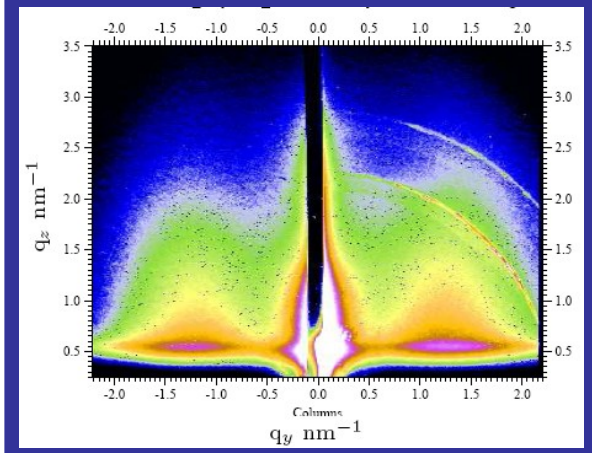
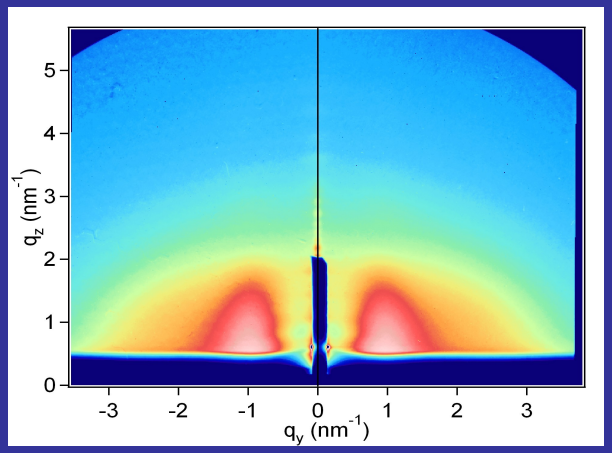
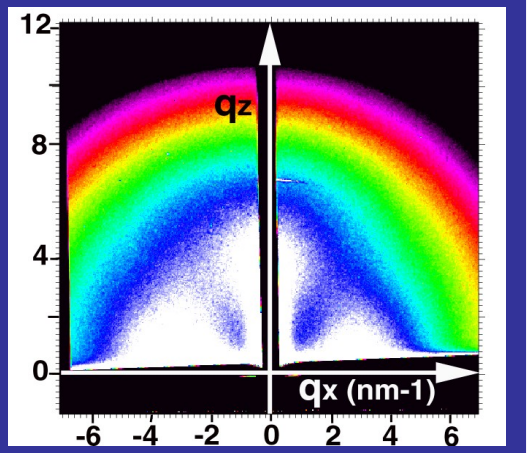
Grazing Incidence Small Angle X-ray Scattering (GISAXS) at the CRG-D2AM beamline







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An advanced powerful technique to investigate nano-objects using the high brilliance and tuneability of SR

WHY?

- Statistical information on the size, shape, orientation and spatial organization of nano-objects (1-100nm) distributed in 2D or 3D.

- Grazing incidence ($\alpha_i \sim \alpha_c$): surface sensitive (enhancement of layer scattering with respect to substrate scattering)

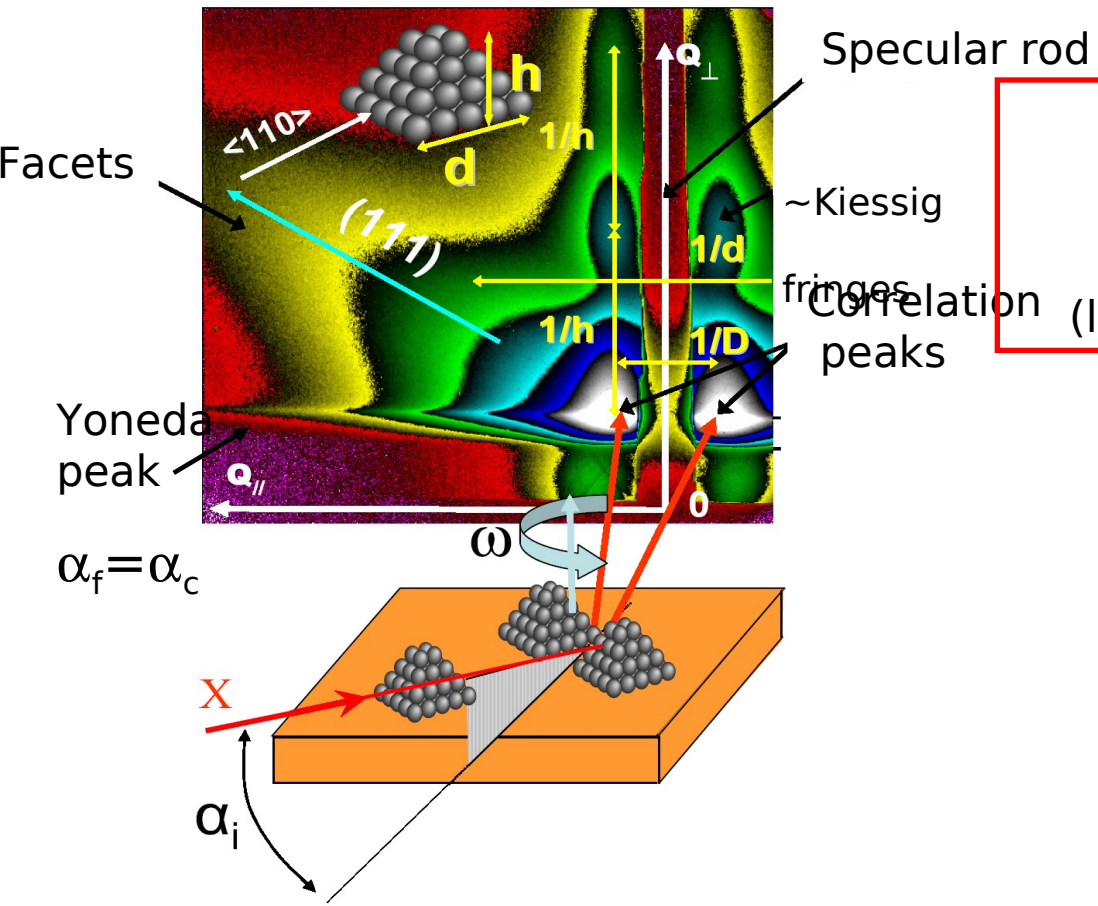
- Element sensitive using anomalous effect

- Applicable to various systems:
  - Nanostructures supported on substrates
  - Clusters, gaz bubbles, pores embedded in a matrix near the surface

- Appropriate also for in-situ investigations: growing particles in UHV chambers, sintering of particles induced by gas or shape evolution of metal particles during catalytic reaction.

Principle of GISAXS

Image of the reciprocal space around the intense specular rod hidden by a beamstop



$$I(q) \approx \langle |F(q)|^2 \rangle \times S(q)$$

(local monodisperse approximation)

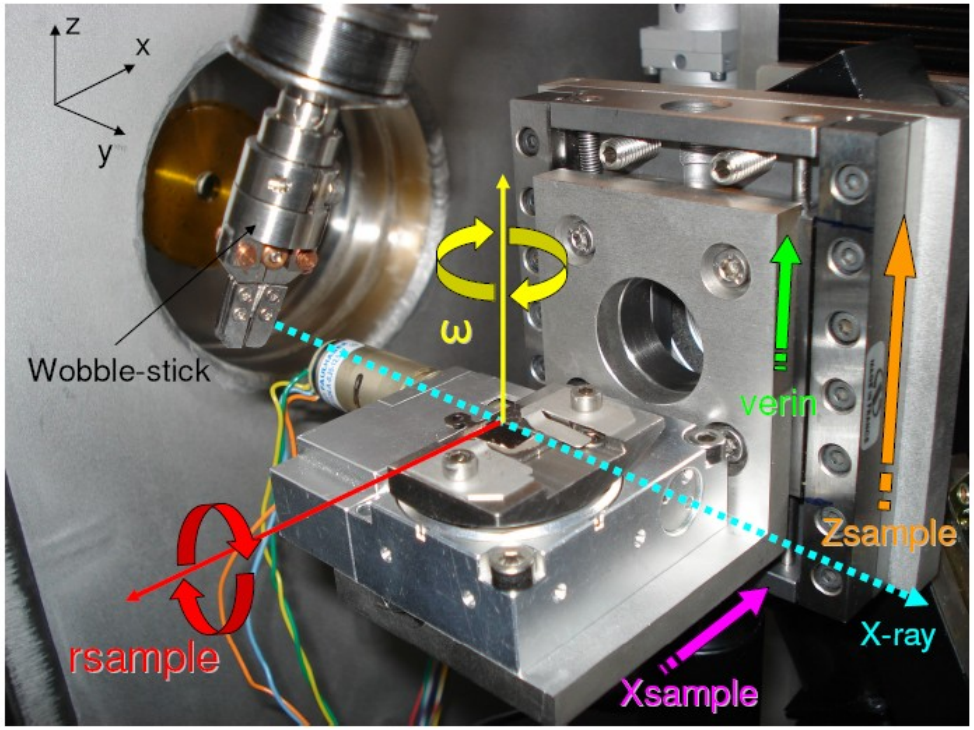
<u>Form factor F(q):</u>
shape, orientation,
size distribution (R,H)

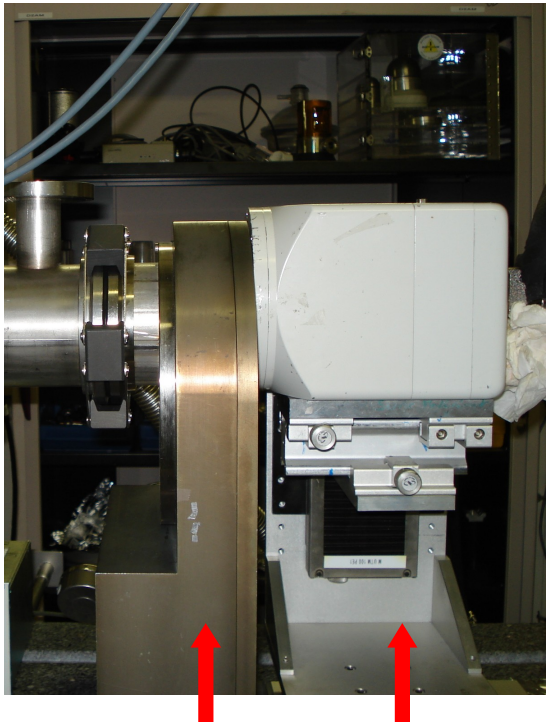
<u>Interference function S(q):</u>
- separation distance:D

Example: Ag(2nm)/MgO(001) at 500K

GISAXS set-up on BM02

e q-range:
m^{-1}





Beam-stop chamber

CCD camera

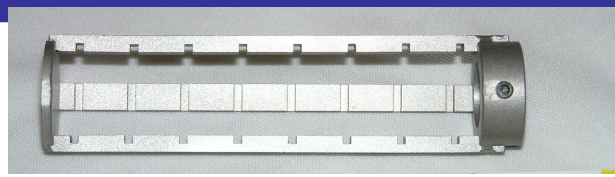
Antiscattering slits

Sample chamber (10^{-6}torr)

Monitor

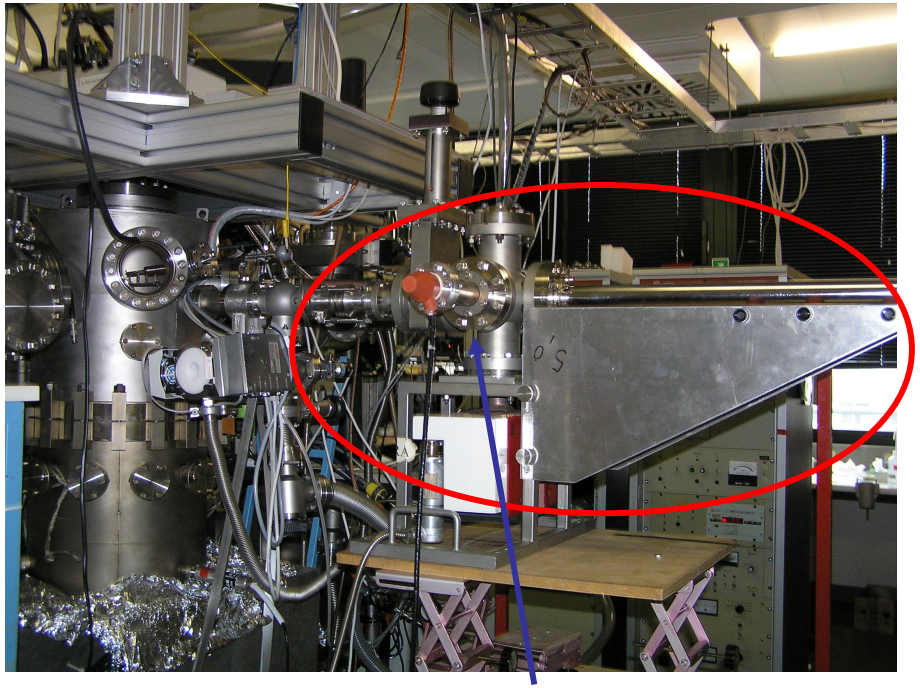
D_{SD} variable from 400 to 1200 mm

Sample transfer from UHV preparation chamber to GISAXS vessel using a vacuum suitcase

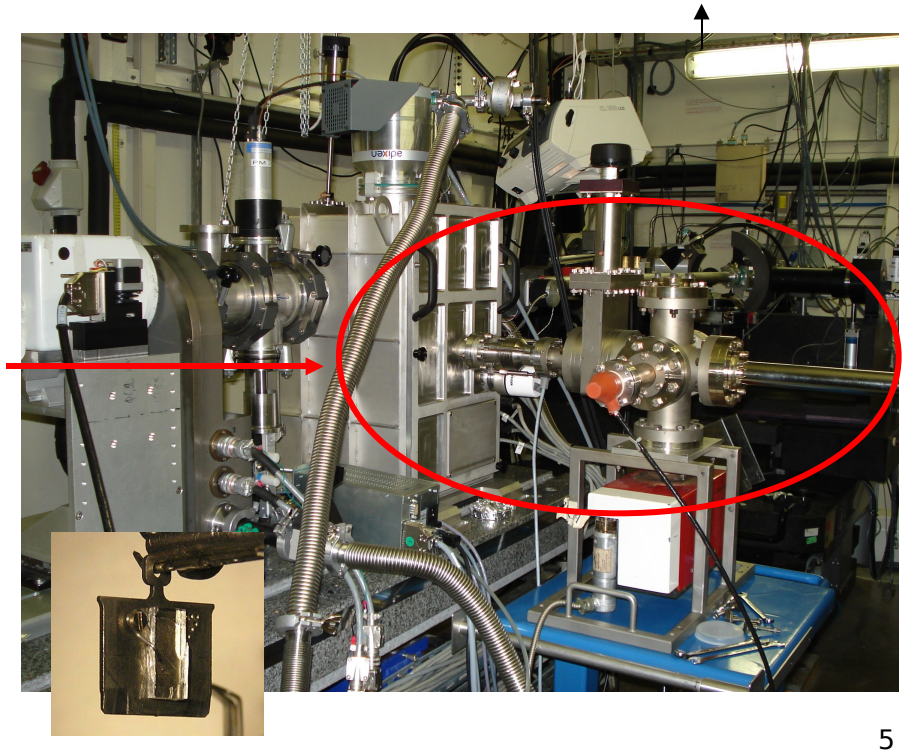


Main advantage:

Measurements on a series of sensitive samples without air exposure.



10^{-8} -10^{-10} mbar



1

Magnetic alloy nanostructures self-assembled on low energy surfaces: NaCl(001) and WSe_2(0001)
(future high density magnetic recording media)

Aims of GISAXS measurements:

- influence of the lattice symmetry of substrate on the size and shape of nanostructures

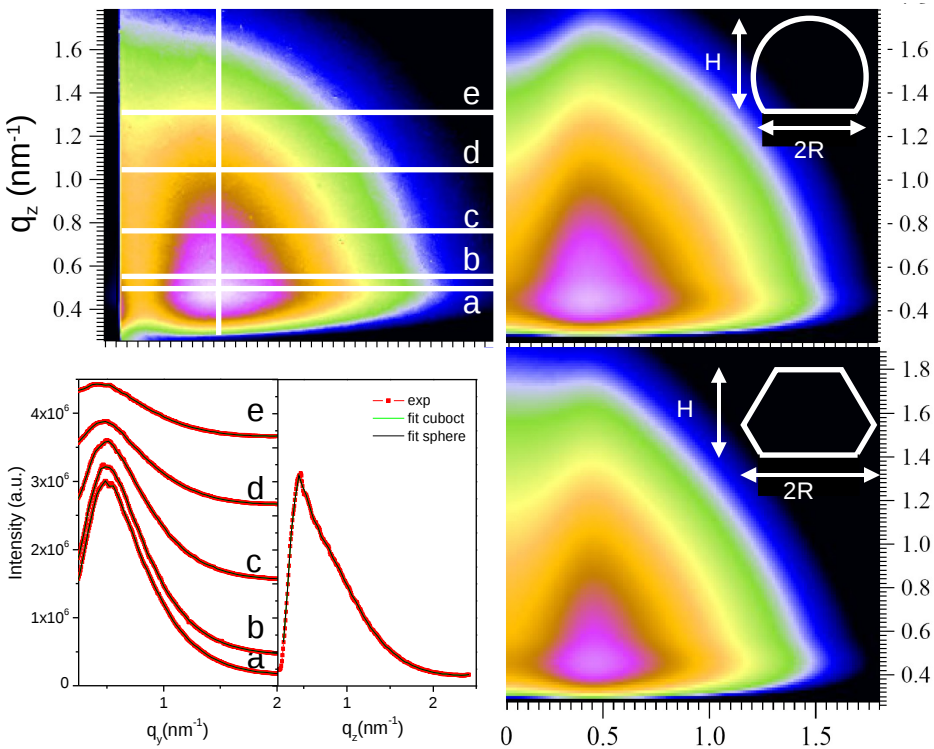
- growth mechanism for continuous deposition of metal atoms

$CoPt_3$ nanostructures on NaCl(001) (SIMaP, Uni Roma Tre & Chemnitz, Néel Institute)

0.5 nm $CoPt_3$ Tg=520K

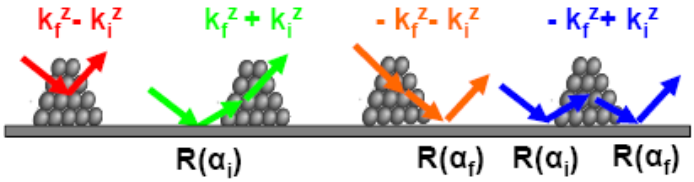
Experimental (α_i=0.4°)

Simulation with IsGISAXS[1]



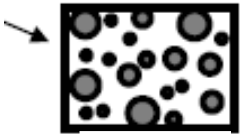
Approximations:

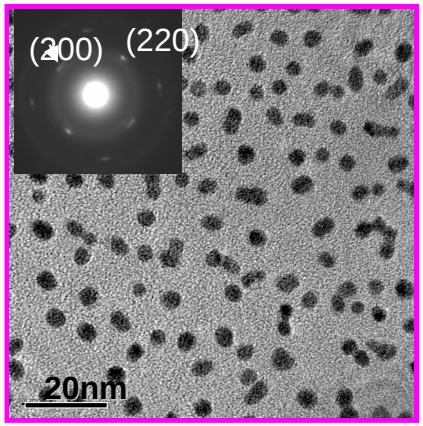
DWBA

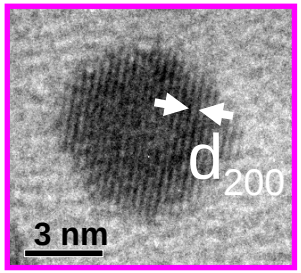


SSCA[2]

$D=D_0+\kappa(\Delta R_i+\Delta R_j)$







HRTEM image

2R=4nm H=3.1nm, H/2R=0.8

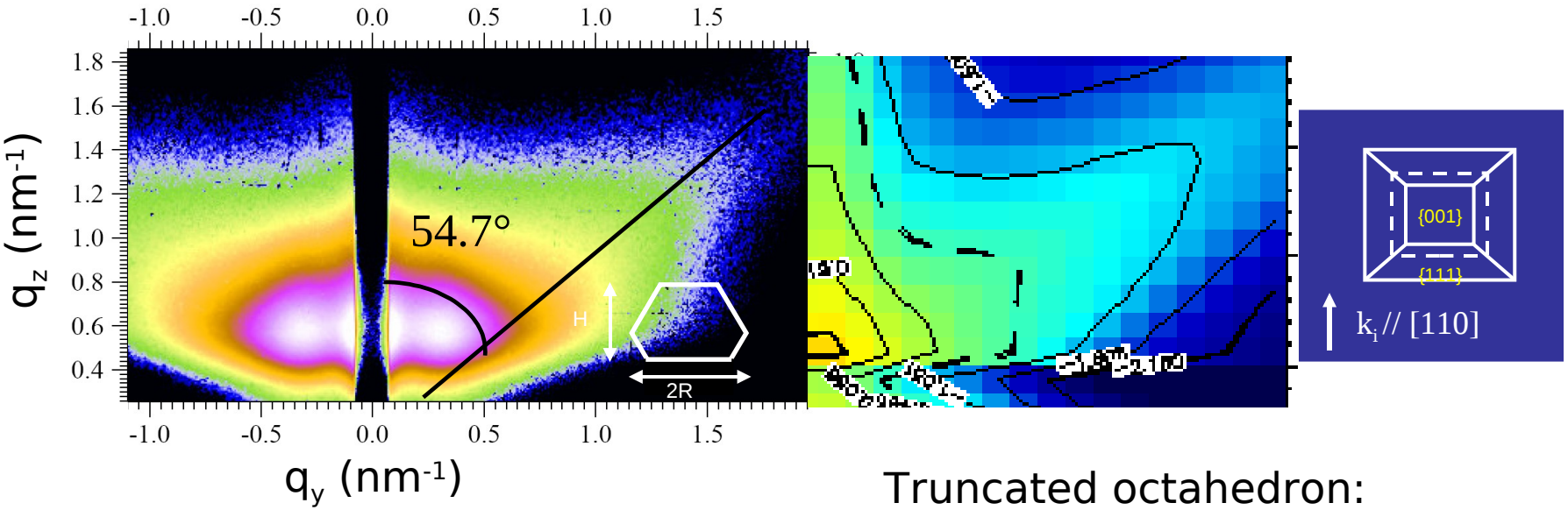
Average volume of particles= 26nm^3

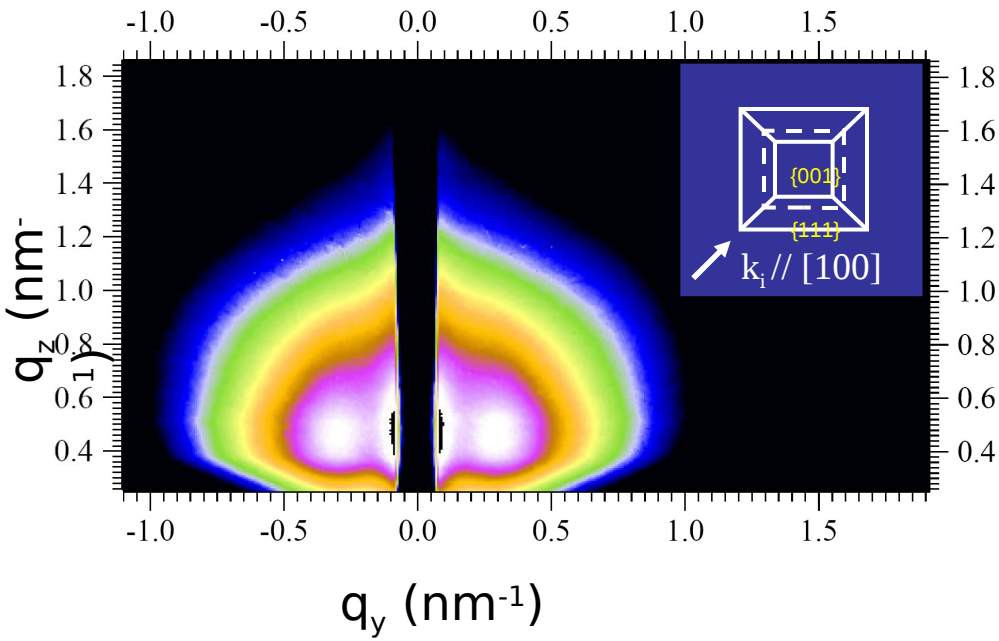
Separation distance: D=8.2nm

[1] *R. Lazzari J. Appl. Cryst. (2002)* ***35****, 406*

[2] *R. Lazzari et al, Phys. Rev. B (2007) 76, 12541*

3nm $CoPt_3$ @570K on NaCl(001)



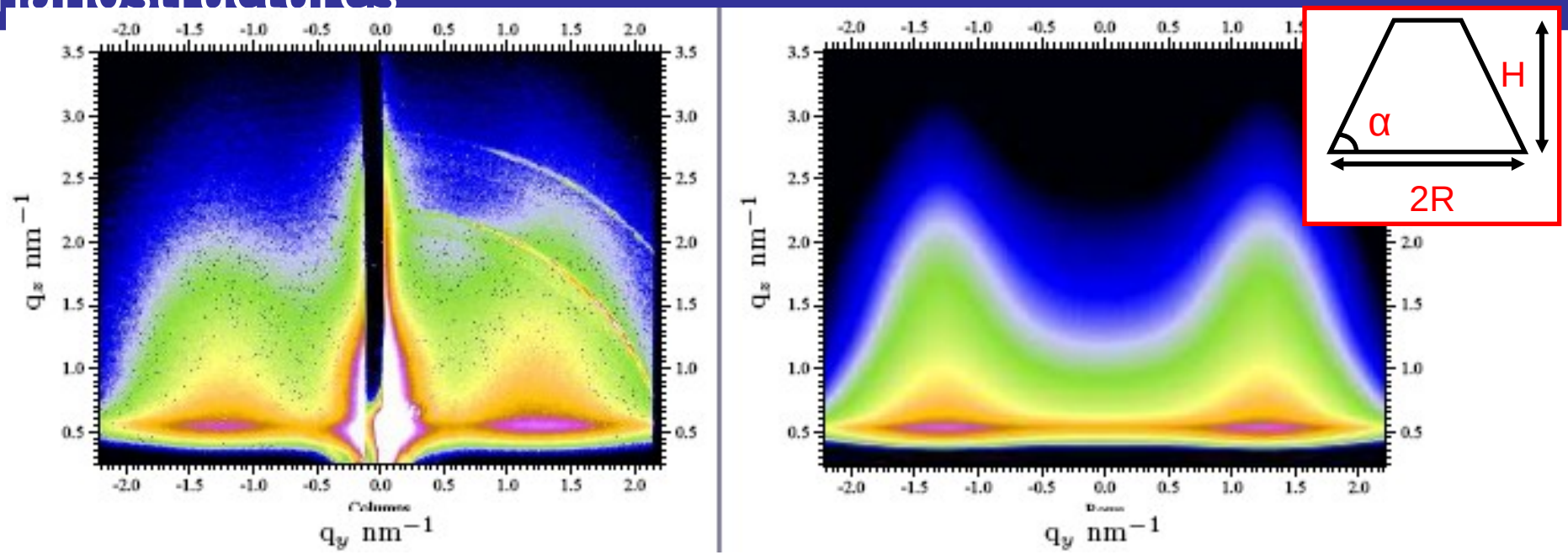


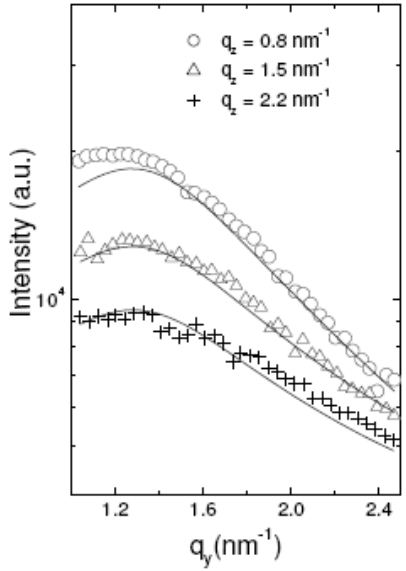
Truncated octahedron:

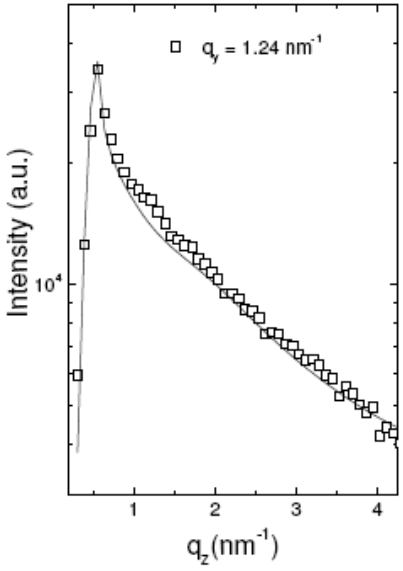
H=8nm, 2R=10nm vol=330 nm^3

For epitaxial and large (10nm) particles GISAXS sensitive to the nanostructure shape

CoPt(1nm) on WSe_2 at RT: dense assembly of nanostructures





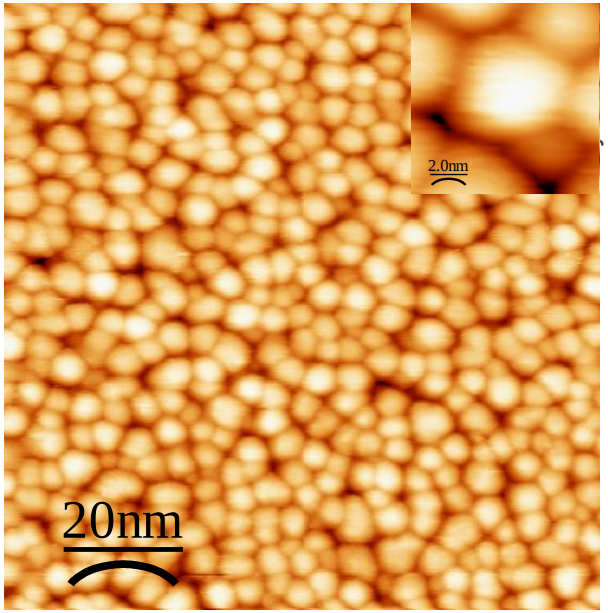


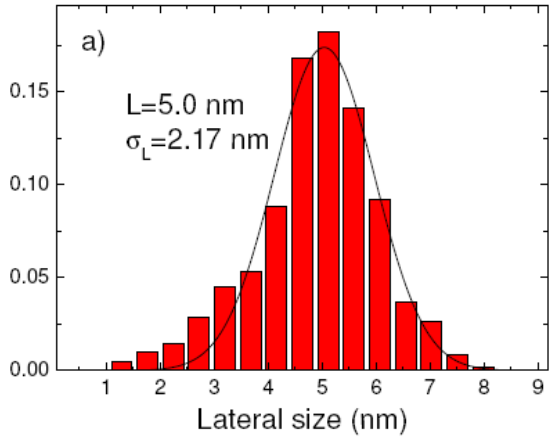
2R=2nm σ_R=1nm
H=0.7nm σ_H=0.8 α=60°
VCoPt=1.5 nm^3 H/2R= 0.35 D=3.2nm => d=0.11part/nm^2

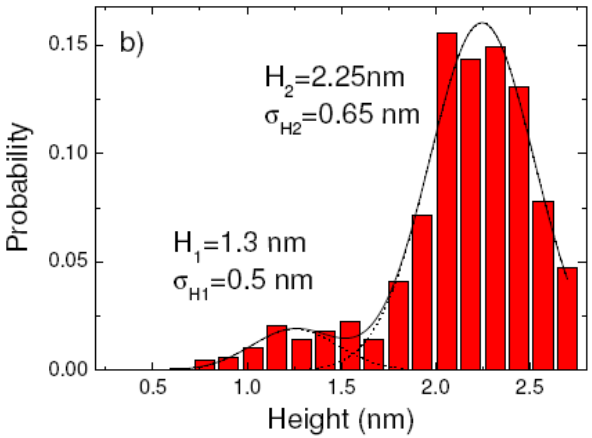
thickness=0.15nm << 1nm!

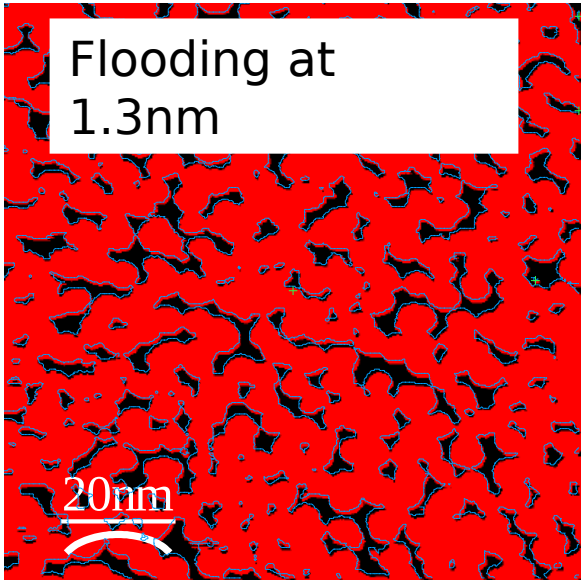
PHD thesis of Fabiola LISCIO (2009)

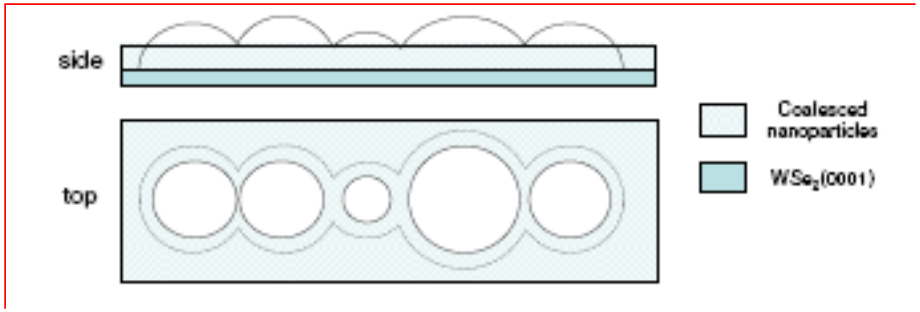
Combined GISAXS with STM measurements : CoPt (1nm) RT









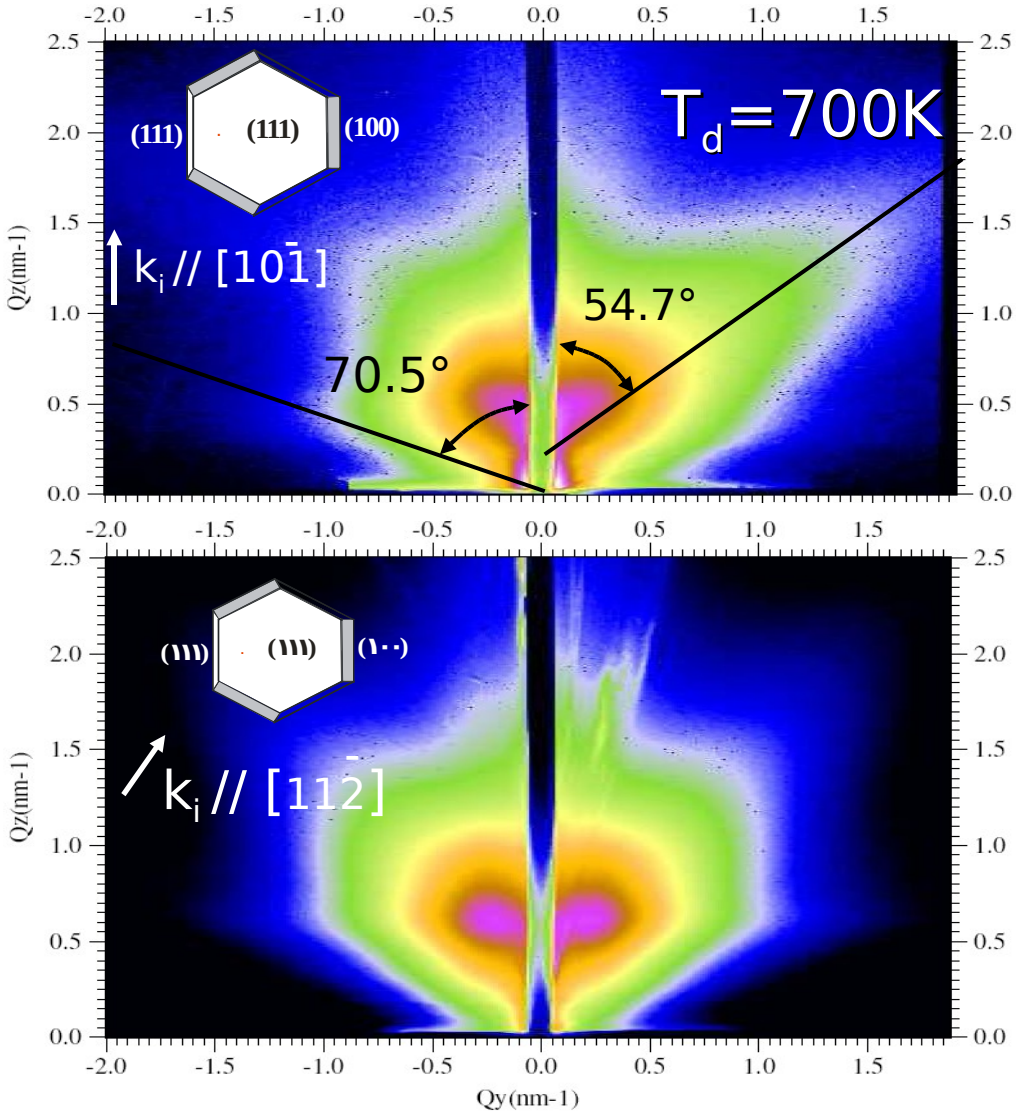


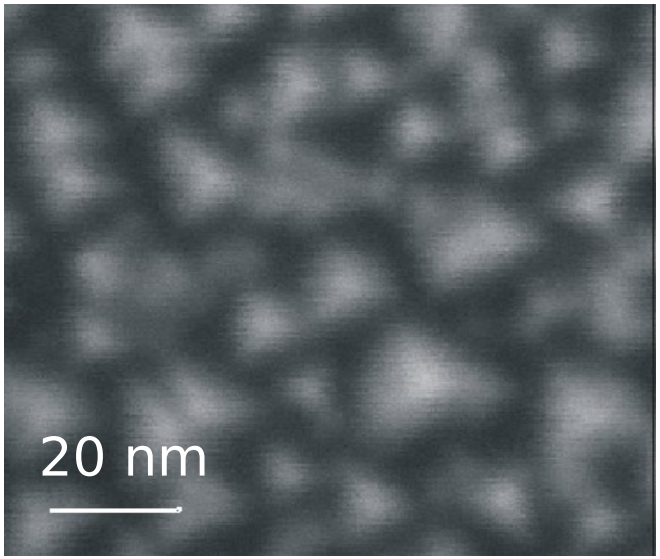
Only the upper parts of nanostructures contribute

to GISAXS pattern

=> GISAXS well suited for studying coalescence effects

GISAXS patterns for 3nm deposit of $CoPt_3$ on $WSe_2(0001)$





Triangular particles observed by Field emission-SEM image,

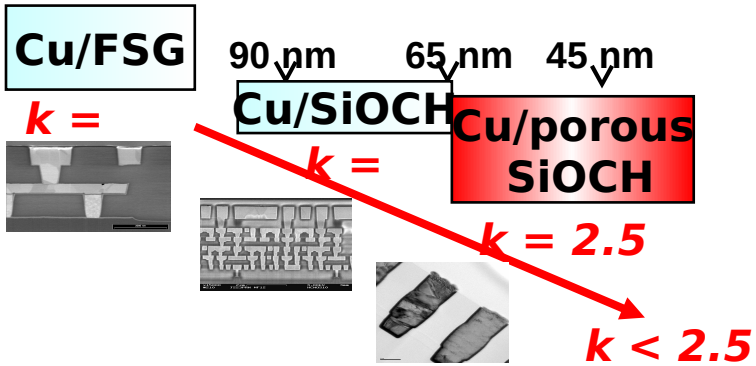
Low GISAXS sensitivity to the steep {111} side-wall facets

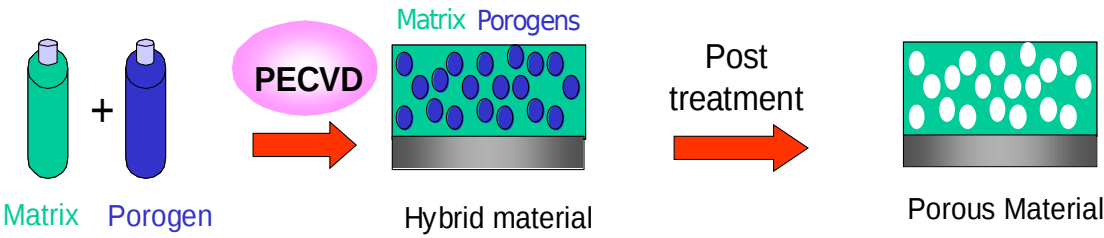
- L=13nm, H=4.5nm
- Aspect ratio of 0.35 << 0.8 value on NaCl

2

GISAXS study of size and organization of pores in low k SiOCH dielectrics prepared on Si wafers

Porous SiOCH dielectrics used in advanced microelectronic interconnections *(LETI/CEA Grenoble, SIMaP)*





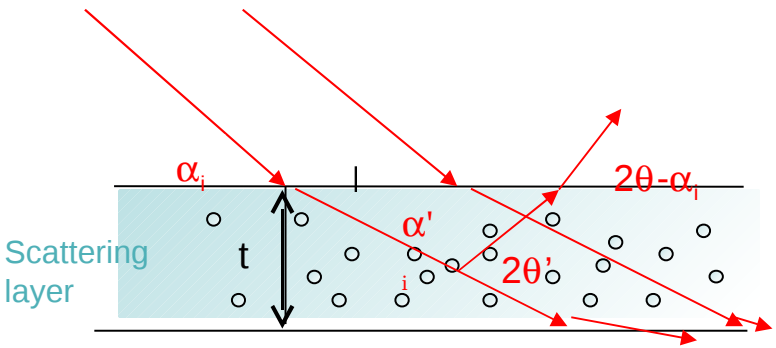
1) Blend of a hybrid material (SiOCH skeleton) with an organic precursor as porogen by spin coating or PECVD
2) Thermal treatment (~400°C,assisted by UV or e-beam):
- Elimination of organic molecule (pores-> low k),
- Improvement of mechanical resistance with strong Si-O-Si bonds

Quantitative measurements of porosity since

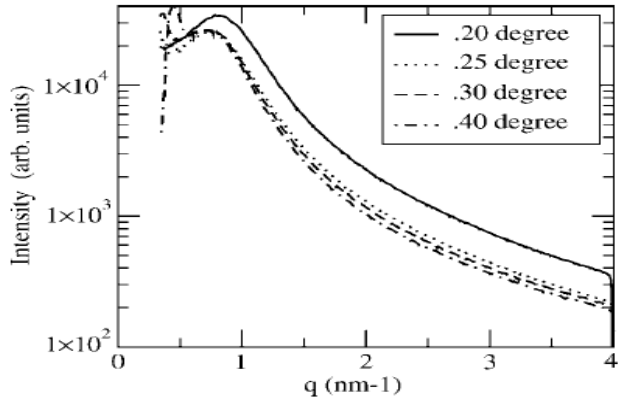
sample length (40-80mm)> footprint (35mm α_i=0.25°)

J-P. Simon, V. Jousseaume, G. Rolland, J. Appl. Cryst 40 (2007) s363

GISAXS patterns for different low k dielectrics



Analysis of GISAXS patterns using Babonneau's program with refraction reflection-transmission and absorption corrections

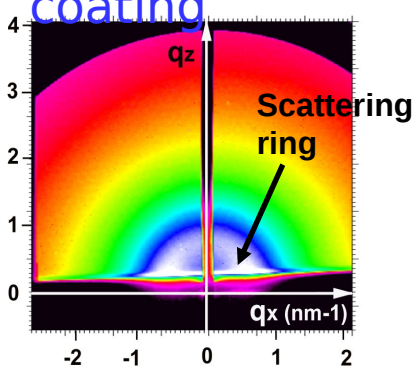


Intensities divided by the probed volume

$\alpha_i > \alpha_c$ (Si) $> \alpha_c$ (SiOCH)

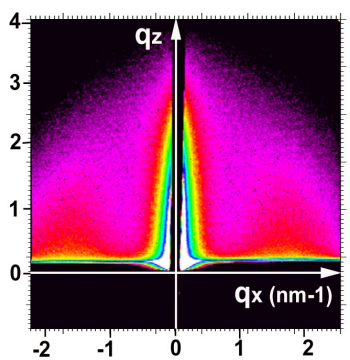
at 8keV, α_c (Si) =0.24°

Spin coating



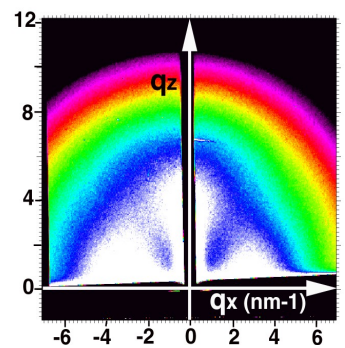
Isotropic scattering Ø=4nm, d=10nm

PECVD1 (e-beam assisted)



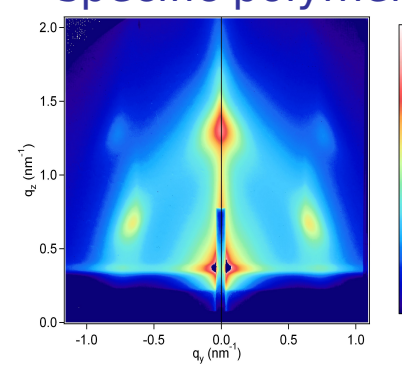
Lateral order d=3.5nm

PECVD2



Ø=0.6nm, vertical and lateral orders (d=1.75nm)

Spin coating using specific polymer



Pore array

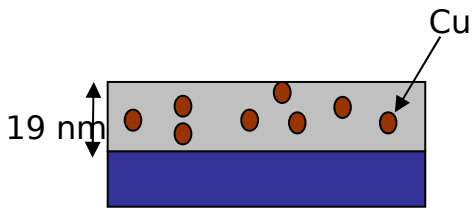
3

Anomalous GISAXS of carbon-encapsulated Au and Cu clusters.

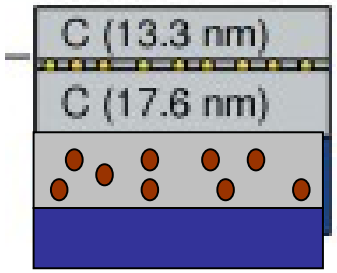
The choice of this system is related to previous GISAXS studies performed in nanocermets giving rise to surface plasmon resonance phenomenon

AGISAXS study of carbon-encapsulated Au & Cu clusters (PHYMAT- Poitiers, SIMaP)

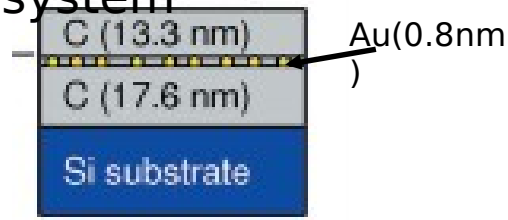
C/Cu binary system

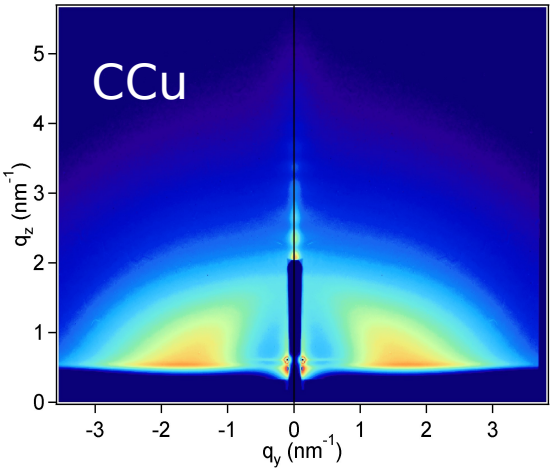


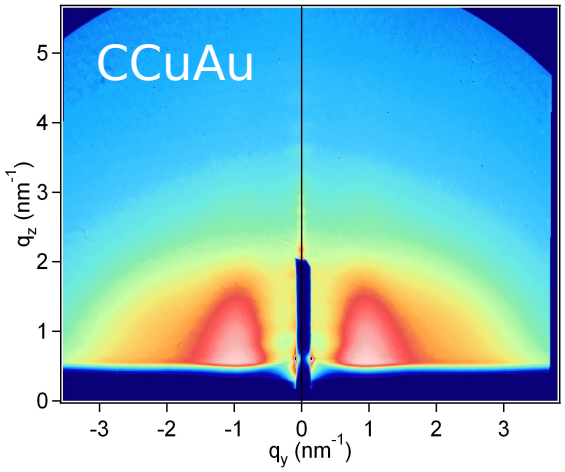
C/Au/C-Cu ternary system

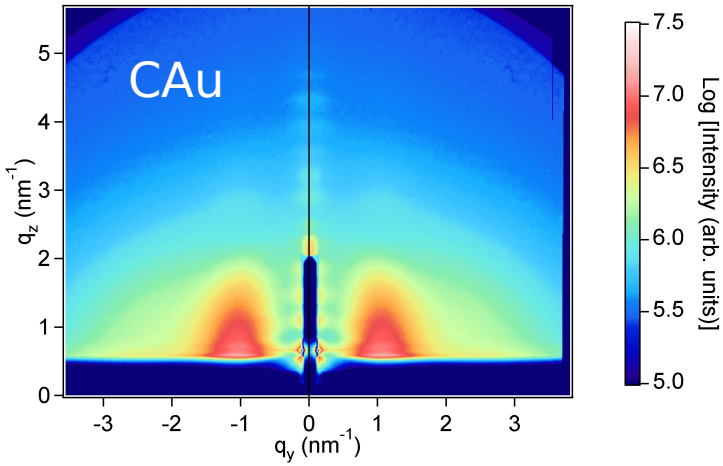


C/Au binary system









Scattering ring => isotropic distribution

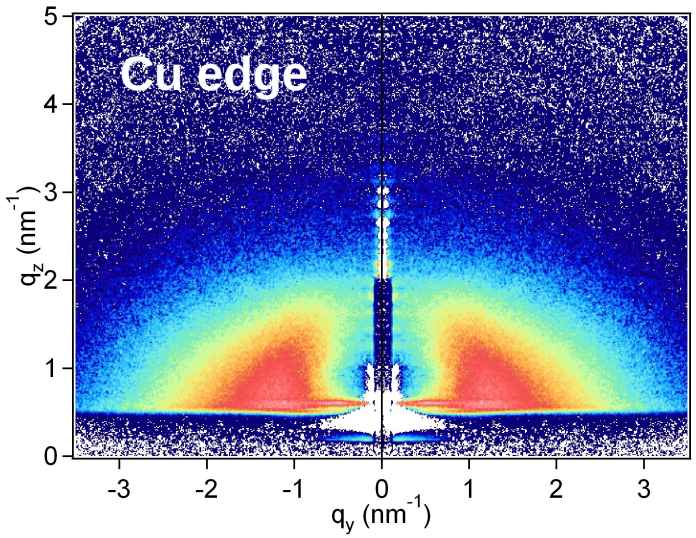
Interference peaks => lateral order

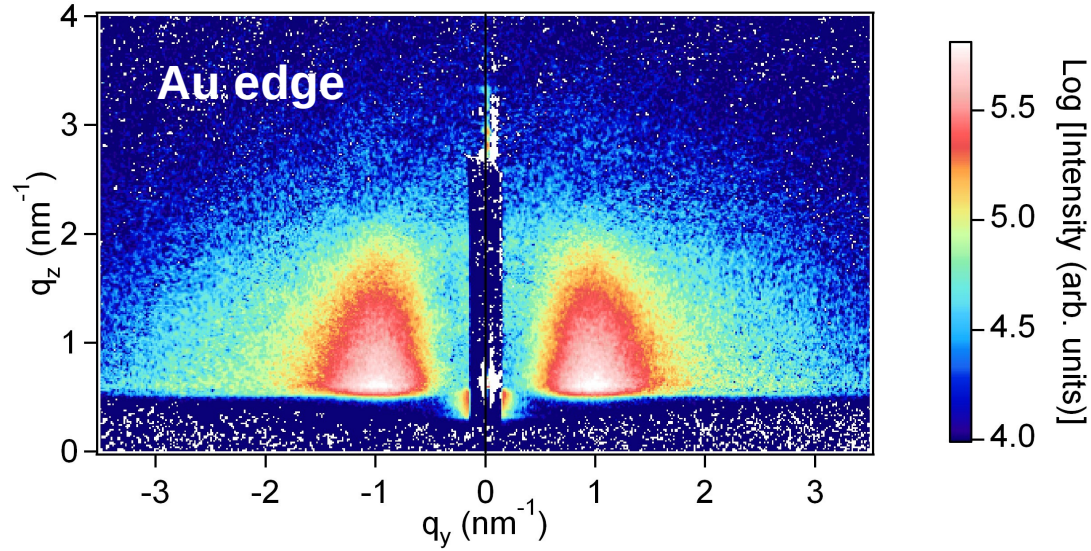
l=1.5nm h=2.7nm

l=3.4nm , h=2nm

(J.P. Simon, D. Babonneau, M. Drouet , O. Lyon, J. Appl. Cryst. 42 (2009) 312)

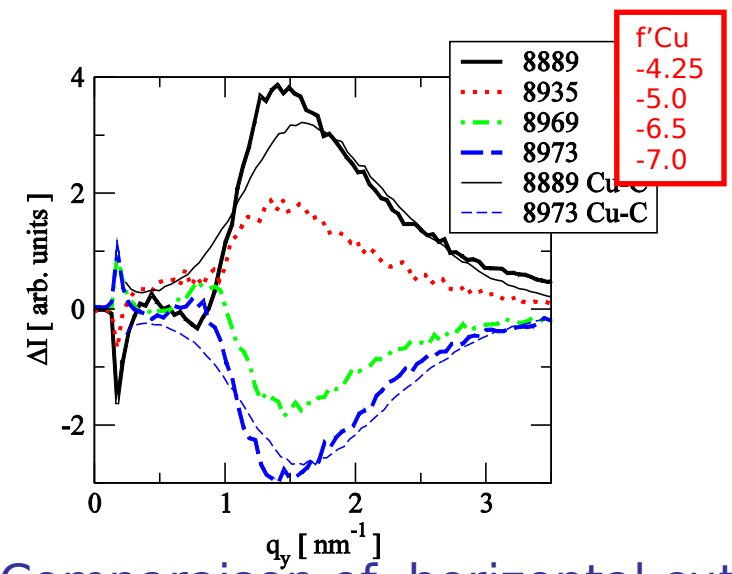
Difference method: very efficient!

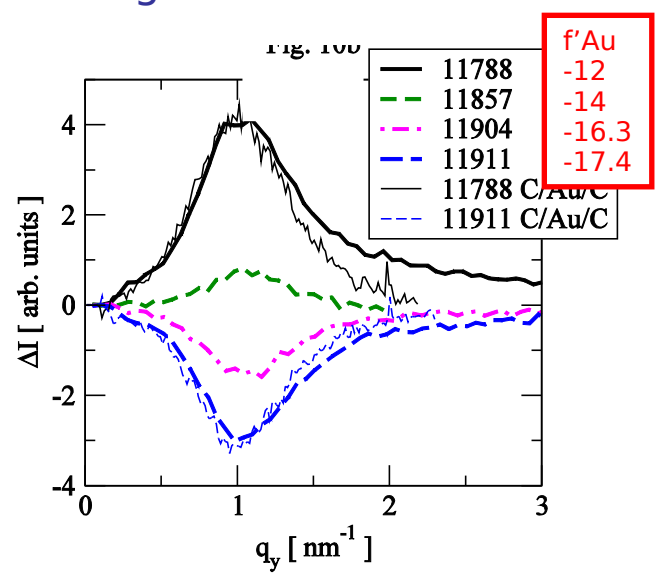




Signal 8973eV – mean signal near Cu-edge

Signal 11911eV – mean signal near Au-edge





Comparaison of horizontal cuts (q_z=0.7nm^{-1}) between ternary & binary systems

Summary & Perspectives

- GISAXS camera : user-friendly, variable sample-detector distance for the characterization of nano-objects with sizes 1-100nm.
- Temperature-dependent measurements under vacuum of 10^{-6}Torr.
- Characterization of sensitive samples introduced in the sample vessel from a vacuum suitcase.
- Taking advantage of the anomalous technique => study of core-shell systems but requires large samples for accurate normalization.