Combinaison quantitative GISAXS et STM: un outil pour sonder les interfaces enterrées.

Exemple du Co/Au(111).

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Laboratoire Louis Néel (CNRS), Grenoble

!

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DRFMC/SP2M/IRS (CEA), Grenoble

J.-P. Deville, A. Barbier, F. Scheurer, J. Mané-Mané
IPCMS (CNRS/ULP/ECPM), Strasbourg

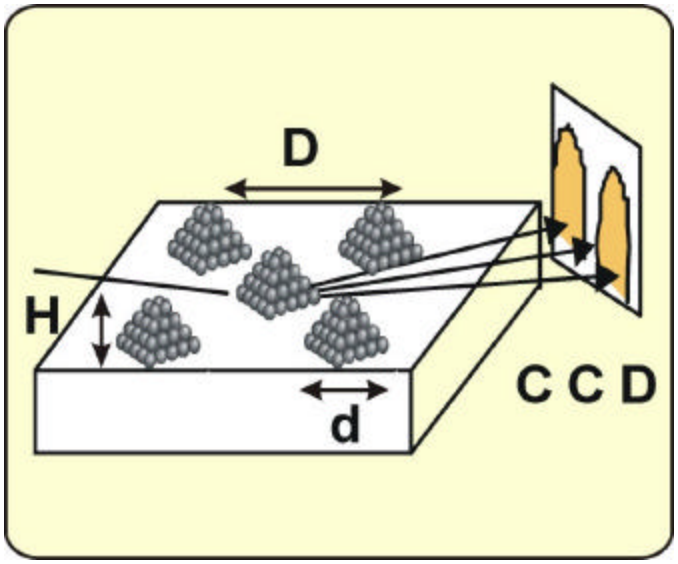
V. Repain, G. Baudot, S. Rousset
GPS-Jussieu, Paris

GISAXS: Grazing Incidence Small Angle X-ray Scattering

Objects >> atoms

Surface sensitive

PRINCIPLE



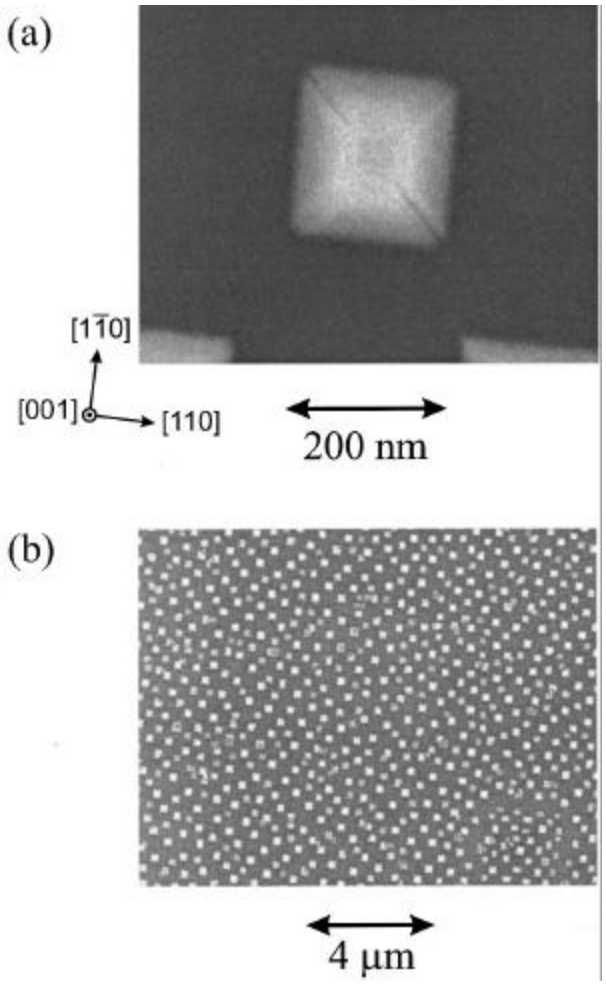
- In-plane / out-of-plane diffusion
- Probes size (H,d), shape, correlations

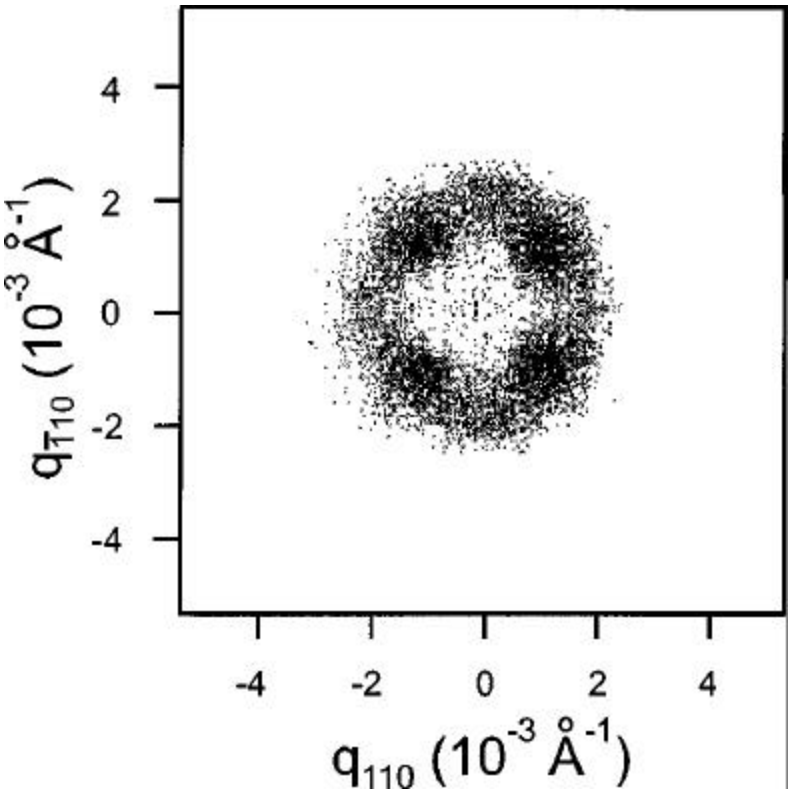
TECHNICAL ASPECTS

- **ID32 beamline at ESRF**
- **In-situ under UHV:**
  - **real time**
  - **background substraction**
- **No window before sample : low background**

Ex situ GISAXS on self-assembled dots : lateral information

$Si_{1-x}Ge_x$ islands



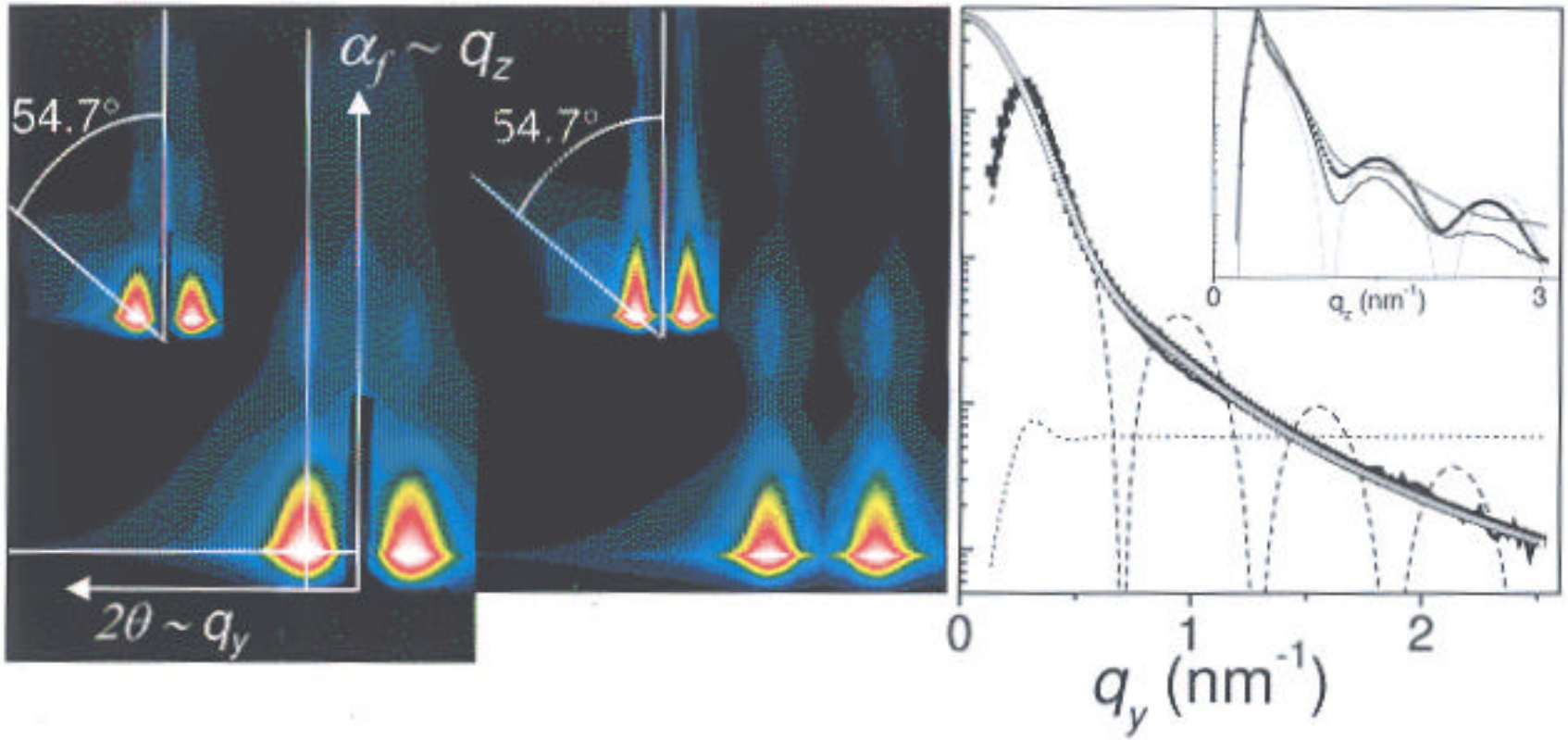


Information on dots shape and lateral order.

M. Schmidbauer et al., PRB58, 10523 (1998)

Ex situ GISAXS on self-assembled dots

Pd/MgO(001) islands



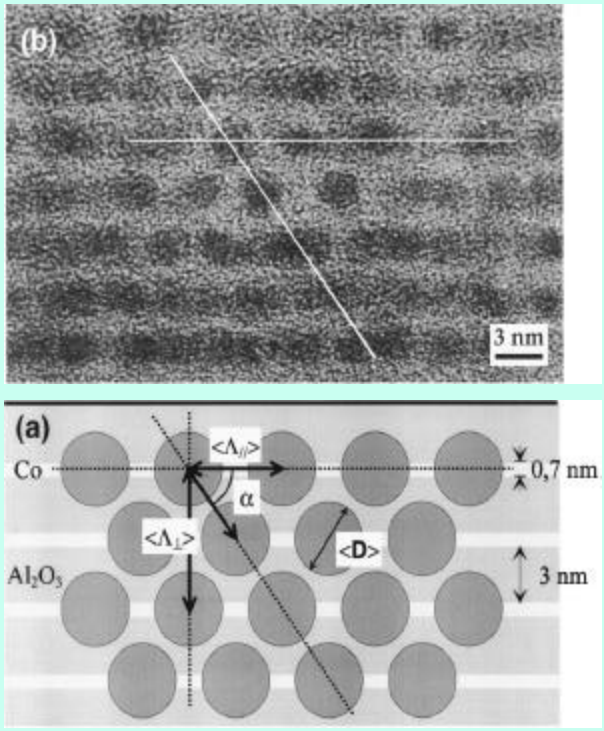
G. Renaud et al., unpublished

Co/Al_2O_3 granular system (sputtering)

$(Co: 0.7\ nm/Al_2O_3: 3\ nm)_{14}$

REAL SPACE

TEM cross-section (Sequential sputtering)



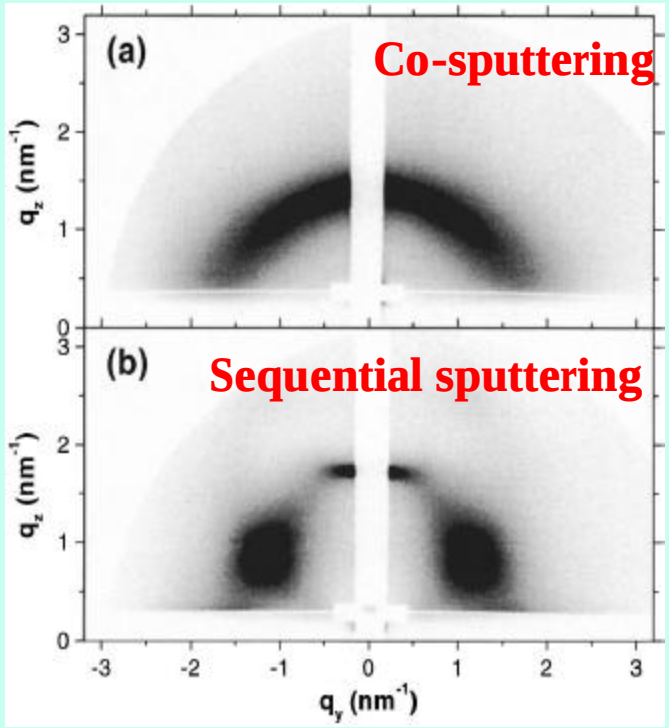
➢ FCC vertical stacking (not epitaxial !)

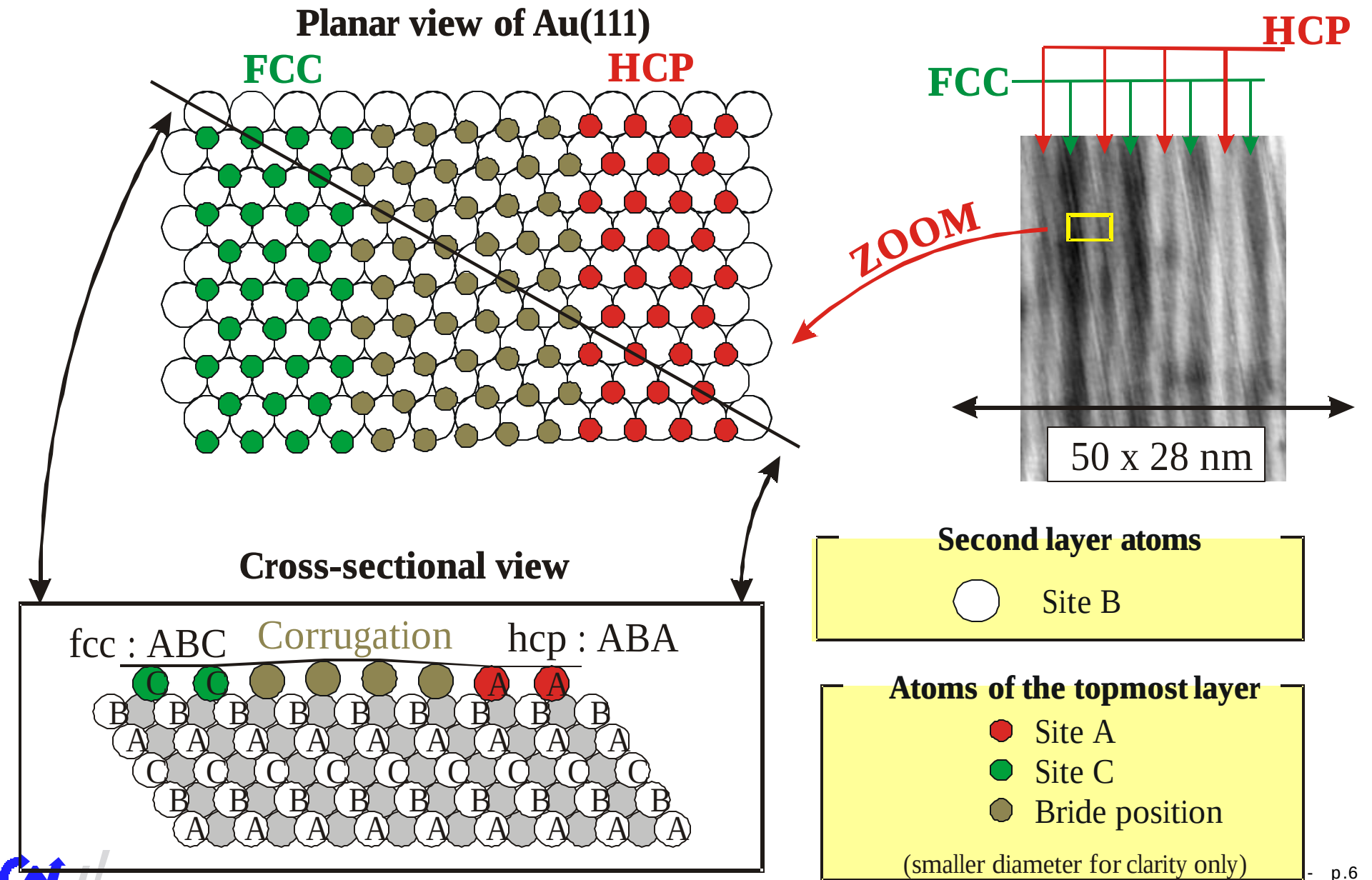
D. Babonneau, Appl. Phys. Lett. 76, 2892 (2000)

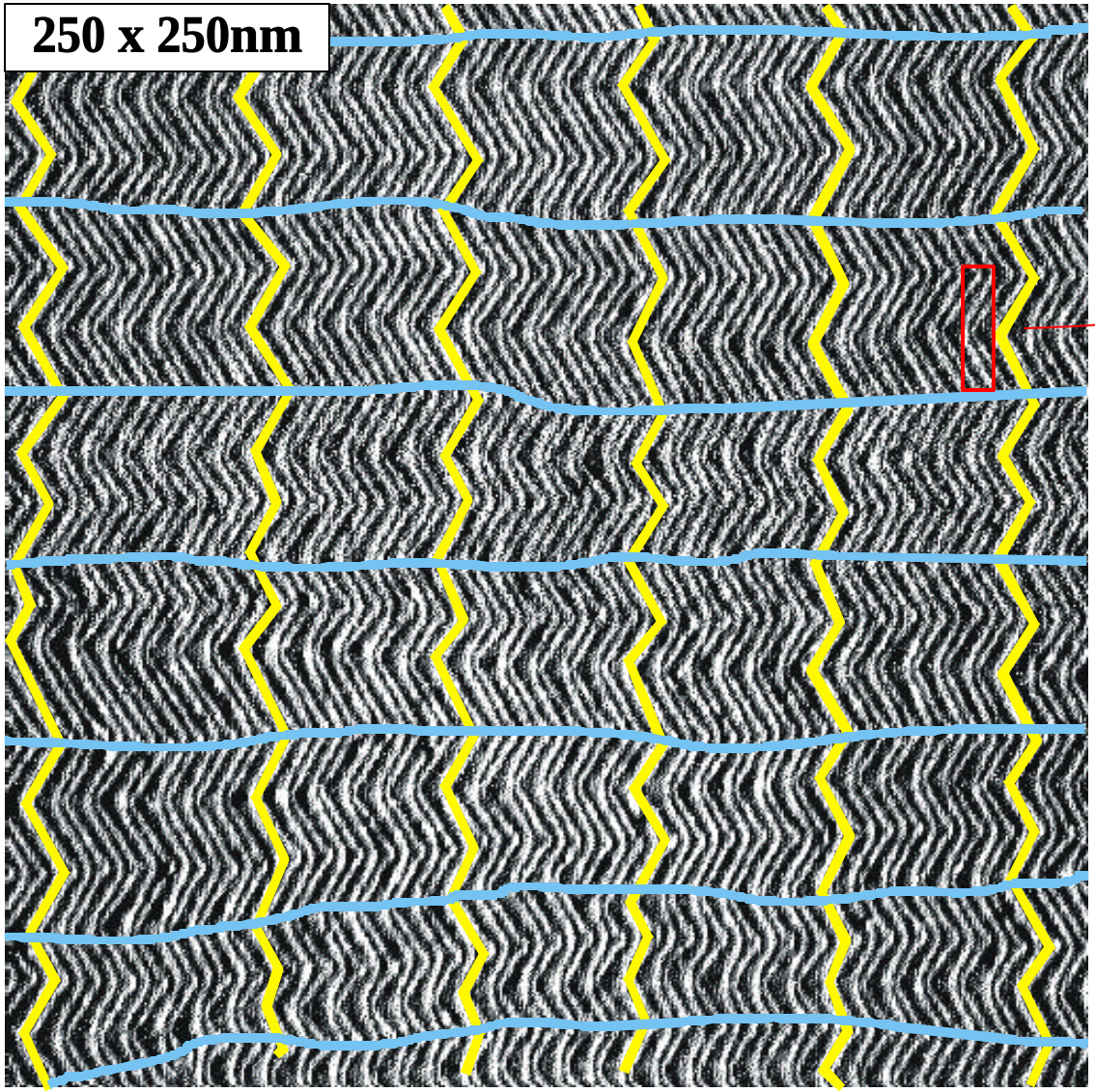
RECIPROCAL SPACE

GISAXS:

Grazing Incidence Small Angle X-Ray Scattering




Planar view of Au(111)
FCC
HCP
HCP
FCC
ZOOM
50 x 28 nm
Cross-sectional view
fcc : ABC
Corrugation
hcp : ABA
Second layer atoms
Site B
Atoms of the topmost layer
Site A
Site C
Bride position
(smaller diameter for clarity only)



Corrugation ~ 0.2 Å

Unit cell size :
~ 7.5 x 25nm

J. V. Barth et al., Phys. Rev. B 42 (15), 9307 (1990)

A.R. Sandy et al., Phys. Rev. B 43 (6), 4667 (1991)

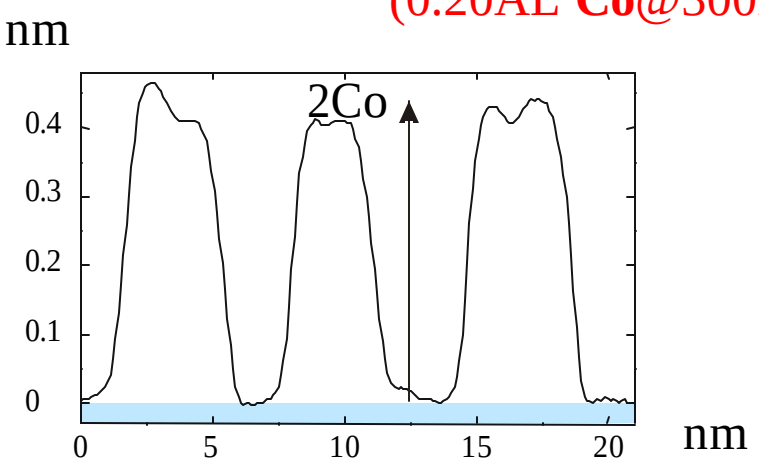
↳ Isotropic surface relaxation

FACTS:

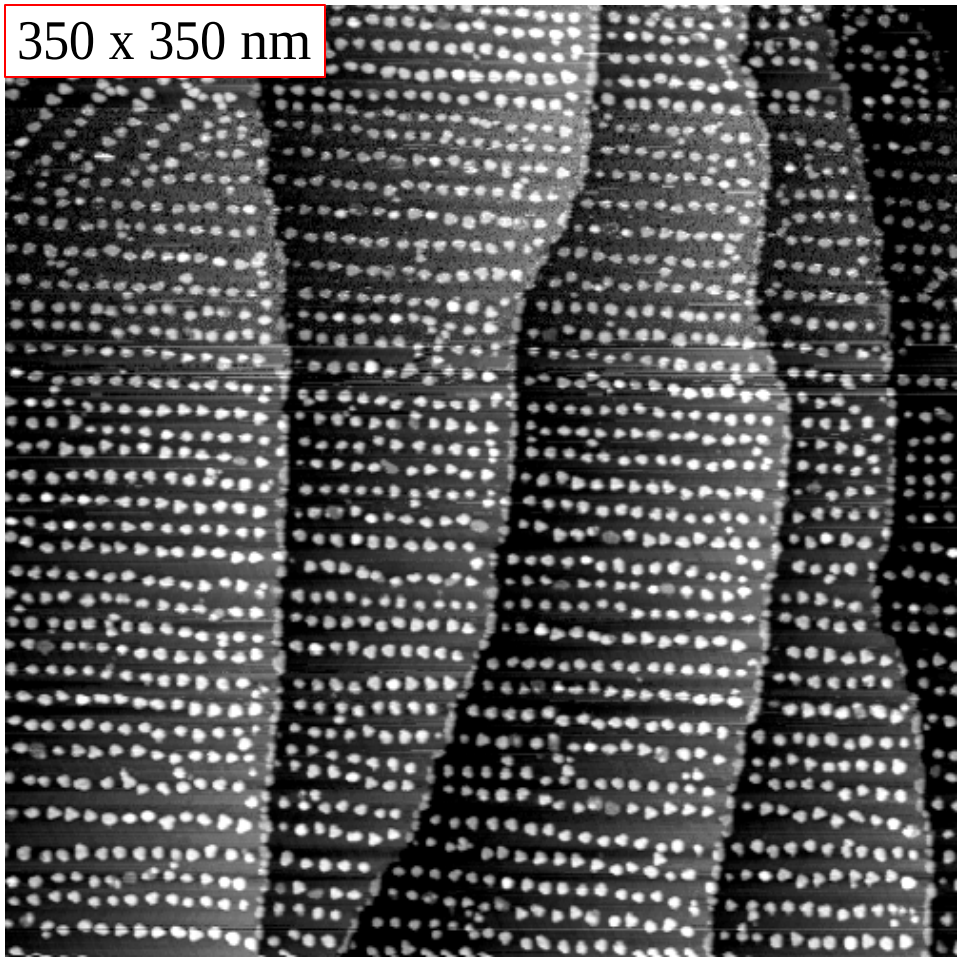
Co, Ni, Fe, Cu, Rh growth on Au(111) gives rise to self-organized arrays of dots

ORIGIN ?

(0.20AL **Co**@300K)



Fe, Ni : 1 AL-high dots
Co : 2 AL-high dots



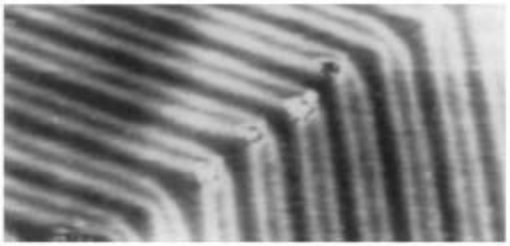
See also:

D.D. Chambliss et al., PRL 66, 1721 (1991)
B.Voigtlander et al., PRB 44, 10354 (1991)

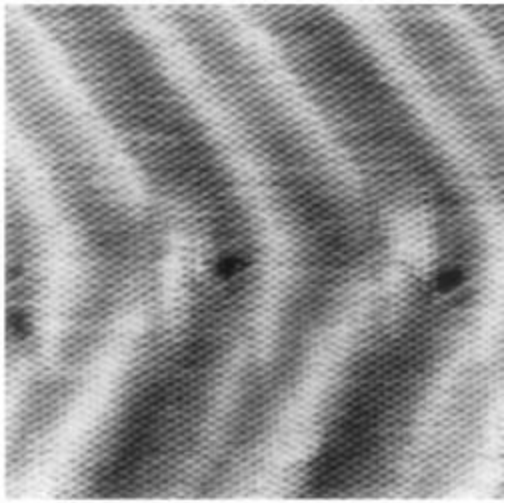
Fe, Co, Ni (etc.) nucleation: atomic place exchange mechnism with Au atoms

Example: 0.002ML Ni@300K

a)



b)

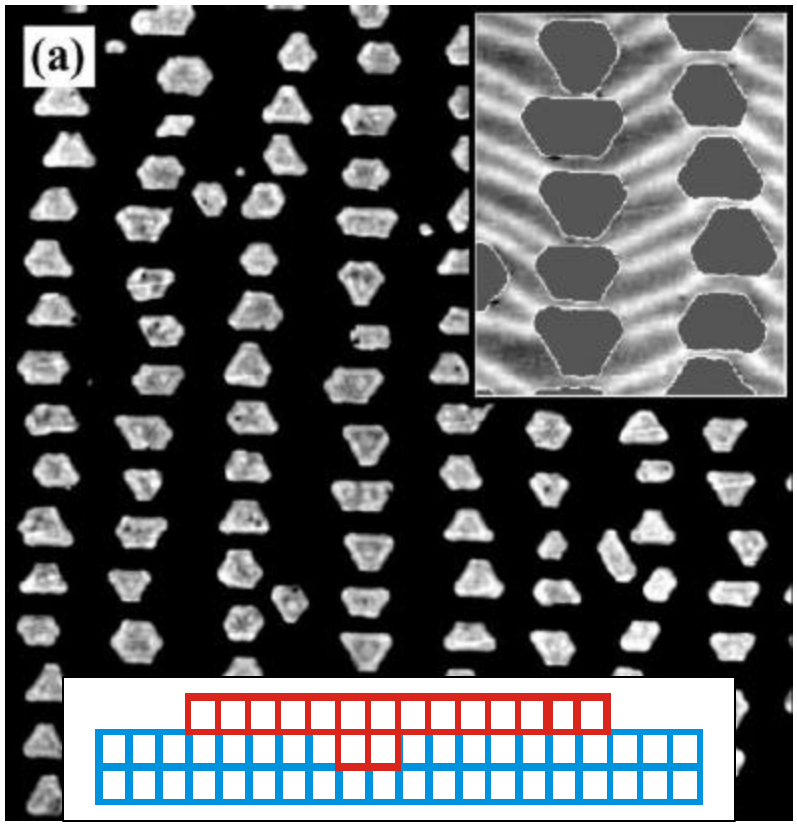


Element	Surface free energy (eV)	Heat of sublimation (eV)
Ag	0.50	2.95
Al	0.56	3.39
Cu	0.69	3.51
Au	0.72	3.79
Ni	0.90	4.45
Co	0.94	4.40
Fe	0.96	4.32

J.A.Meyer et al., Surf.Sci.**365**, L647 (1996)

See also: S. Rousset et al.

0.25ML Ni @300K : 1ML-high dots



W. G. Cullen et al., Surf. Science 420, 53 (1999)

Leading parameter (?): deposit has a higher surface energy.
(and Au atoms stress near chevrons)

Continuous films

t > 2 AL

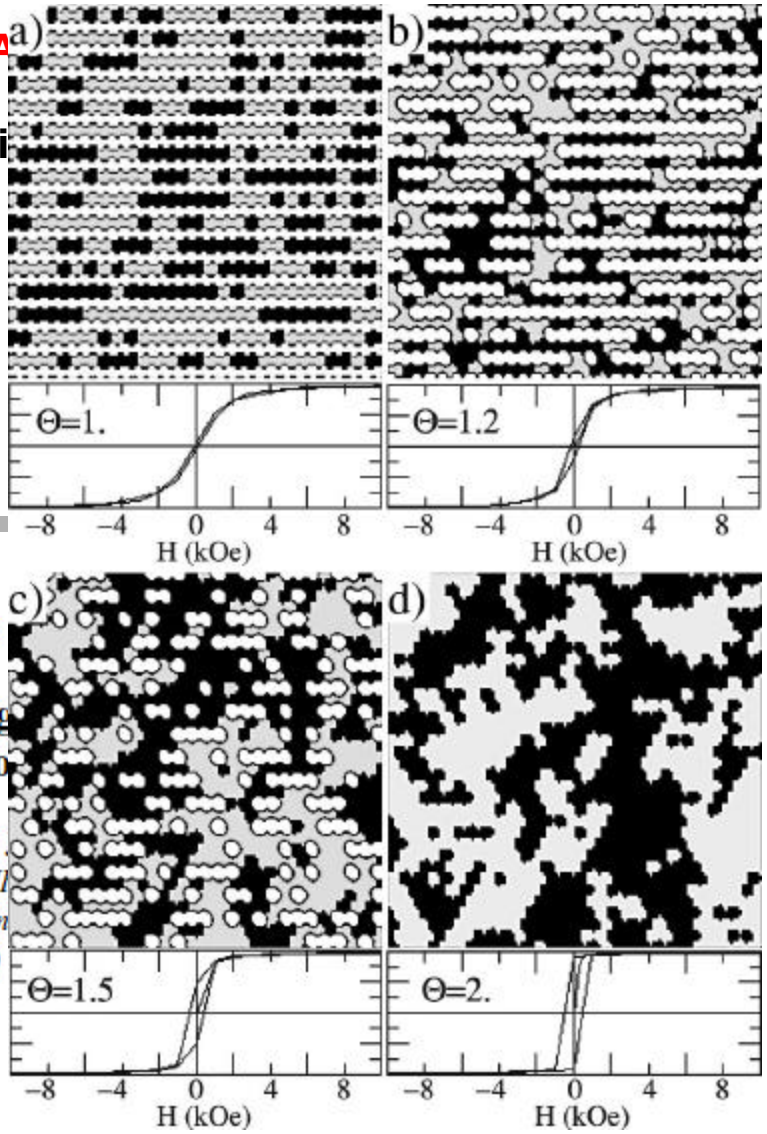
Continuous films

J. Pommier el al., Phys. Rev. Lett. 65, 2054 (1990)
M. Speckmann et al., Phys. Rev. Lett. 75, 2035 (1995)

Etc.

t > 5-7 A

Perpendi



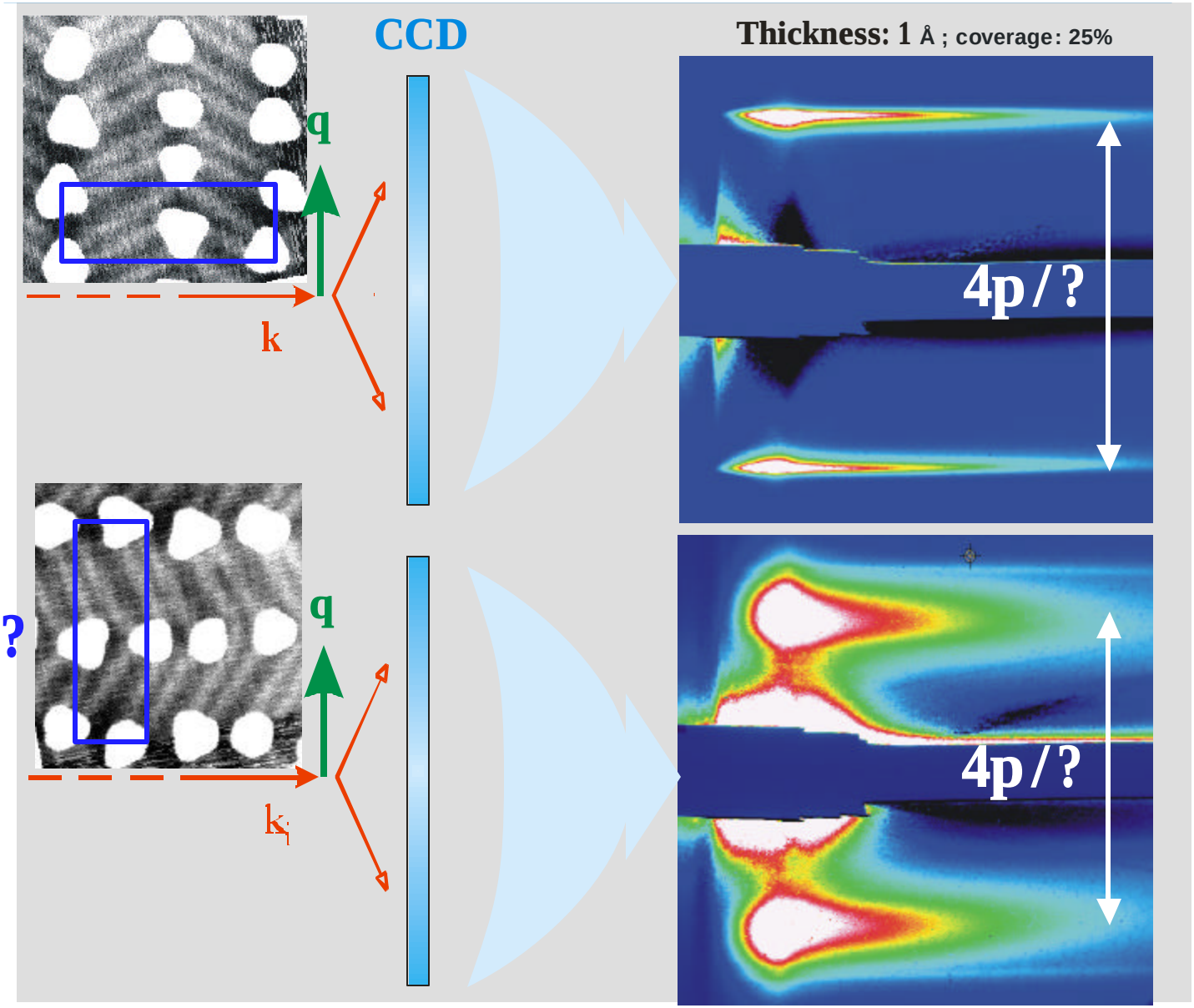
From dots to films

PHYSICAL REVIEW B VOLUME 59, NUMBER 18

Transition from zero-dimensional superparamag
ferromagnetism of Co clusters o

S. Padovani, I. Chado, F. Scheurer, and
Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504 CNI
F-67037 Strasbourg Cedex, Fran
(Received 9 November 1998)

S. Padovani et al., Phys. Rev. B 59, 11887 (1999)

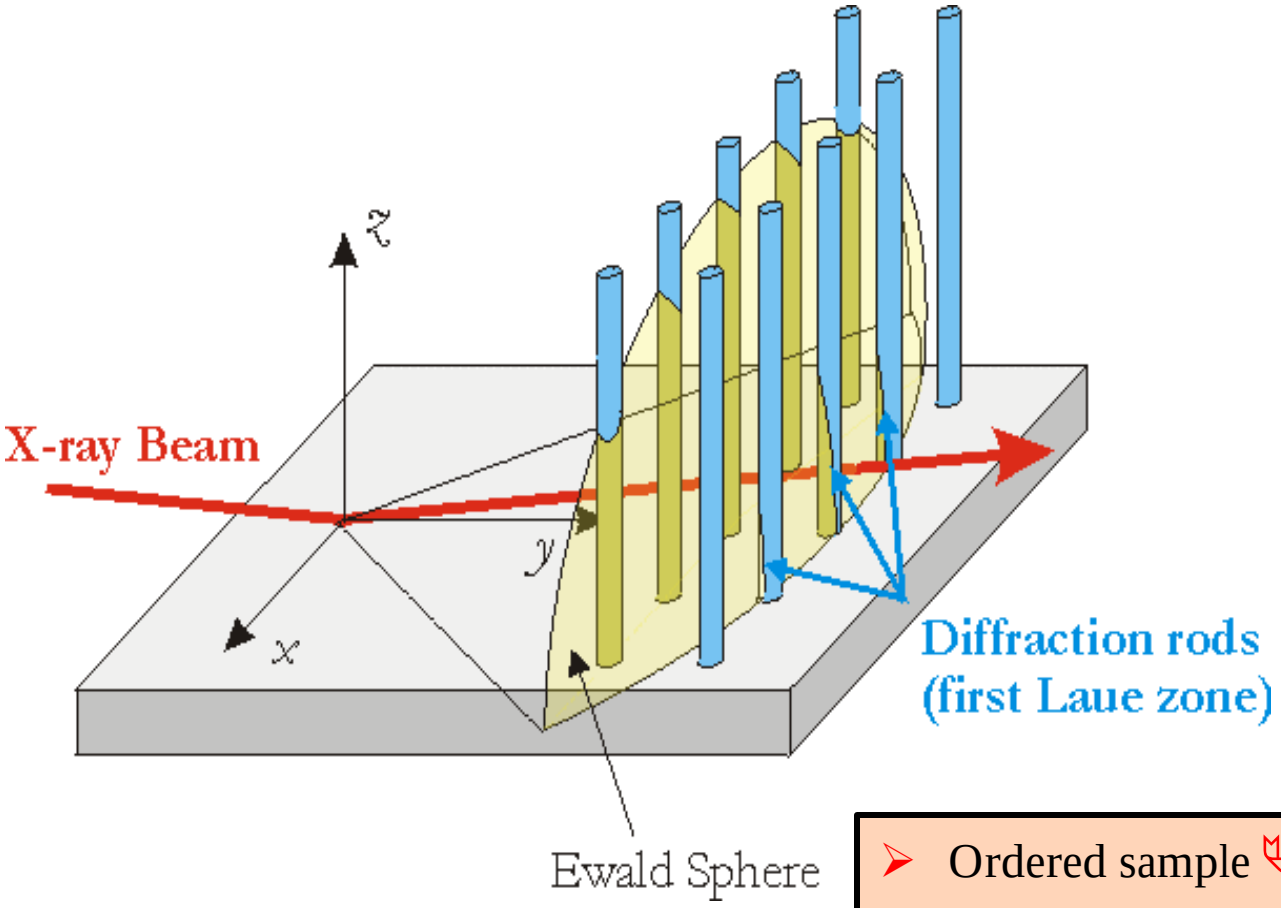


INTRA-ROW ORDER: SUPER-CRYSTAL

DQ / Q = 3 %

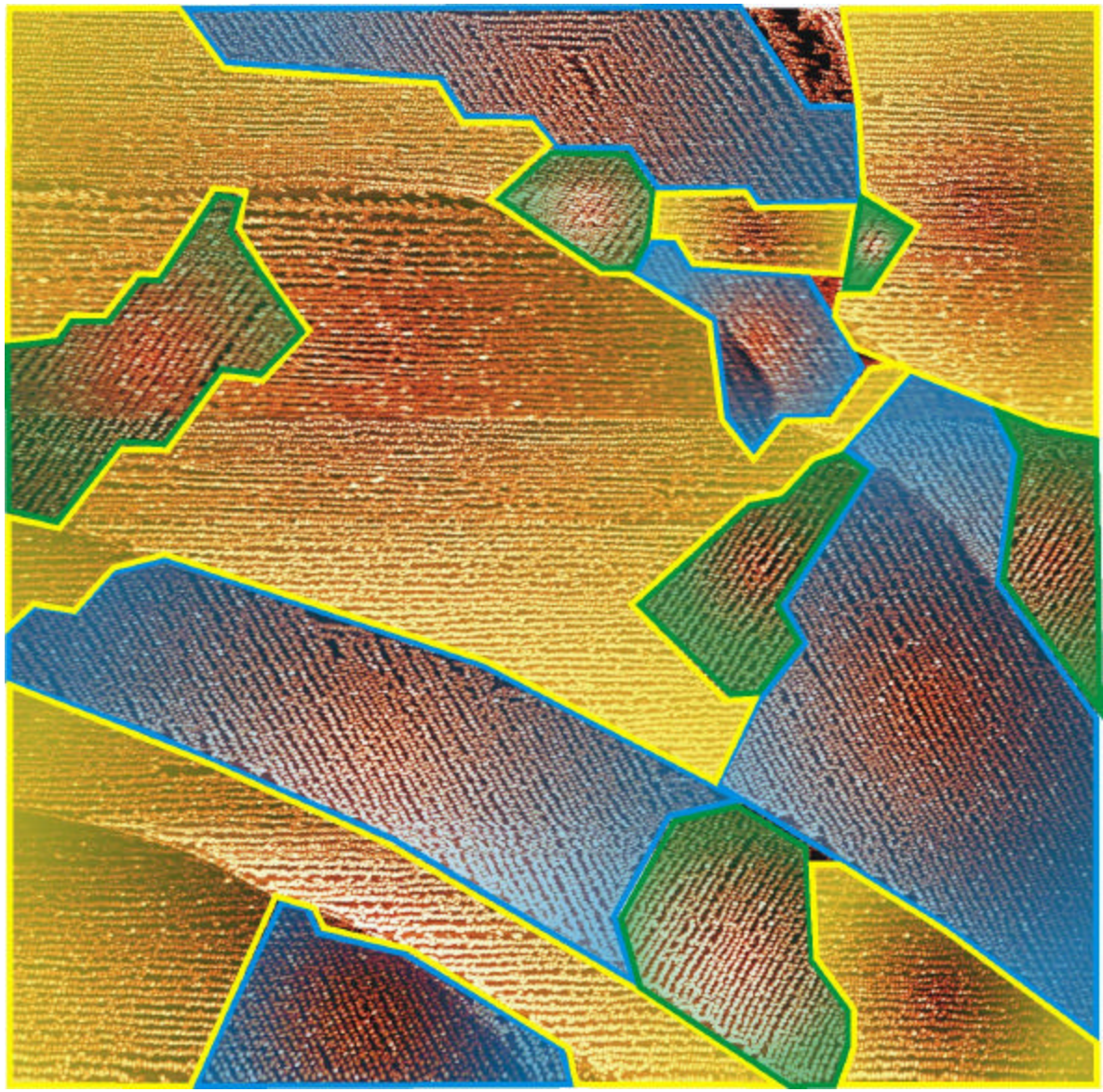
INTER-ROW ORDER: LIQUIDE-TYPE

K = 8.5nm
s = 2.1nm



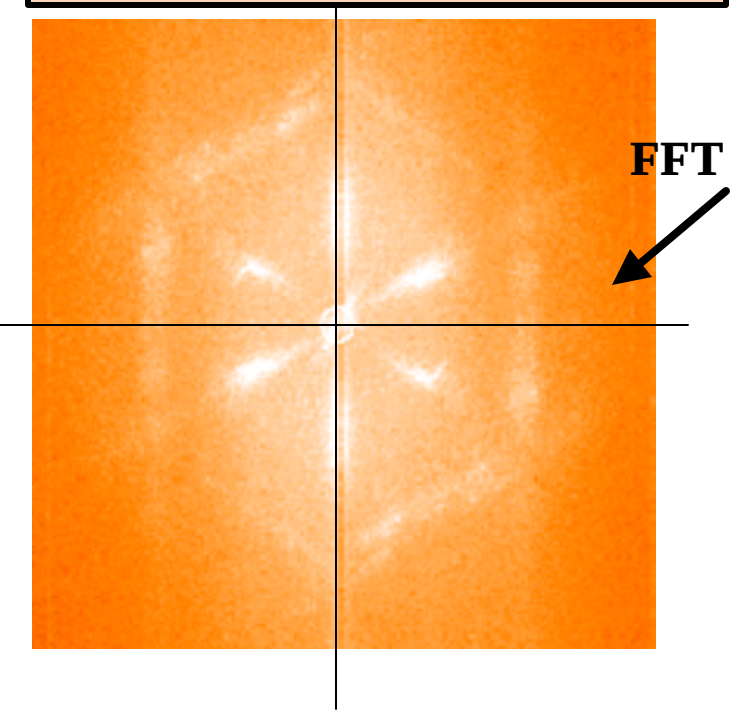
- Ordered sample ↳ 'super' reciprocal space ?
- Grazing incidence and 2D detector
  ↳ similarity with RHEED

1.5mm x 1.5mm STM image

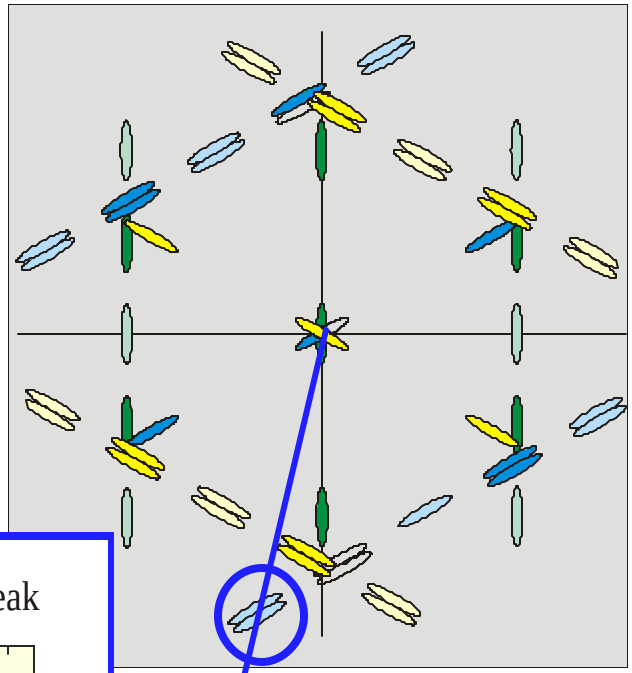


3-fold symmetry of Au(111) crystal

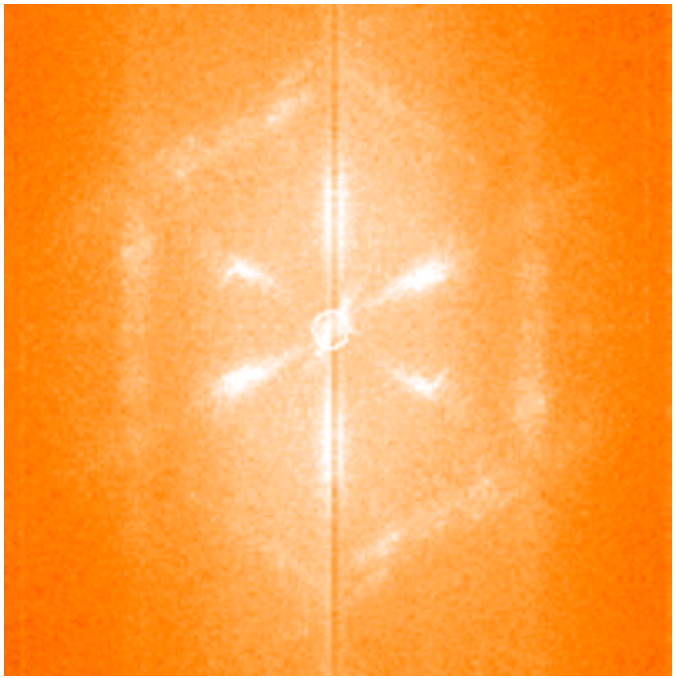
- 3 ‘equivalent domains’



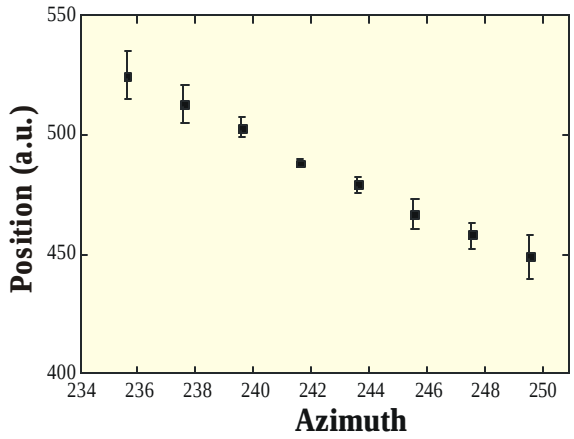
GISAXS



FFT of STM



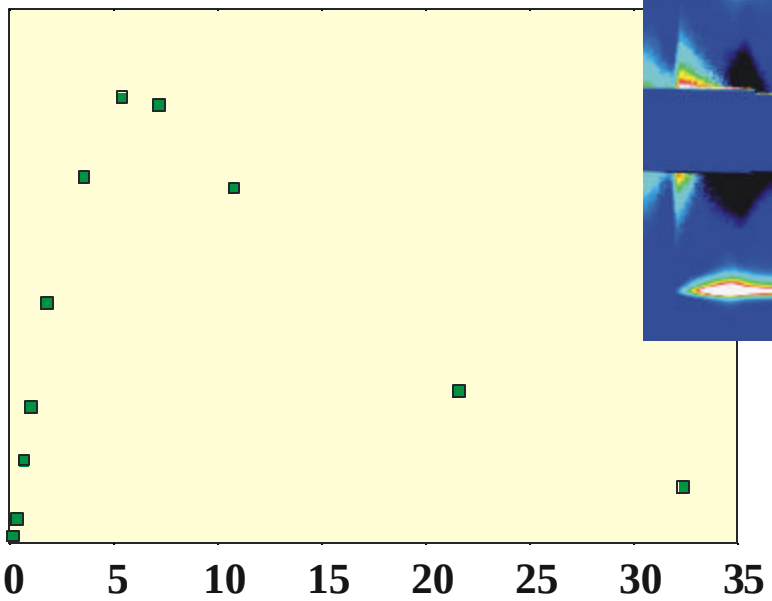
Transverse cross-section of a peak

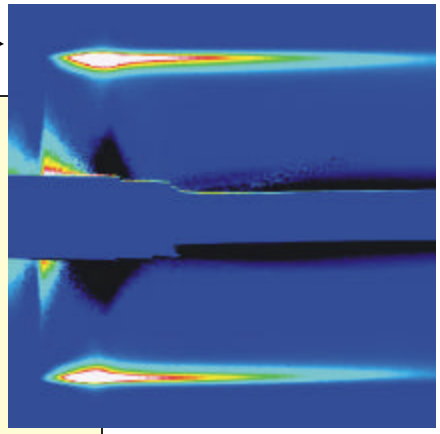


Similar patterns and good understanding

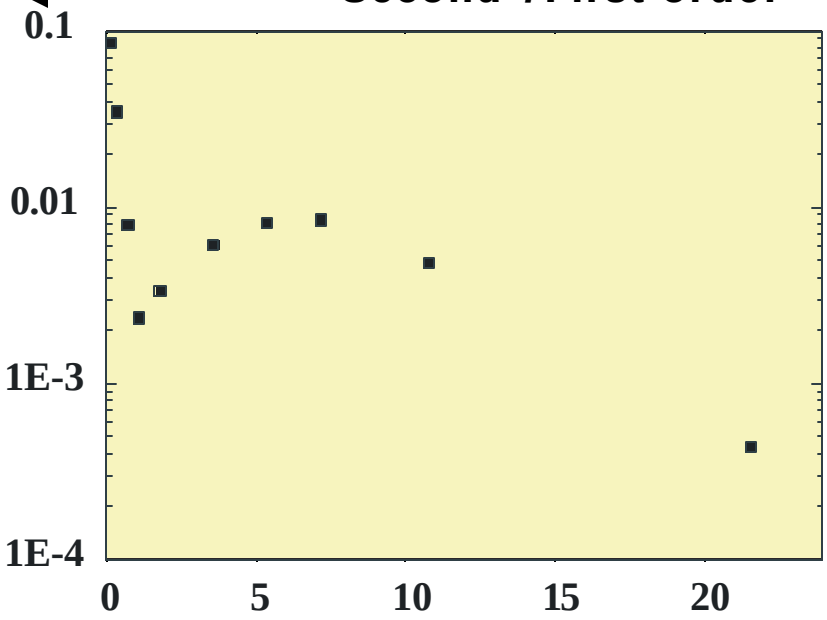
- Do we gain any new information from GISAXS ?

First order peak intensity





Second / First order



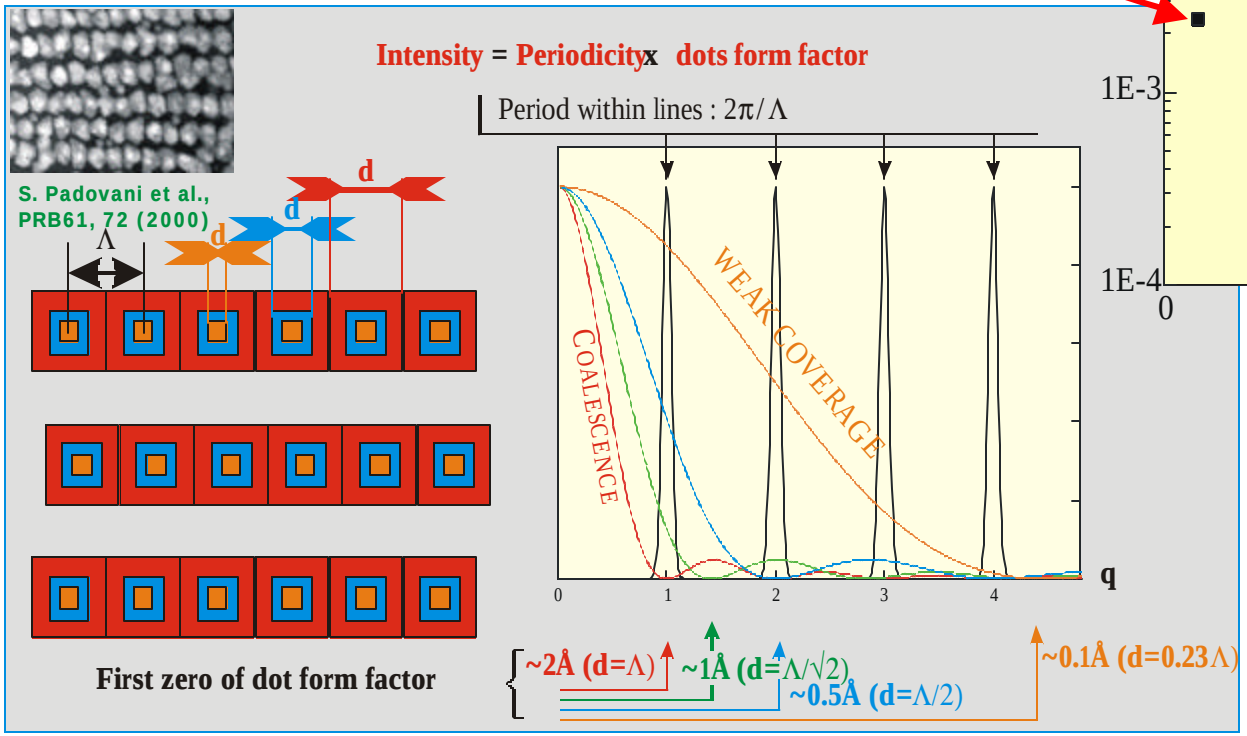
Features to explain

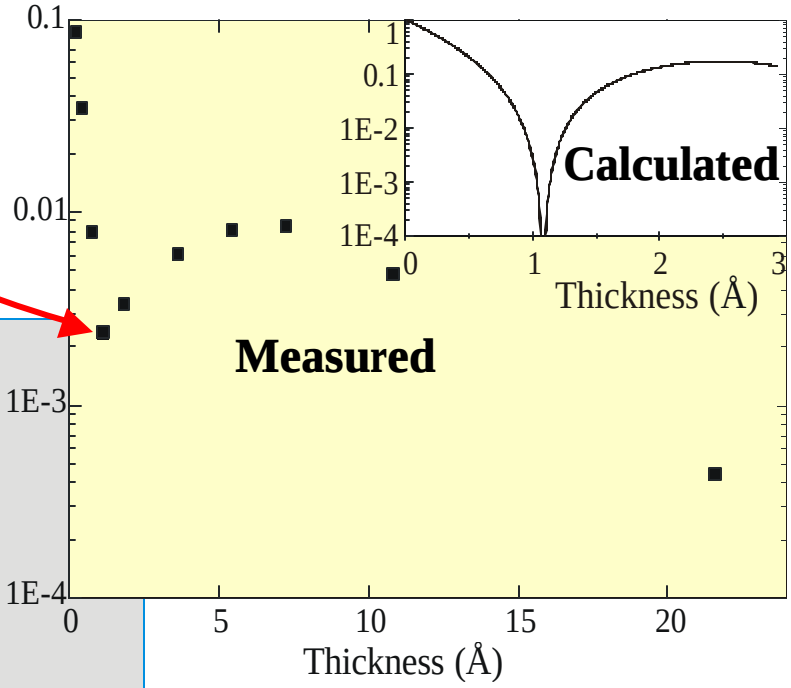
- Maximum at 6Å = 3 atomic layers ?
- Significant intensity for continuous film ?
- Weak intensity ?
- Intermediate minimum ?

RATIO: Second /First order peak intensity

➢ **Deposition rate calibration**

Simple model of 1D coalescence

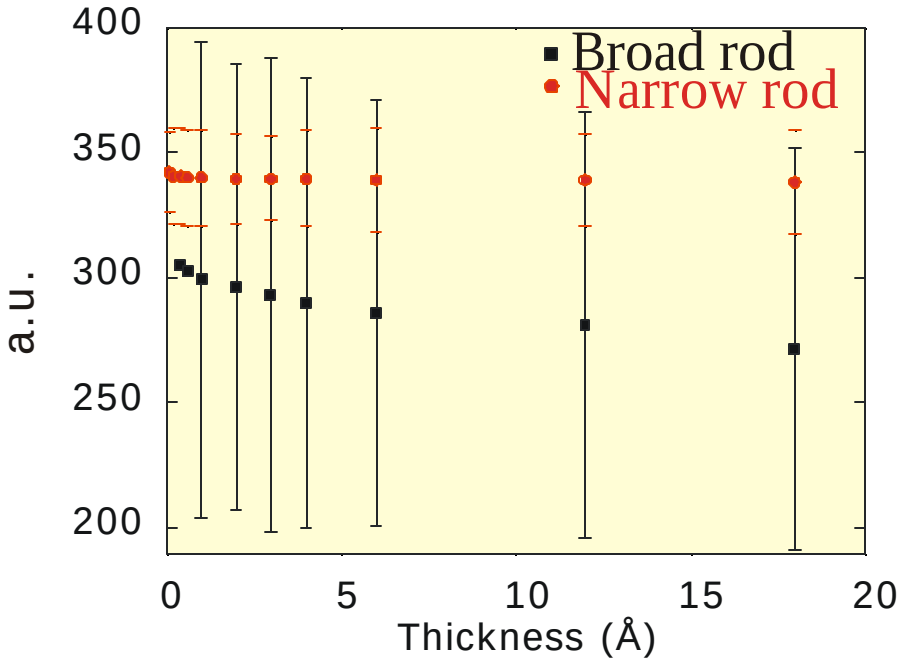




$F_{dot}(Q)$ **vanishes rapidly for 'reasonable' dot size**

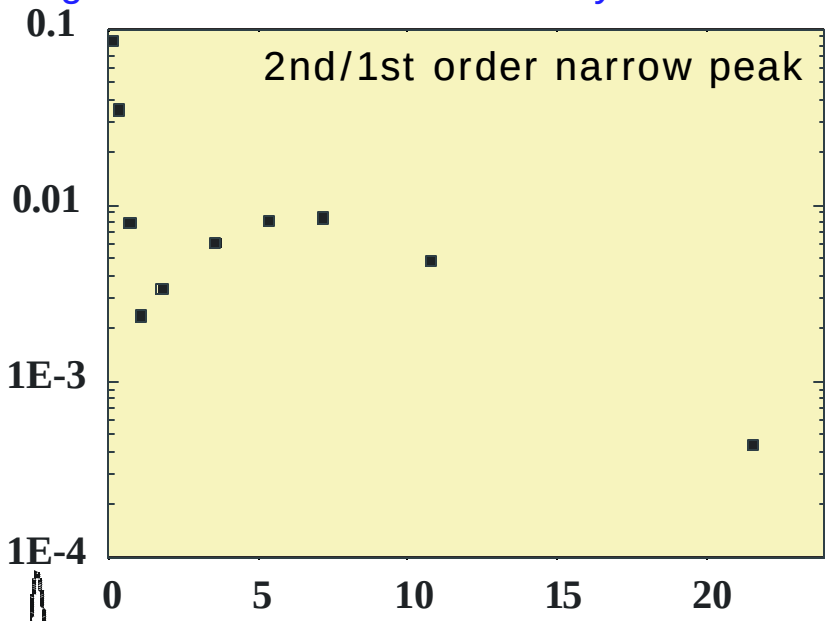
Peak position

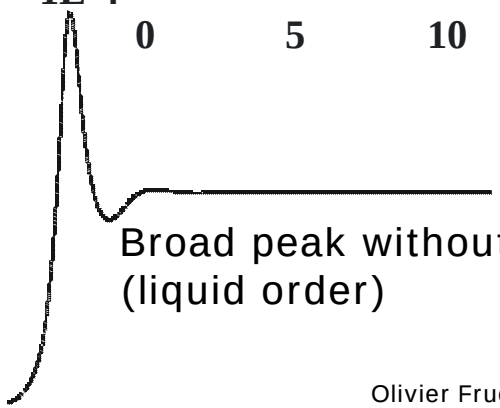
Maximum displaced from 2π/a



Peak magnitude

Higher orders: weak intensity





Broad peak without shape factor
(liquid order)

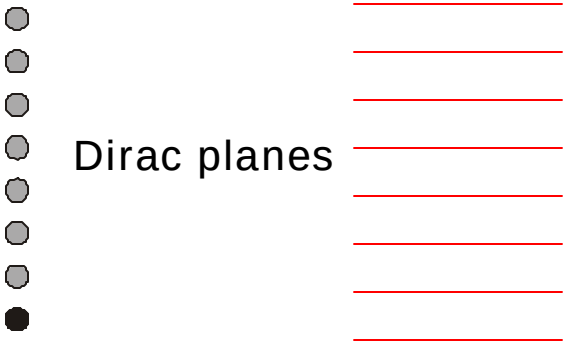
Building brick : 1 dot

$F_{dot}(Q)$ ↳ Shape factor

Bessel functions, etc.

Row of dots

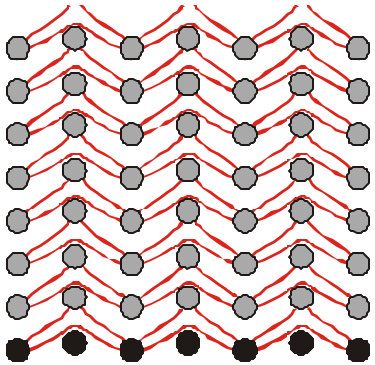
$F_{row}(Q)$



Dirac planes

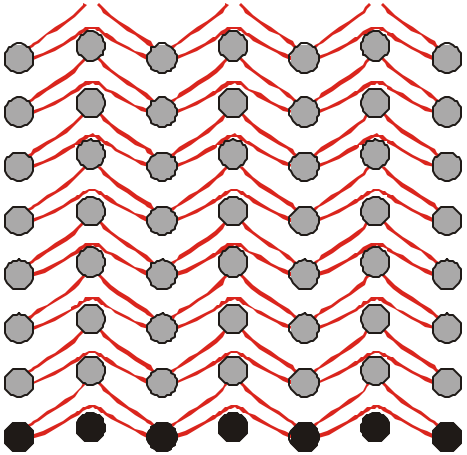
Inter-row liquid order

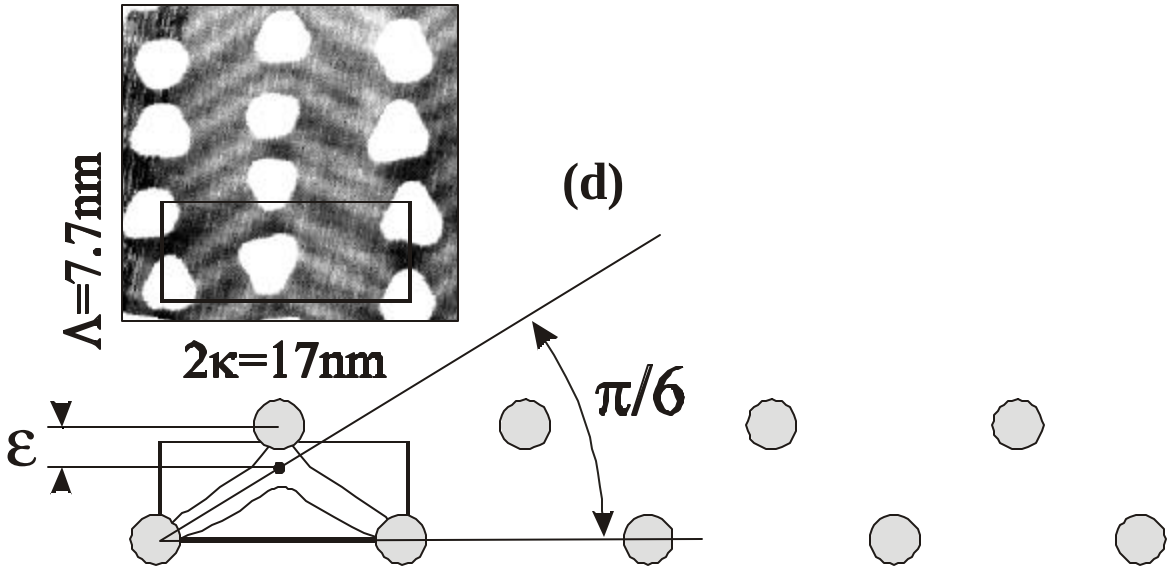
$F_{liq}(Q)$ ↳ Structure factor



$$I = |F_{\mathrm{dot}}|^2 \times |F_{\mathrm{row}}|^2 \times |F_{\mathrm{liq}}|^2$$

Inter-row liquid order



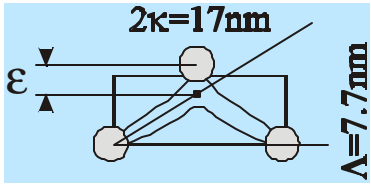


Pair correlation function

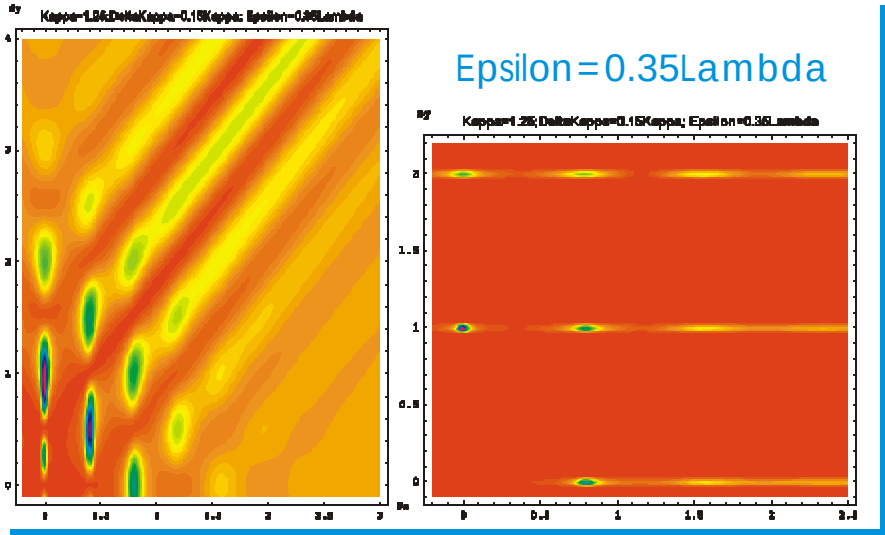
$$h^{\pm}(x,y) = \frac{1}{\sqrt{2\pi\sigma_\kappa^2}} \exp\left[-\frac{(x-\kappa)^2}{2\sigma_\kappa^2}\right] \delta(y \pm \frac{1}{2}x \pm \epsilon)$$

Analytical formula

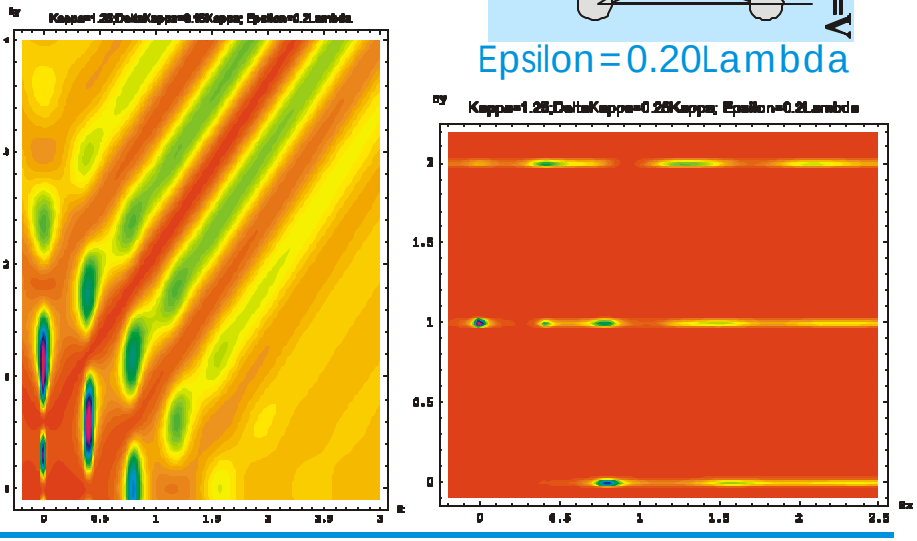
From side-centered to cell-centered…
(peak **position** is affected)



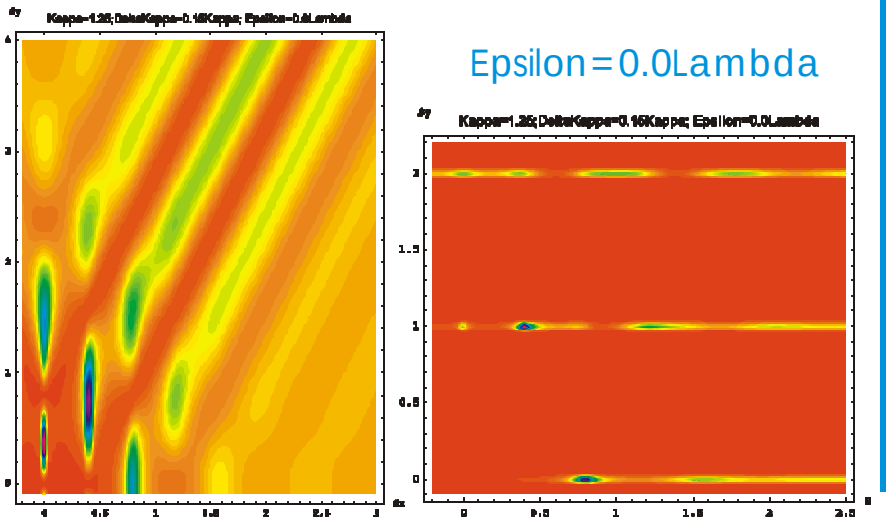
Epsilon=0.35Lambda



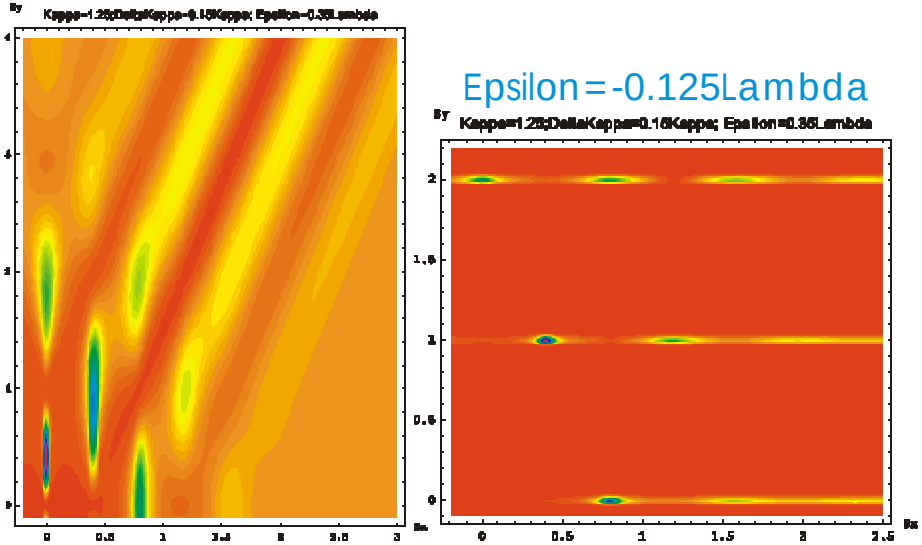
Epsilon=0.20Lambda



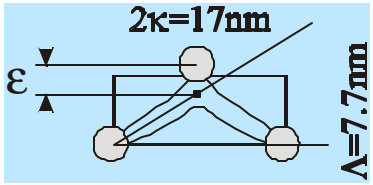
Epsilon=0.0Lambda



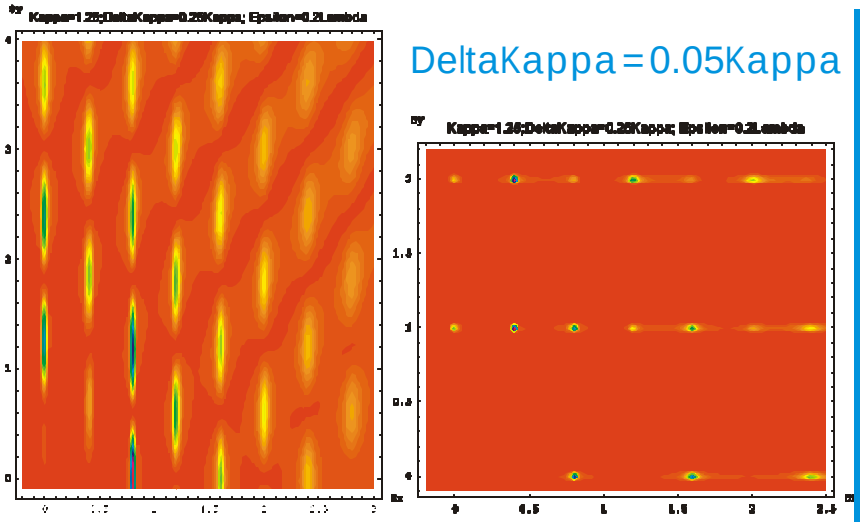
Epsilon=-0.125Lambda



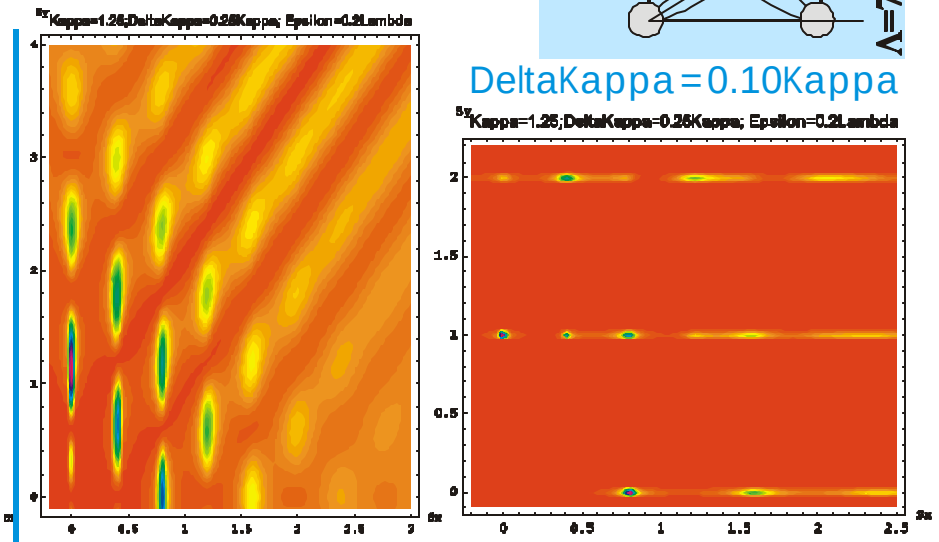
From crystal to liquid
(peak **position** affected at high Q)



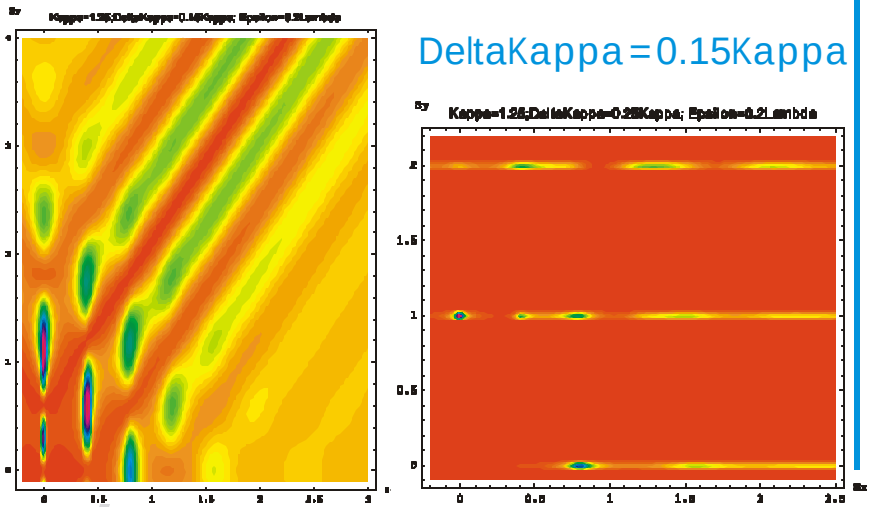
DeltaKappa=0.05Kappa



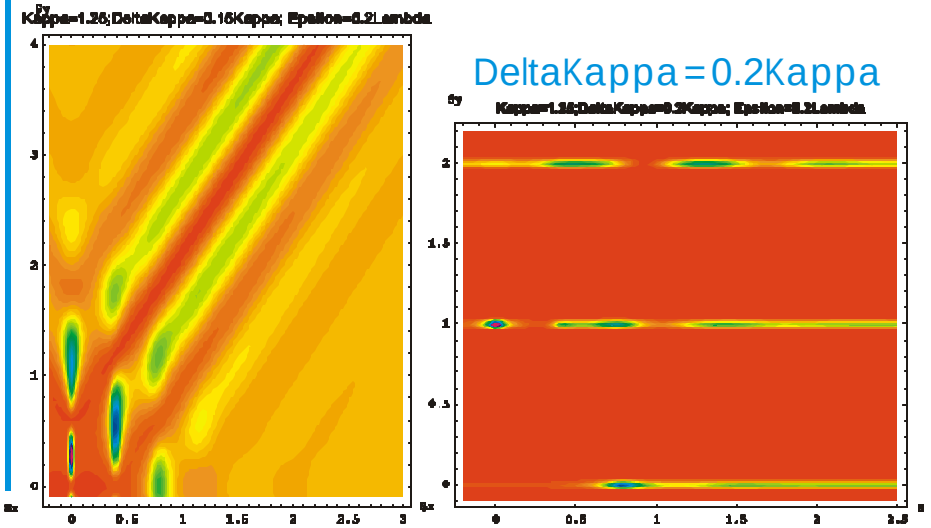
DeltaKappa=0.10Kappa



DeltaKappa=0.15Kappa



DeltaKappa=0.2Kappa



Peaks position

- **Close to origin**: determined by cell size
- **Far from origin**: determined by structure factor
  (two slits interference)

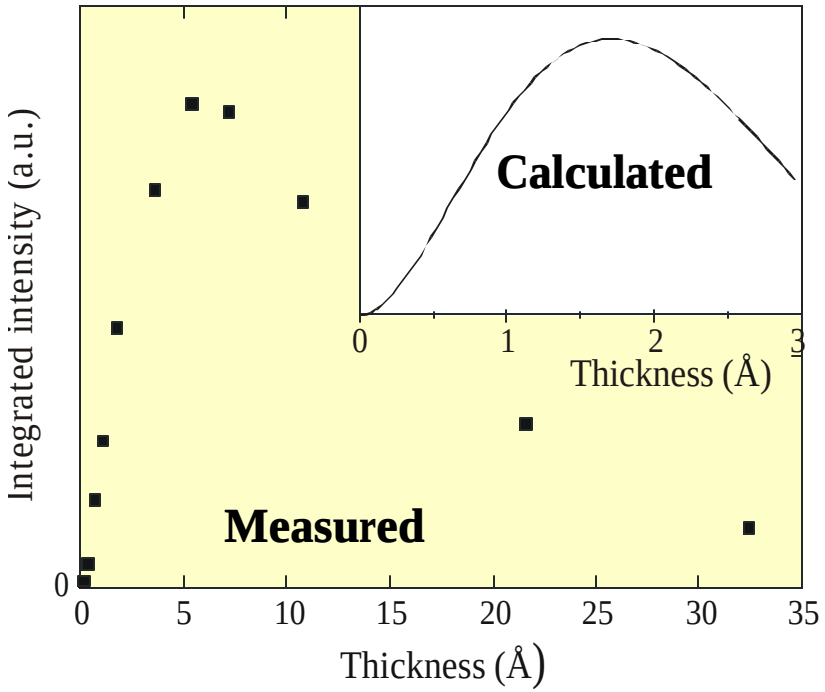
Peaks intensity analysis

- **Explains weakness of I2/I1:** disorder and cell 'centering'
- Knowledge of disorder > deduce centering $e = 2.5 \pm 1.5\,\mathrm{nm}$ (for 0.5 AL)

Perspective

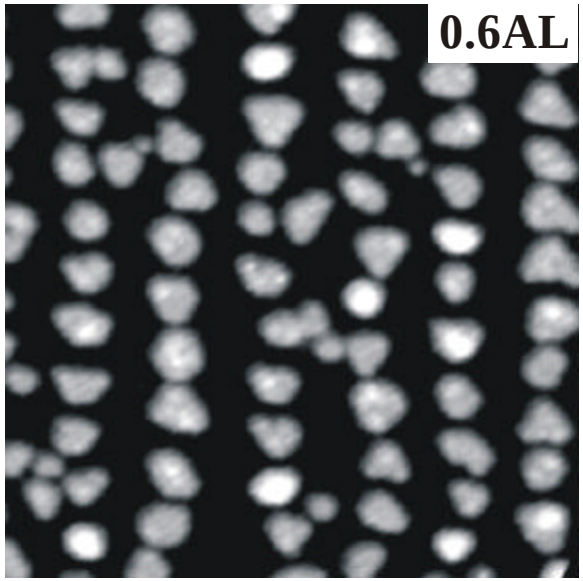
- **Measure many more peaks**
- **Full 'crystallographic' analysis**

First order peak intensity : discrepancy

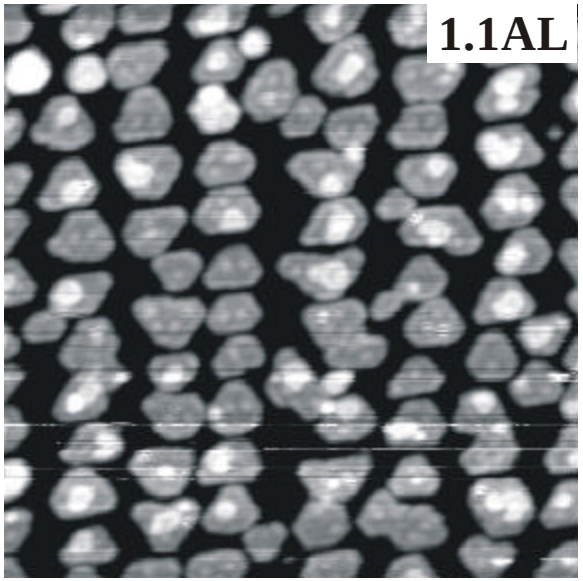


- **Qualitative agreement**
- **Quantitatively : maximum for higher coverage**
  - **Is the model too simple ?**
  - **Does the roughness vanish at coalescence ?**

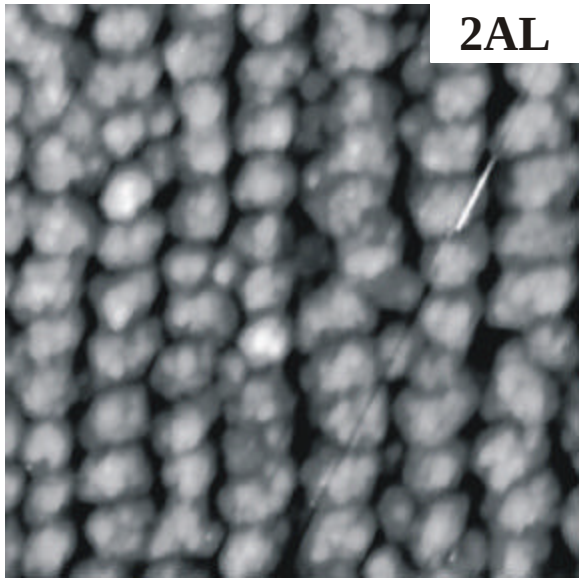
STM pictures



Fruchart et al.



S. Rousset et al.

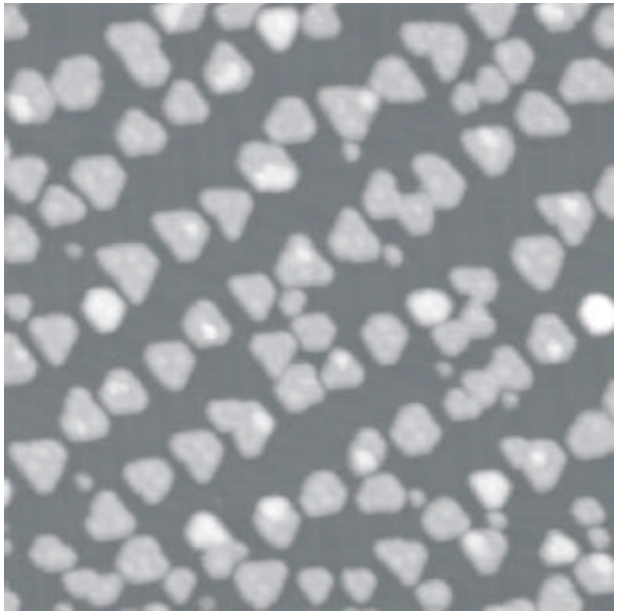


S. Padovani et al., Phys. Rev. B 59, 11887 (1999)

Can residual rougness explain the discrepancy ?

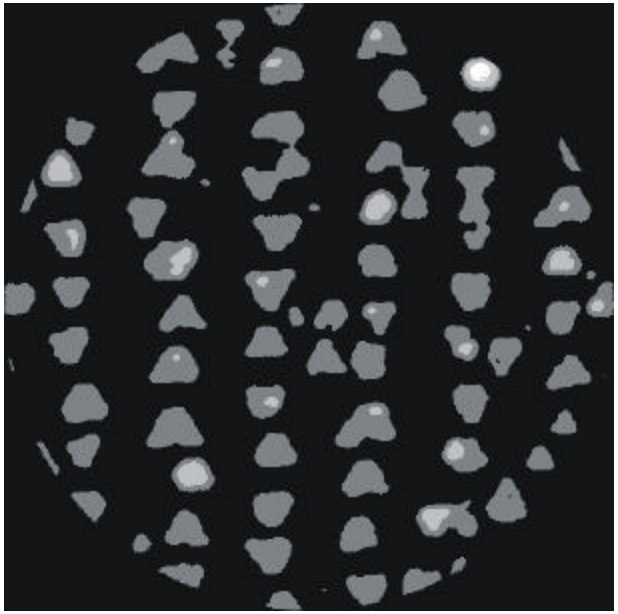
Experimental procedure (example : 0.5AL)

Raw image

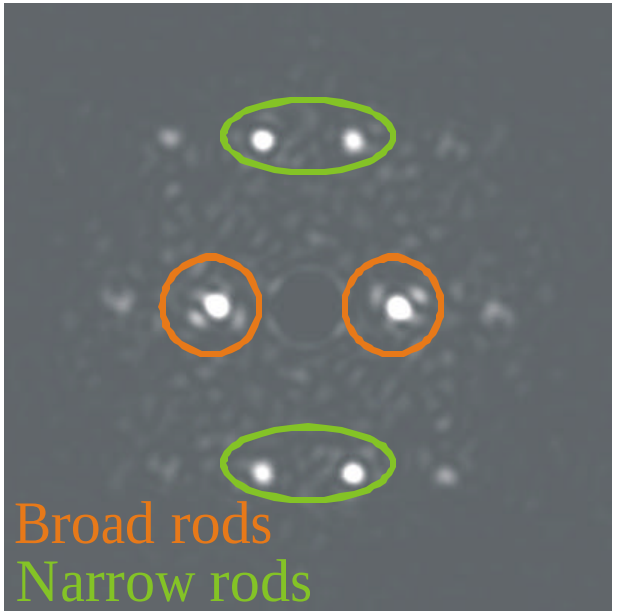


Disk-shaped crystallite

Gray level discretization



Calculated diffusion



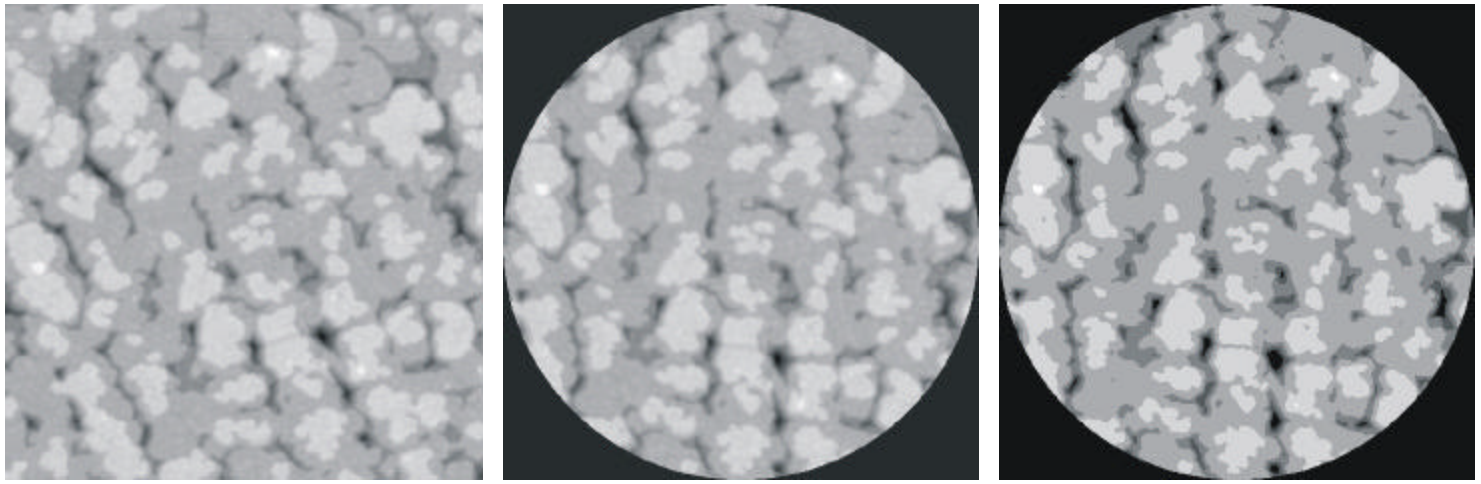
- **Speckle effect (‘beam’ coherence over the image)**
  averaging is necessary
- **Backs up model: reciprocal space is not a simple rectangle**

Experimental procedure (example : 4AL)

Raw image

Disk-shaped crystallite

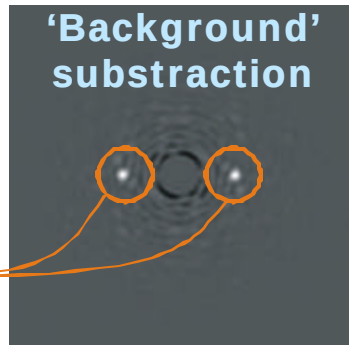
Gray level discretization



S. Rousset et al.

Raw diffusion

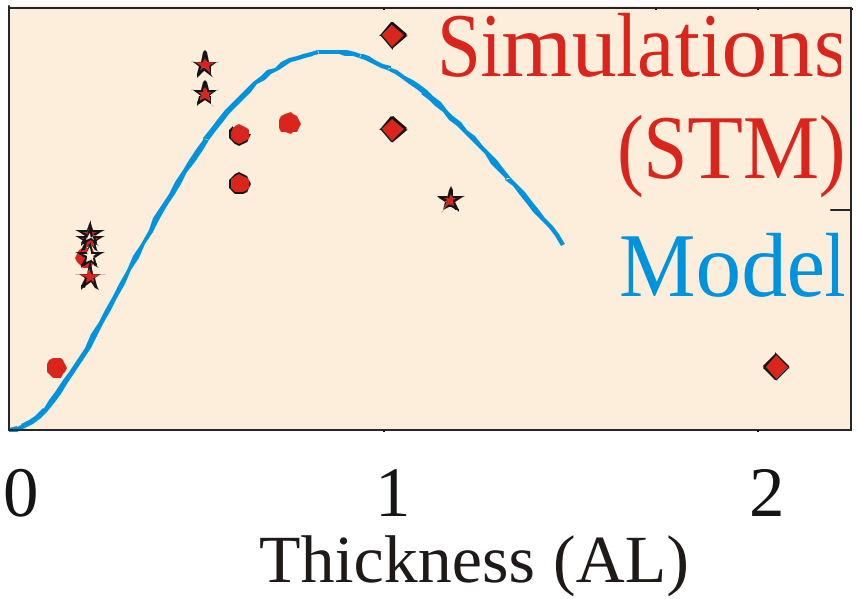
'Background' substraction



Broad peaks only (inter-row)

Narrow peaks vanish

Model versus STM



O. Fruchart et al.

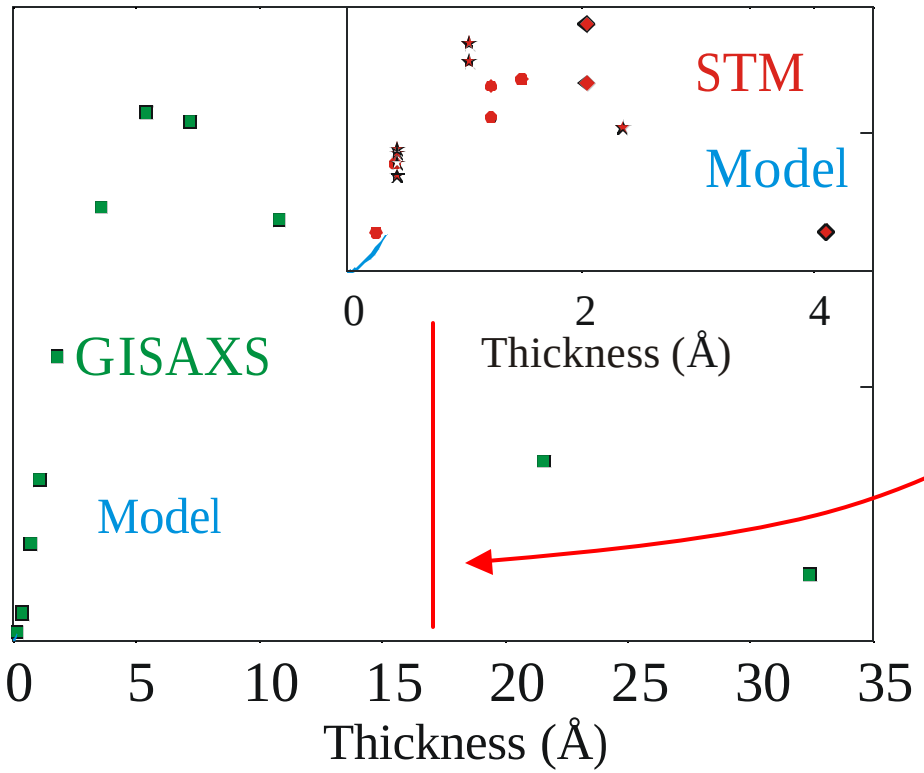
GPS

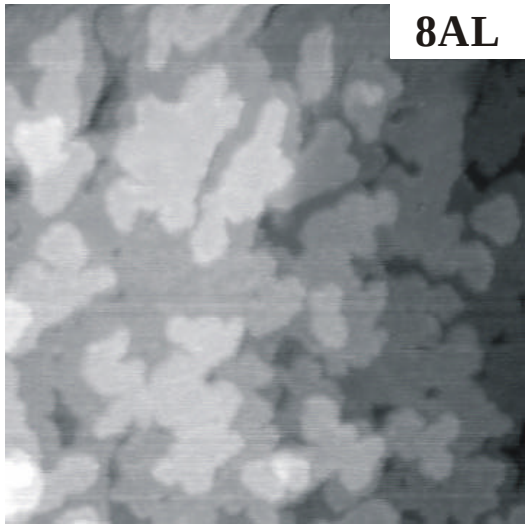
Padovani et al.

S. Padovani et al., Phys. Rev. B 59, 11887 (1999)

- **Tip shadowing effect on calculated GISAXS**
  - **overestimates for low coverage**
  - **underestimates for high coverage**
- **Group and tip independant**

Model versus STM: discrepancy remains !



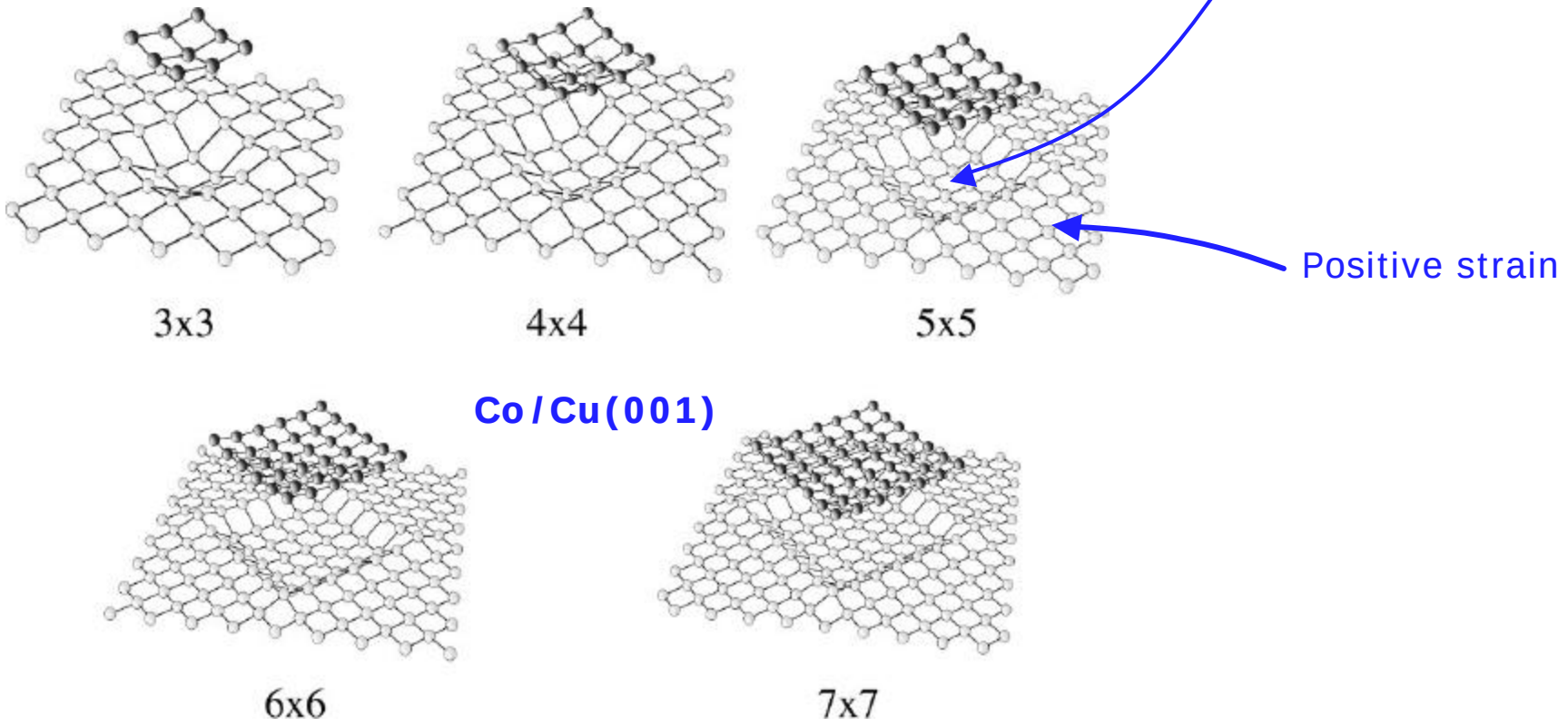


GISAXS intensity remains for continuous films with insignificant surface roughness

Could a periodic stress induced in the Au(111) substrate by the dots contribute to GISAXS ?

Elastic theory, atomistic calculations

Example:

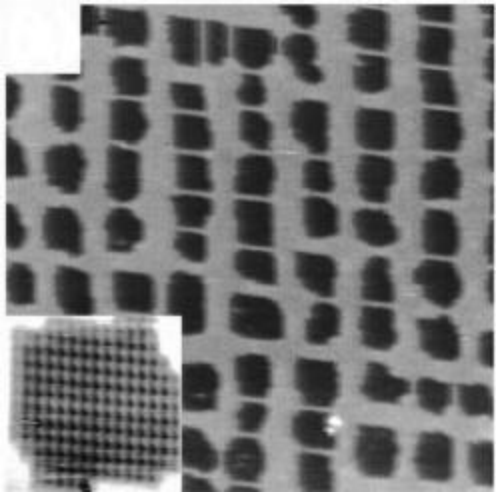


V. S. Stepanyuk et al., Phys. Rev. B 62, 15398 (2000)

- **Modulation of substrate lateral density.**
- **Depth similar to lateral scale**

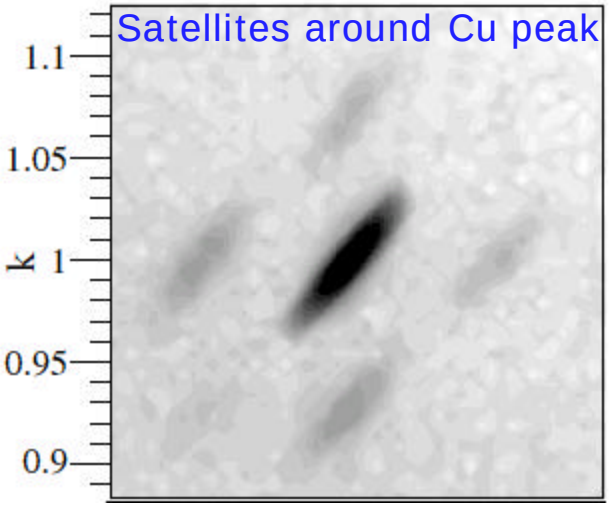
SXRD: self-organized N/Cu(001)

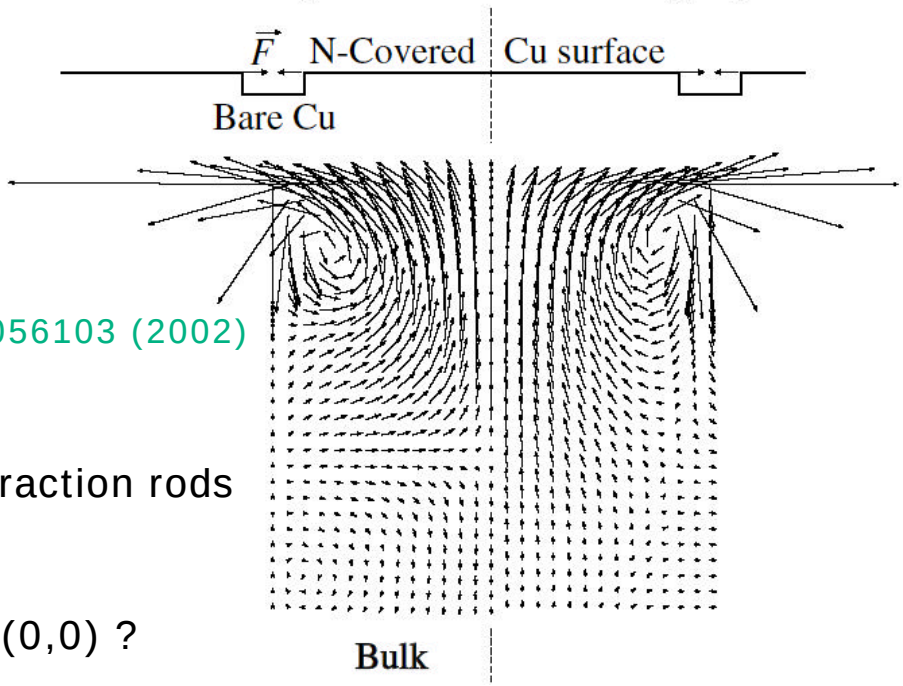
0.2AL N/Cu(001)



S.L. Silva, APL76, 1128 (2000)

F.M. Leibsle, SS317, 309 (1994)





B. Croset, PRL88, 056103 (2002)

- Periodic surface strain can induce satellite diffraction rods
- Depth similar to period
- Small-angle : diffraction satellites around rod (0,0) ?

Objection

- Co: Z_{CO} versus vacuum
- Au: $Z_{AU}(1+\varepsilon)$ versus Z_{AU}

➥ **x 10^{-3}**

Effects affecting magnitude

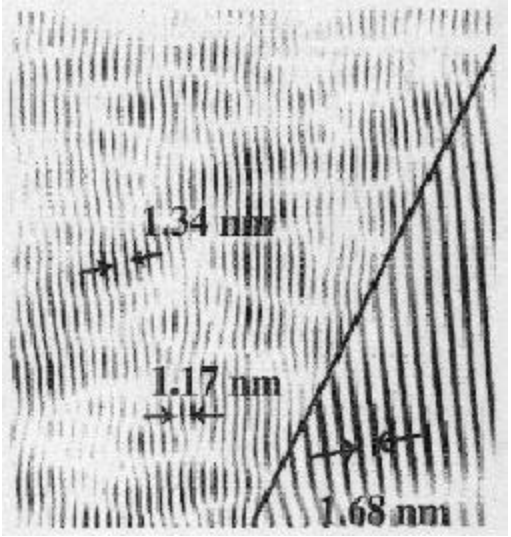
- **$Z_{AU} > Z_{CO}$** ➥ **x 10**

- **Depth of modulation t**
  - Shortening of diffraction rods: Qz ~ 1/t ➥ **x 10**
  - Number of atoms ~ t ➥ **x 10**

➥ Similar orders of magnitude for Co and Au scattering

TEM, plane views

H. Ardhuin, J. Cryst. Growth 182, 394 (1997)



➥ e_{Co} = **3-3.5 %** **@ 4AL**

EXAFS

Marsot et al.

➥ e_{Co} = **2-3 %** **@ 2AL**

SXRD

Marsot et al., Thesis, unpublished.

➥ e_{Co} = **5±1 %** **@ 2AL**

STM dislocation Moirés

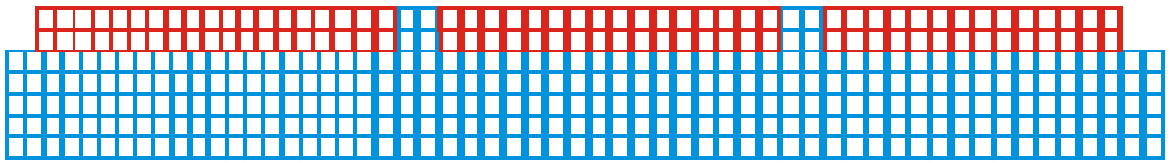
S. Rousset et al., unpublished ?

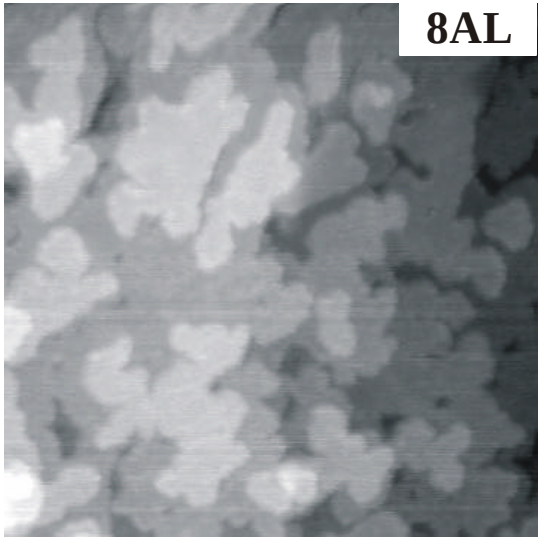
➥ e_{Co} = **3 %** **@ 2AL**

➥ e_{Au} [3] **0.1 %**

Imperfect percolation ?

➥ **Au atoms upcoming from substrate ?**



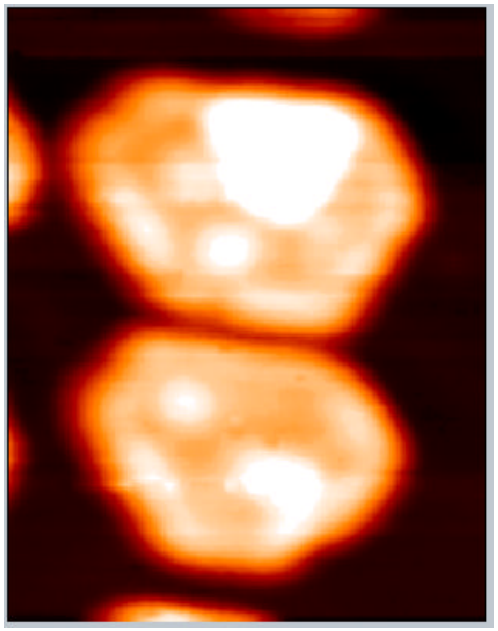
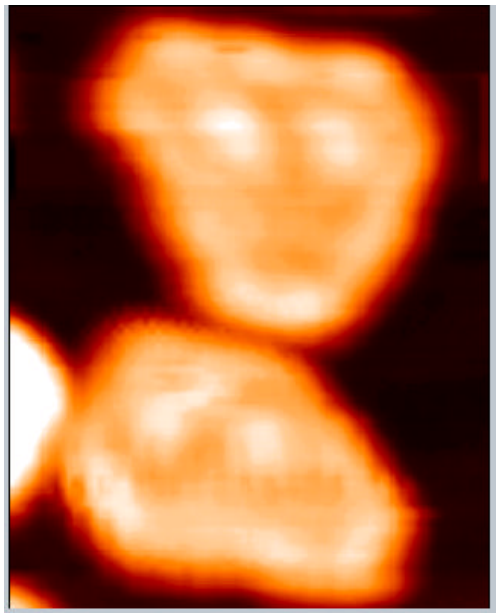
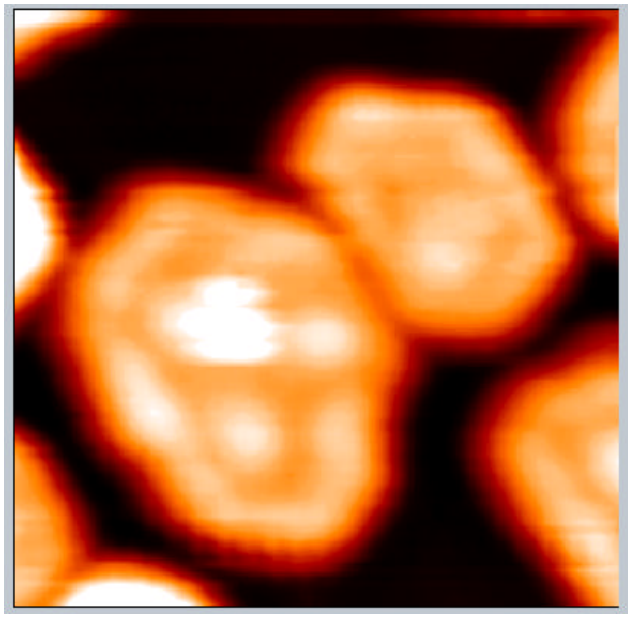
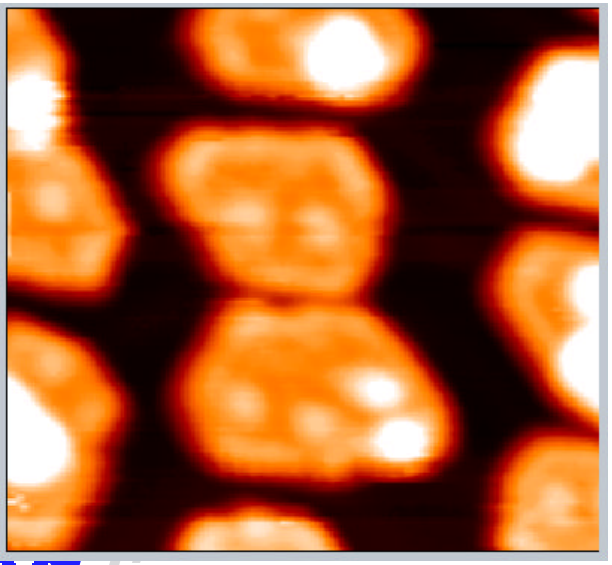
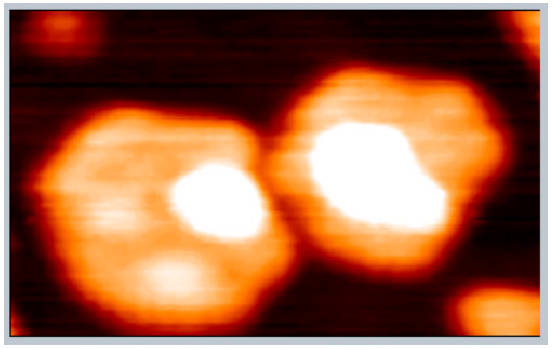
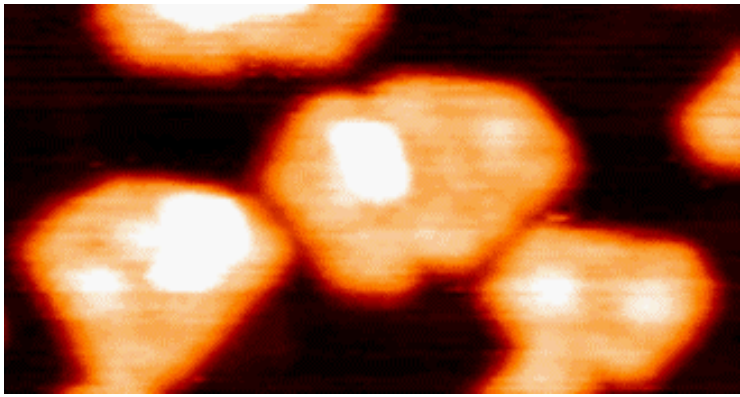


WHY : expanded area attracts Au atoms, not Co atoms

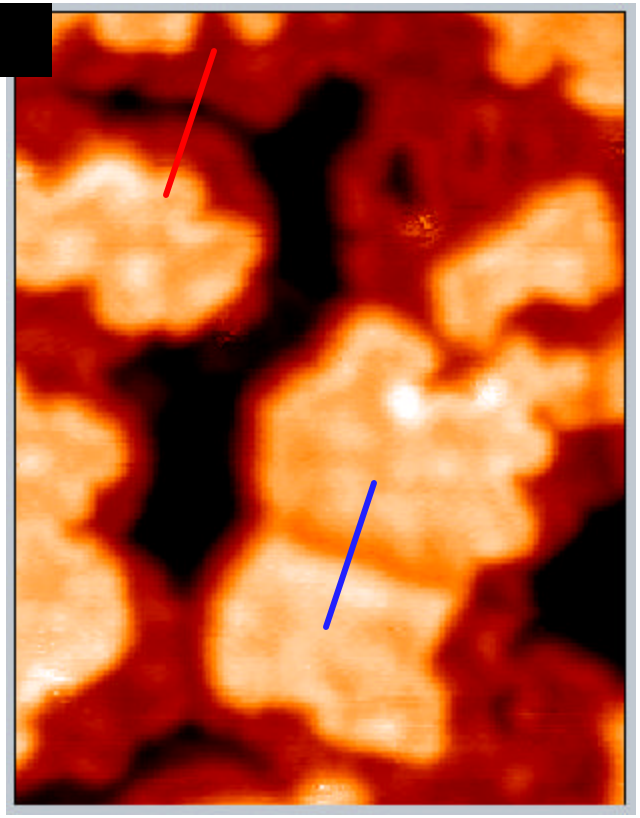
(chemical potential)

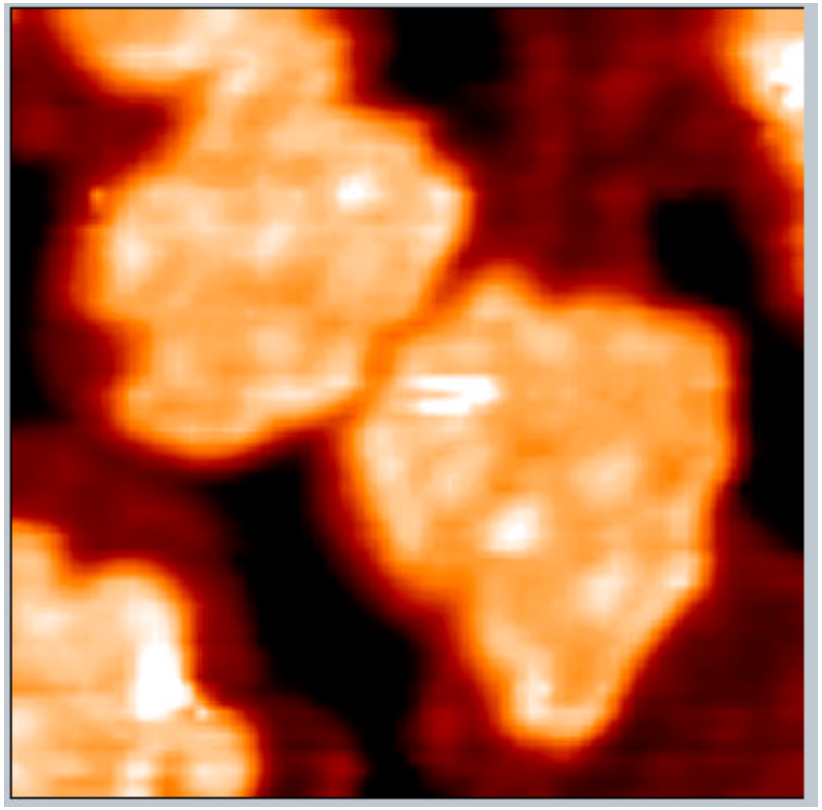
CONSEQUENCE : stabilizes strain modulation
(also reduces the total elastic energy)

1.1 AL Co / AU(111)

4 AL Co / AU(111)





tan = 2Å/nm tan = 1.3Å/nm

Depth = 2Å Depth = 1Å

- **Au up-diffusion ?**
- **Stacking faults, grain boundaries?**

Annealing

M. Speckmann et al., Phys. Rev. Lett. 75, 2035 (1995)

System: Co(5AL)/Au(111)

Experiment: Annealing (240°C, 10-15min)

Evidence: Auger, Magnetic anisotropy

➥ **Diffusion channels ?**

'Intermixing'

N. Marsot, Surf.Sci. 377, 225 (1997)

System: Co(≥2AL)/Au(111)

Experiment: Growth

Evidence: Au Core-level spectroscopy

➥ **Au up-diffusion**

Lifting the Au(111) reconstruction

N. Marsot, unpublished

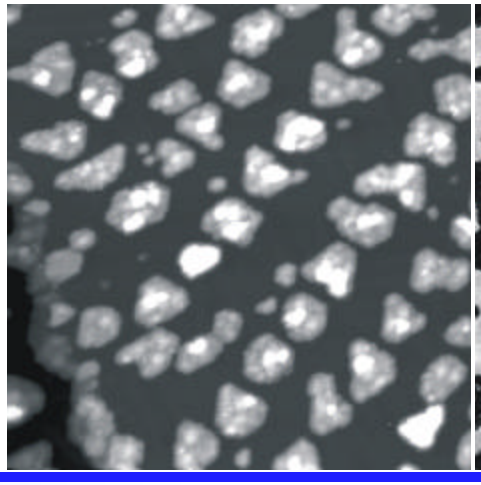
System: Co(<2AL)/Au(111)

Experiment: Growth

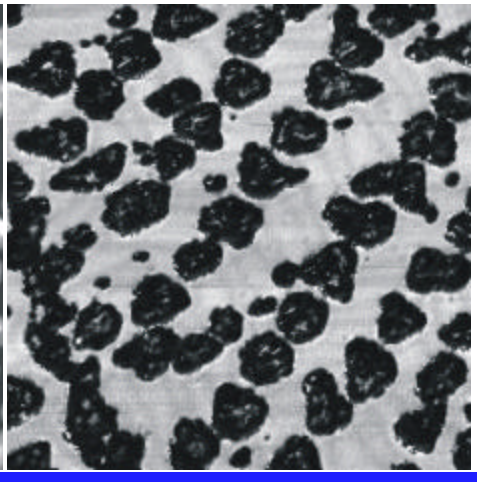
Evidence: SXRD

➥ **Where do 4% Au atoms go ? (not as 3rd layer !)**

Topo



Spectro



Conclusions

- « Super-diffraction » in-situ sur 0.05MC: études ‘cristallographiques’
- Complémentarité au STM: déformations, percolation, etc.
- Rappel: interface peut rester rugueuse même si surface libre se lisse

Perspectives

- Calculs de relaxation élastique (H. Bulou et al.)
- Grand nombre d’ordres de diffraction
- Couplage à la diffraction atomique
- Etude magnétique ?

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IPCMS (CNRS/ULP/ECPM), Strasbourg

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