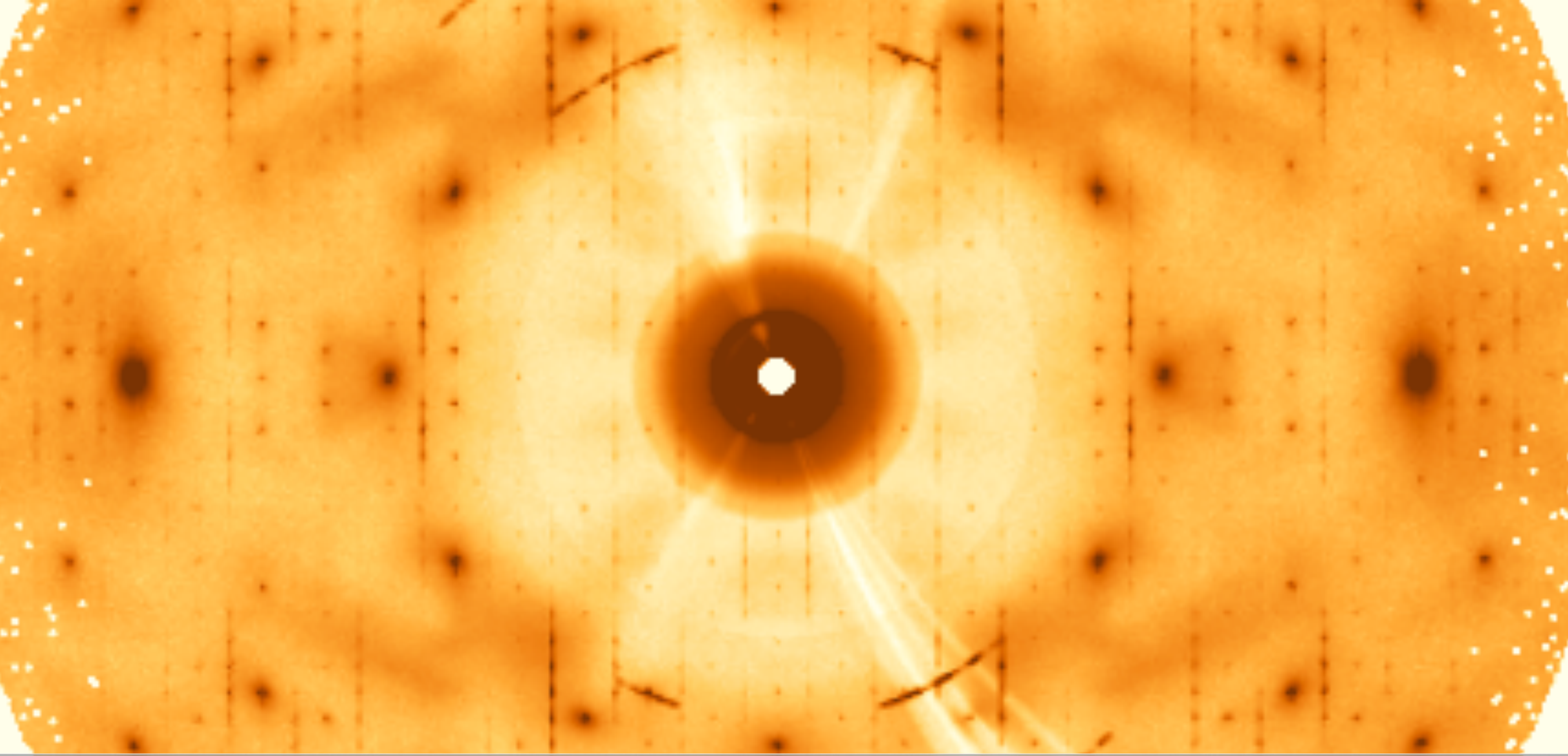


SURFACE X-RAY SCATTERING

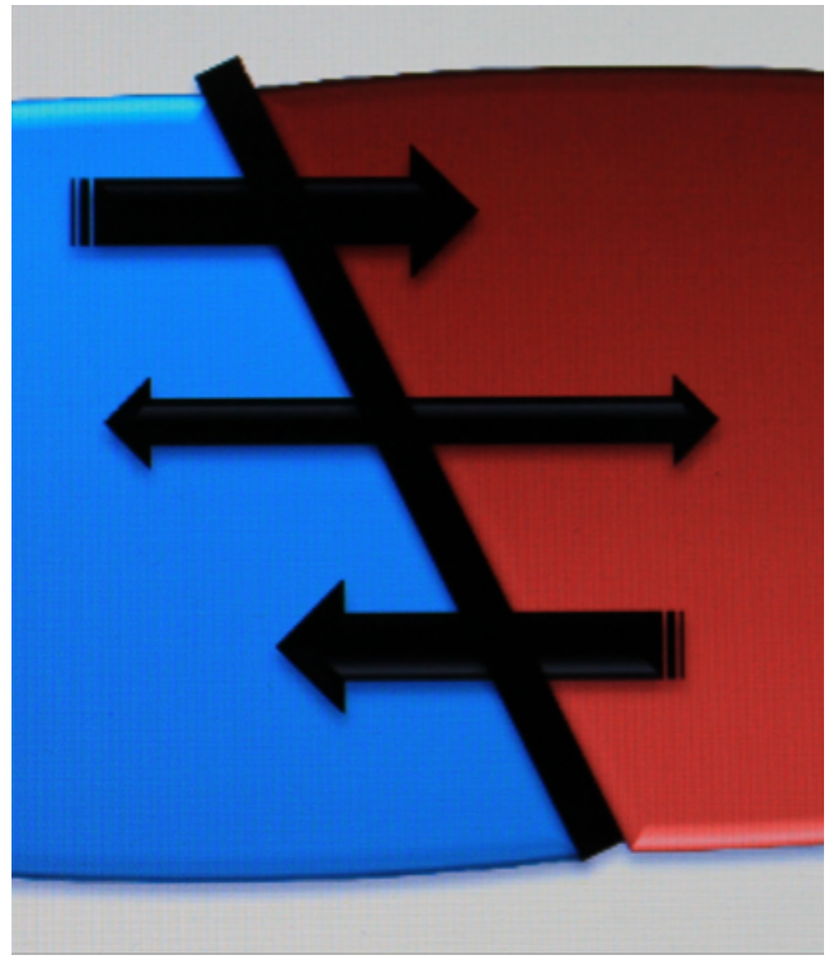
Alessandro Coati
SixS beamline - Synchrotron SOLEIL

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

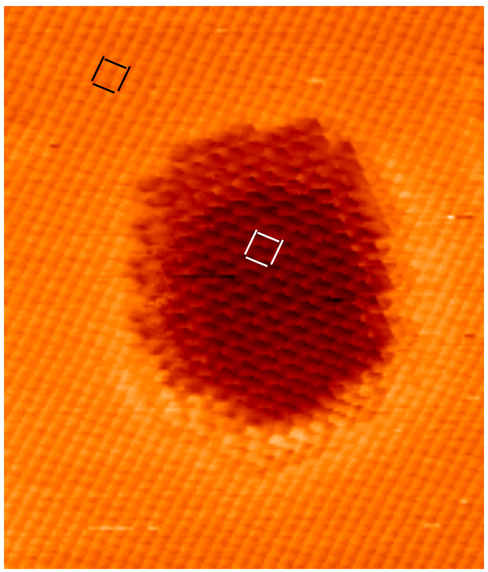
Physical properties (electronic, catalytic, photonics, magnetic):

- 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)

λ=1 Å, E=12,4 keV

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

n = 1-δ : GIXD

Coherence width > 1mm

Electrons

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

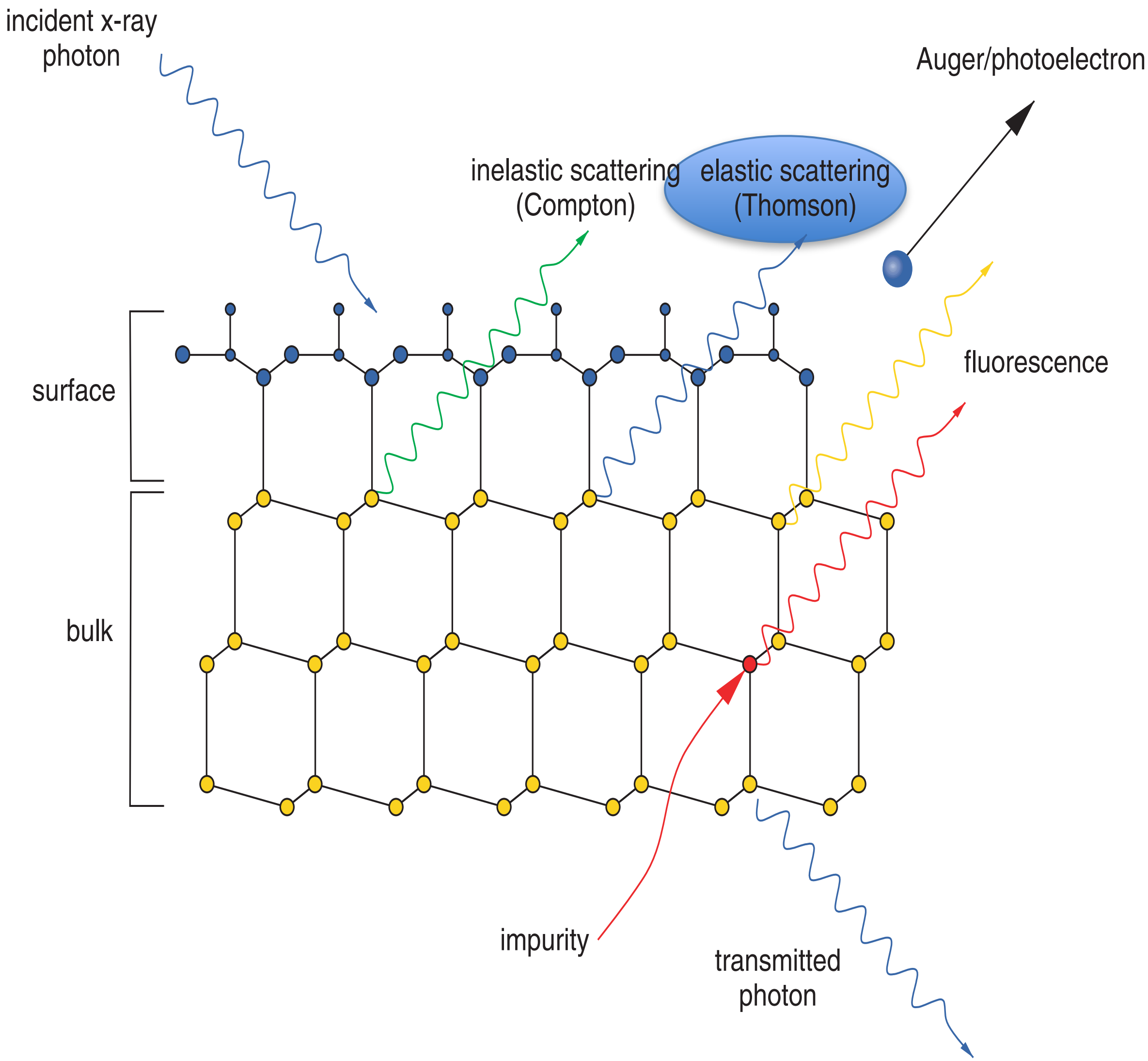
λ=1 Å, E=150 eV LEED
λ=0.1 Å, E=15 keV RHEED

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

$n=1+\delta$

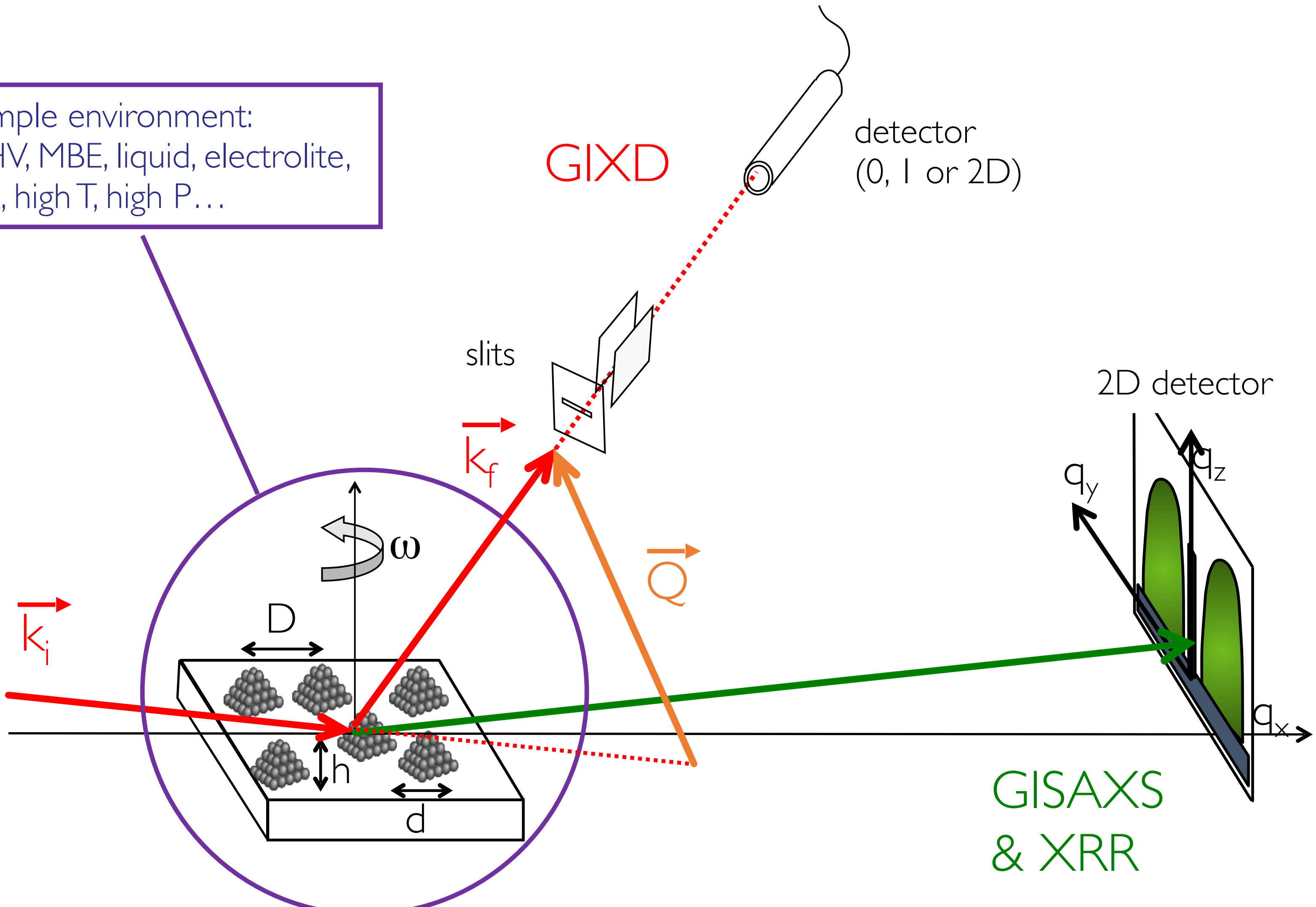
Coherence width < 0.1mm

X-RAY-MATTER INTERACTIONS

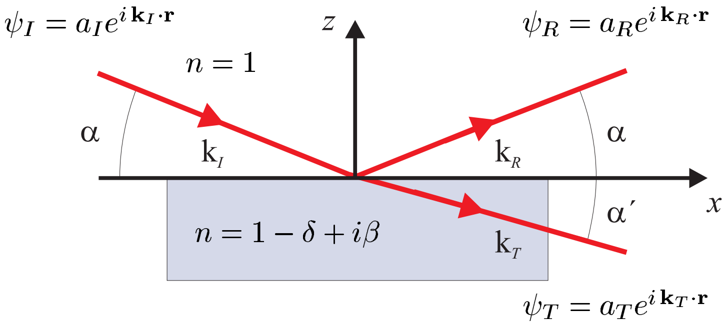


In-situ measurements

Sample environment:
UHV, MBE, liquid, electrolite,
gaz, high T, high P…



TOTAL REFLECTION



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

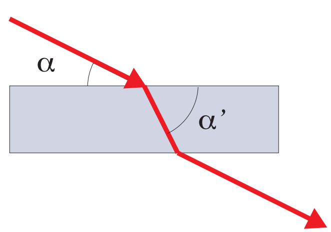
$$\boxed{n = 1 - \delta + i\beta}$$

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

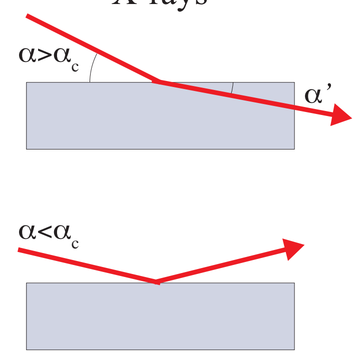
$$\cos(\alpha_c) = \mathrm{Re}(n) = 1 - \delta$$

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

Light

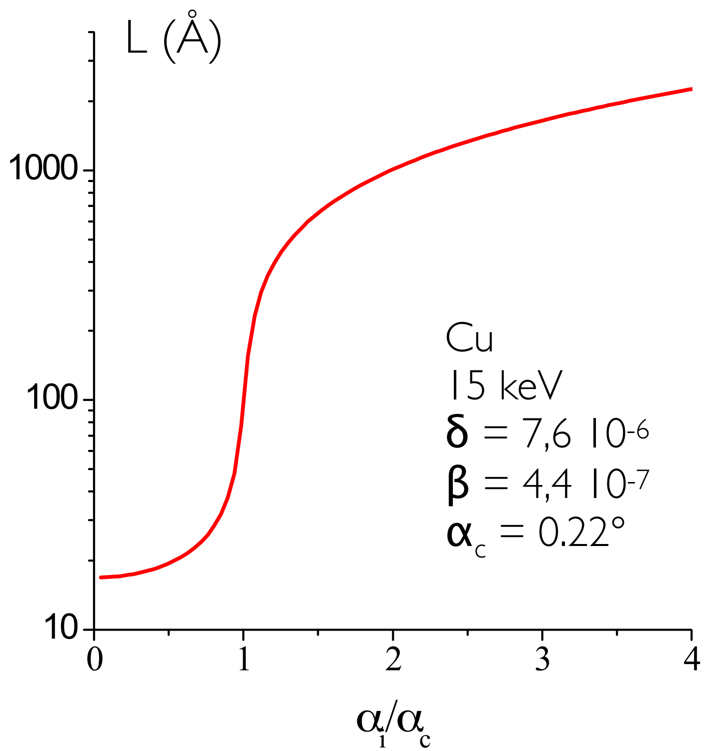


X-rays

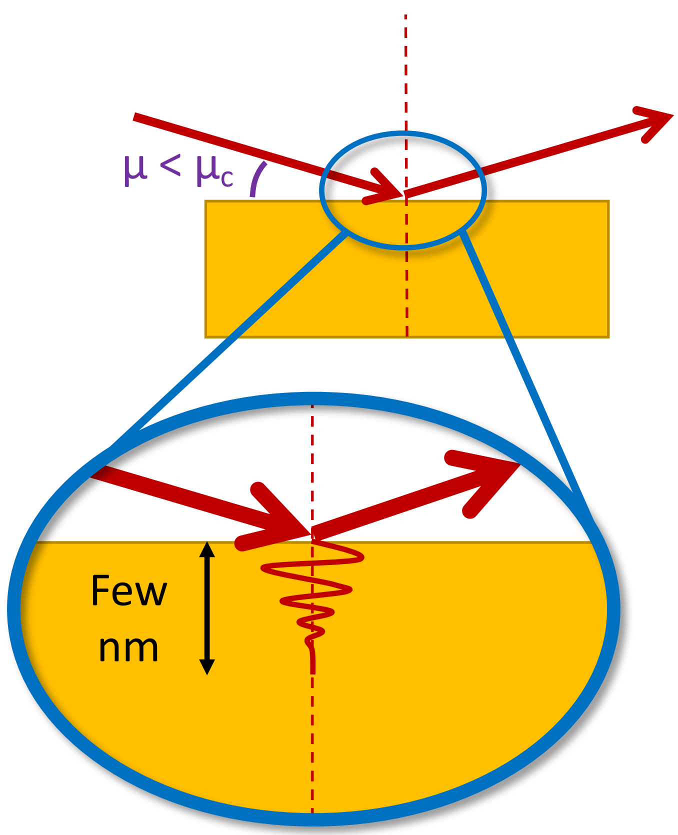


Total external reflection

PENETRATION DEPTH

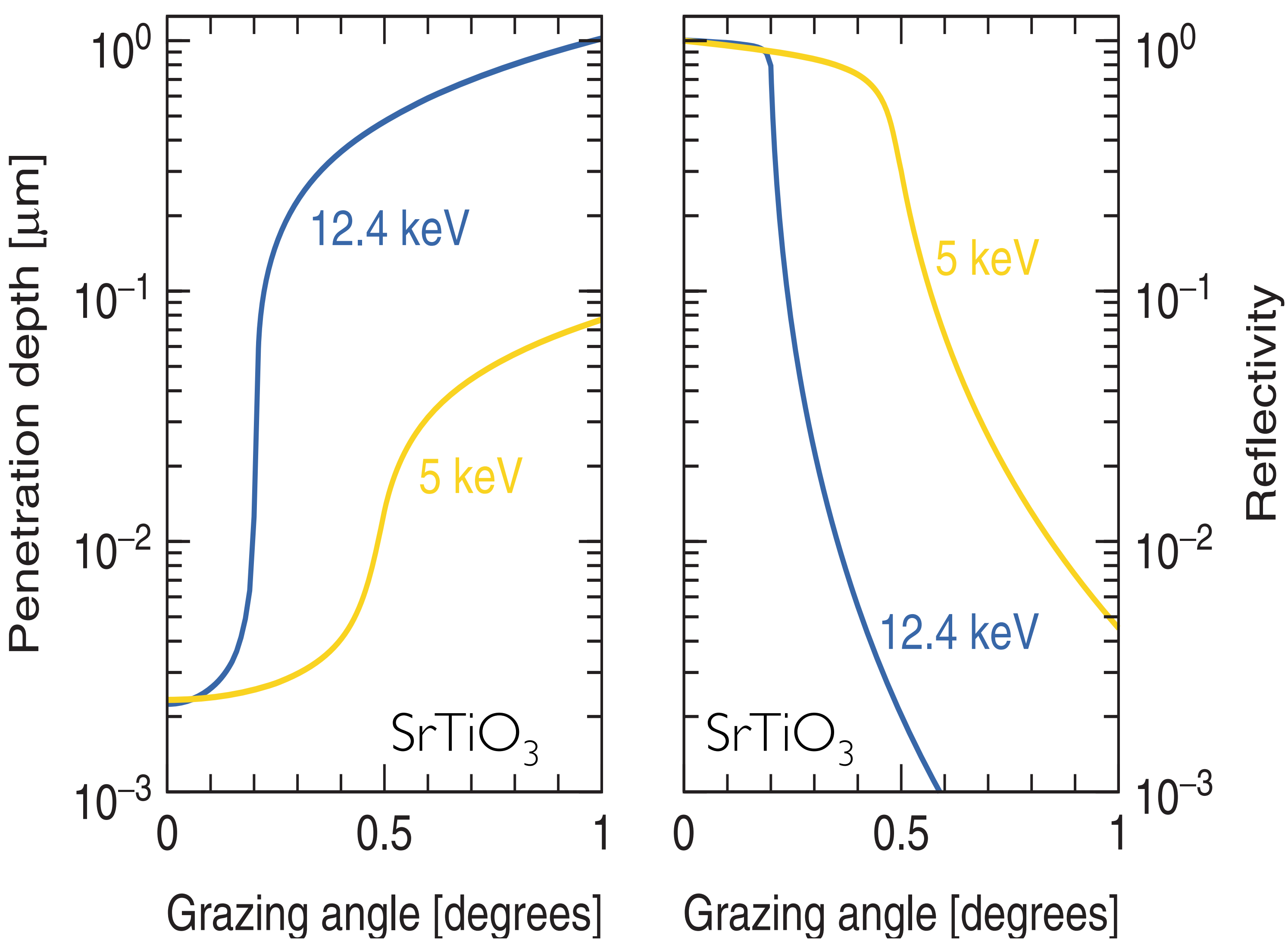


$$L \approx \frac{-\lambda}{4\pi \ \operatorname{Im}\sqrt{\alpha_i^2 - \alpha_c^2 - 2i\beta}}$$



α_i	$0.1\ \alpha_c$	α_c	$2\ \alpha_c$
L (Å)	15	100	1000

Penetration depth



ZnTe/GaAs

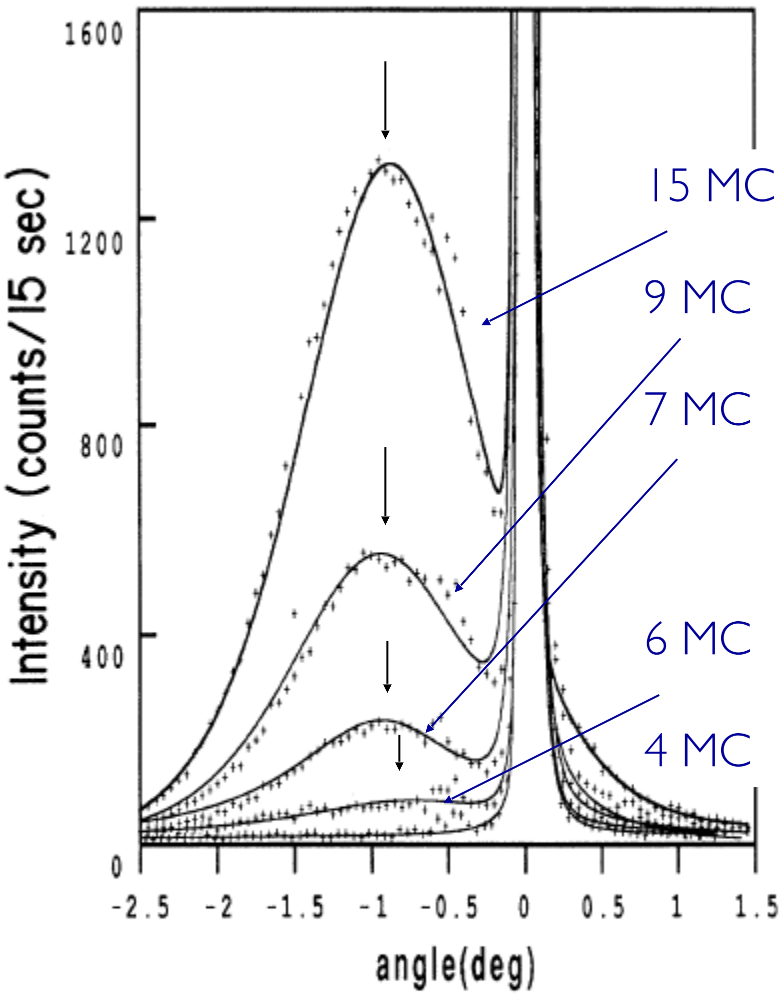


FIG. 1. θ-2θ scans of the (200) reflection from ZnTe/GaAs (001) for heterostructures of increasing thicknesses (4, 6, 7, 9, and 15 ML from bottom to top curve). Profiles are aligned on the substrate Bragg peak.

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

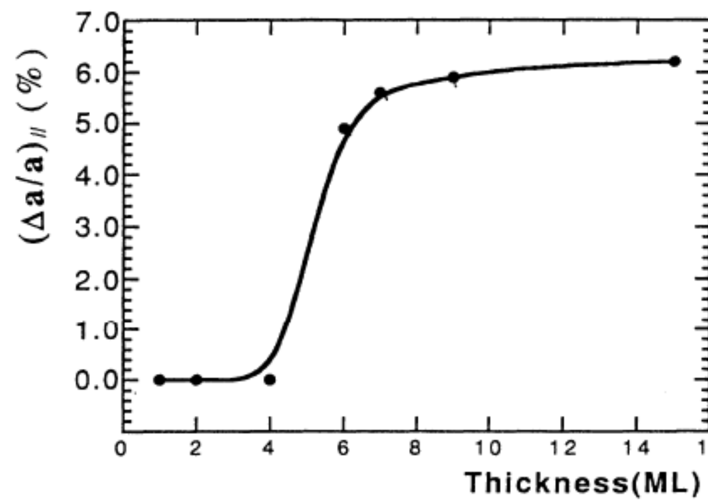
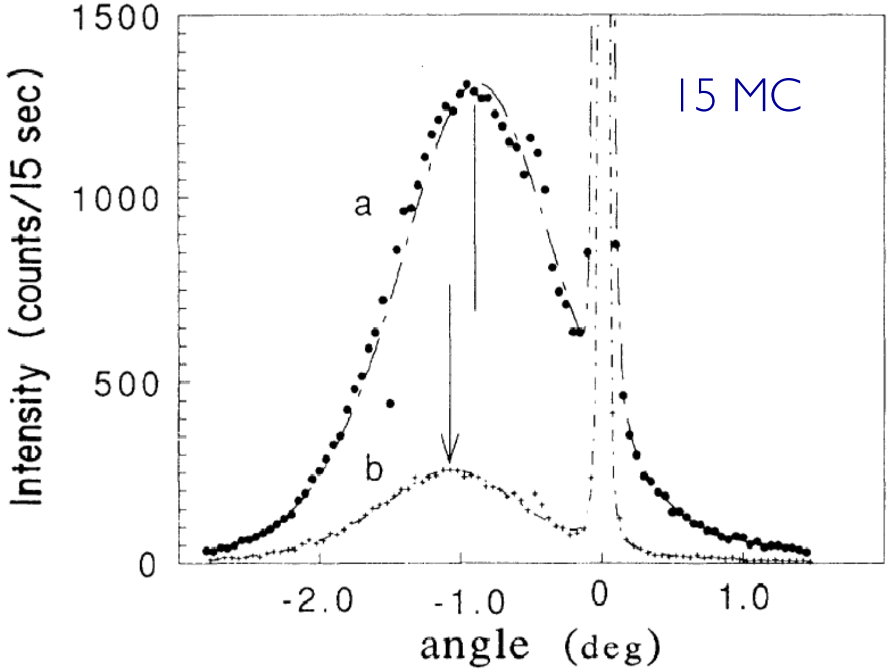


FIG. 2. Variation of $(\Delta a/a)_{\|}$ with the film thickness.

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

ZnTe/GaAs



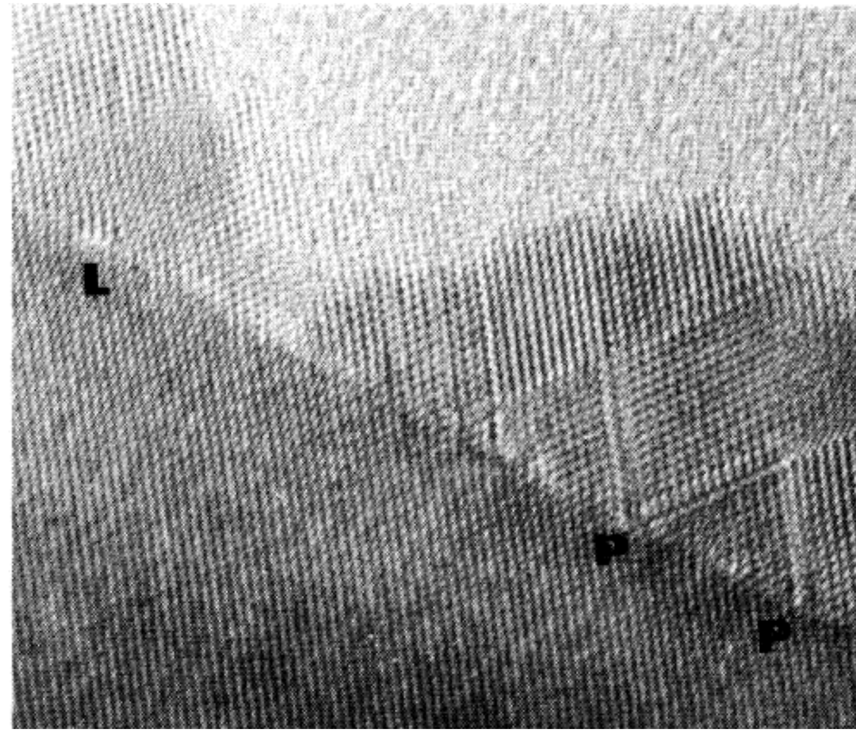
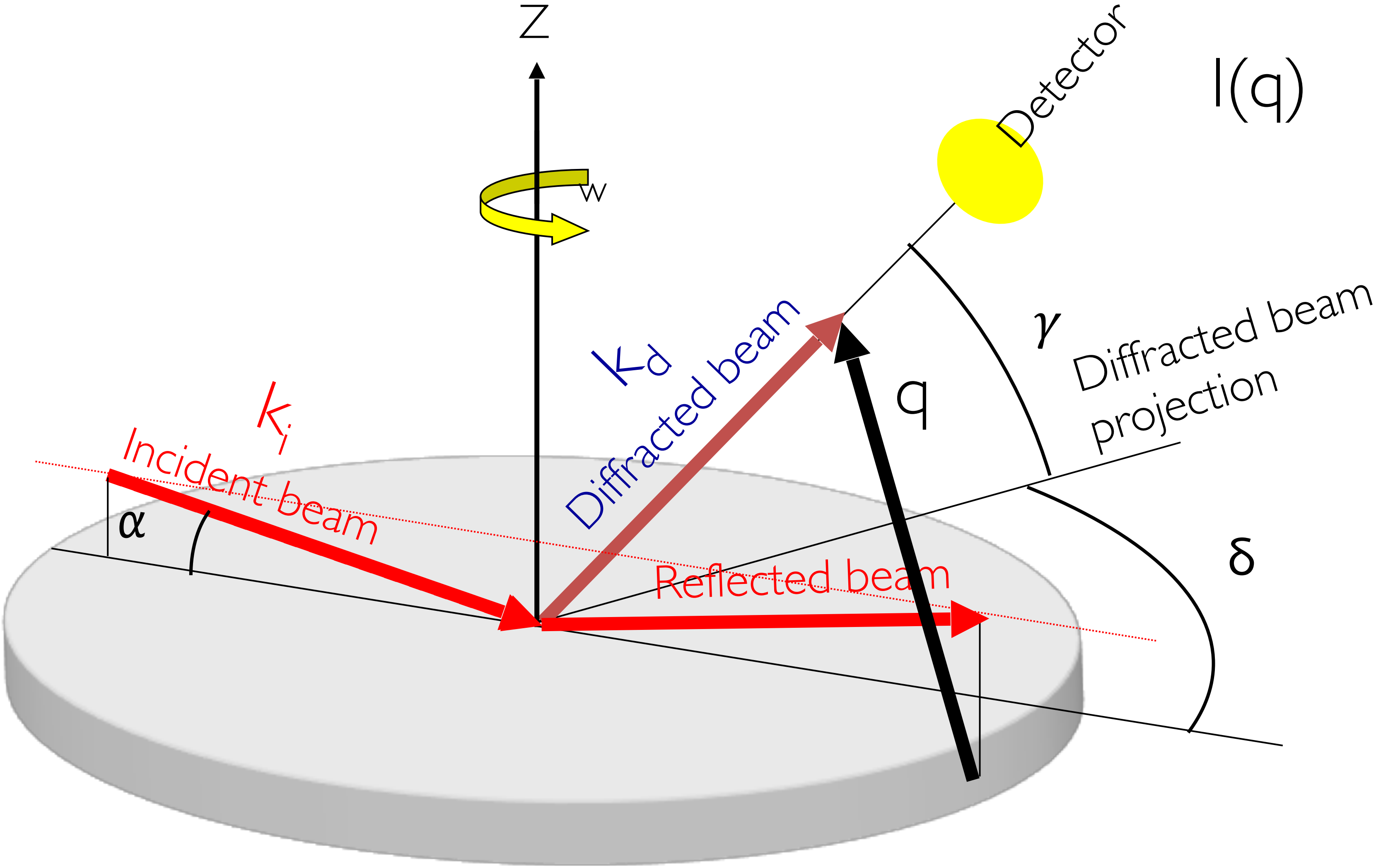


FIG. 6. Radial scans of the 15-ML ZnTe/GaAs at different inside angles. (curve a) $\alpha=\alpha_c$; (curve b) $\alpha=0.3\alpha_c$.

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 : $\mathbf{R}_n$

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

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

The intensity diffused by the crystal is :

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

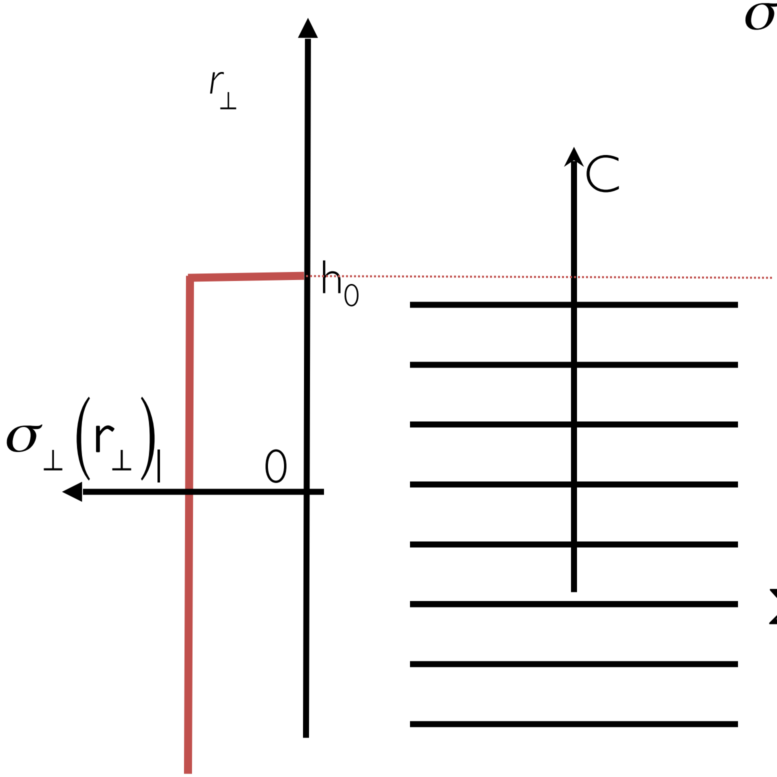
Atomic structure

Finite size effects

periodicity

the atomic form factor is a complex quantity $f(q)=f^0(q) + f' + i f''$
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 $\boldsymbol{\sigma}(r)$: $\displaystyle\sum_{n=-\infty}^{+\infty} \frac{1}{(q_\perp - n\, c^*)^2} = \left(\frac{\pi}{c^* \sin(\pi L)}\right)^2$

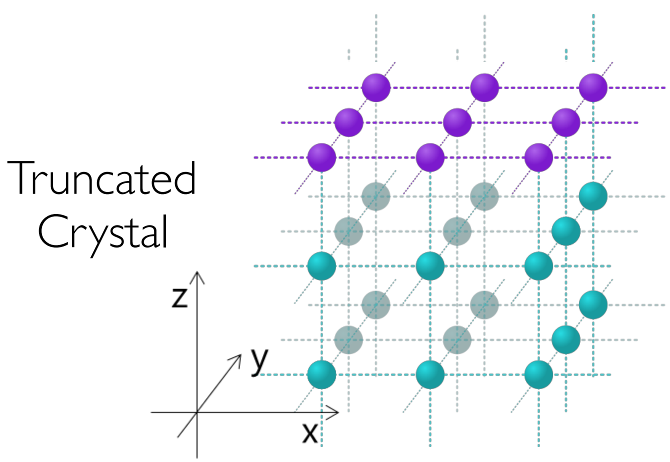
$$\Sigma(q) = \frac{e^{-iq_\perp . h_0}}{-iq_\perp}\ \delta(q_{//}) \Rightarrow \left|\Sigma(q)\right|^2 = \frac{1}{q_\perp^2}\ \delta(q_{//})$$

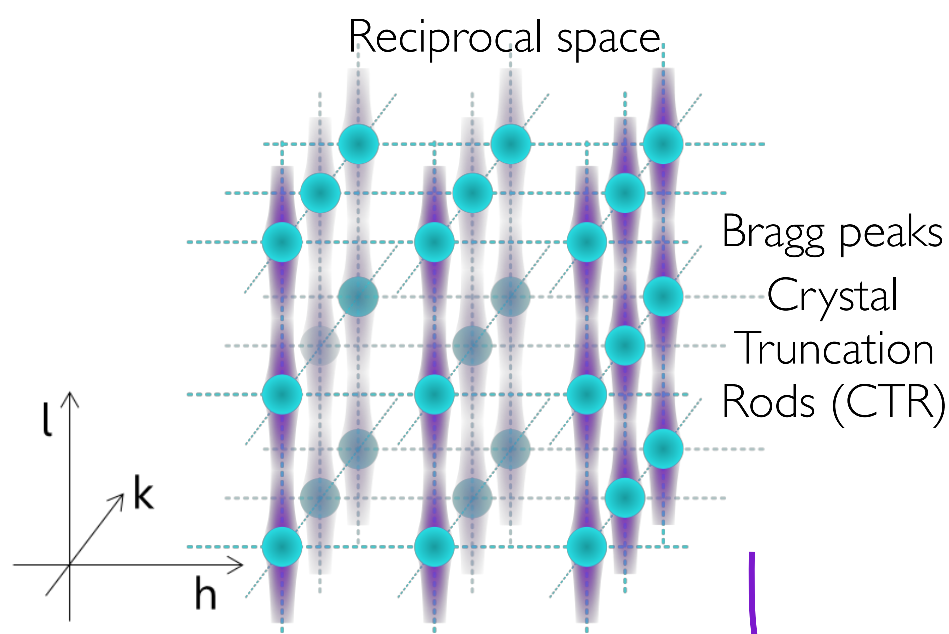
$$\boxed{I(q) = \frac{|F(q)|^2}{s^2}\left(\frac{1}{2\sin(\pi l)}\right)^2\left[\sum_{G_{//}} \delta(q_{//} - G_{//})\right]}$$

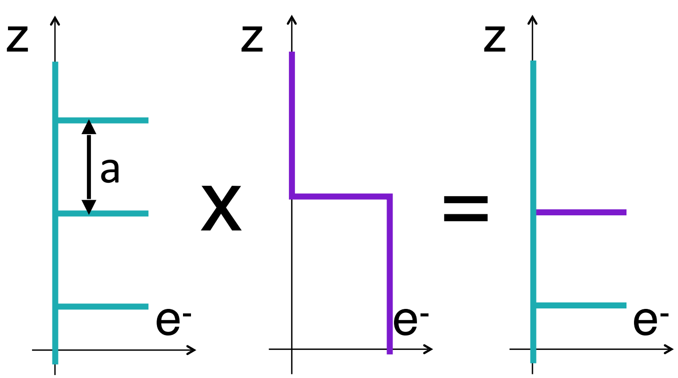
➡ Crystal Truncation Rods (CTR):
issued from Bragg peak & perpendicular to the surface

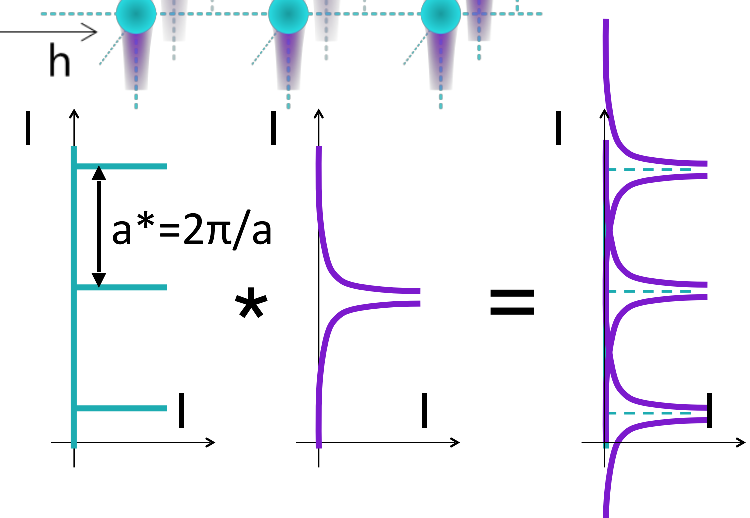
Cristal Truncation Rod (CTR)

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

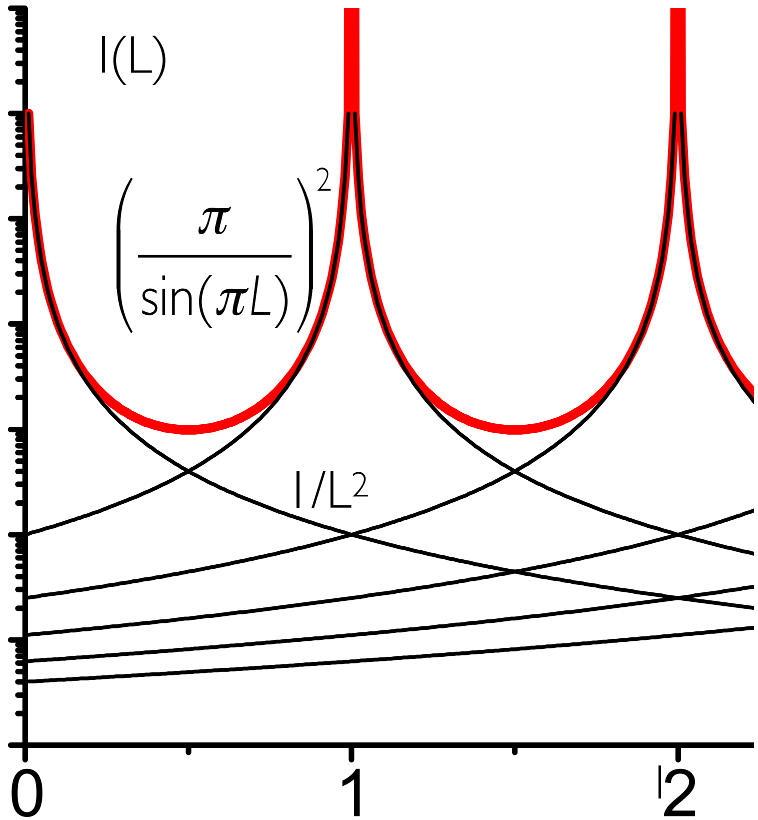






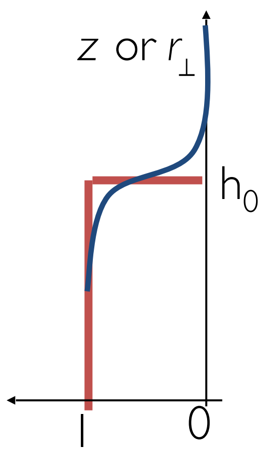


Cristal troncation rod (CTR)



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

Surface roughness



$$\sigma_\perp^{surf}(r_\perp) = 1 \quad \text{for } r_\perp < h_0$$

$$\sigma_\perp^{surf}(r_\perp) = 0 \quad \text{for } r_\perp > h_0$$

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

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

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

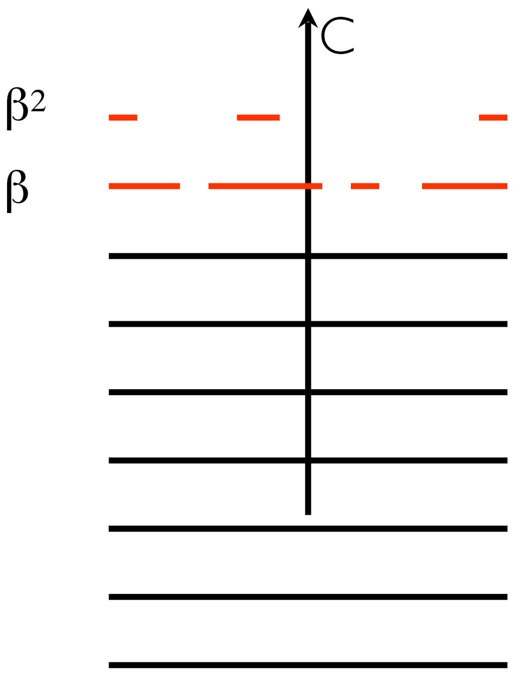
Roughness models:

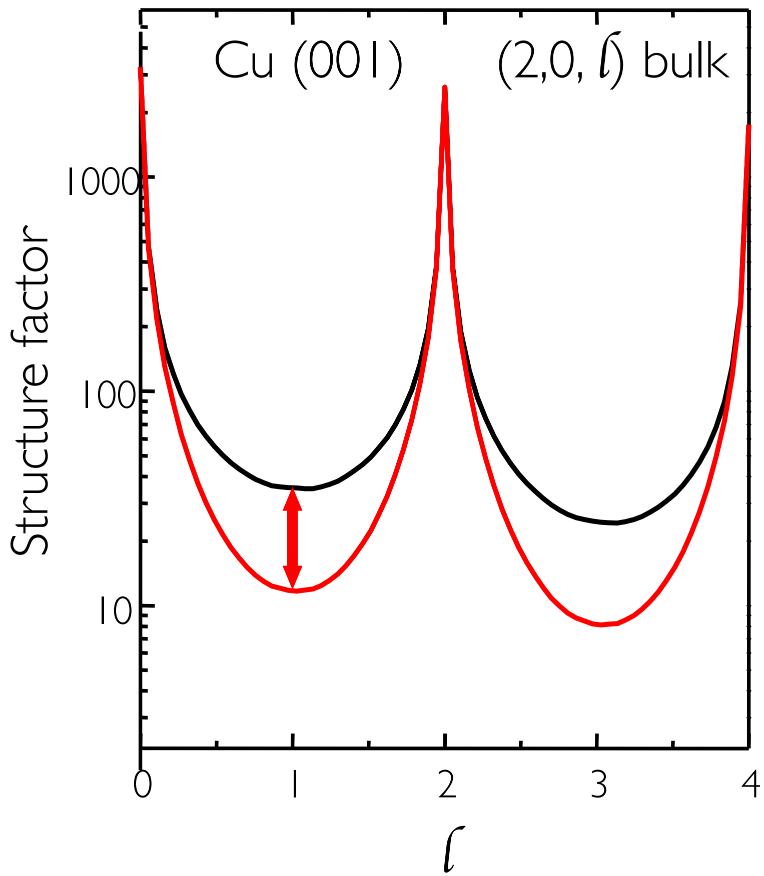
i. a simple two level model (E. Vlieg)

ii. an exponential decay (I. Robinson)

iii. a gaussian distribution of successive layers occupancy (P. Guenard)

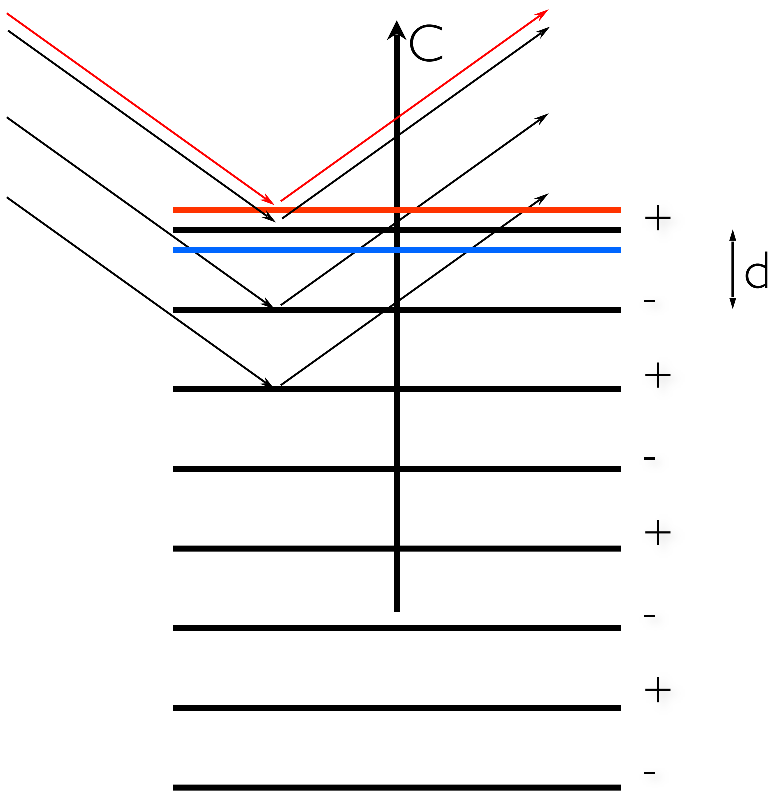
CTR FROM A ROUGH SURFACE

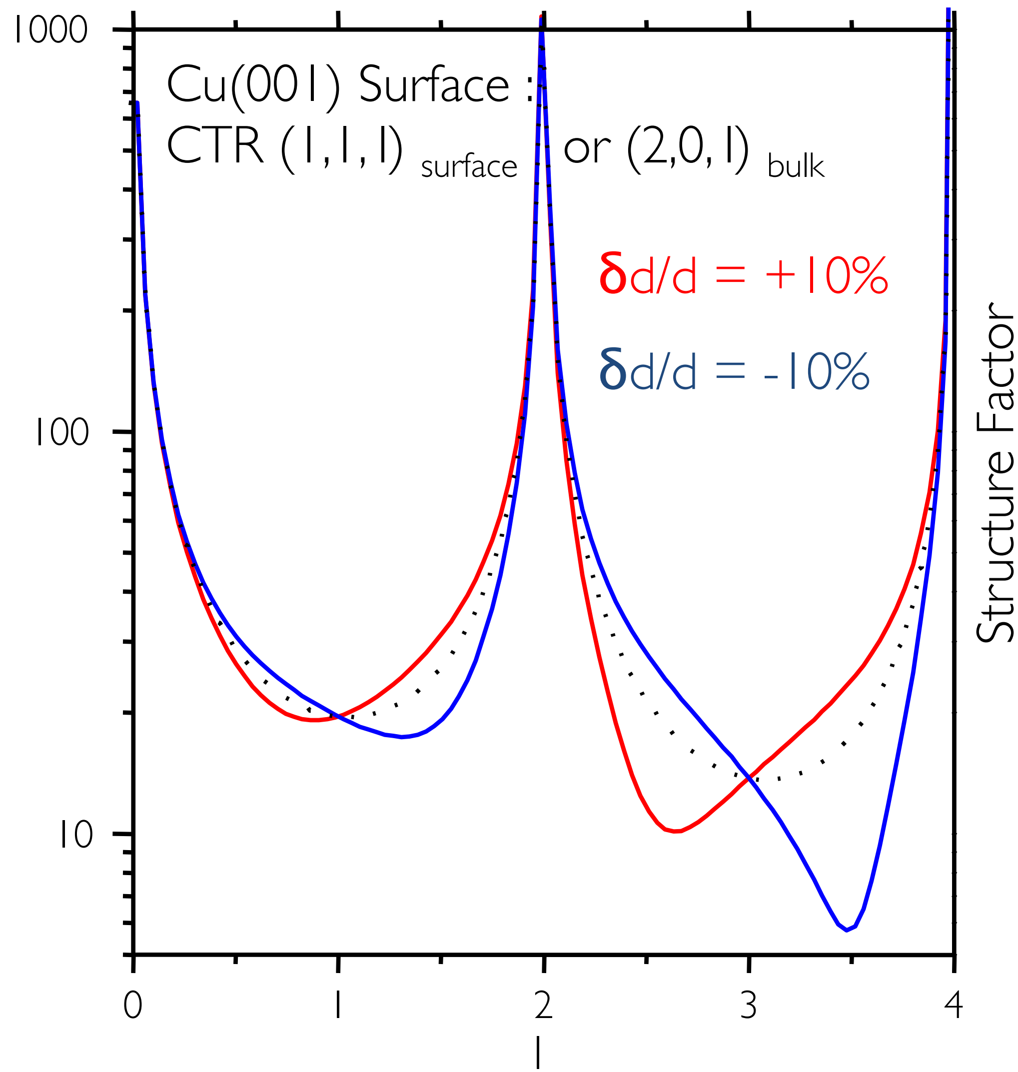




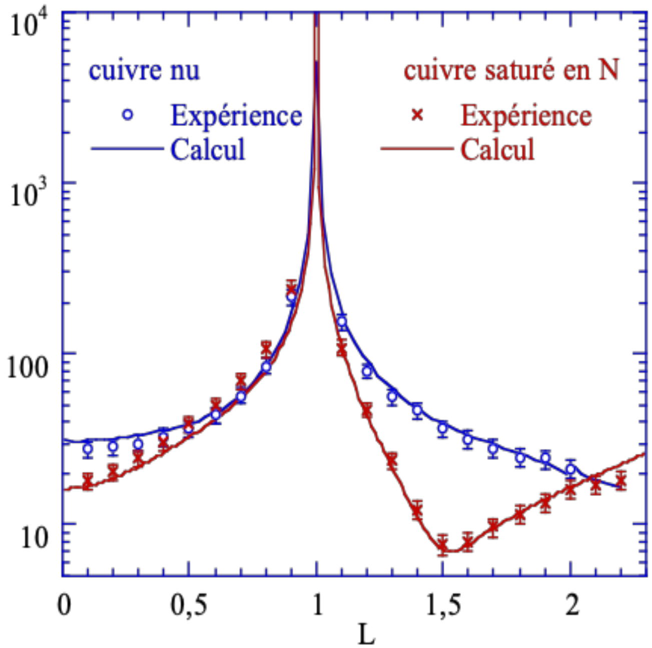
Optimal sensitivity in « anti-bragg » position, used to monitor layer by layer growth through pseudo-periodic oscillations

CTR : Effect of the relaxation

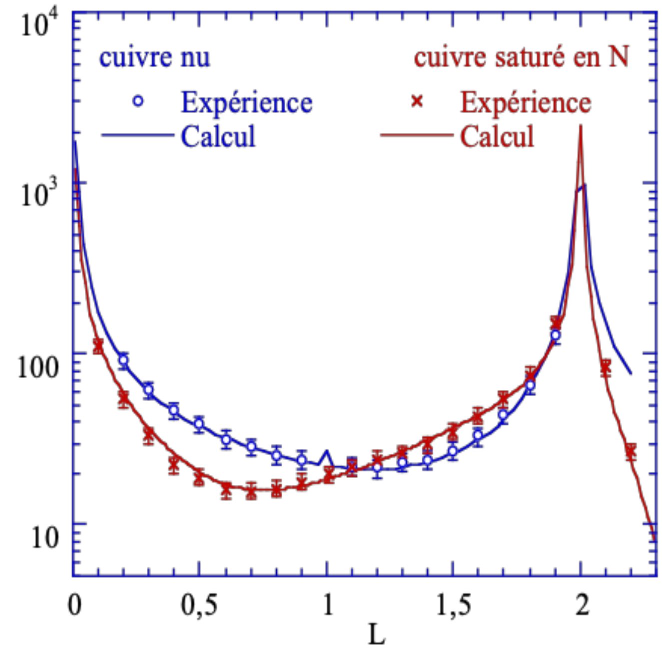




CTR : Cu (001) et N/Cu(001)



Rod (1,1,L)



Rod (2,0,L)

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

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

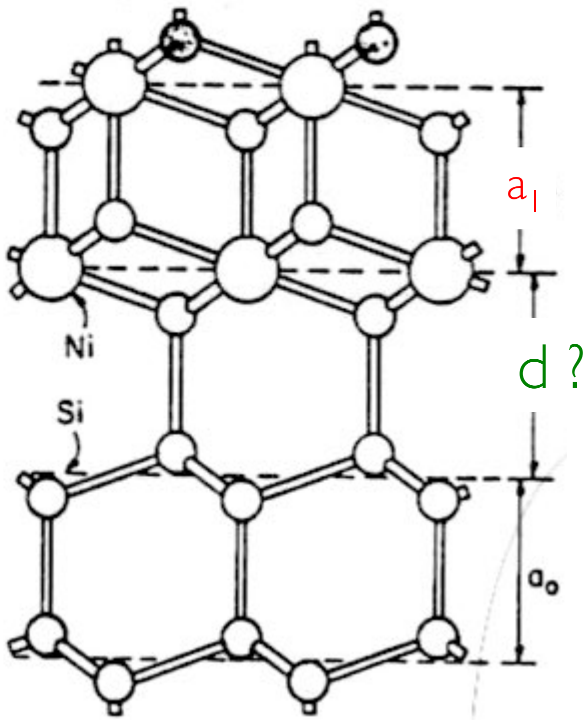
CTR AND INTERFACES

$SiNi_2$/Si(111) interface

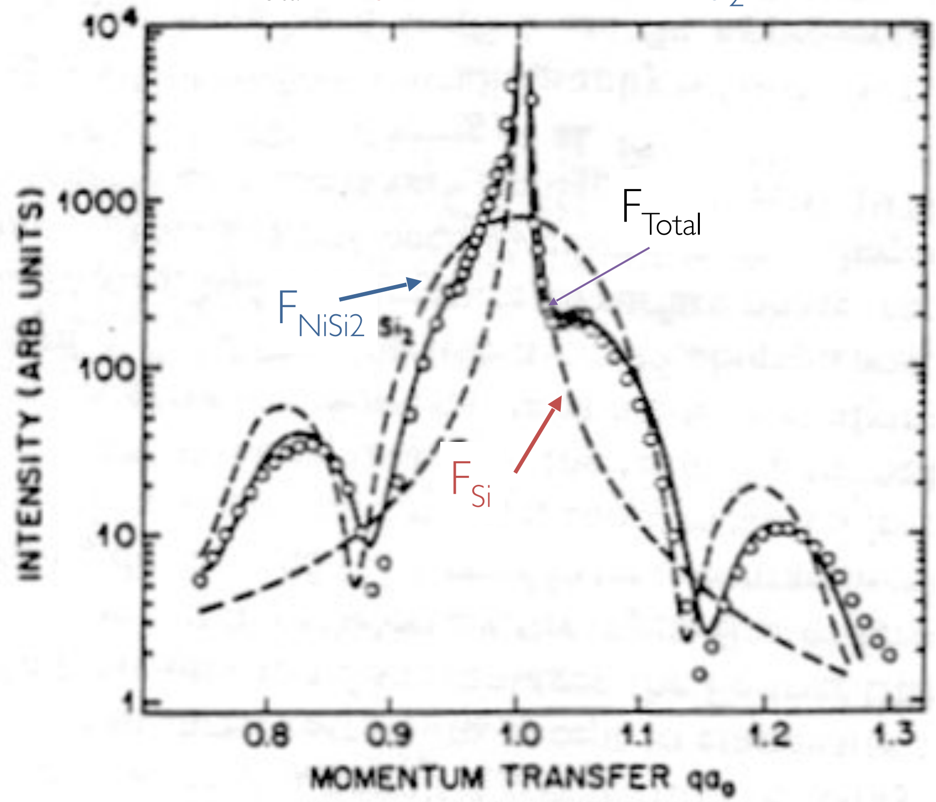
around Si(111) Bragg peak

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

$NiSi_2$ 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

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

$$\sigma_{\perp}(\mathrm{r}_{\perp}) = \delta(\mathrm{r}_{\perp})$$

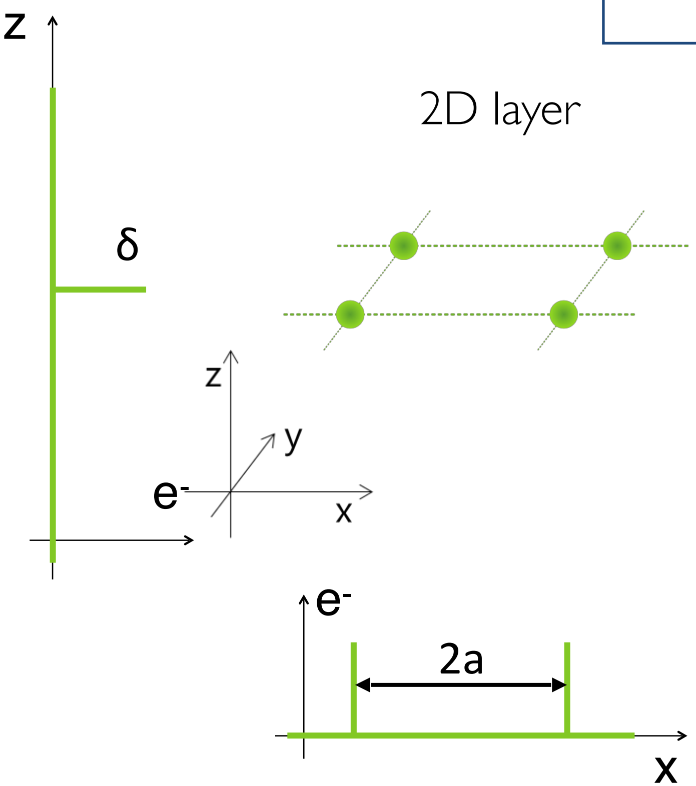
Fourier transform of $\boldsymbol{\sigma}(\mathrm{r})$:

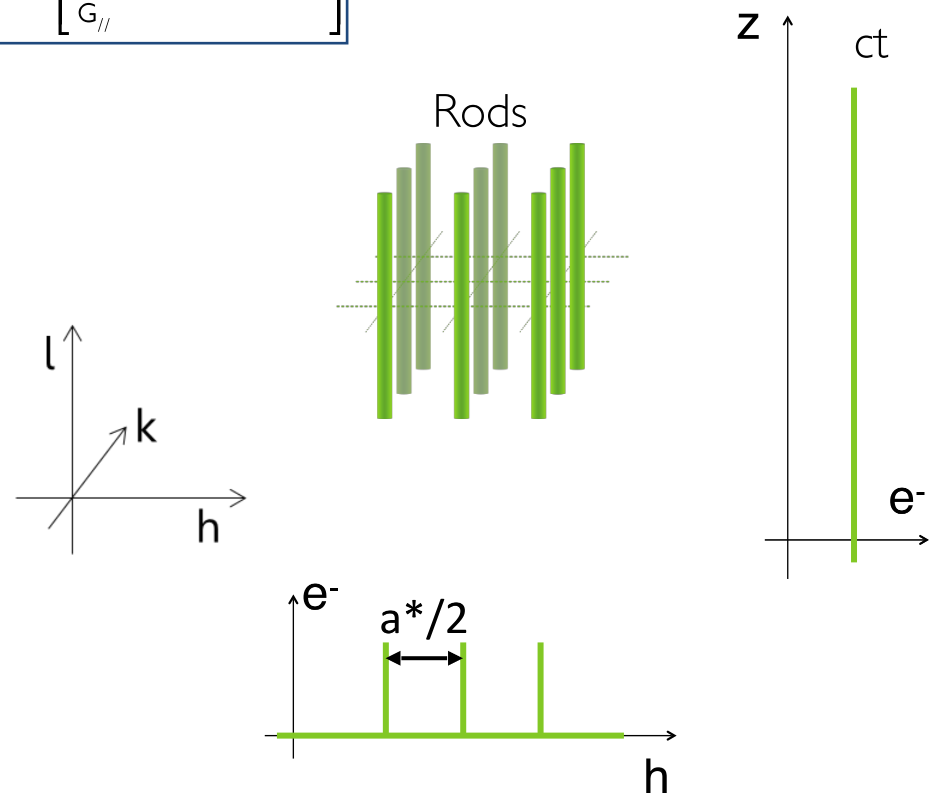
$$\Sigma(\mathrm{q}) = const\ \delta(\mathrm{q}_{//}) \Rightarrow \left|\Sigma(\mathrm{q})\right|^2 = const^2\ \delta(\mathrm{q}_{//})$$

Real space

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

Reciprocal space



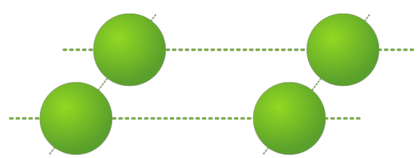


2D CRYSTAL

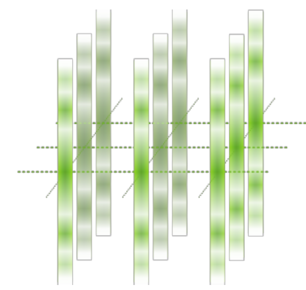
$$I(\mathrm{q}) = \frac{\left|F(\mathrm{q})\right|^2}{s^2} const^2 \left[\sum_{\mathrm{G}_{//}} \delta\left(\mathrm{q}_{//} - \mathrm{G}_{//}\right) \right]$$

2D layer
of spheres

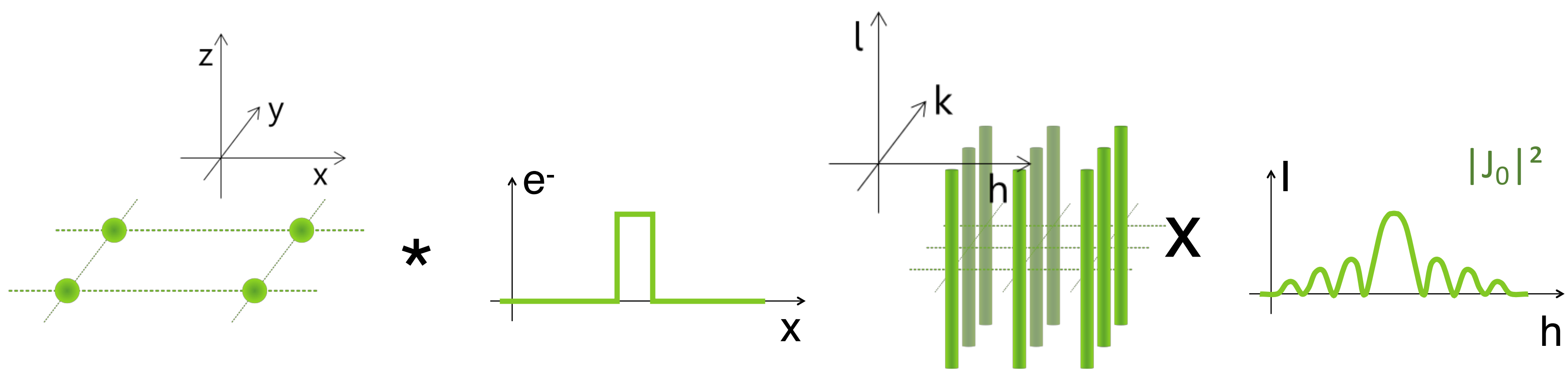
Real space



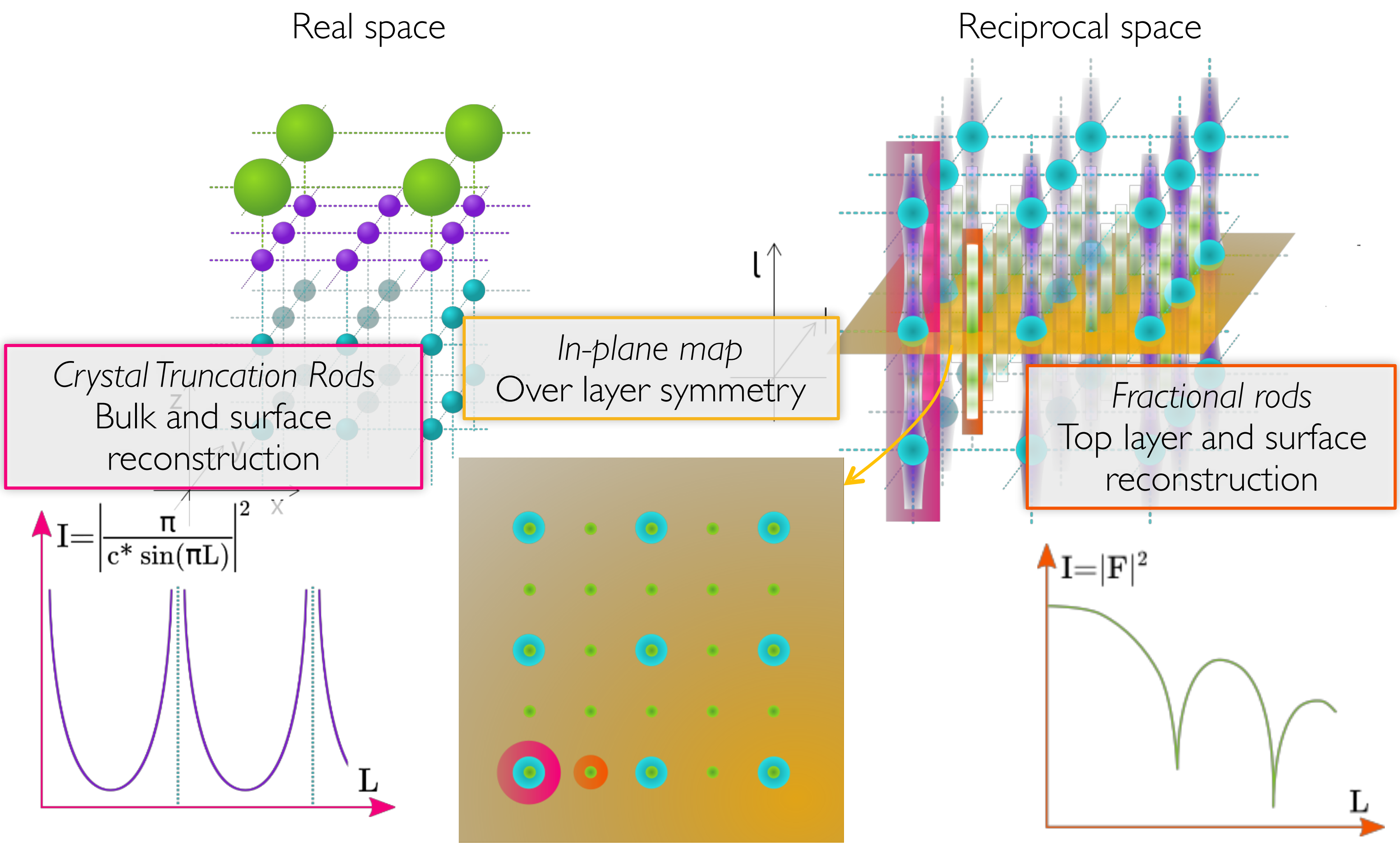
Reciprocal space



Modulated
intensity

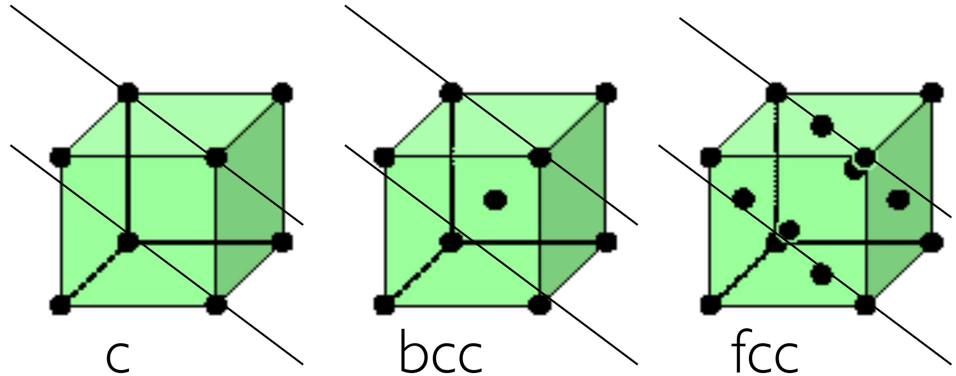


SURFACE X-RAY DIFFRACTION

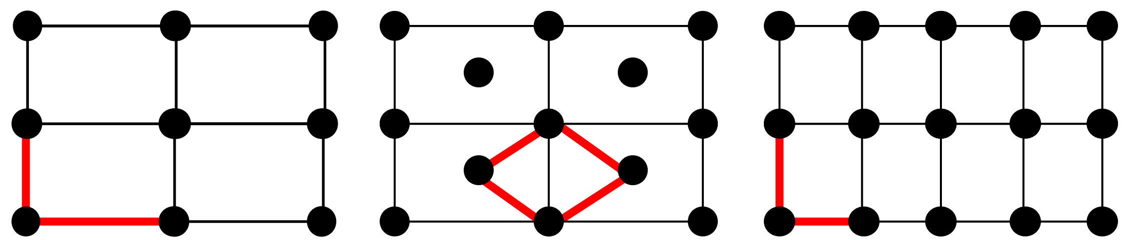


SURFACE CRYSTALLOGRAPHY

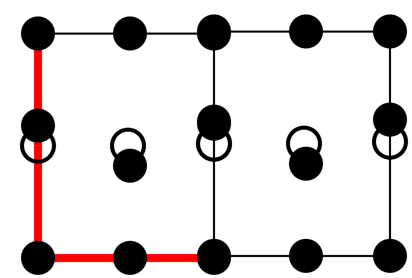
Ex: (110) cut in the
3 cubic lattices



Basis vectors a_s b_s
of the 1x1 surface cells



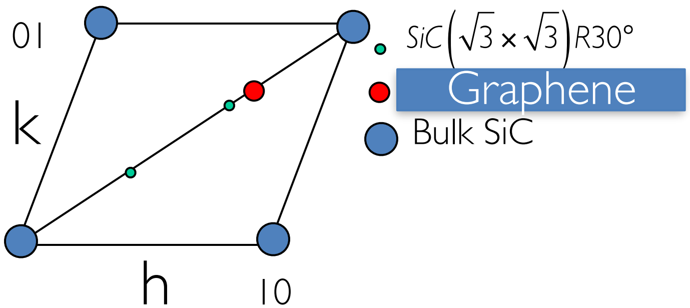
Basis vectors of a 2x2 unit cell on a
reconstructed (110) surface of an fcc lattice

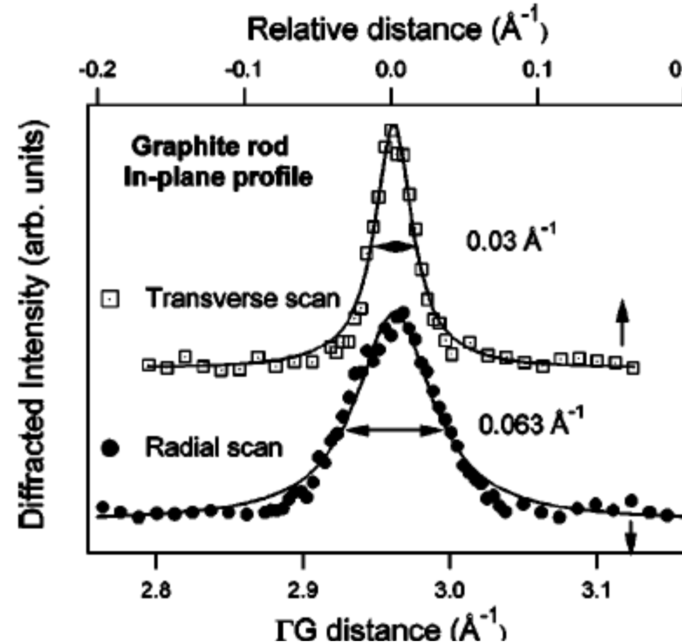


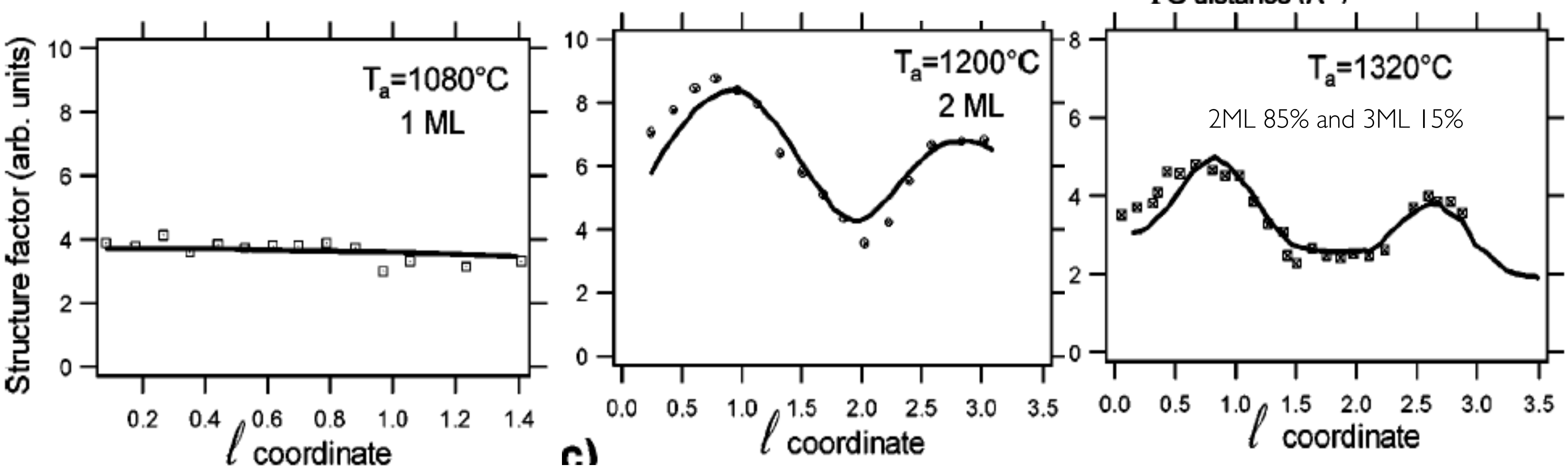
More generally mxn reconstruction

GRAPHENE GROWTH

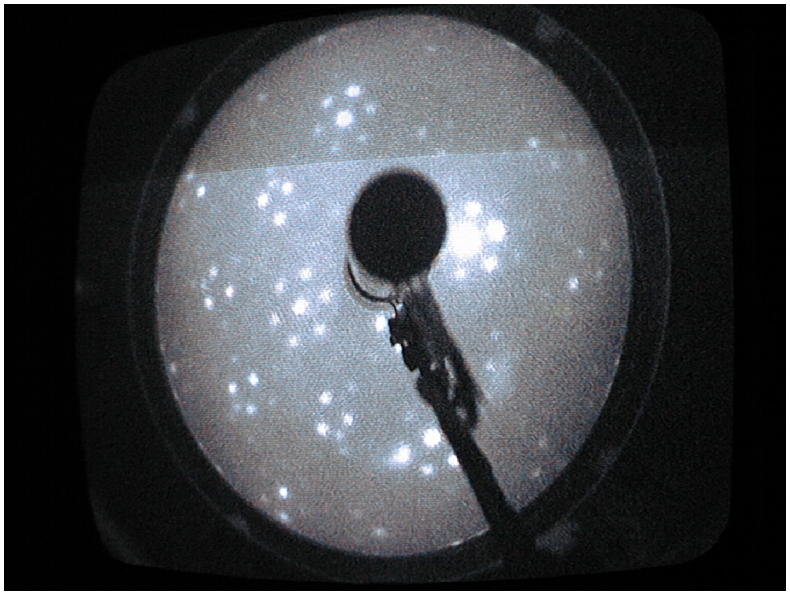
Charrier et al. J. Appl. Phys. 92, 2479(2002)

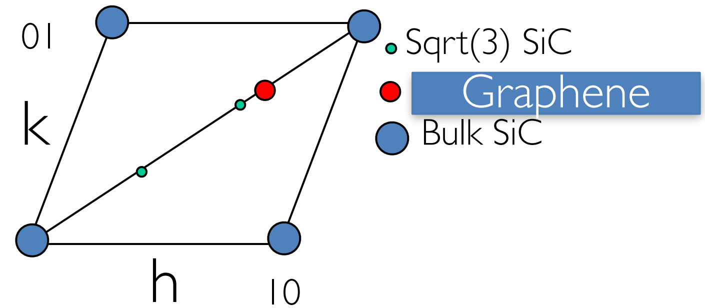






LEED VS GIXD





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

A fully relaxed graphene plane in registry with the SiC substrate

Multiple scattering versus single scattering

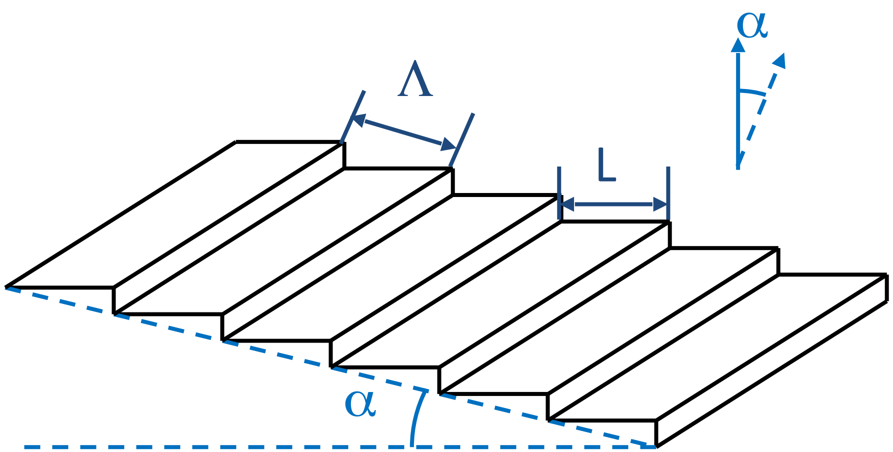
ROD SOFTWARE

The « ROD » code

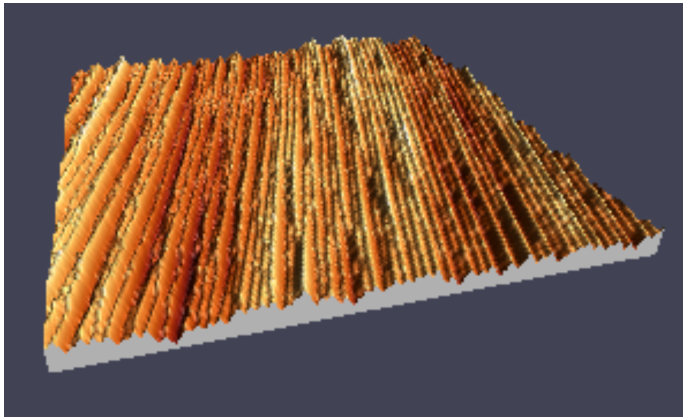
E. Vlieg, J. Appl. Cryst, 33, 401 (2000)
➔interactive webpage ANA-ROD

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

Vicinal Surface

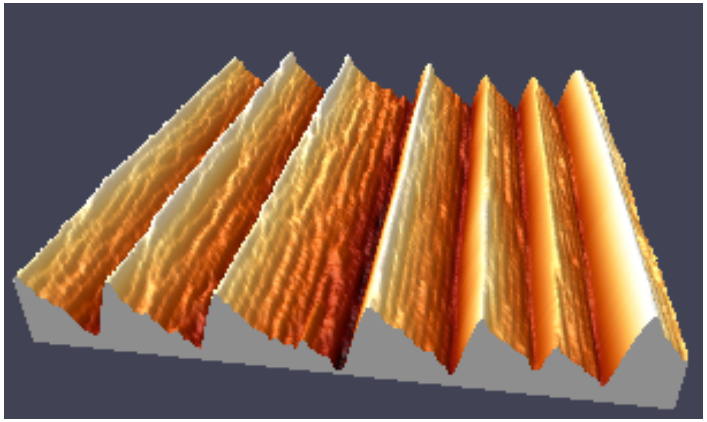


Cu(433) (100x100) nm

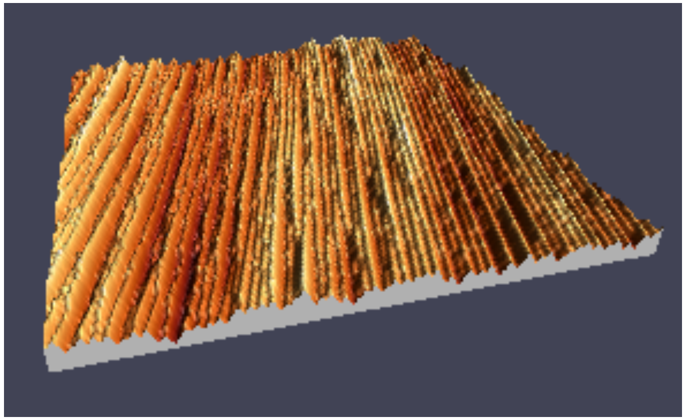


SELF ORGANISATION: AG/CU

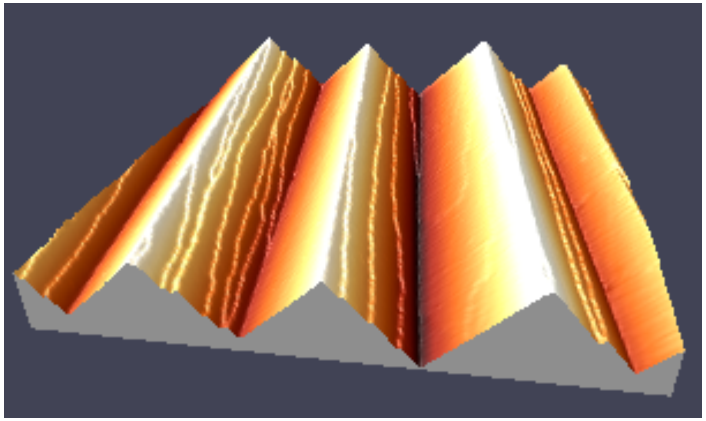
0.3 ML Ag/Cu(433) (200x200) nm



Cu (433) (100x100) nm

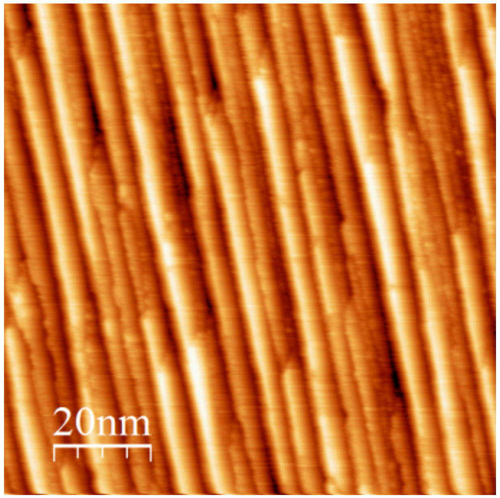


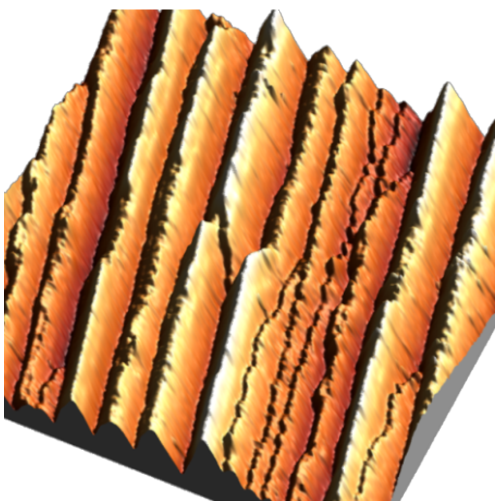
0.6 ML Ag/Cu(433) (200x200) nm



Self Organisation: Ag/Ni

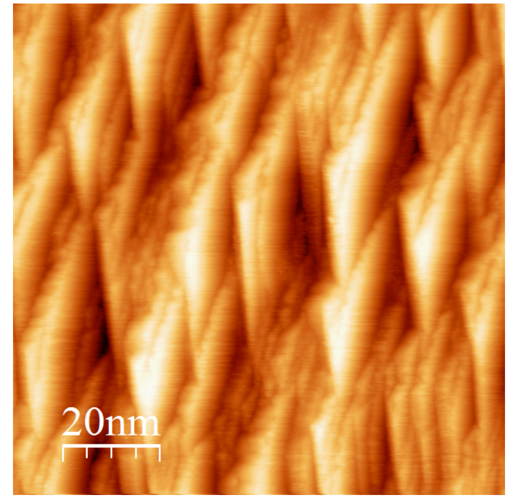
Ag/Ni(11 9 9)

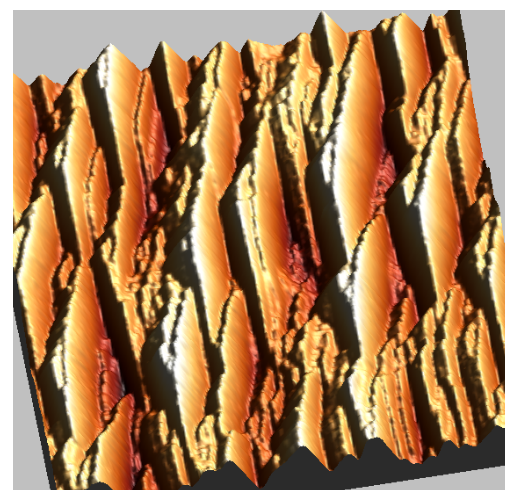




Organisation 1D

Ag/Ni(27 17 19)

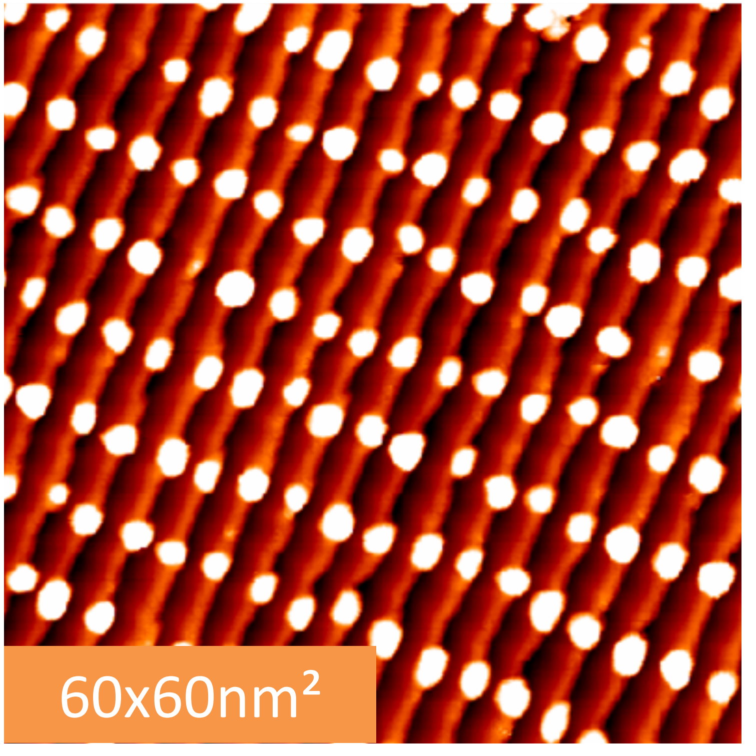




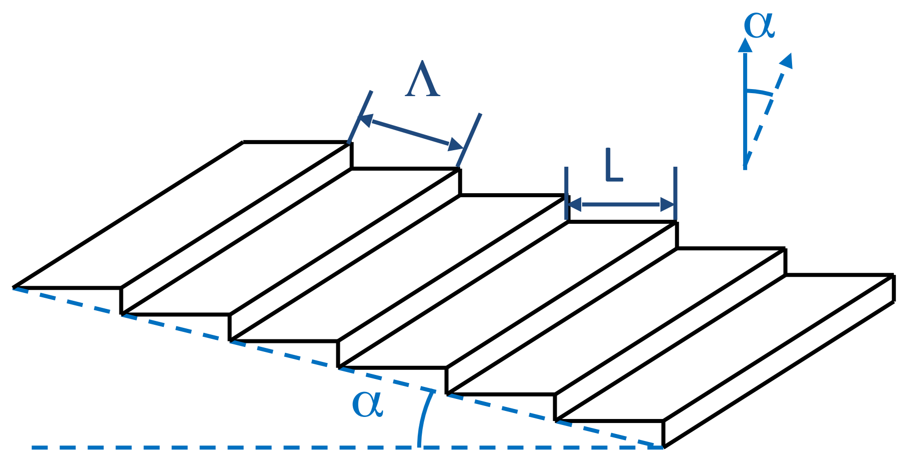
Organisation 2D

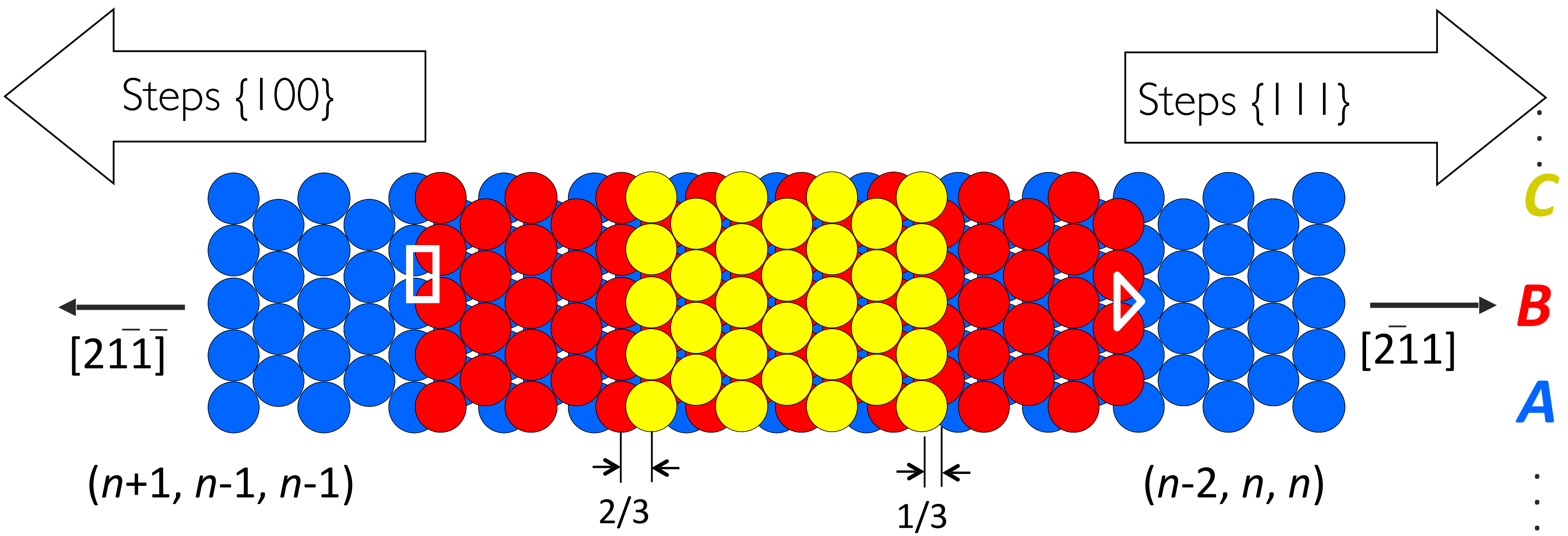
Self Organisation: Co/Au

Co/Au(788)



Vicinal Surfaces (111) fcc

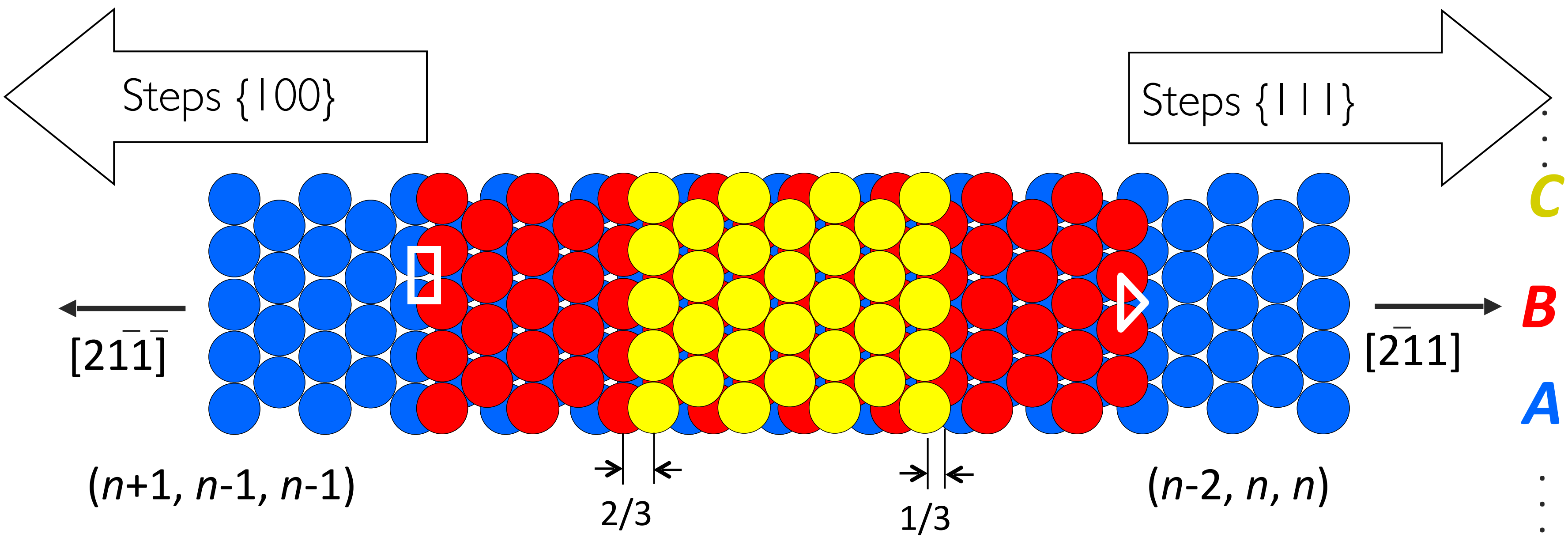




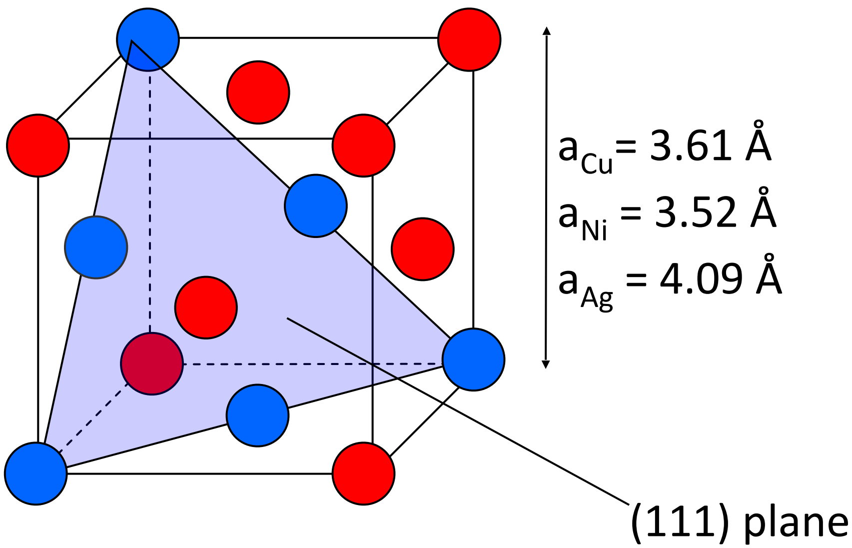
VICINAL SURFACES (111) FCC

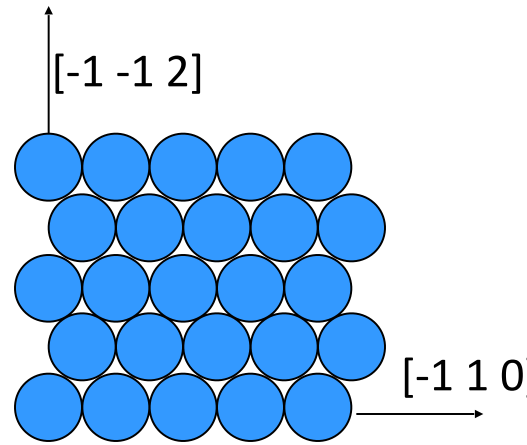
	Angle (°)	Lines	Λ (nm)
Cu(211)	(-)19.5	2+2/3	0.626
Au(322)	(-)11.4	4+2/3	1.17
Ni(1199)	(-) 5.57	9+2/3	2.096

	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



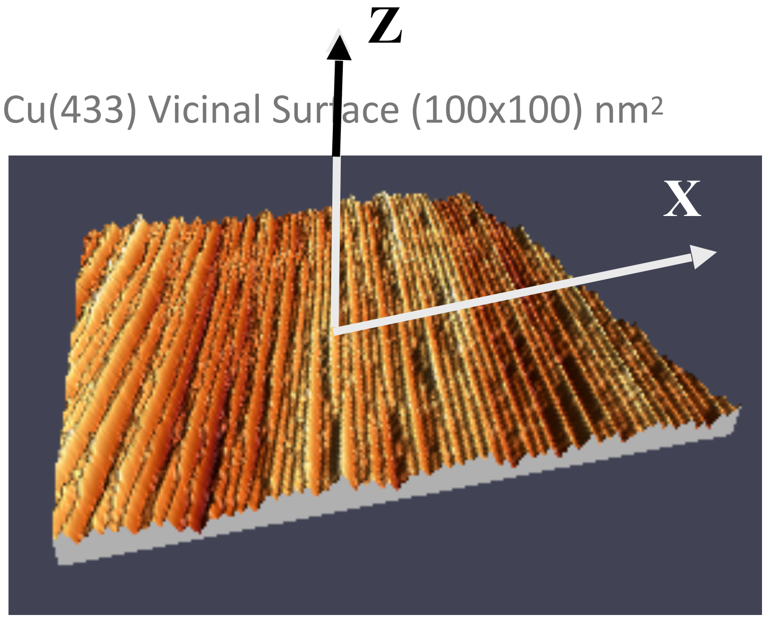


- fcc structure
- Immiscibles
- atomic radii r_{Ag}/r_{Cu}=1,13 r_{Ag}/r_{Ni}=1,15
- cohesion energies : E_{NCu}=-3,50 eV E_{cNi}=-4,44 eV E_{cAg}=-2,96 eV

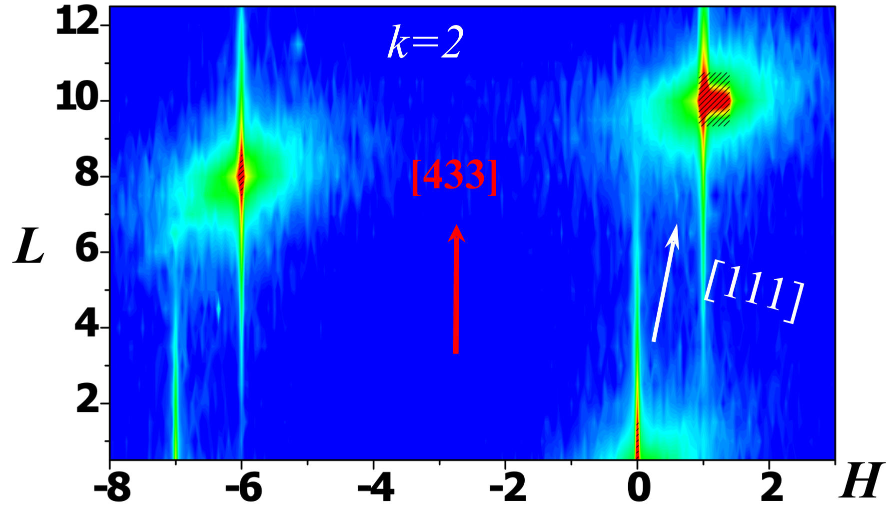
Ag segregates on Ni or Cu
Abrupt Interfaces

ABSORBATE INDUCED FACETING : X-RAY MEASUREMENTS

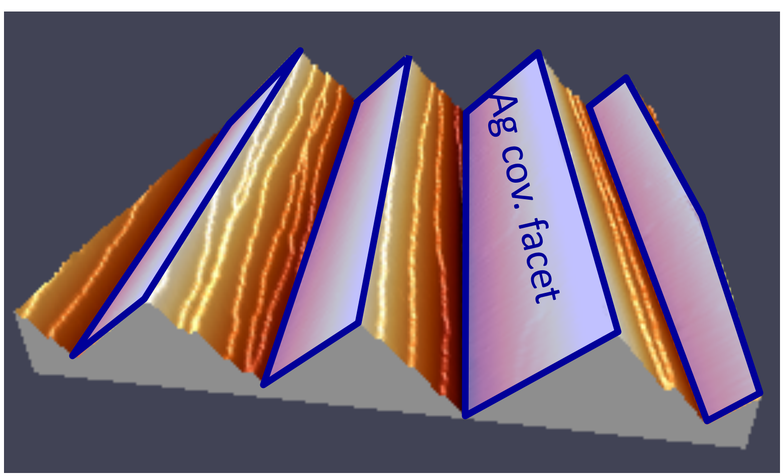
Cu(433) Vicinal Surface (100x100) nm^2



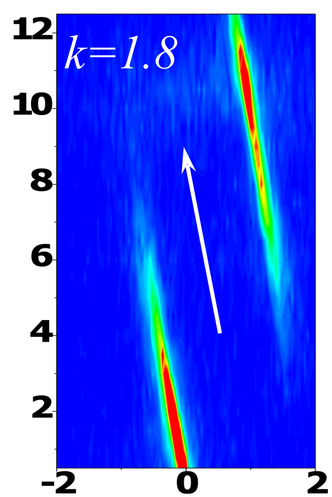
X-ray measurement : Cu(433)

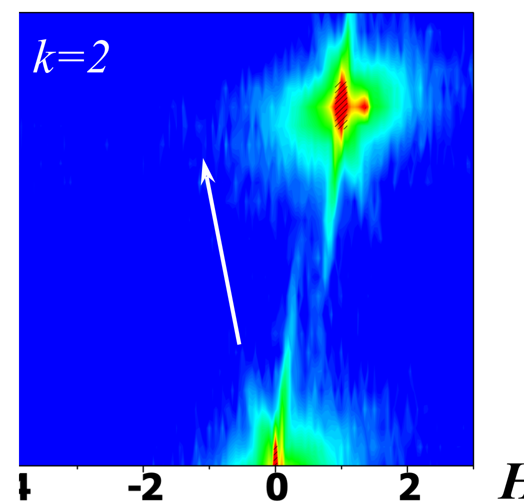


~1/3 ML Ag/Cu(433) (200x200) nm^2

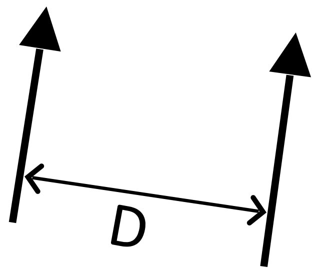


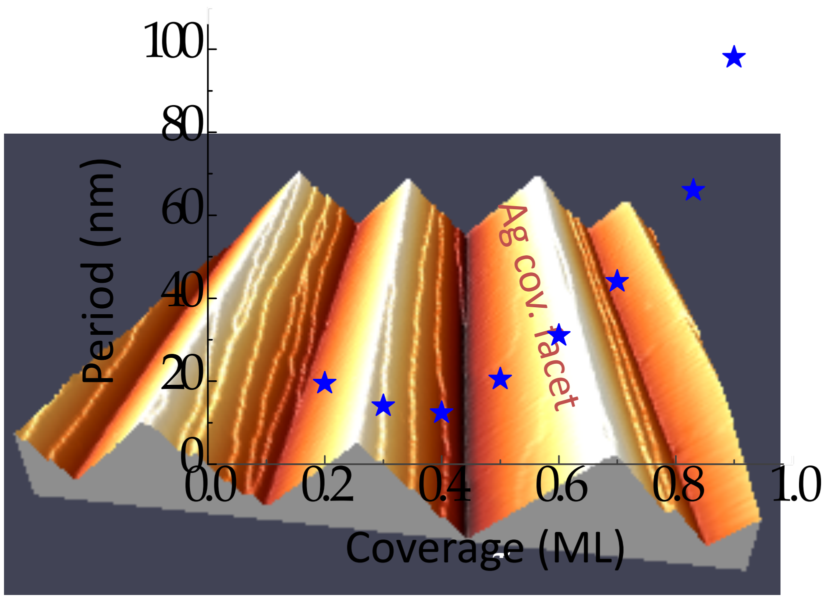
After Ag deposition and annealing

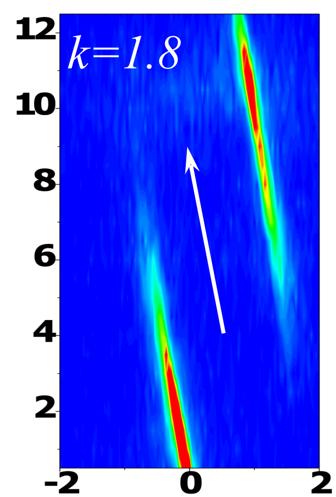


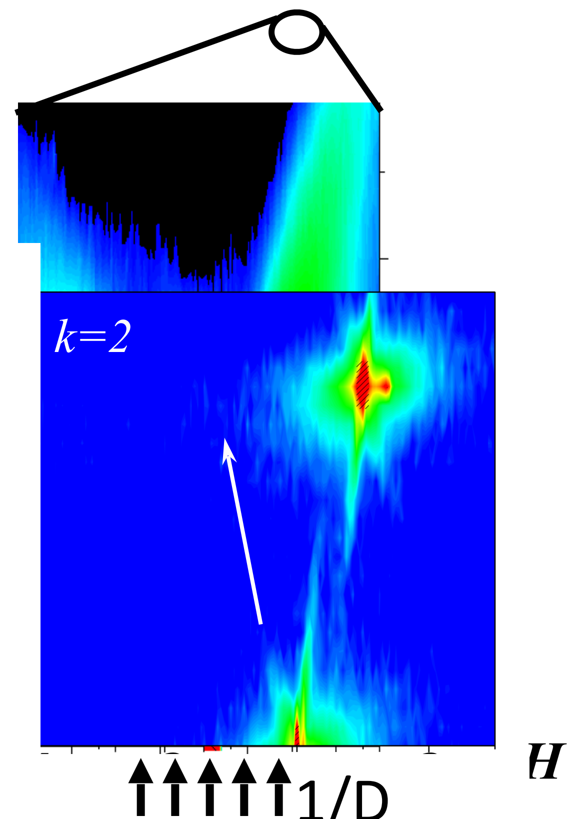


Absorbate induced faceting : X-ray measurements

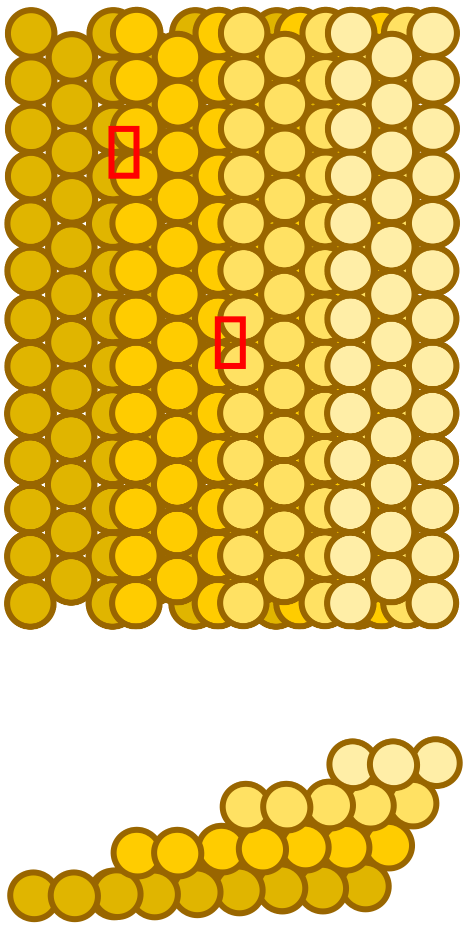


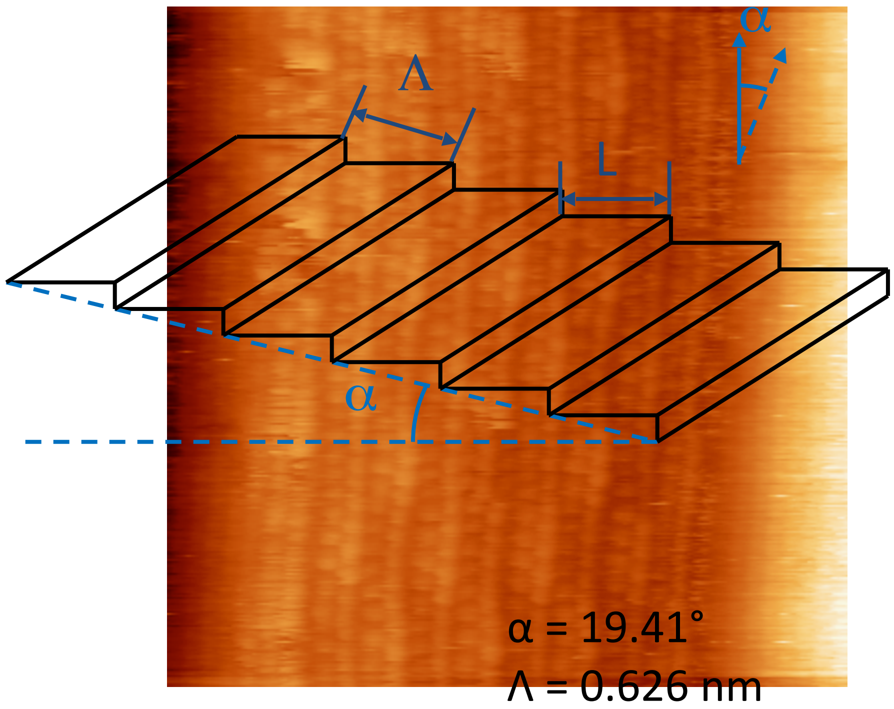




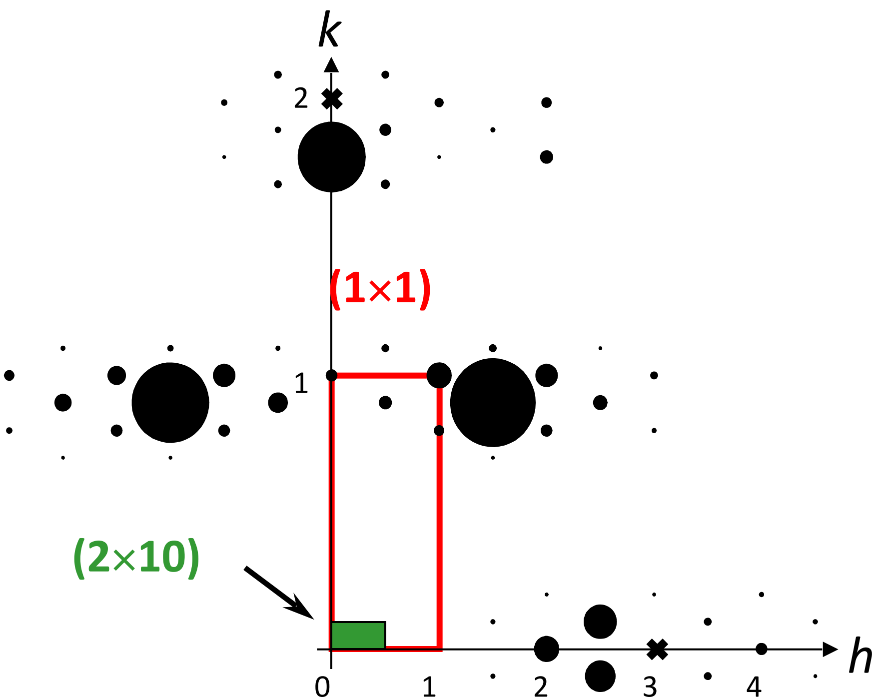


1 ML Ag/Cu(211)

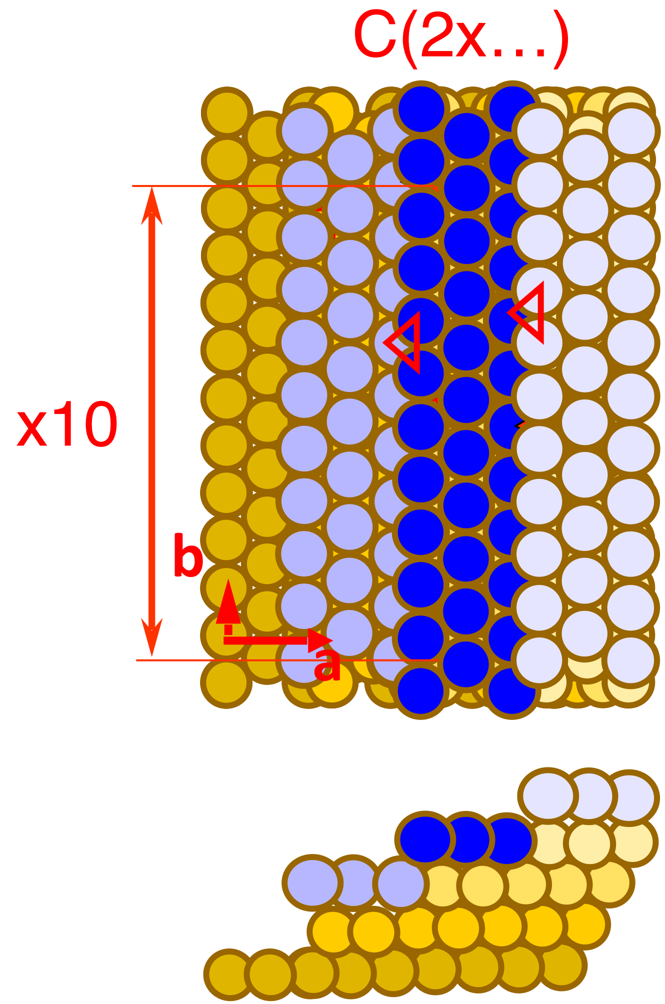




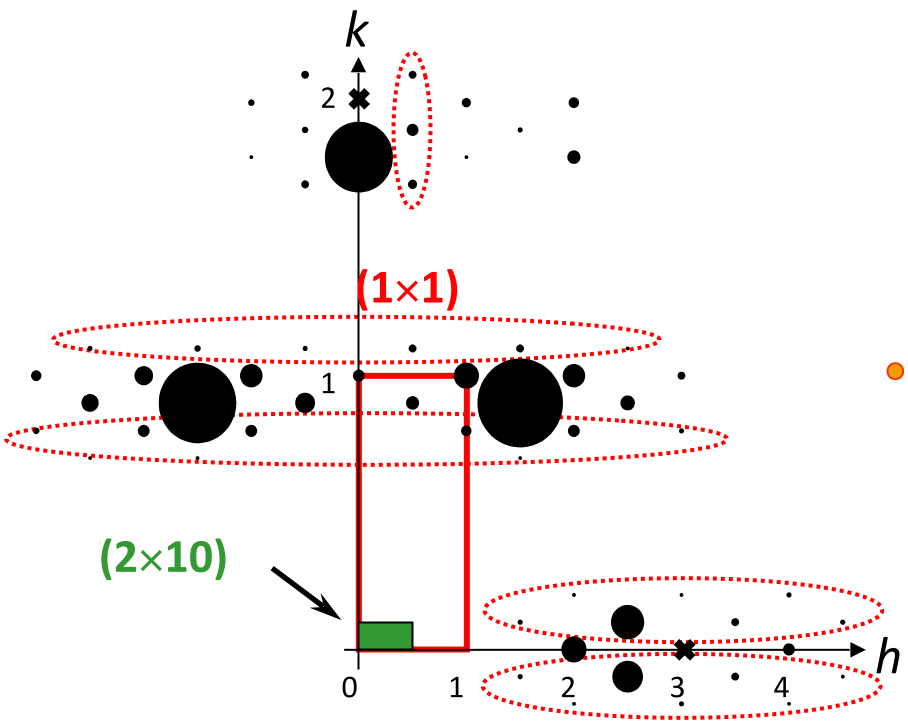
1 ML Ag/Cu (211) - reconstruction C(2x10)



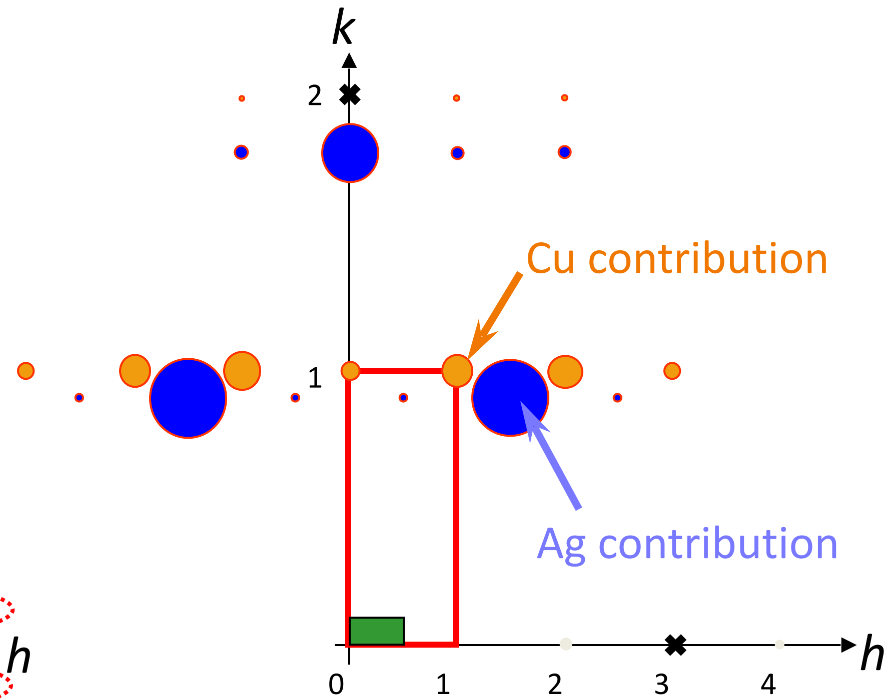
GIXD measurements



1 ML Ag/Cu(211) – GIXD



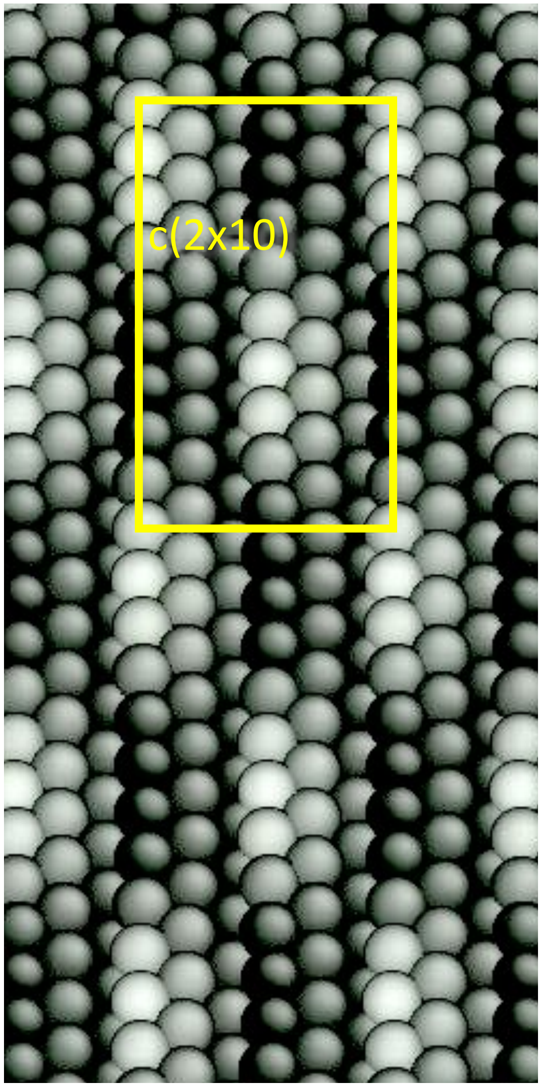
GIXD

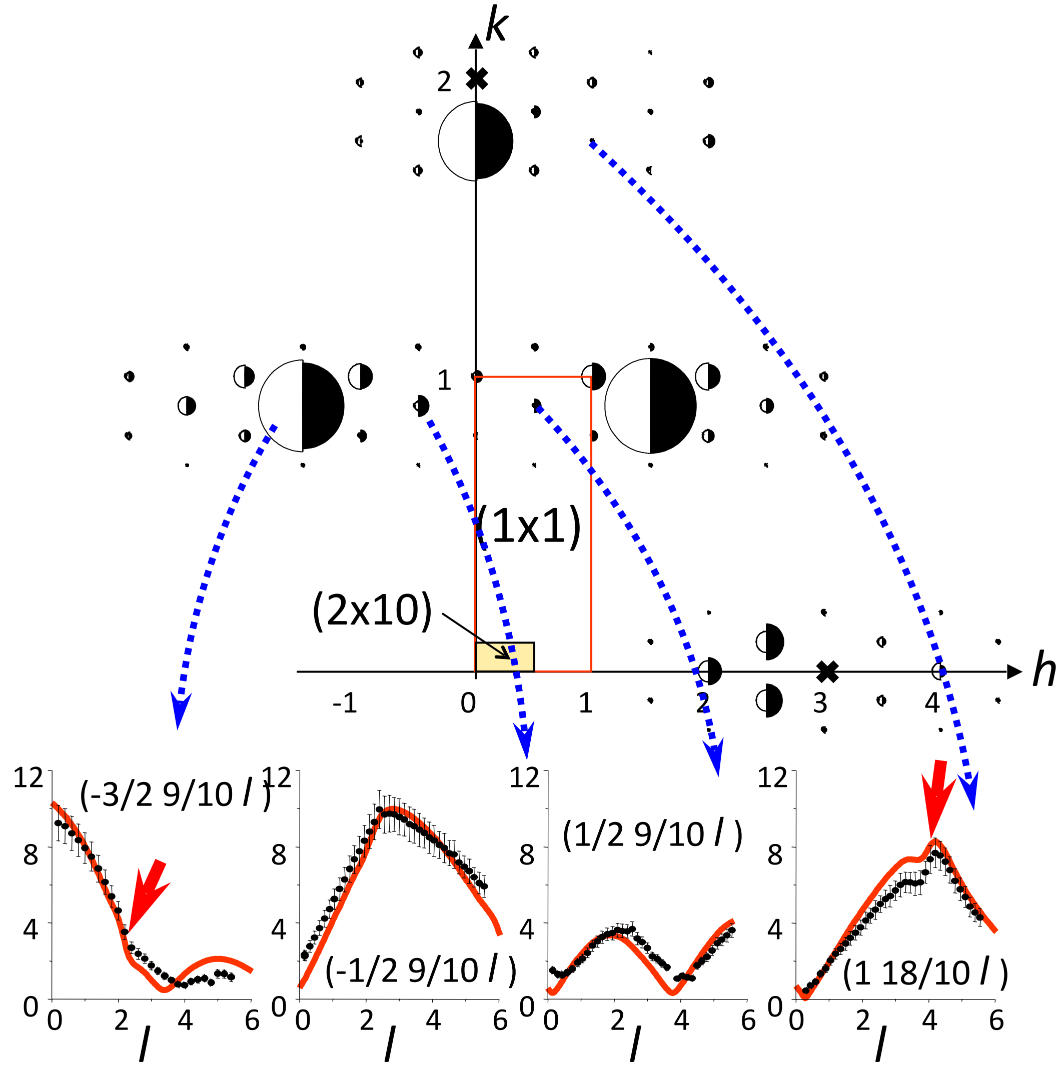


Simulation

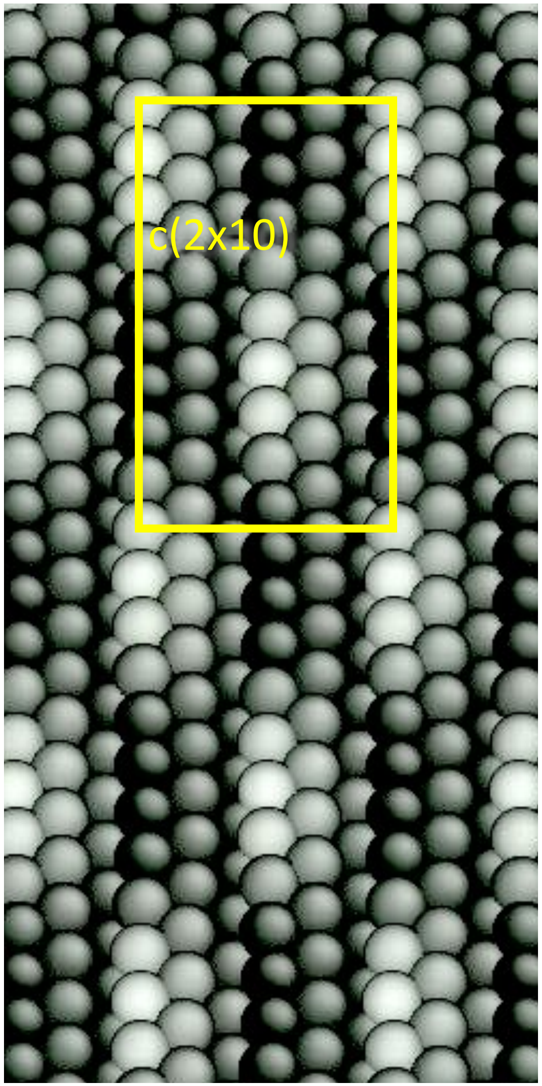
The structure is not relaxed !

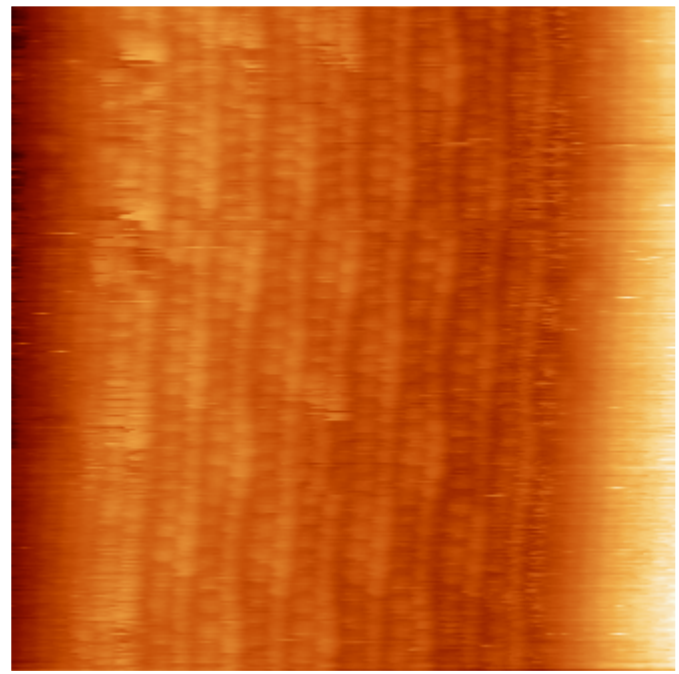
1 ML Ag/Cu(211) - GIXD et QMD





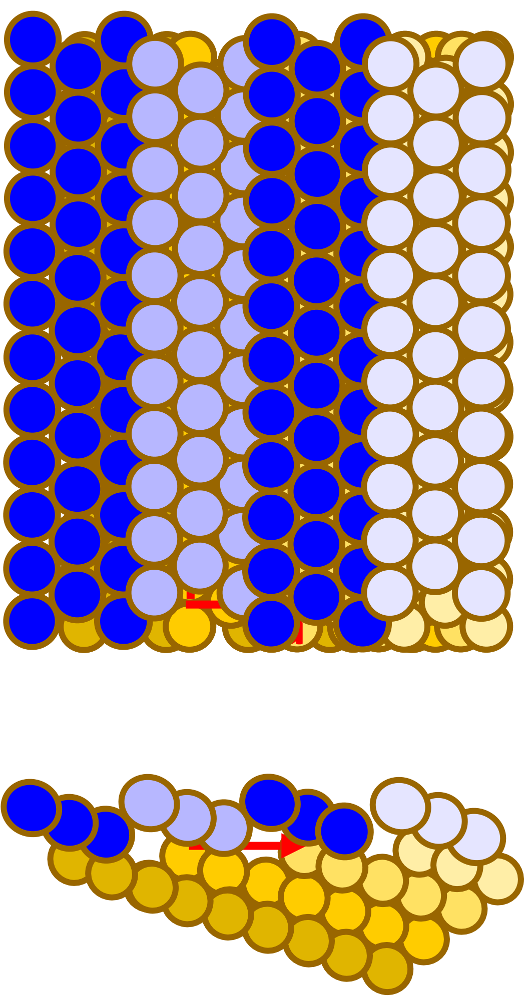
1 ML Ag/Cu(211) - GIXD & STM

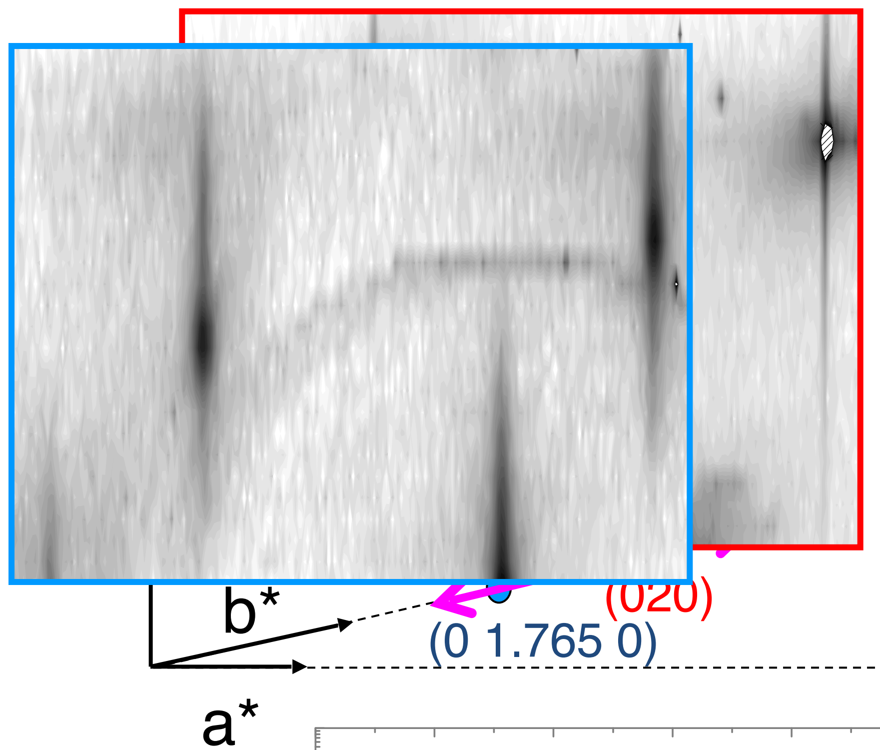


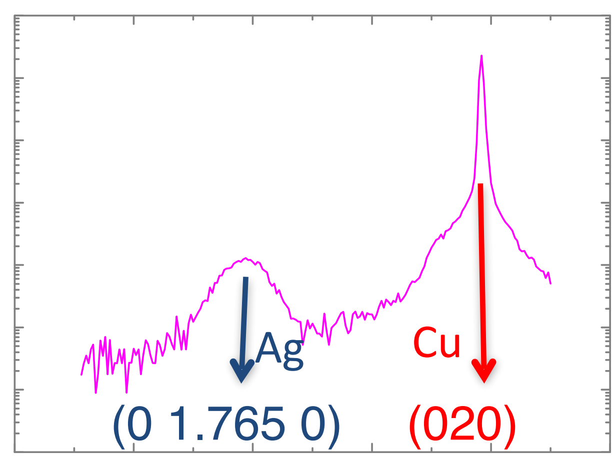


Y. Garreau, A. Coati, A. Zobelli, and J. Creuze
Phys. Rev. Lett. 91, 116101

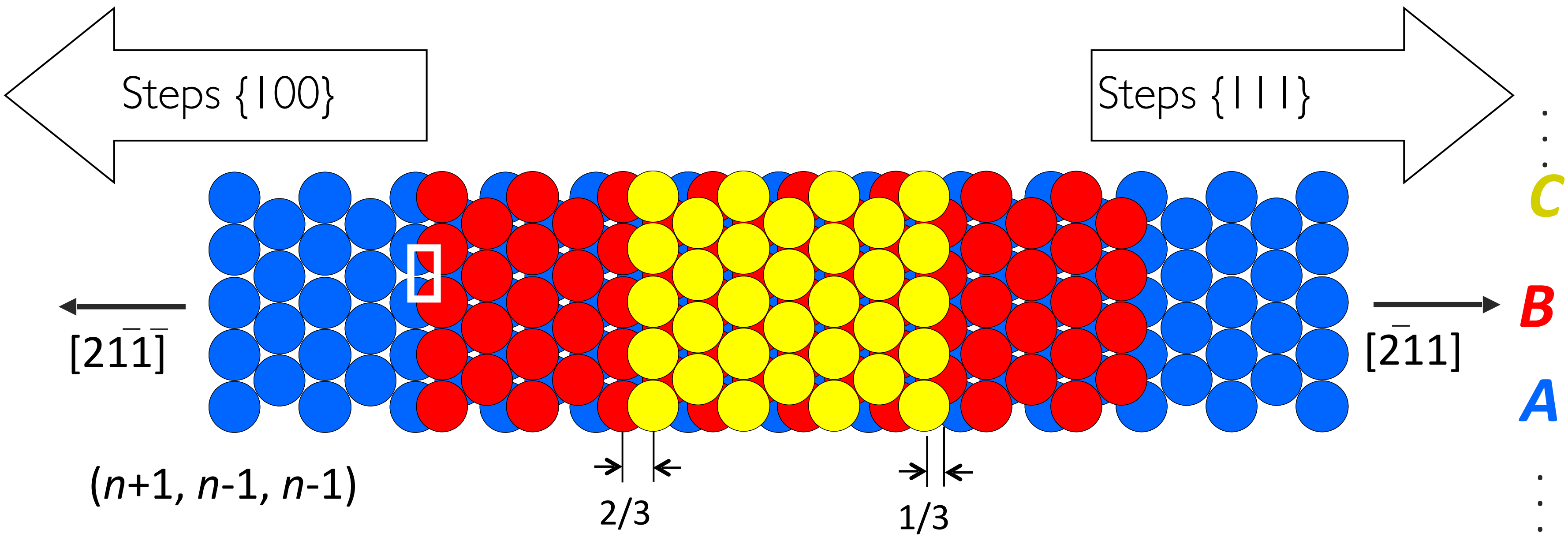
“Magic” Heteroepitaxy

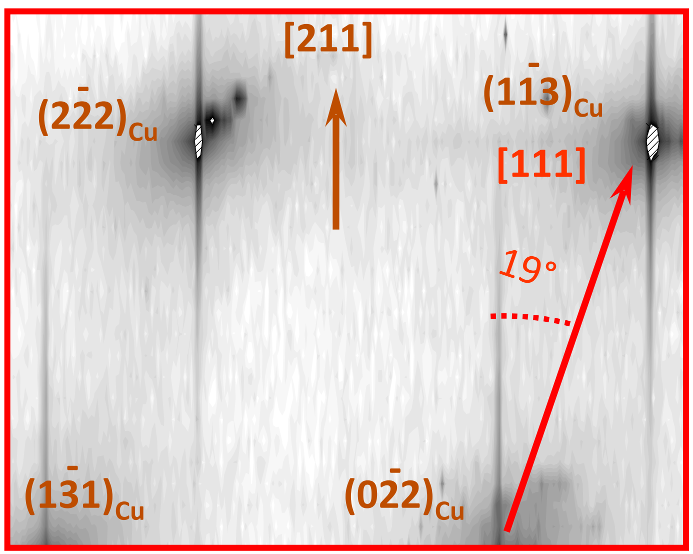


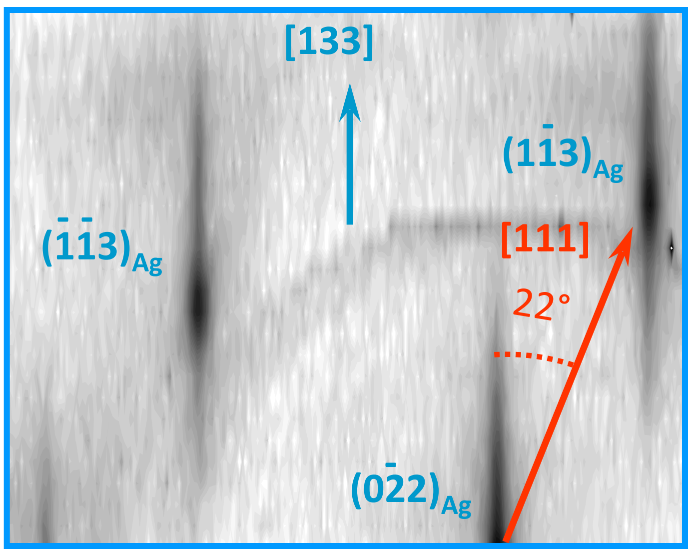




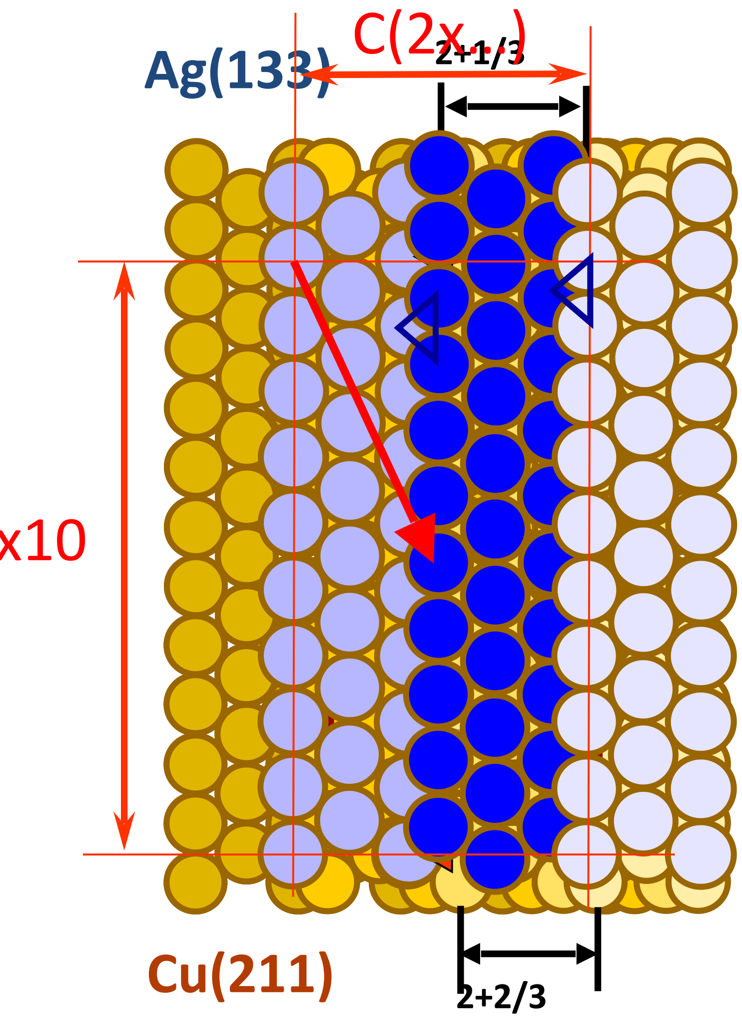
"MAGIC" HETEROEPITAXY

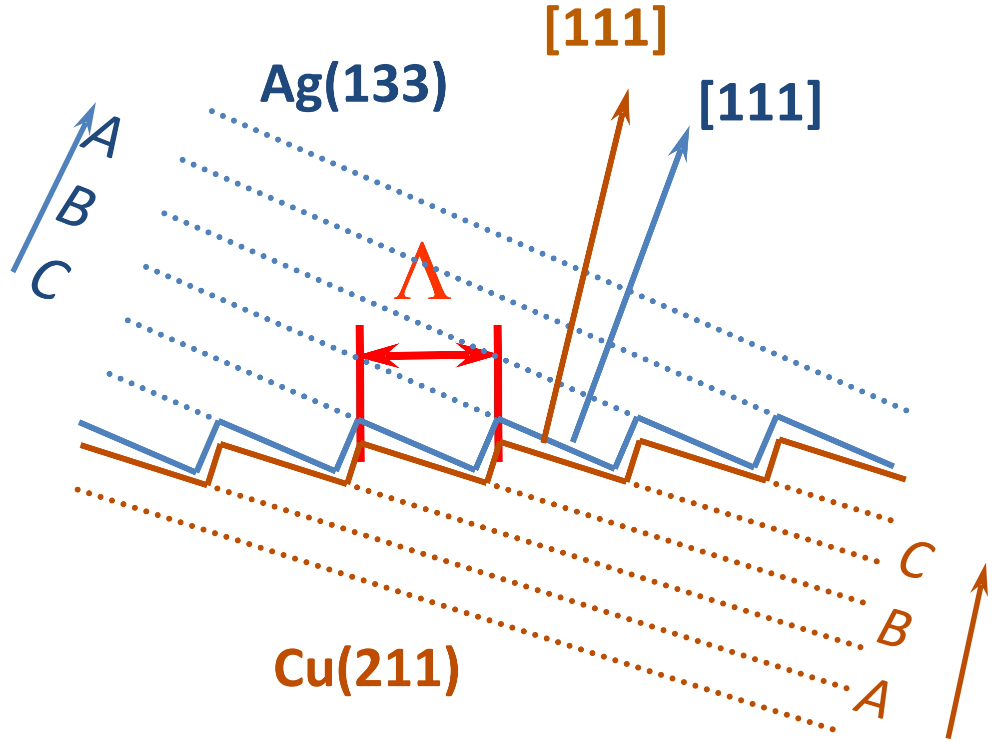






"MAGIC" HETEROEPITAXY

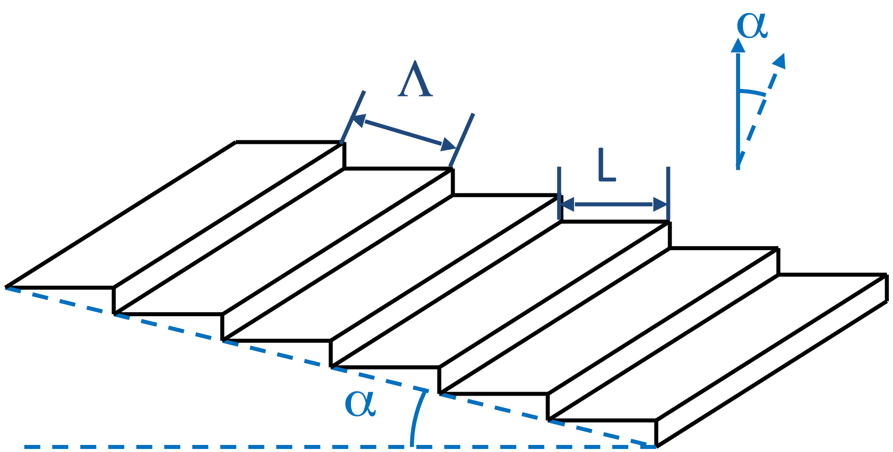




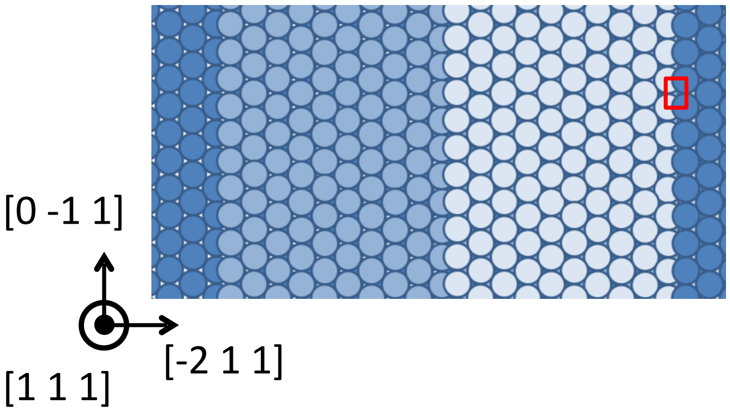
$$\frac{\Lambda_{Cu(211)}}{\Lambda_{Ag(133)}} = \frac{\left(2+\frac{2}{3}\right)}{\left(2+\frac{1}{3}\right)} = 1.14 \approx \frac{a_{Ag}}{a_{Cu}} \quad 0.4\%$$

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

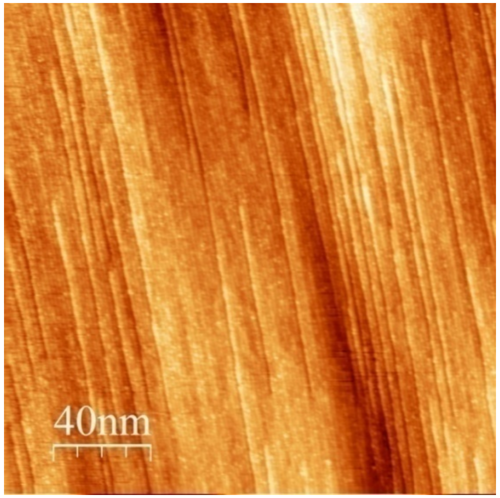
Ni(1 1 9 9)



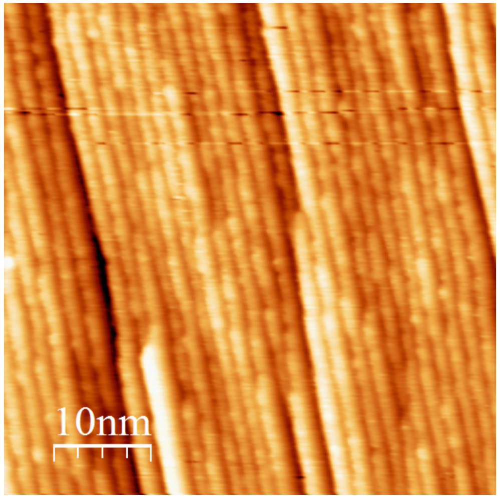
α = 5.57°
L = 2.1 nm



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



V_s=875mV, I_t=0.22nA



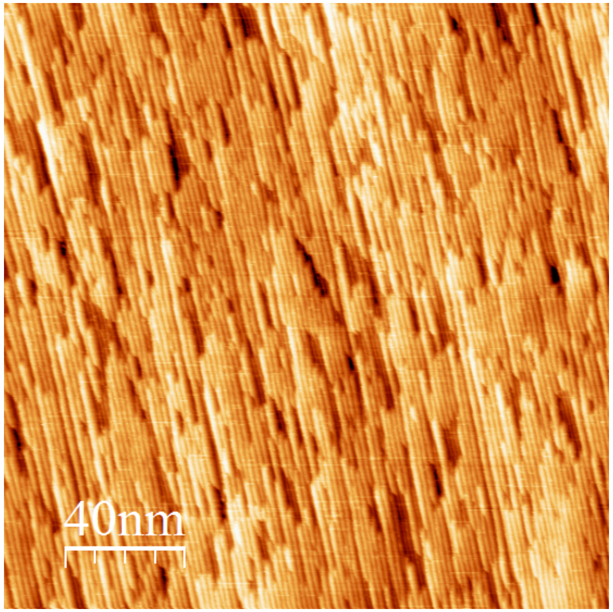
V_s=895mV, I_t=0.11nA

L = 2.09 ± 0.41 nm

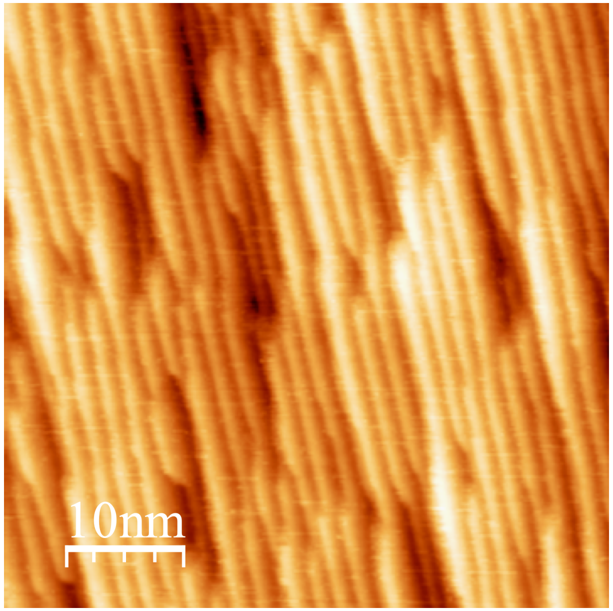
Bellec, A., et al., Physical Review B., 96(8): art.n° 085414. (2017)

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

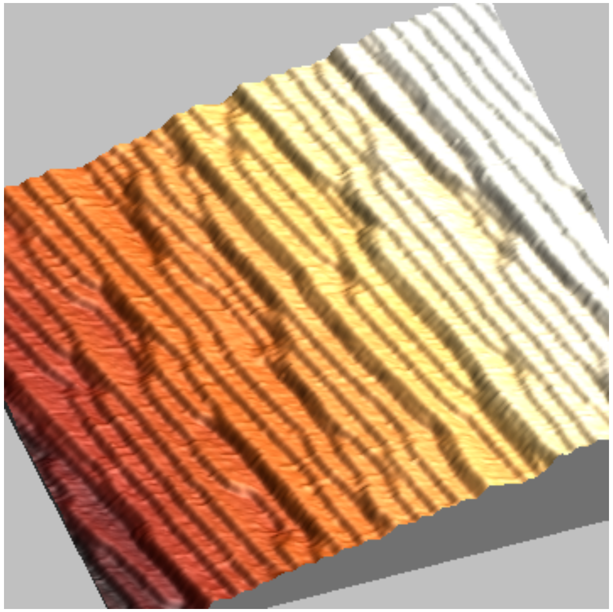
Recuit à 190°C



200x200nm² - V_S=0.85V - I_t=0.15nA

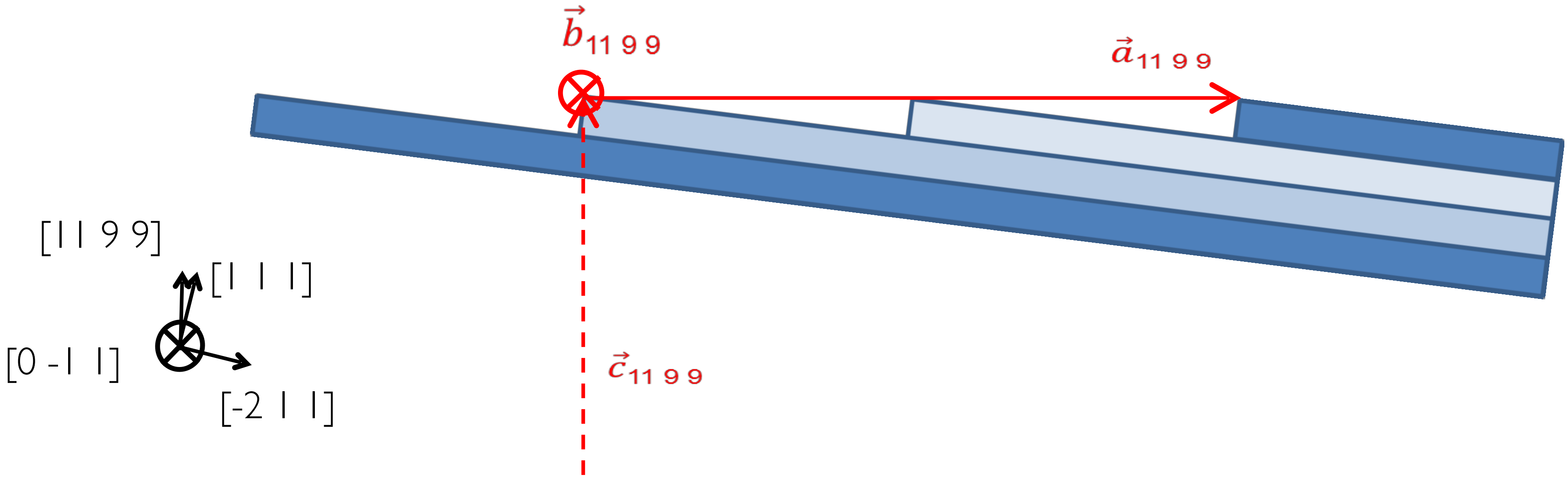


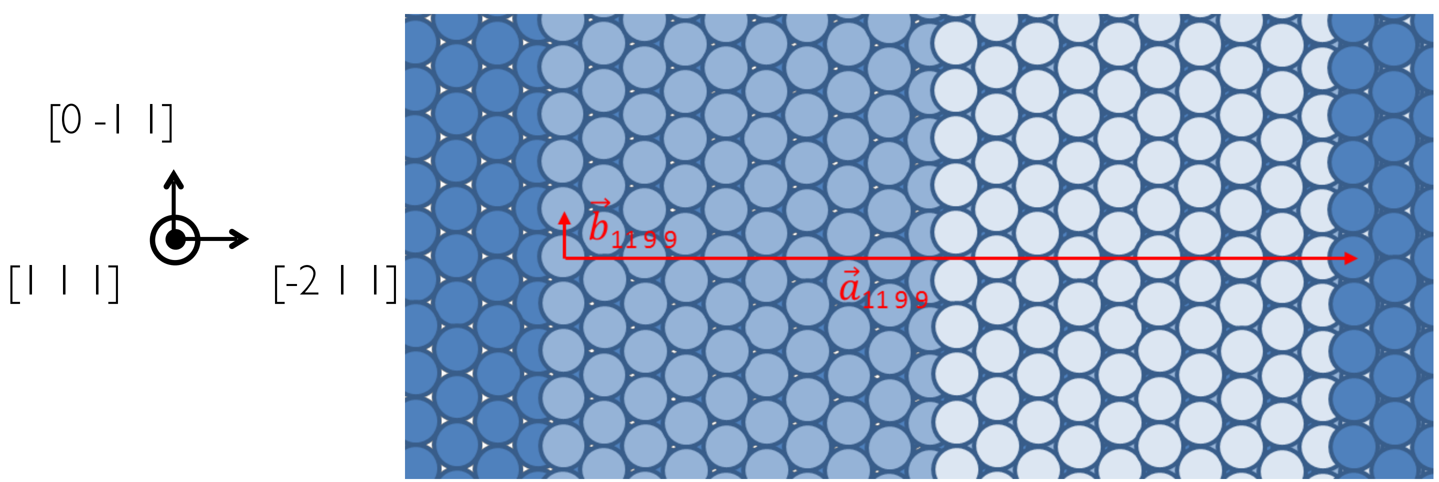
50x50nm² - V_S=0.85V - I_t=0.15nA



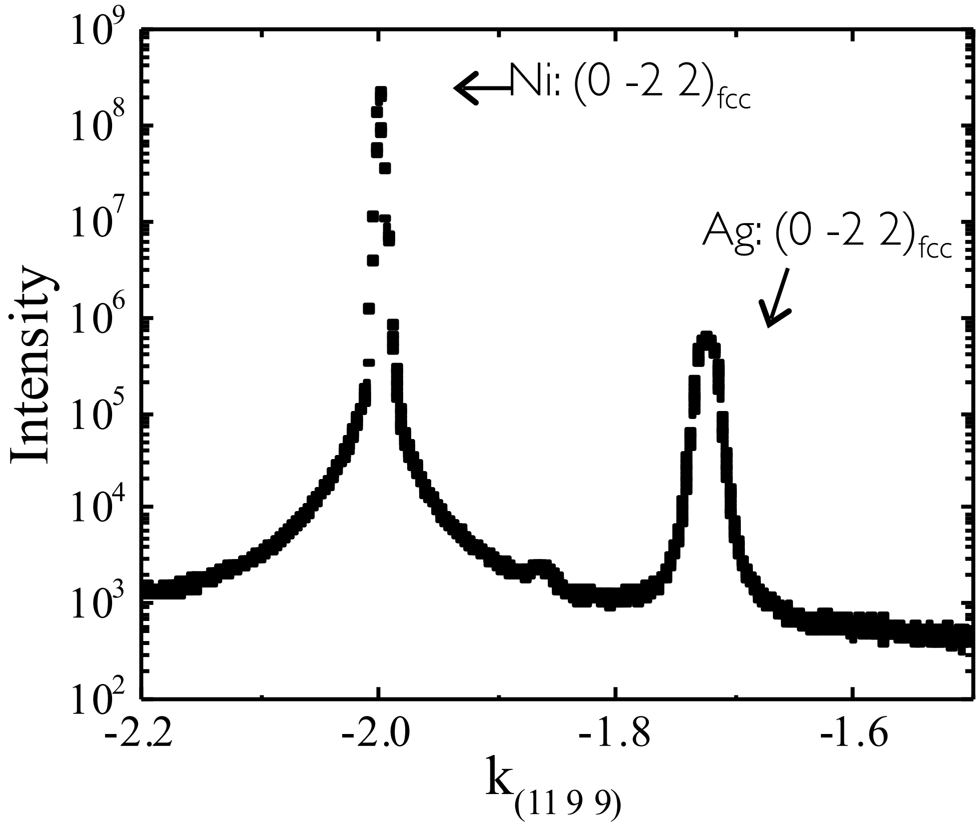
Largeur des terrasses mesurée : L =2.1± 0.3 nm

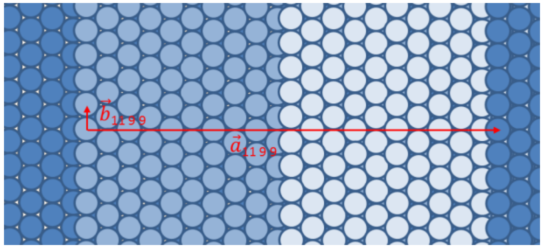
Ag/ Ni(11 9 9): Vicinal basis





ALONG STEP EDGES





Lattice mismatch:

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

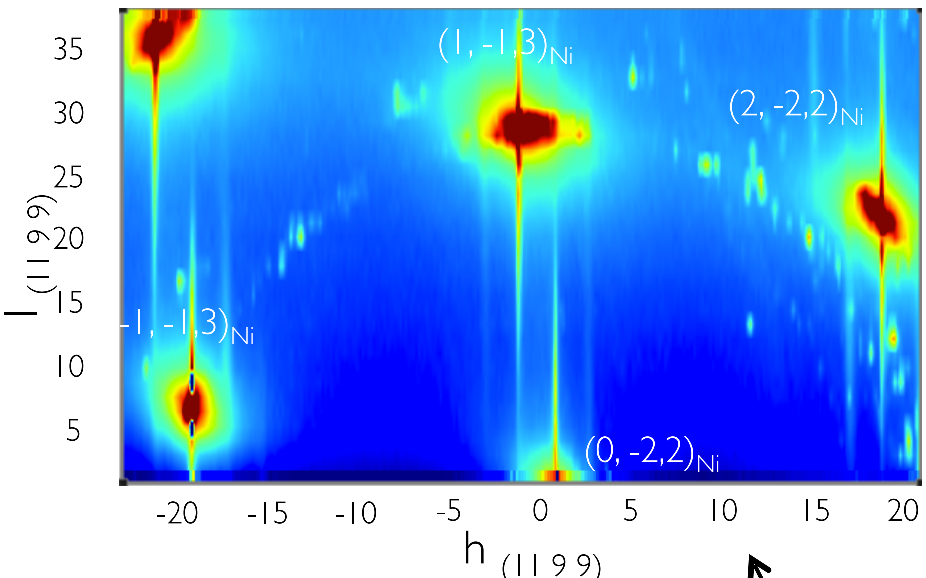
Measure:

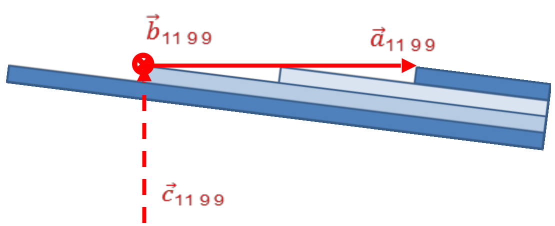
$$\left|\frac{a_{Ni}^{//} - a_{Ag}^{//}}{a_{Ni}^{//}}\right| = 0{,}161$$

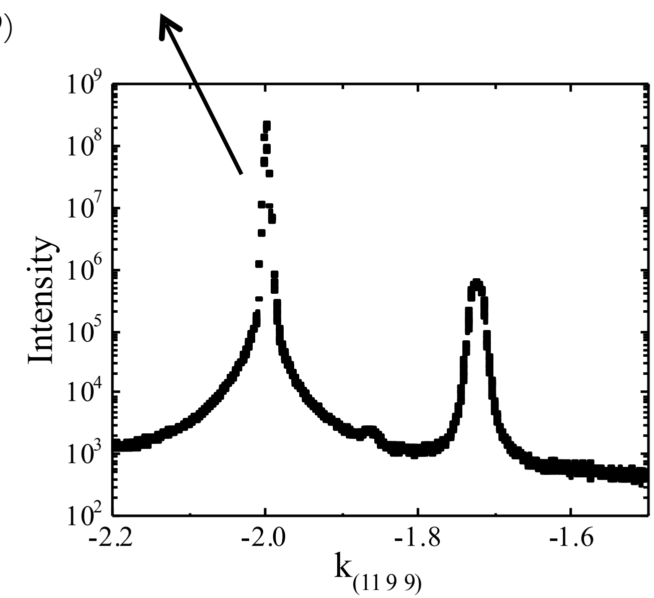
Ag is relaxed along the step edges

Reciprocal space mapping

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

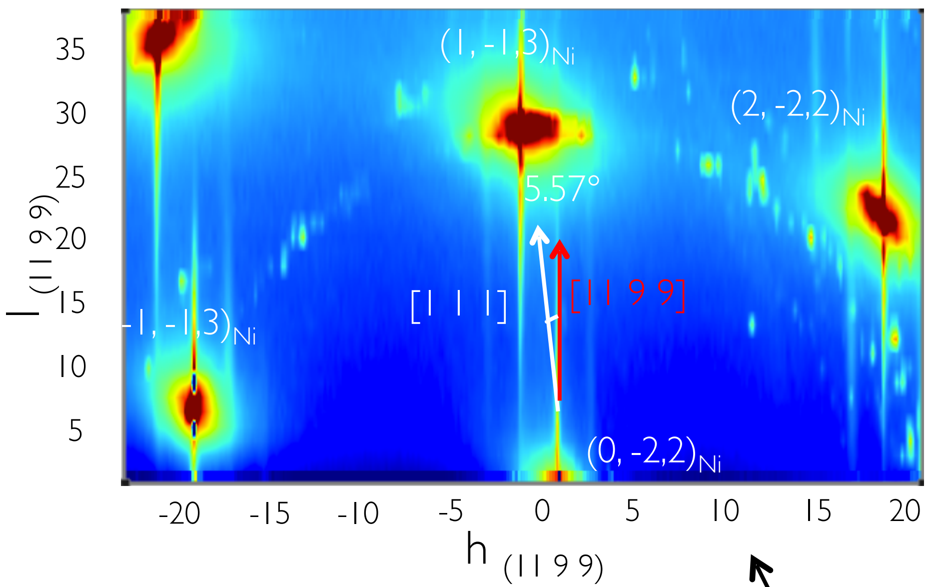


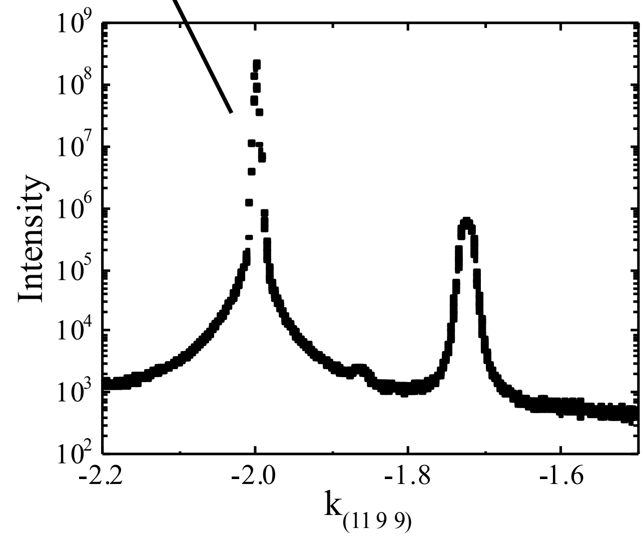




RECIPROCAL SPACE MAPPING

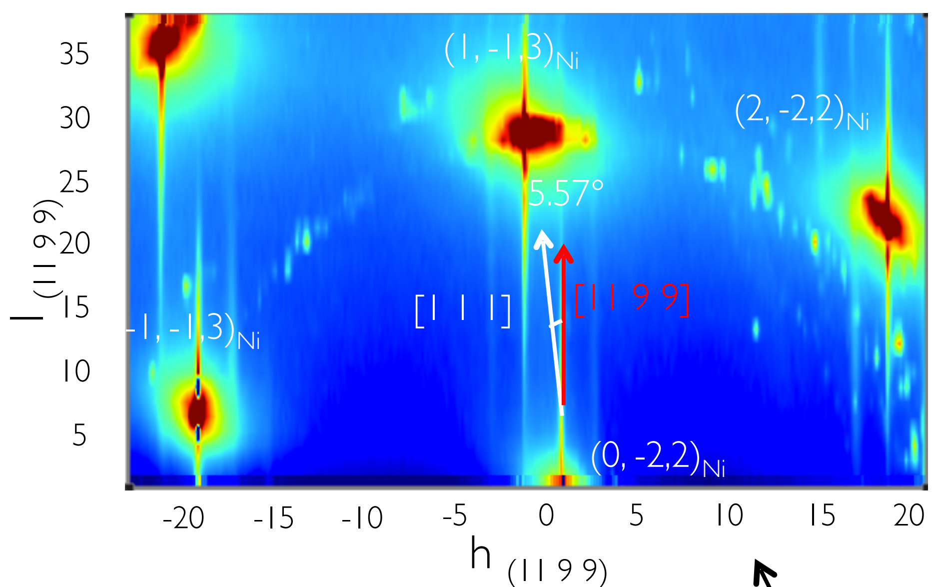
Ni map - $k_{11\,9\,9} = -2$



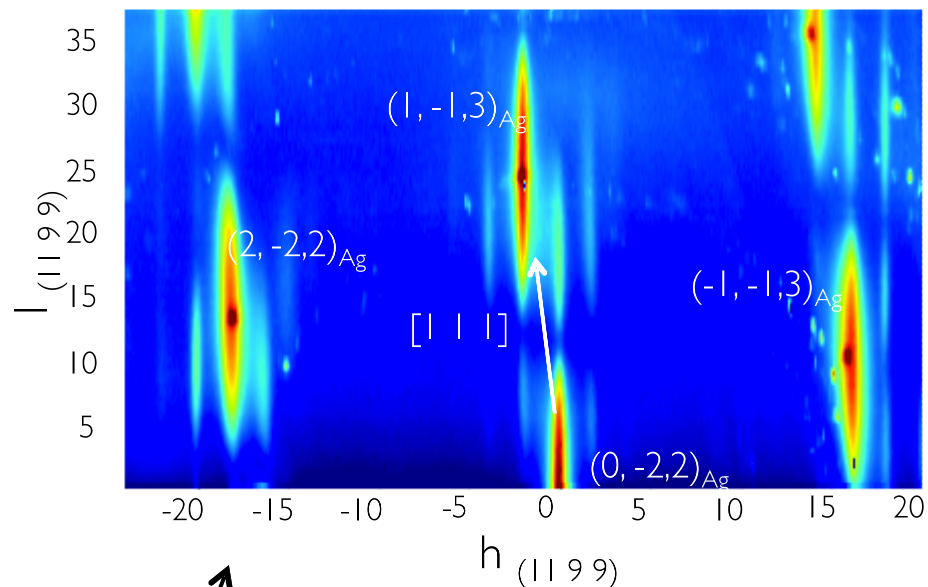


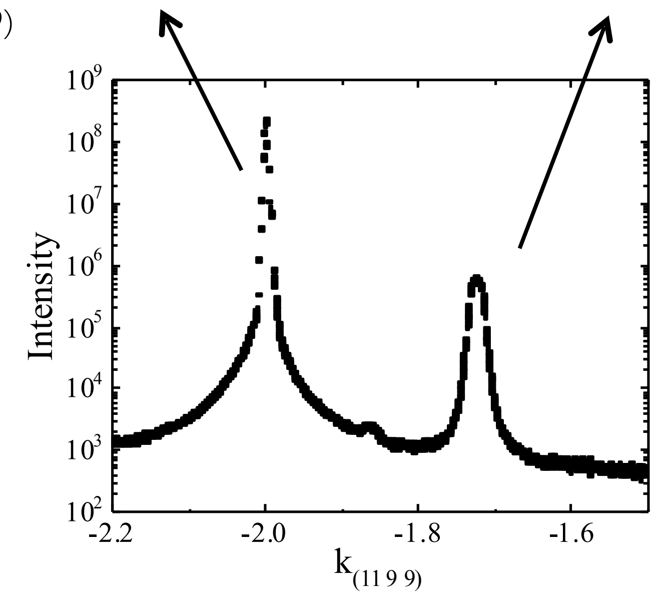
Reciprocal space mapping

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



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



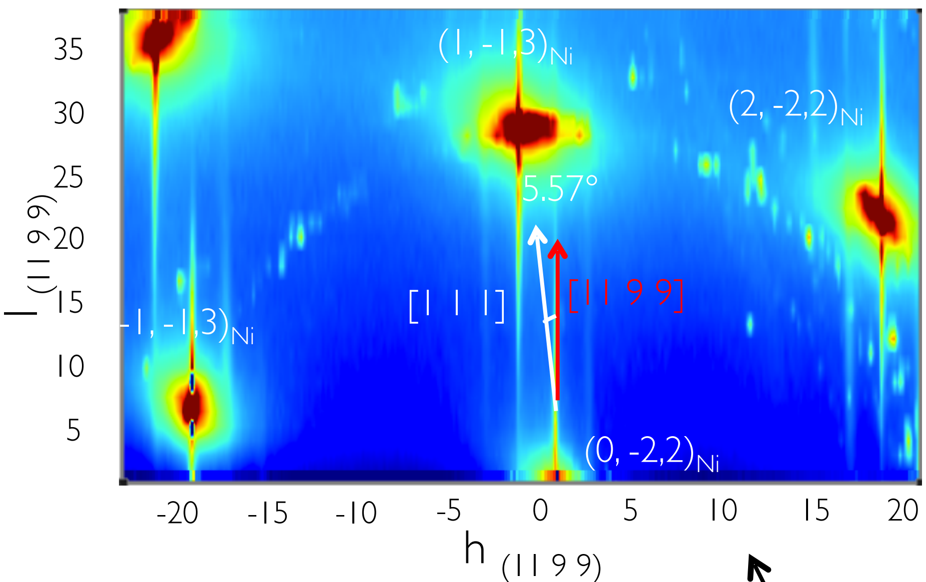


Ag layer presents a fcc structure

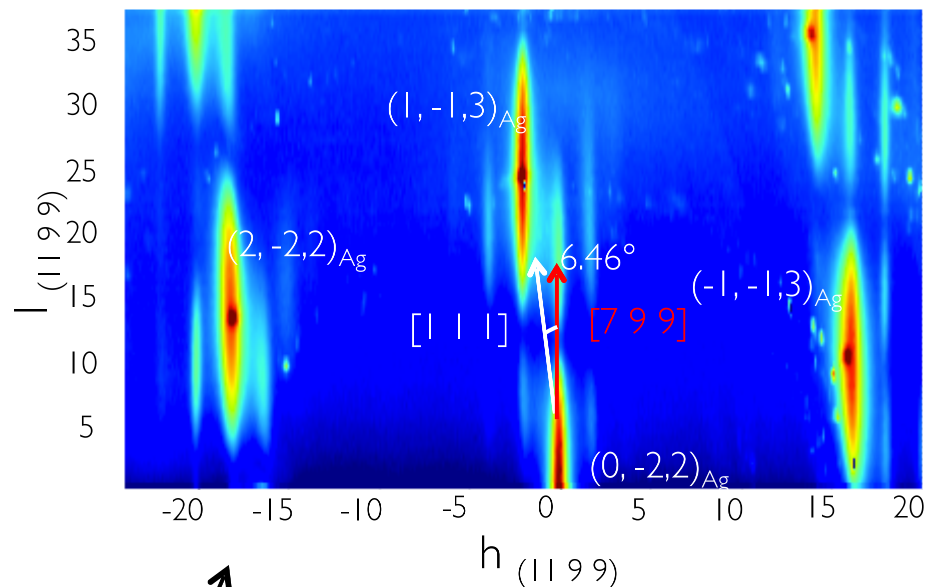
Inversion of the stacking between the Ag layer and the Ni substrate

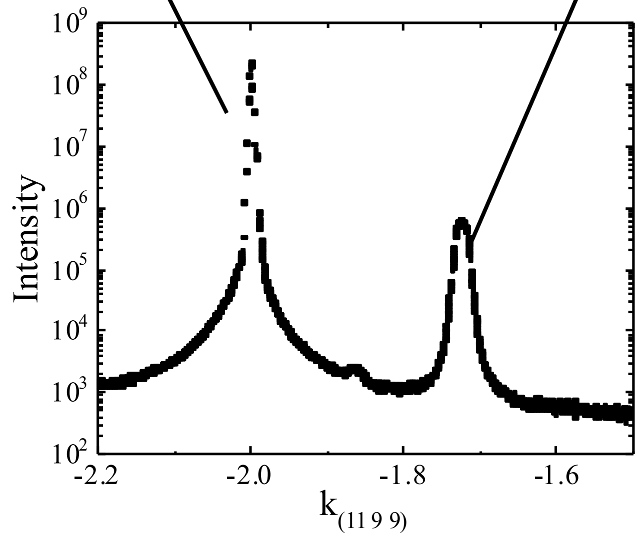
Reciprocal space mapping

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



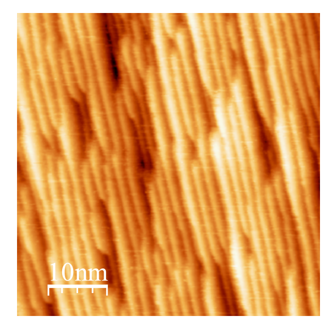
Ag map - $k_{11\,9\,9} = -1.73$





Ag: vicinal surface [7 9 9]

$\Lambda_{Ag(7\,9\,9)} = 20.95Å$



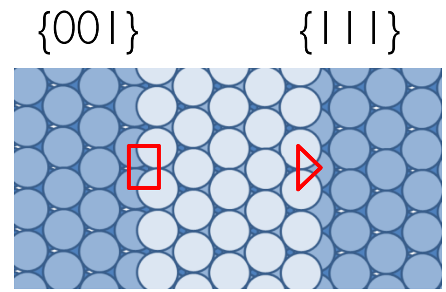
L = 20.7 ± 5.1 Å

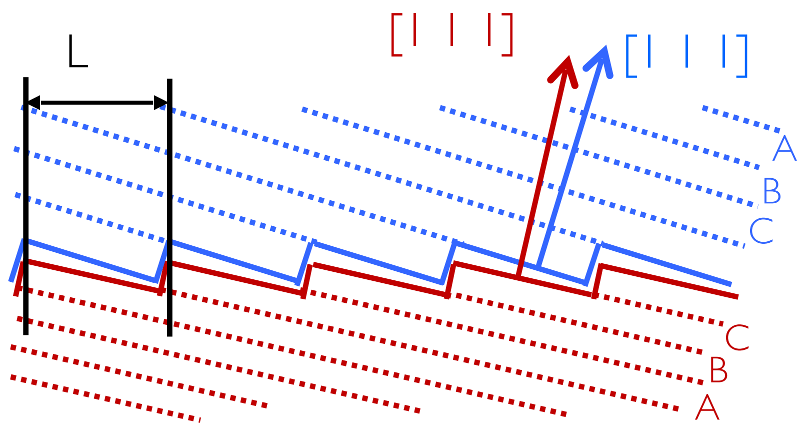
"MAGIC" HETEROEPITAXY

Formation of Ag homogeneous thin film

<u>Ni (11 9 9)</u>: terraces (111)
steps (001)

<u>Ag (7 9 9)</u>: terraces (111)
steps (111)



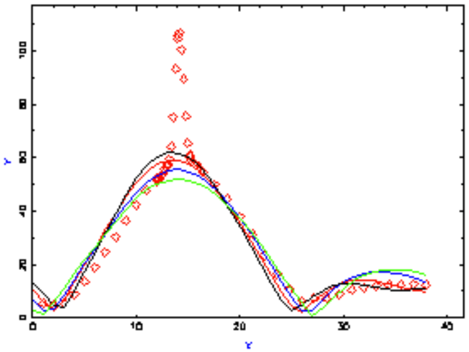


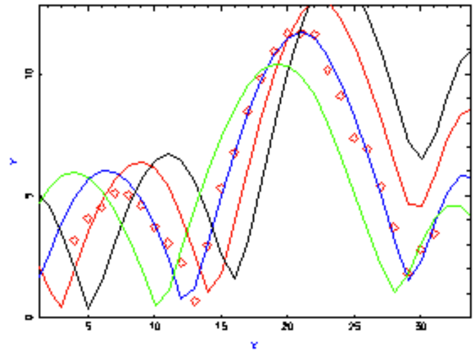
$$\Lambda_{Ag(7\,9\,9)} = 20.95\text{Å}$$

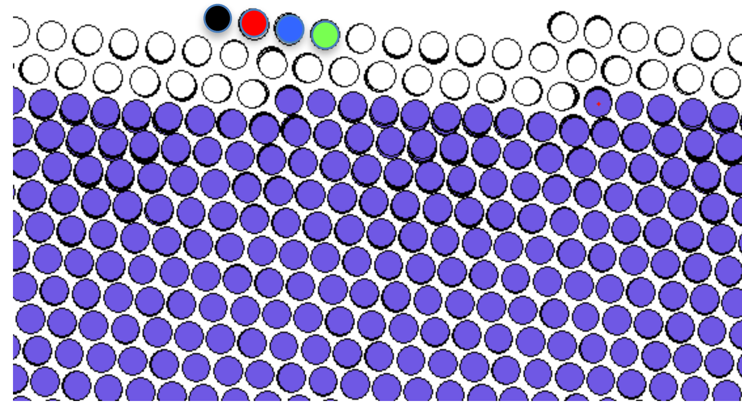
$$\Lambda_{Ni(11\,9\,9)} = 20.96\text{Å}$$

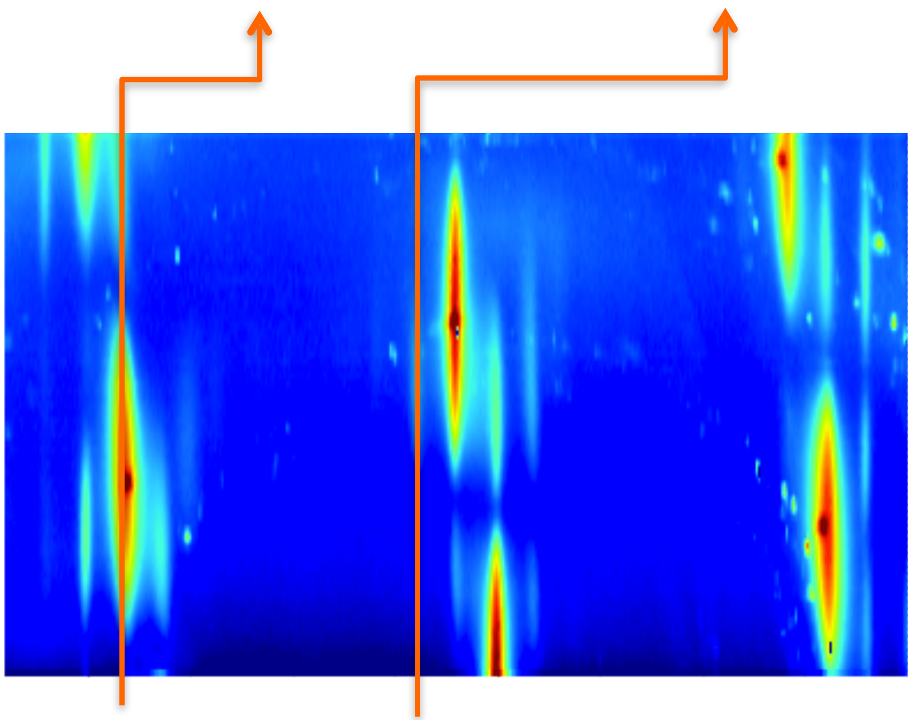
Step period governs the growth of the Ag layer

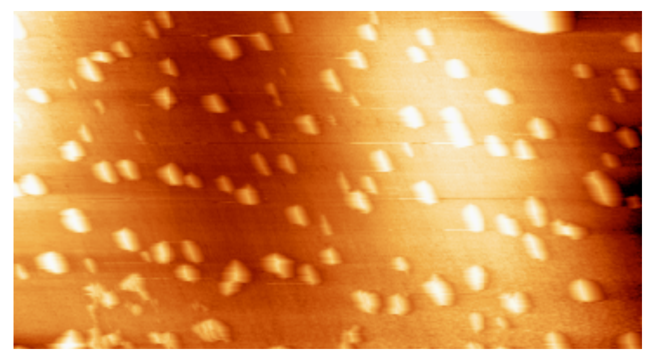
Ag Islands





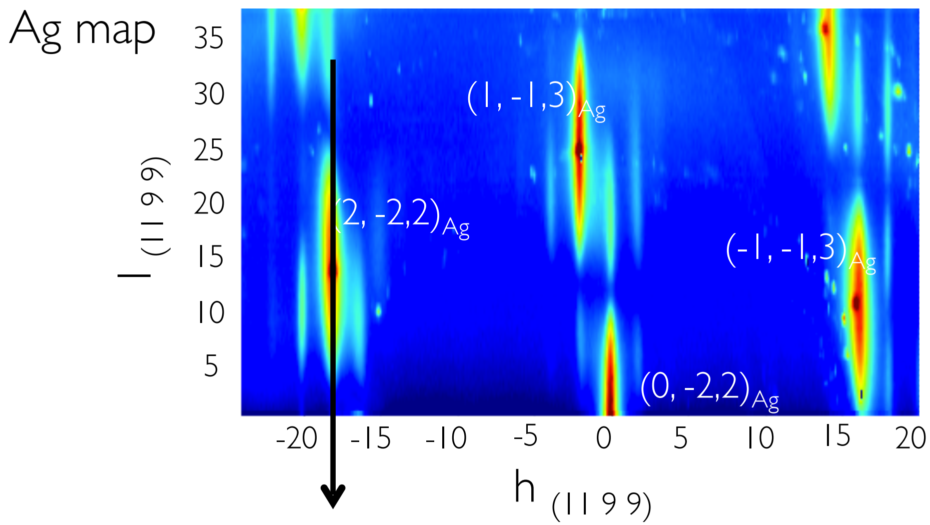


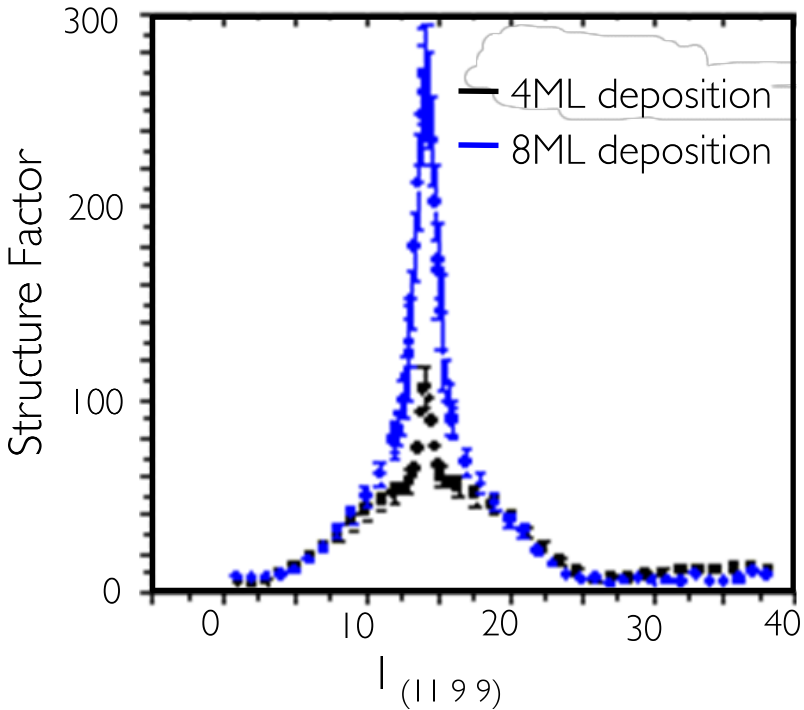


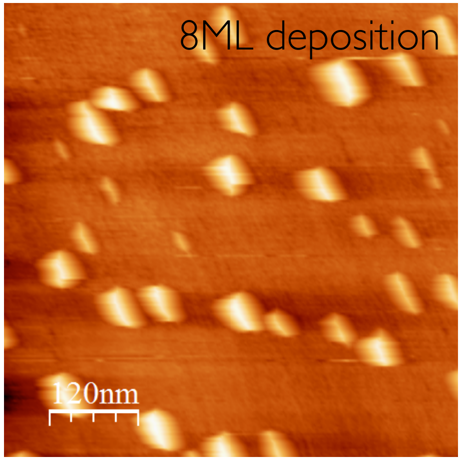


1500 x 750 nm2

Ag Islands







600x600nm^2, 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

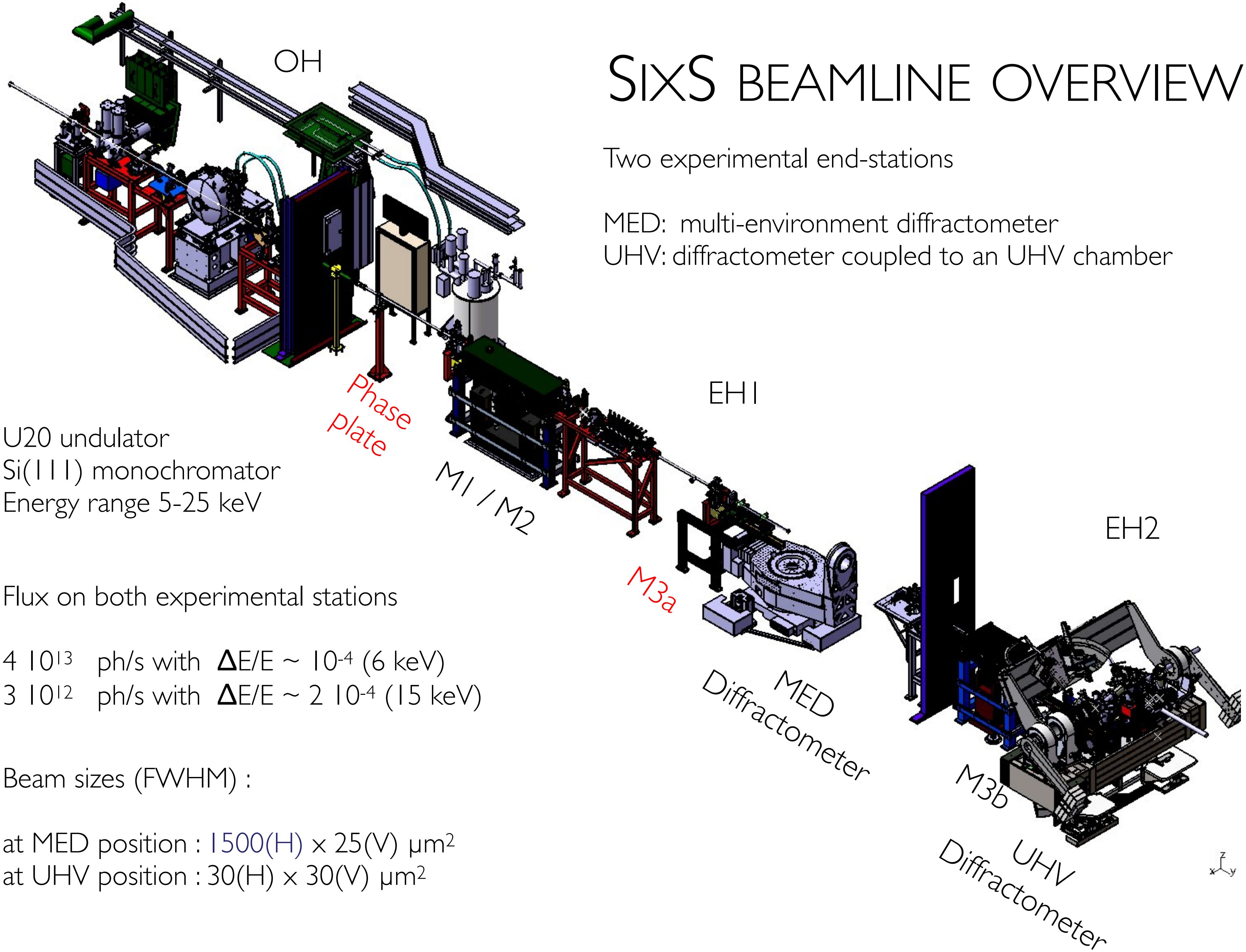
Solid surfaces and interfaces structures
Nanostructures
Self-organised surfaces
Original in-situ growths
Surface magnetic X-ray diffraction
Surfaces in catalytic environment
Solid-liquid electrochemical interfaces
Buried soft interfaces
Liquid-liquid interfaces
……..

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



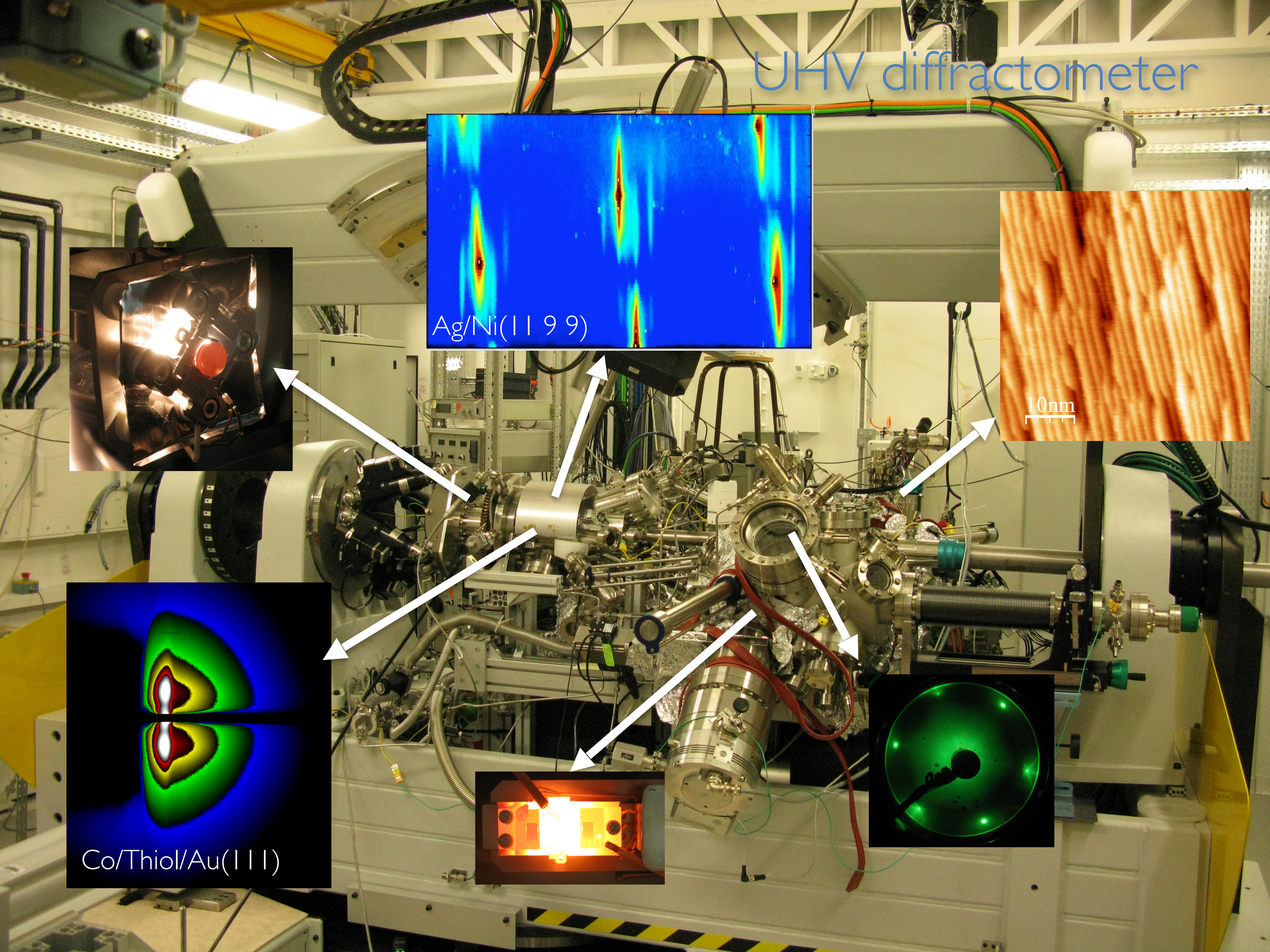
U20 undulator
Si(111) monochromator
Energy range 5-25 keV

Flux on both experimental stations

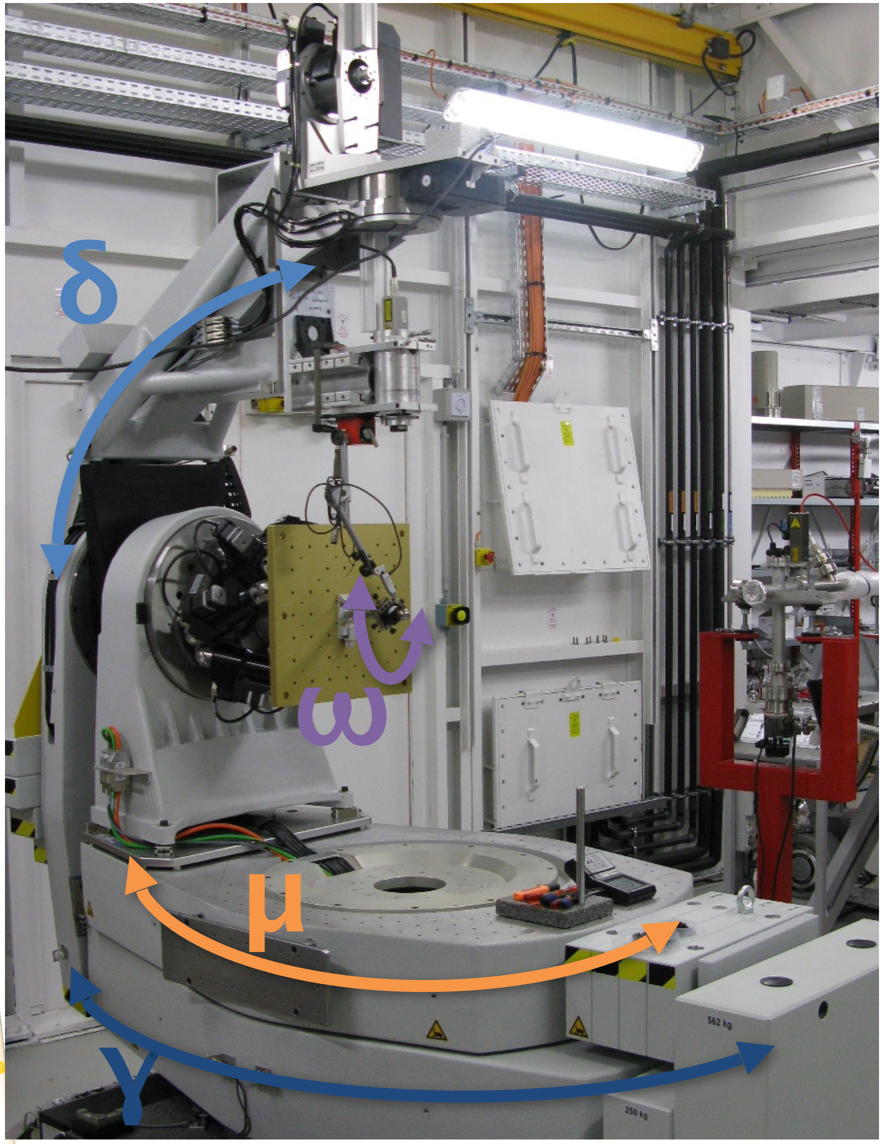
$4\ 10^{13}$ ph/s with $\Delta E/E \sim 10^{-4}$ (6 keV)
$3\ 10^{12}$ ph/s with $\Delta E/E \sim 2\ 10^{-4}$ (15 keV)

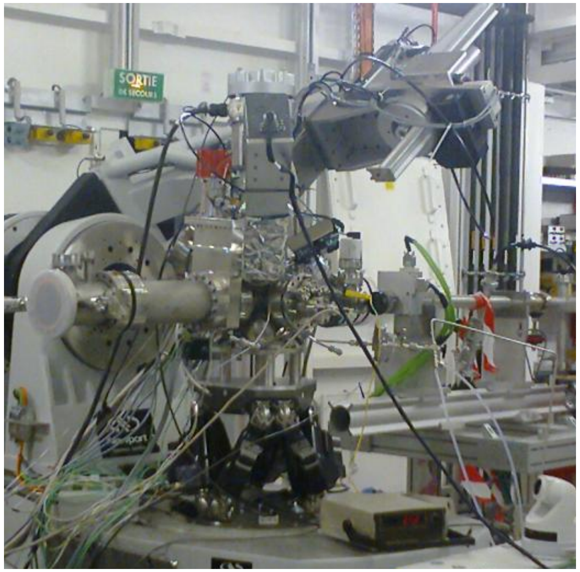
Beam sizes (FWHM) :

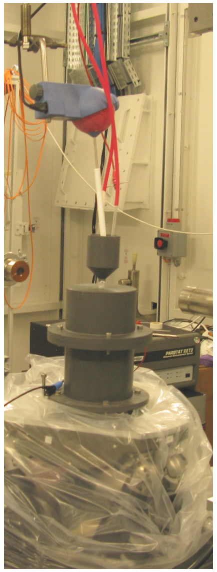
at MED position : 1500(H) x 25(V) μm^2
at UHV position : 30(H) x 30(V) μm^2

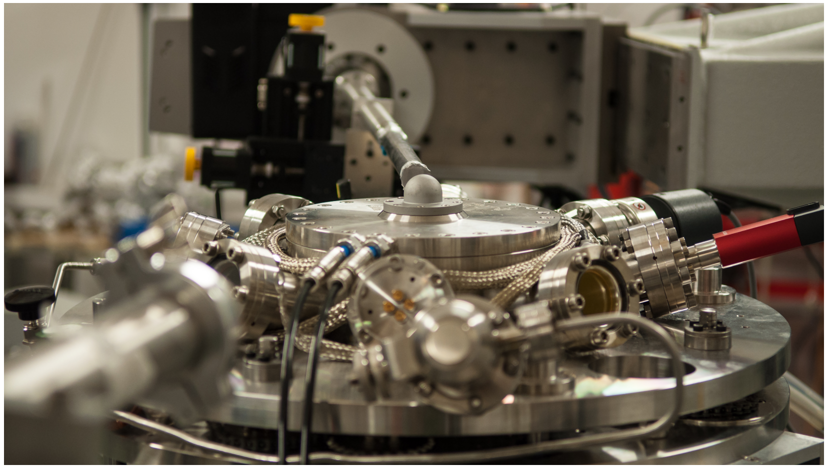

UHV diffractometer
Ag/Ni(11 9 9)
10nm
Co/Thiol/Au(111)

MED end-station









Continuous scan mode

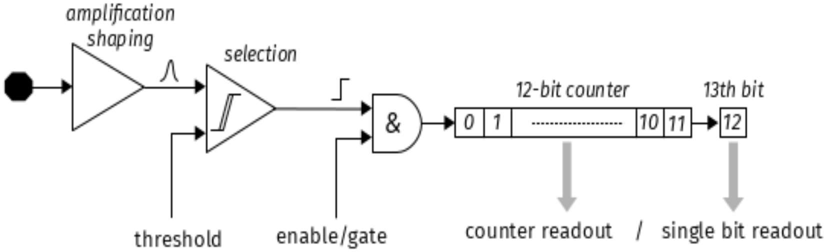
- Time saved
- Full encoder resolution exploitation
- HKL trajectories > non-linear grouped motors
- Trajectories (XPS controller – DC motor with PID)

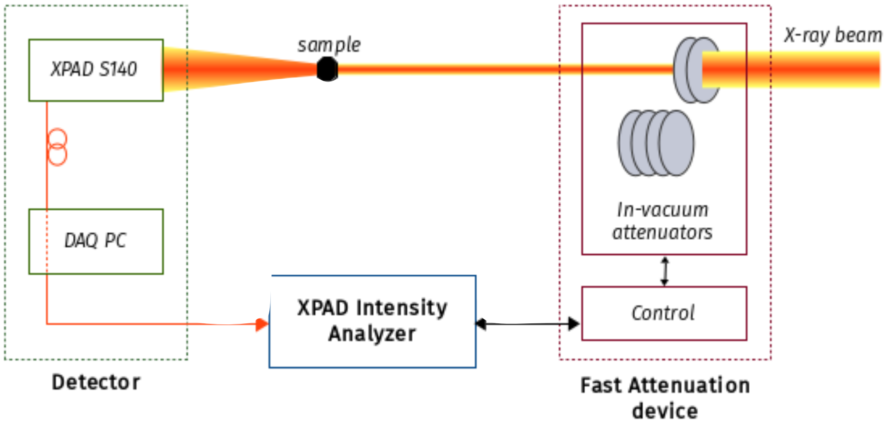
- Need to integrate properly 2D detectors
- Generalization of the trajectories on other motors

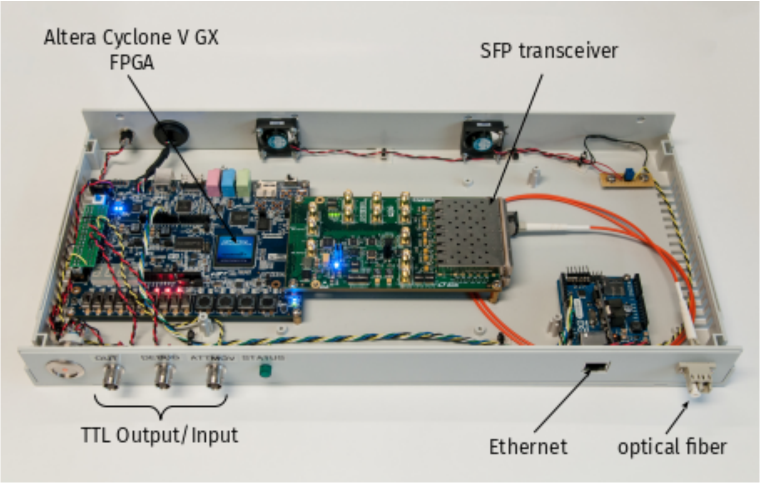
>>> Flyscan <<<

2D detector (XPAD-S140)

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





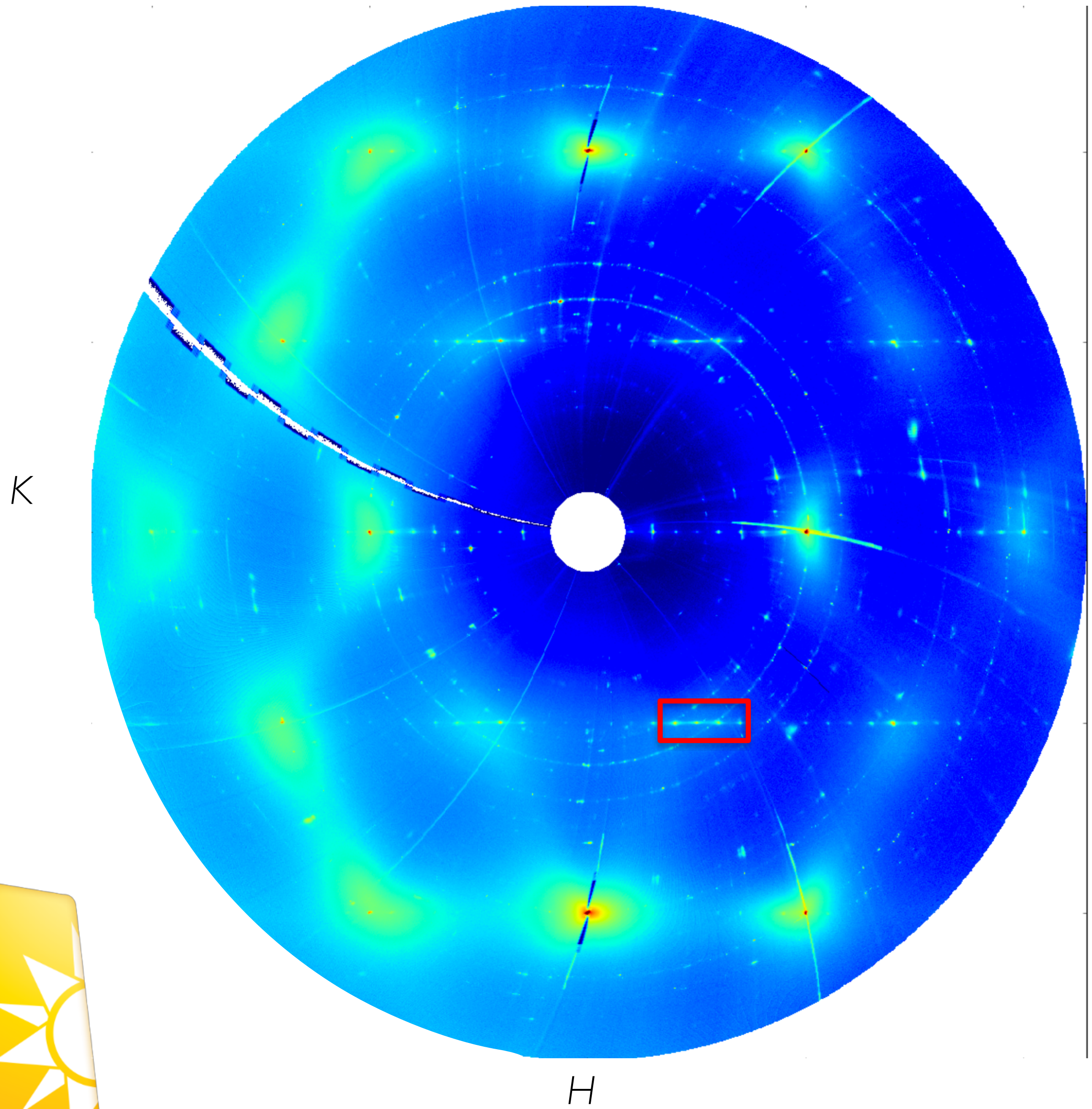


Reciprocal Space Visualisation - BINOCULARS

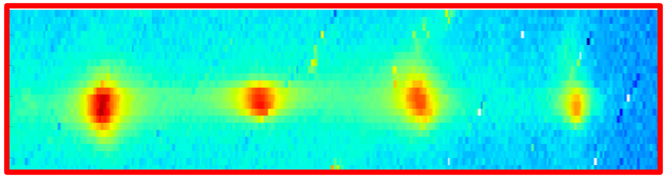
- Installed on the SOLEIL high performance cluster SUMO
  - Data
    - Reduction
    - Representation
    - Projection
  - Build a reciprocal space volume in
    - Q-space
    - (hkl) space
    - Angles space (soon)
  - Intensity integration
  - Python

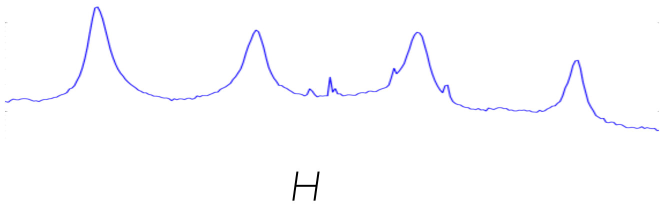
Roobol, S., Onderwaater, W., Drnec, J., Felici, R. & Frenken, J. , J. Appl. Cryst. 48, 1324-1329 (2015)

Pentacene/Cu(322)



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





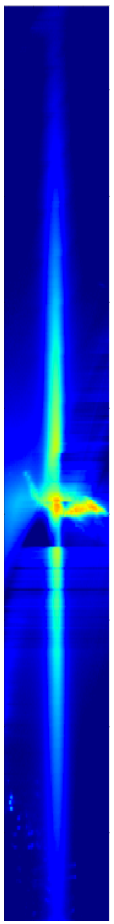
Surface structure
Surface periodicity

Pentacene/Cu(322)

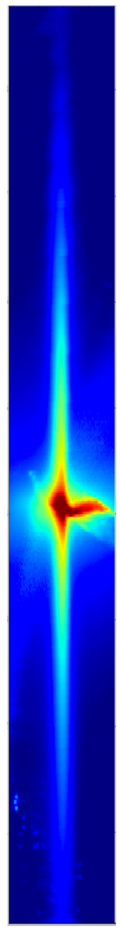
CTR in flyscan

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

L



H



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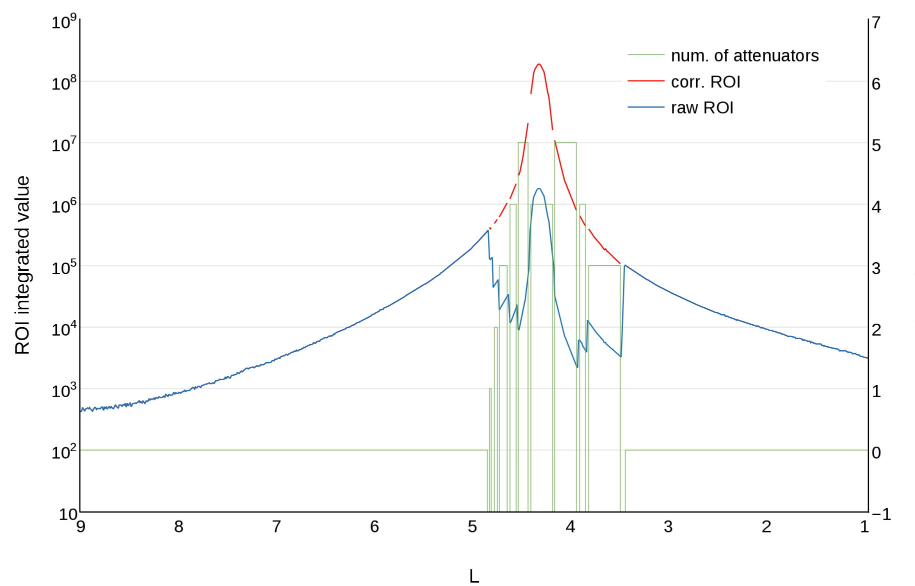
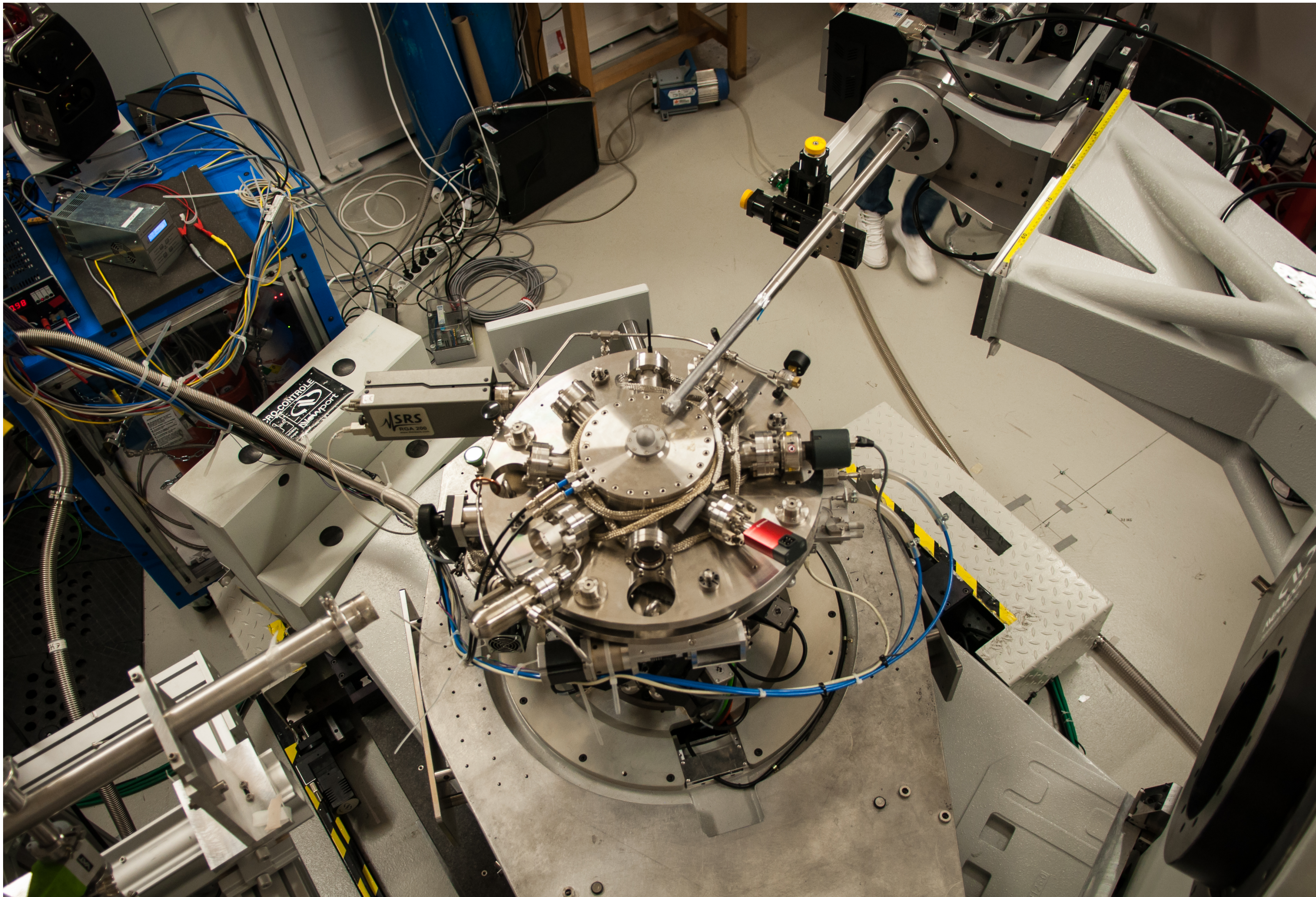


SOLEIL SYNCHROTRON

NanoSciences ILE-DE-FRANCE

XCAT



SOLEIL SYNCHROTRON

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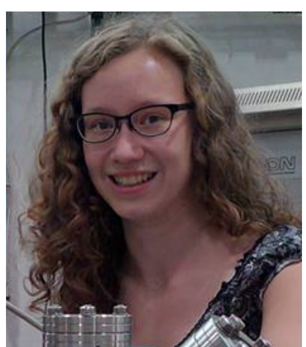
Alina VLAD

Michèle SAUVAGE

SixS

Benjamin VOISIN

Andrea RESTA



Cynthia FOURMENTAL

Corentin CHATELIER

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.