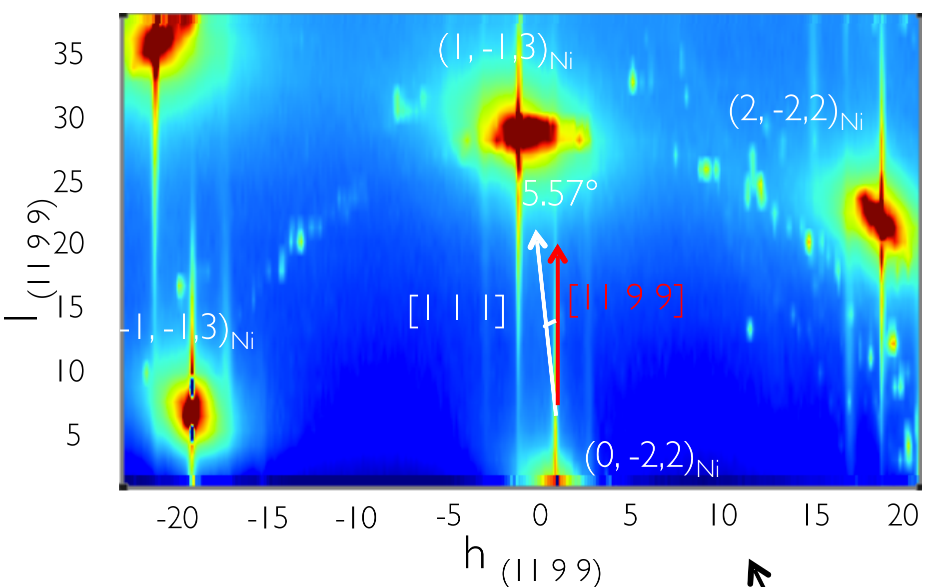




Ag layer presents a fcc structure

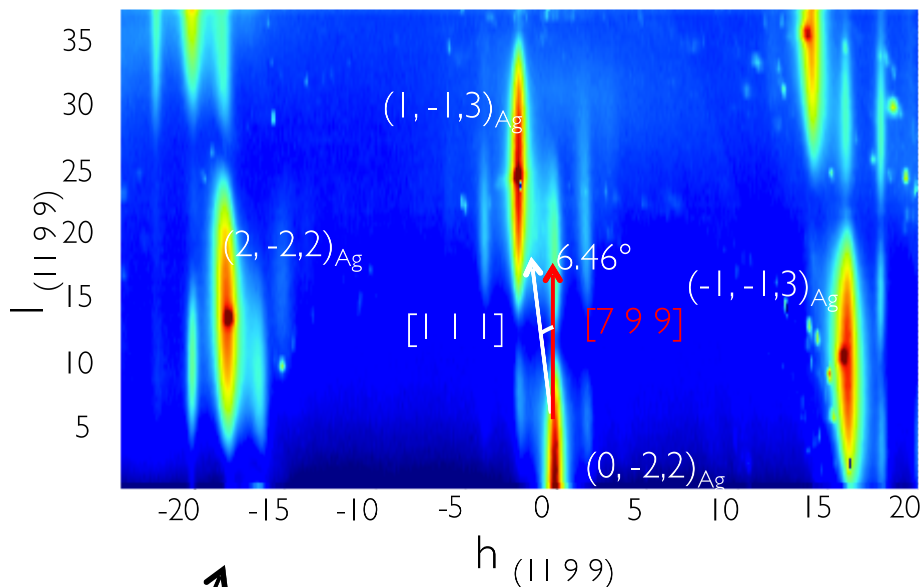
Inversion of the stacking between the Ag layer and the Ni substrate

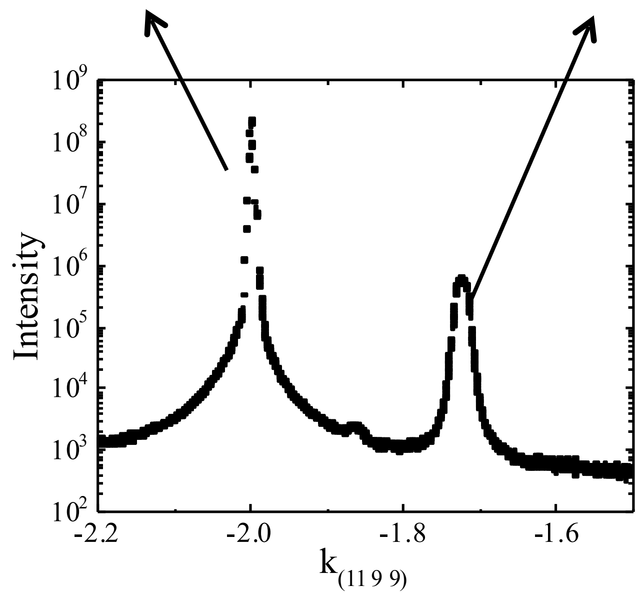
# RECIPROCAL SPACE MAPPING

Ni map - $k_{11\,9\,9} = -2$



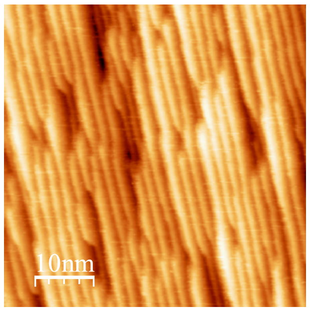

Ag map - $k_{11\,9\,9} = -1.73$




Ag: vicinal surface [7 9 9]

$\Lambda_{Ag(7\,9\,9)} = 20.95Å$



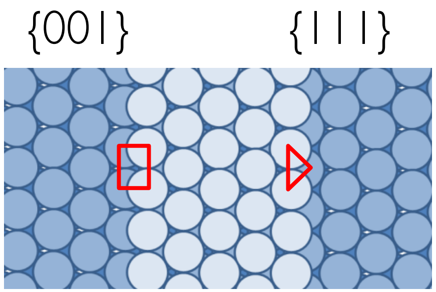

L = 20.7 ± 5.1 Å

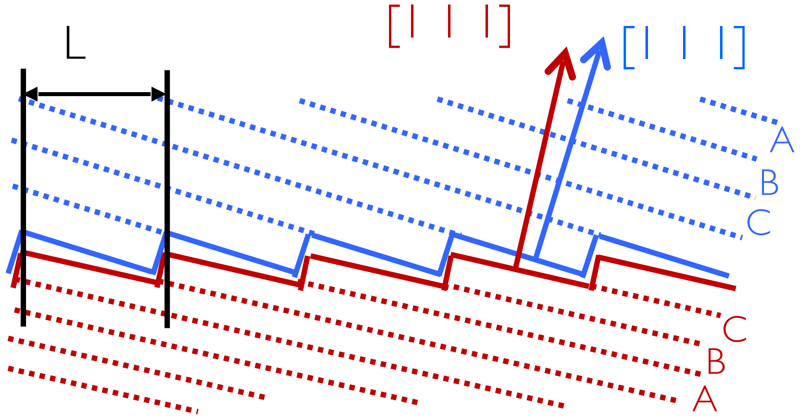
# “MAGIC” HETEROEPITAXY

Formation of Ag homogeneous thin film

Ni (11 9 9): terraces (111)
steps (001)

Ag (7 9 9): terraces (111)
steps (111)



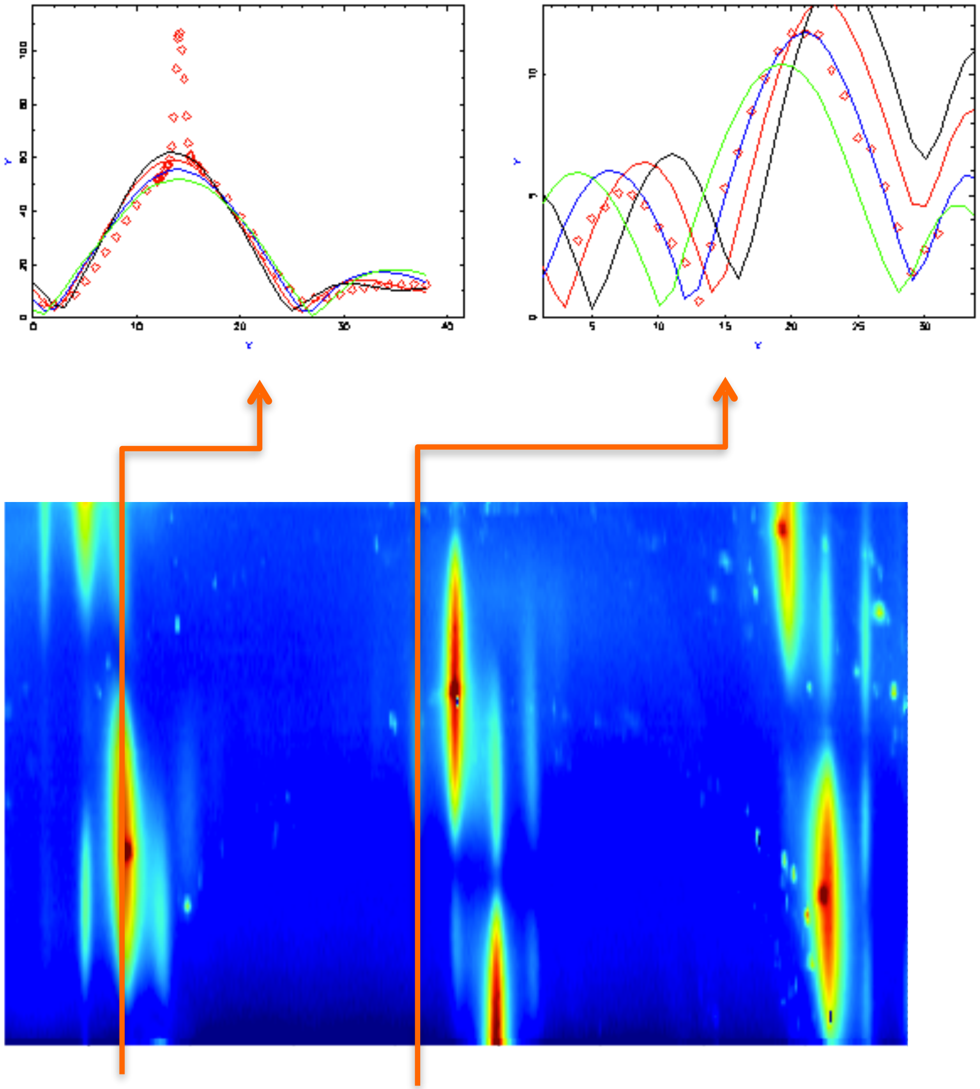



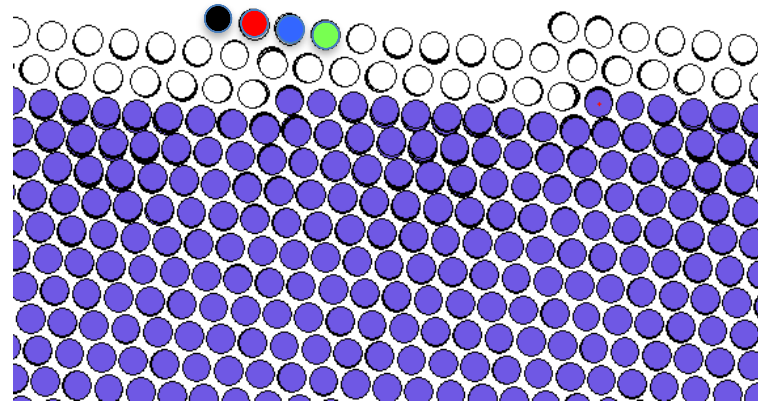

$\Lambda_{Ag(7\ 9\ 9)} = 20.95Å$

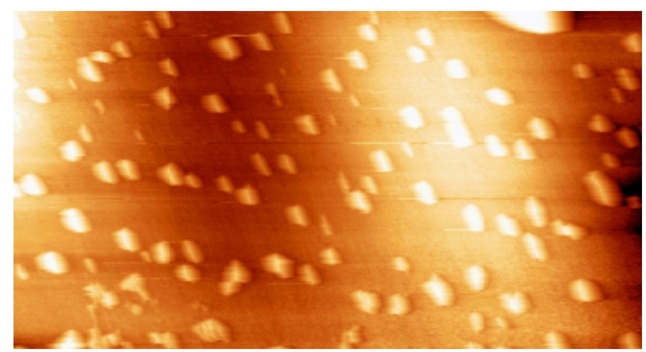
$\Lambda_{Ni(11\ 9\ 9)} = 20.96Å$

Step period governs the growth of the Ag layer

# Ag Islands

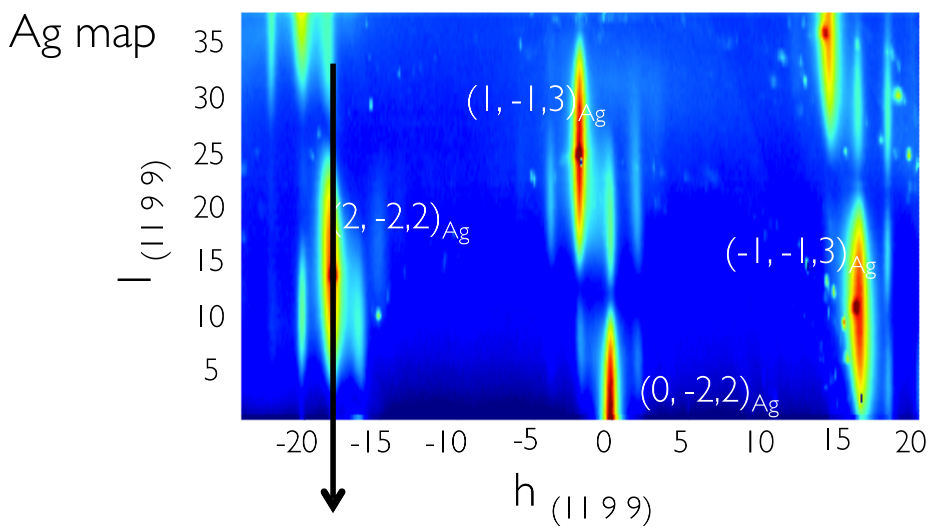


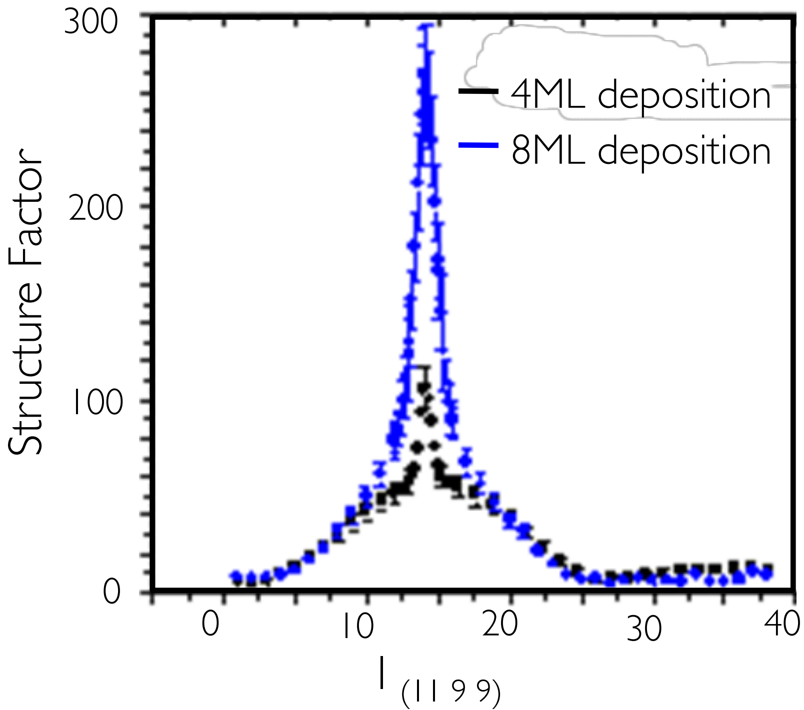


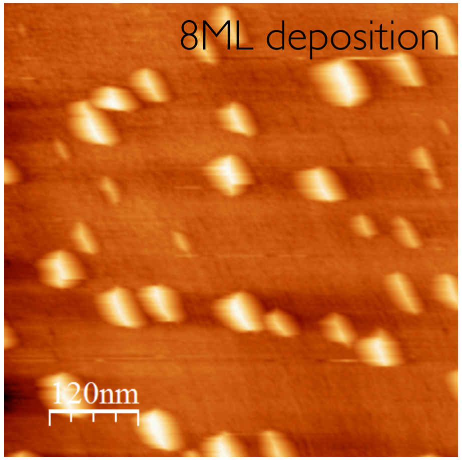


1500 x 750 nm2

# Ag Islands




600x600nm², V=2.4V, I=2.5nA

Island formation on a 2ML Ag(7 9 9) layer

# SURFACE X-RAY SCATTERING

- Reliable quantitative analysis
- Statistical information
- Beyond the surface (buried interfaces…)
- In-situ and operando measurements
- Atomic structure and morphology

# SixS

## Surfaces and Interfaces X-ray Scattering

# SixS

## Surface Interface X-ray Scattering

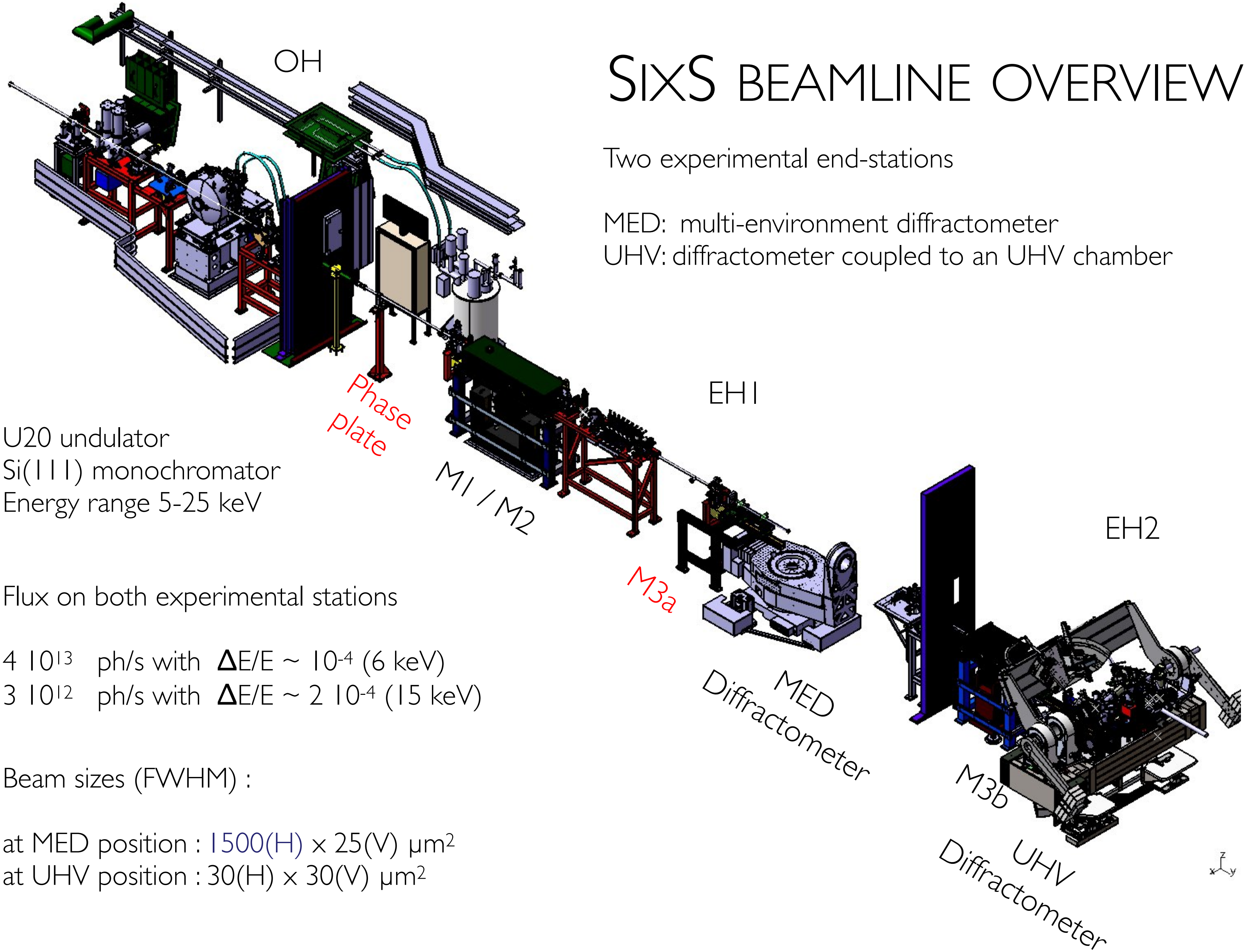
Solid surfaces and interfaces structures
Nanostructures
Self-organised surfaces
Original in-situ growths
Surface magnetic X-ray diffraction
Surfaces in catalytic environment
Solid-liquid electrochemical interfaces
Buried soft interfaces
Liquid-liquid interfaces
……..

GIXD
GISAXS
X-ray reflectivity
Anomalous Scattering
Coherent Scattering
Magnetic Scattering
….

# SIXS BEAMLINE OVERVIEW

Two experimental end-stations

MED: multi-environment diffractometer
UHV: diffractometer coupled to an UHV chamber



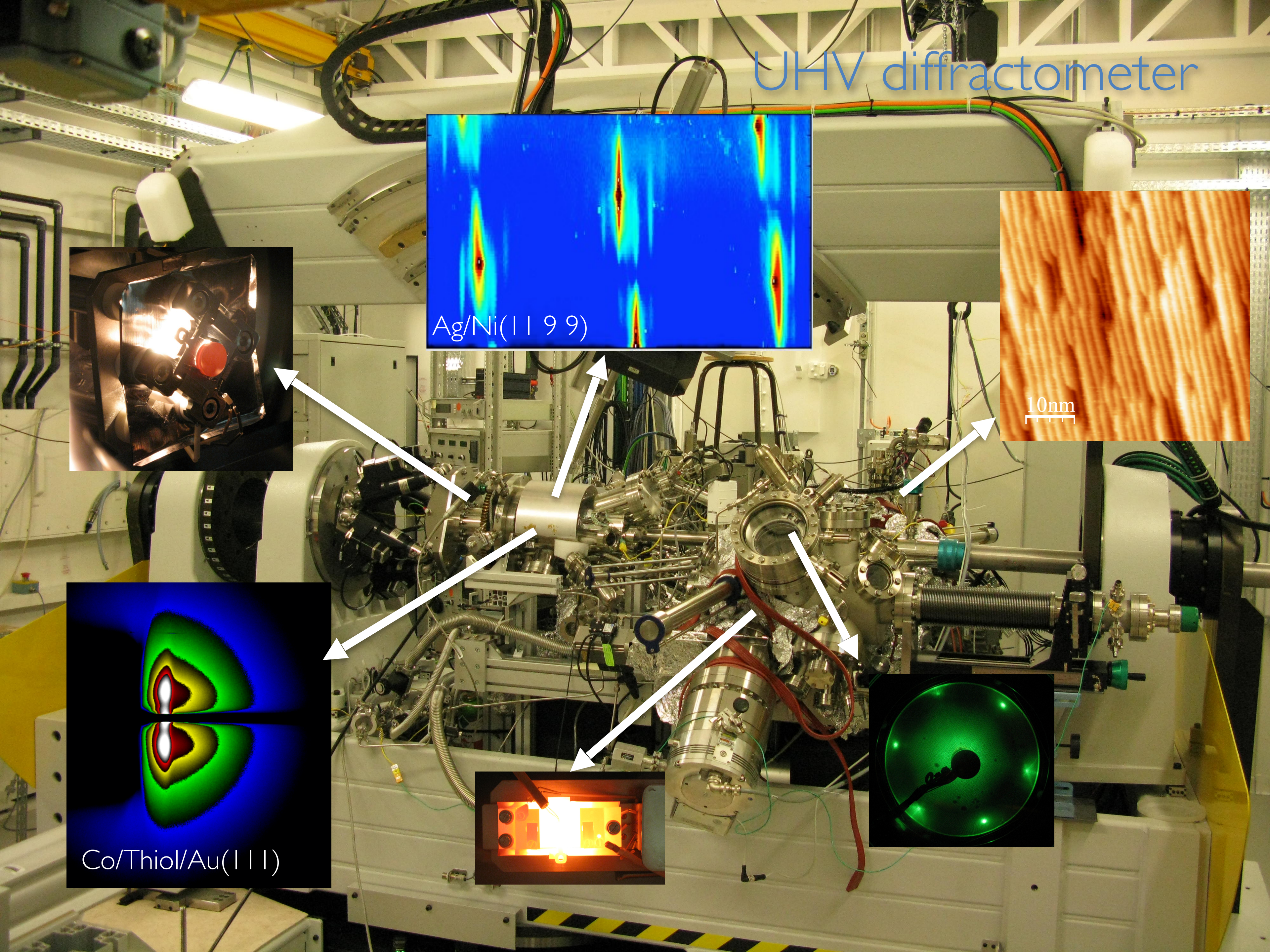

U20 undulator
Si(111) monochromator
Energy range 5-25 keV

Flux on both experimental stations

4 $10^{13}$ ph/s with $\Delta E/E \sim 10^{-4}$ (6 keV)
3 $10^{12}$ ph/s with $\Delta E/E \sim 2\ 10^{-4}$ (15 keV)

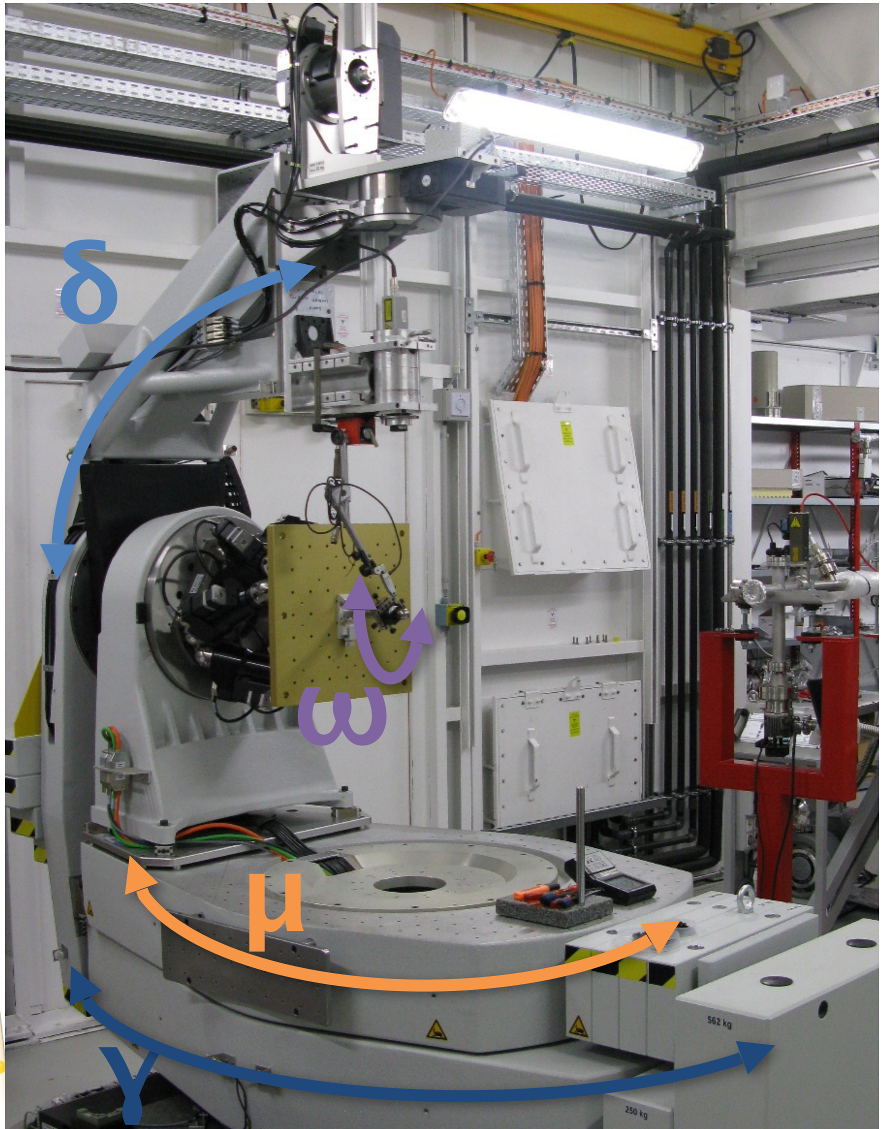
Beam sizes (FWHM) :

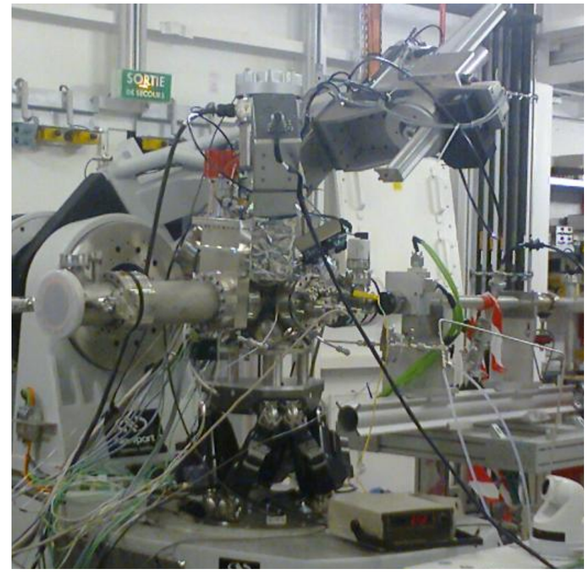
at MED position : 1500(H) x 25(V) μm²
at UHV position : 30(H) x 30(V) μm²

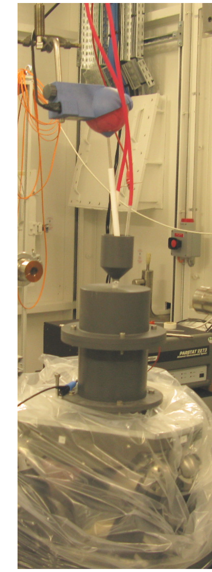

UHV diffractometer
Ag/Ni(11 9 9)
10nm
Co/Thiol/Au(111)

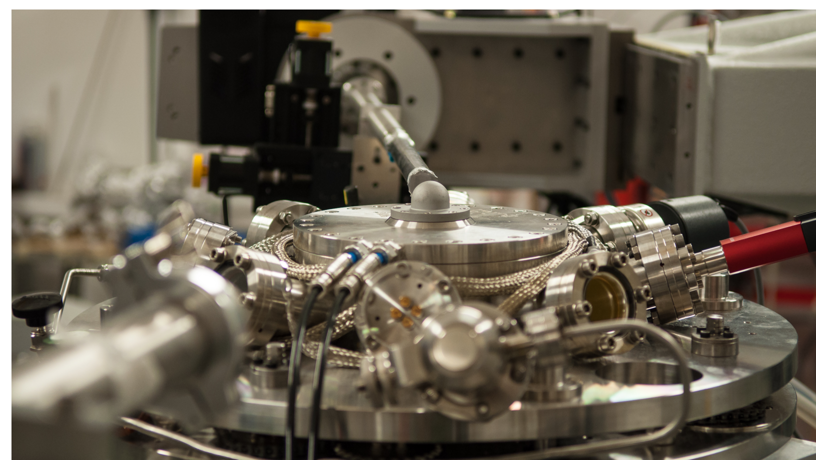
SOLEIL SYNCHROTRON

# MED end-station







# Continuous scan mode

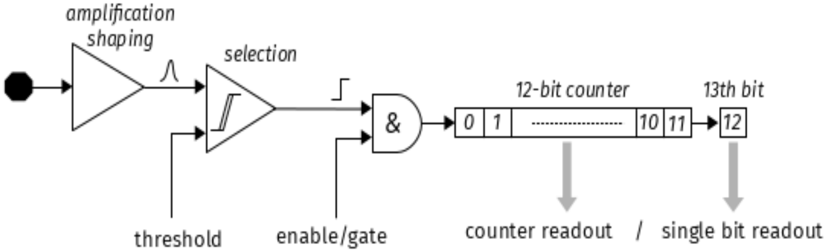
- Time saved
- Full encoder resolution exploitation
- HKL trajectories > non-linear grouped motors
- Trajectories (XPS controller – DC motor with PID)

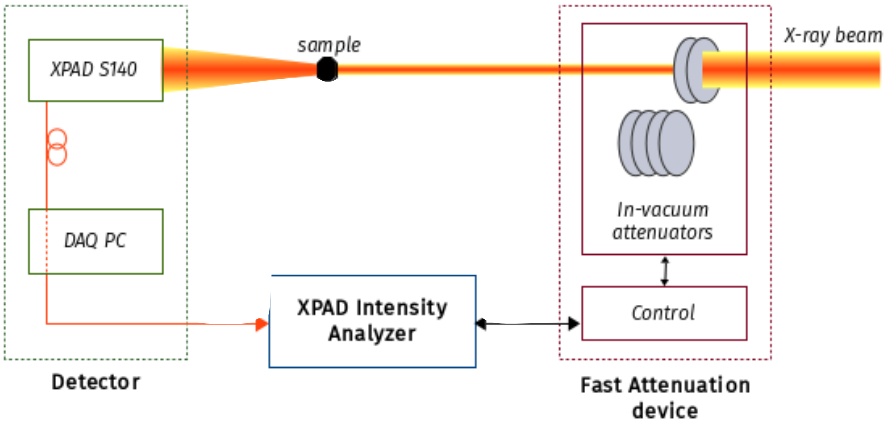
- Need to integrate properly 2D detectors
- Generalization of the trajectories on other motors

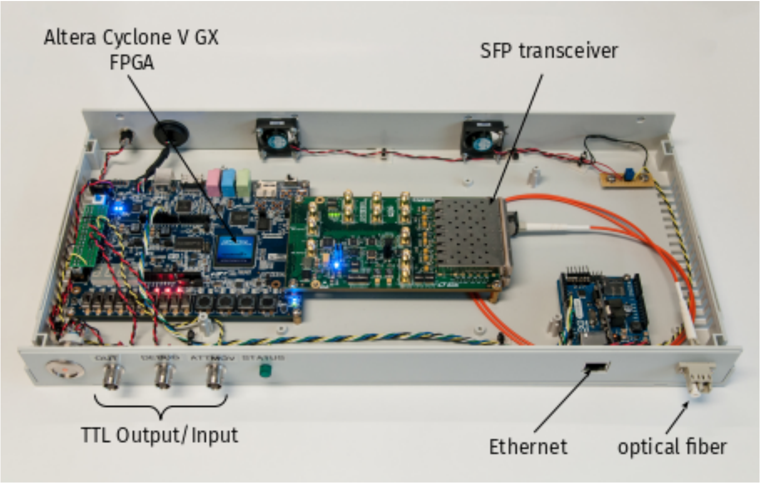
>>> Flyscan <<<

# 2D detector (XPAD-S140)


Pixel dimensions
130x130 µm2
Active surface
240 × 560 pixels
75 × 32 mm2
Counter
12 bits + 1 OVF
250 Hz sampling



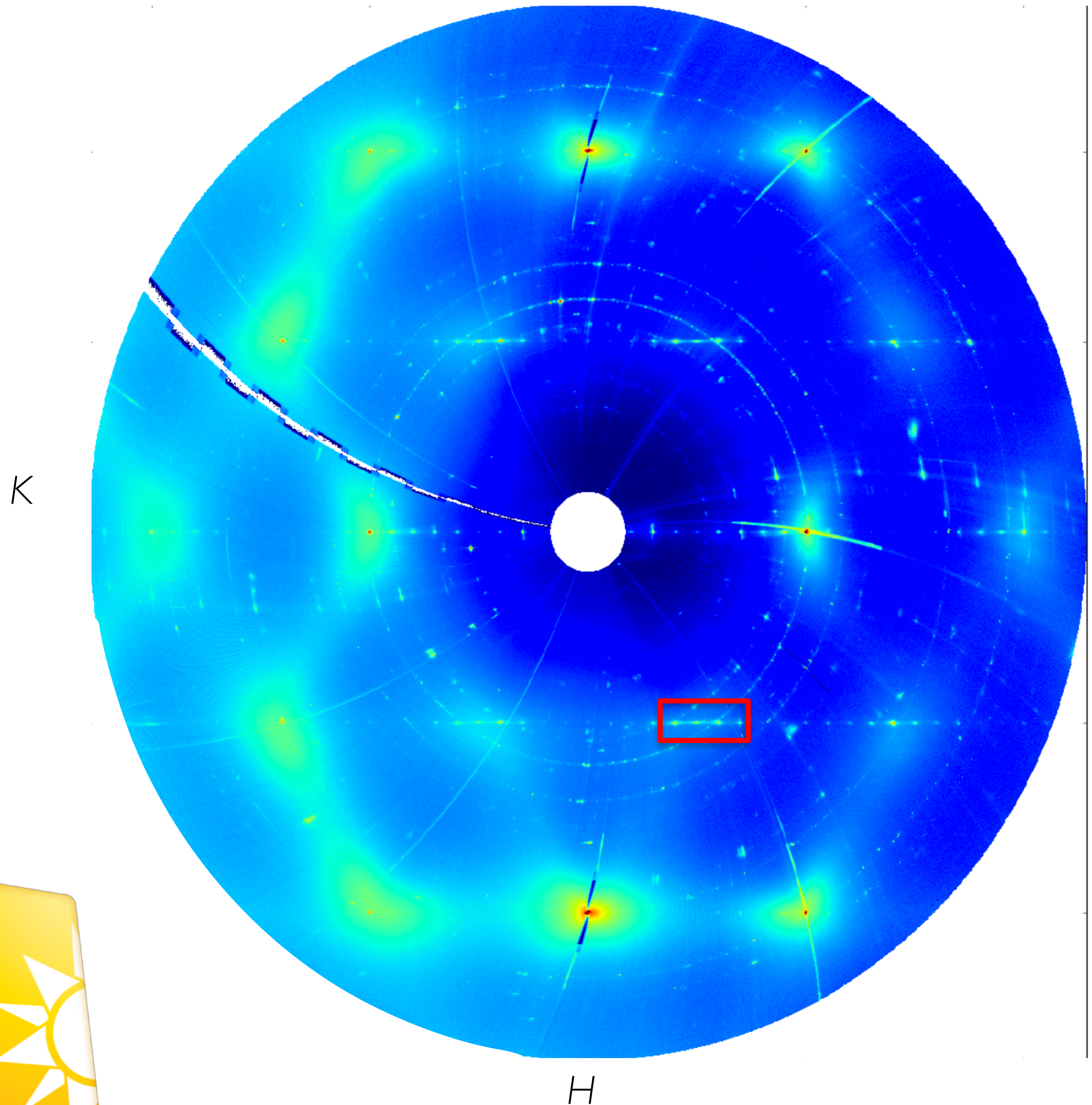



# Reciprocal Space Visualisation - BINOCULARS

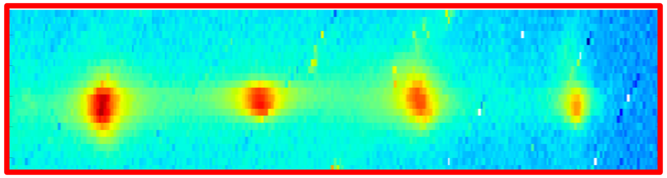
- Installed on the SOLEIL high performance cluster SUMO
  - Data
    - Reduction
    - Representation
    - Projection
  - Build a reciprocal space volume in
    - Q-space
    - (hkl) space
    - Angles space (soon)
  - Intensity integration
  - Python

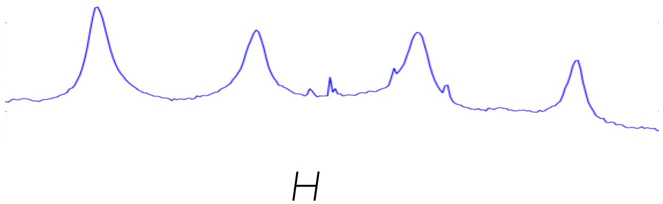
Roobol, S., Onderwaater, W., Drnec, J., Felici, R. & Frenken, J. , J. Appl. Cryst. 48, 1324-1329 (2015)

# Pentacene/Cu(322)



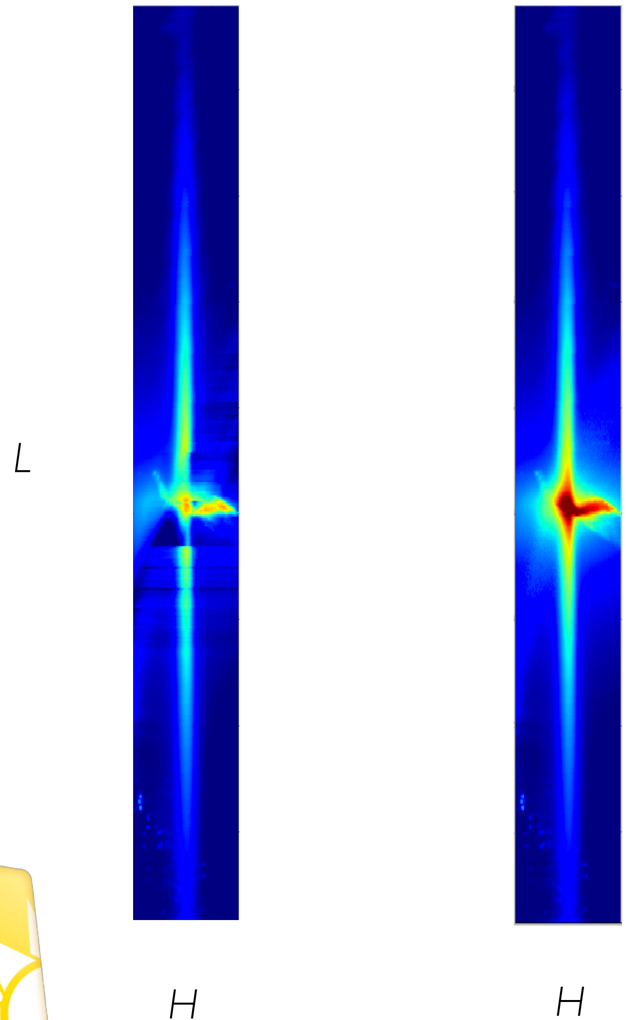

Pentacene/Cu322
(M. Sauvage, K. Muller, A. Kara, et al.)
In-plane (*hk*) – map
1h, 36000 images





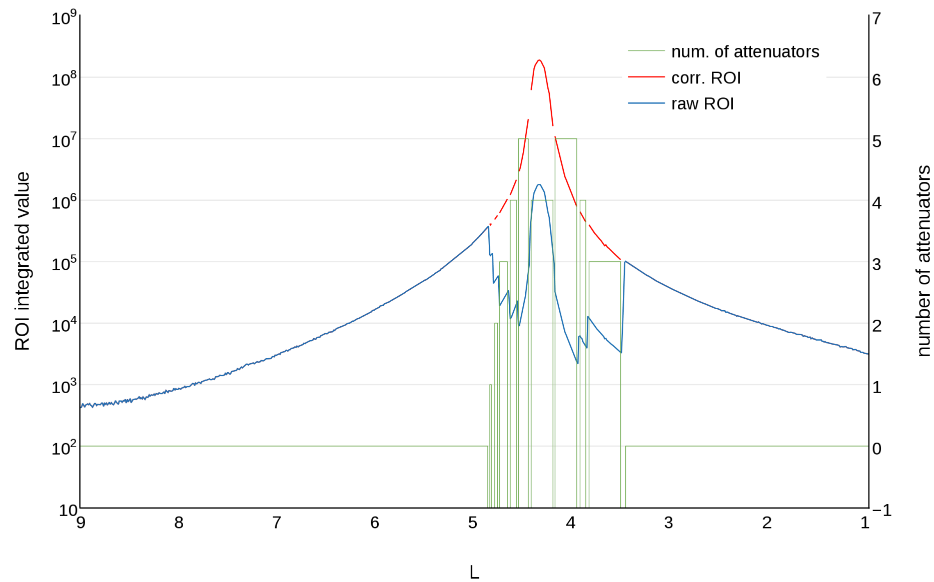

Surface structure
Surface periodicity

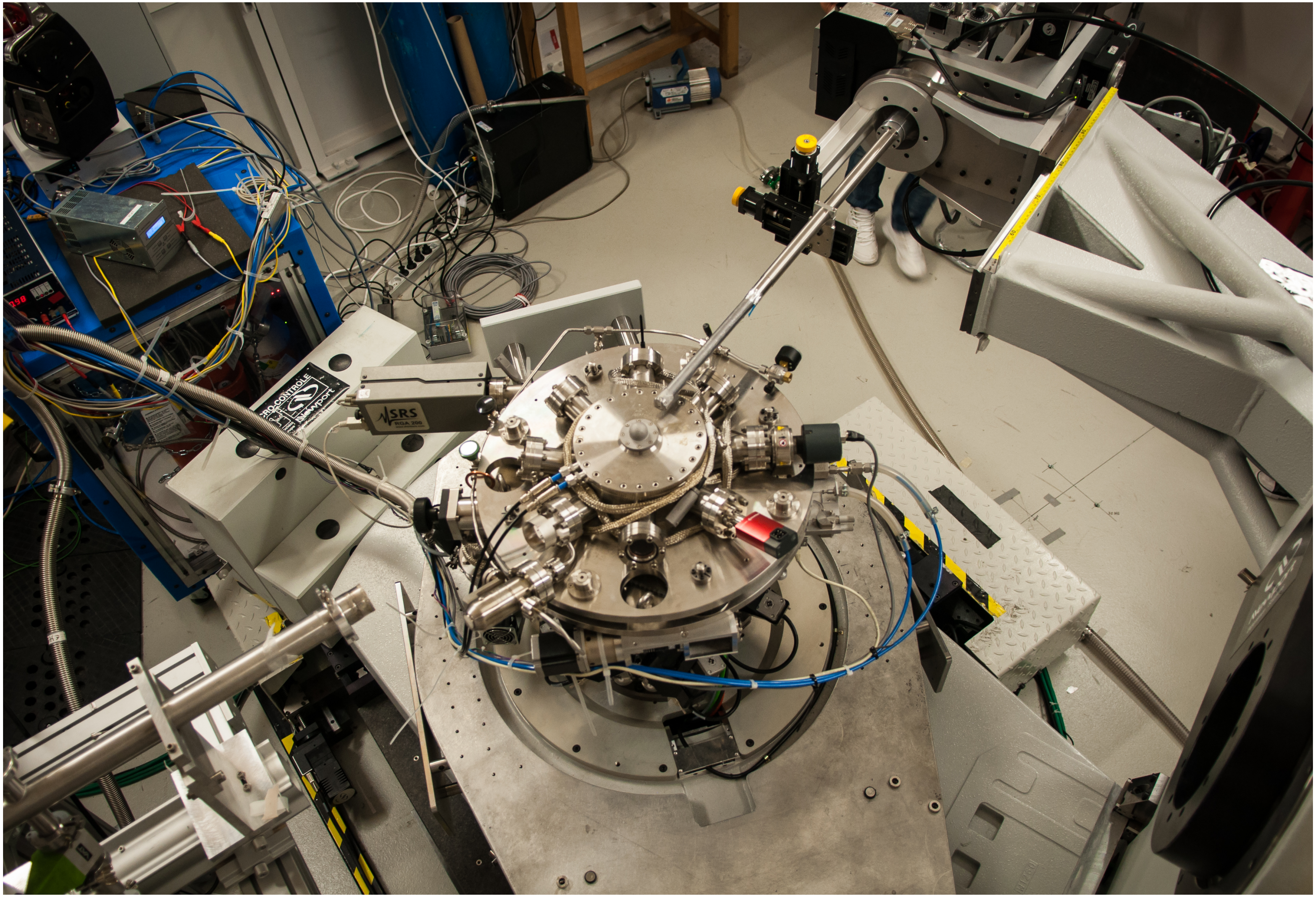
# Pentacene/Cu(322)




CTR in flyscan

- Less than 1 min
- projection in the (*h l*) plane
- Absorbers correction




SRS
RGA 200

SOLEIL SYNCHROTRON

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# References

## Surface diffraction


R. Feidenhans'l, Surface structure determination by X-ray diffraction, Surf. Sci. Reports 10 (1989) 105-188.

I.K. Robinson and D.J. Tweet, Surface X-ray diffraction, Rep. Prog. Phys. 55 (1992) 599-651.