PIER Graduate Week 2017

X-ray Diffraction from Nanosystems

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X-ray Physics and Nanoscience
Deutsches Elektronensynchrotron (DESY)

HELMHOLTZ ASSOCIATION

Outline

1. Introduction: Solid state physics and nanoscience at DESY

2. Synchrotron radiation based methods for the characterization of materials in reduced dimensions (thin films, surfaces, nanopartices) including examples of:

   X-ray Reflectivity (XRR)
   Grazing incidence X-ray Diffraction (GIXRD)
   Surface X-ray Diffraction (SXRD)
   Grazing Incidence Small Angle X-ray Scattering (GISAXS)
   Coherent Diffraction Imaging (CDI)

Solid State Physics and Nanoscience @ DESY

Scattering with coherent X-rays (G. Grübel)	**Complex liquids and glasses** **Ultrafast magnetization dynamics**
X-ray Physics and Nanoscience (A. Stierle)	**Catalytic Reactions on Nanomaterials** **Nanoscale Phenomena** **Oxide Surfaces and Interfaces**
X-ray Crystallography and Imaging (E. Weckert, I. Vartaniants)	**Coherent diffraction from individual semiconductor nanostructures**
Magnetism and Coherent Phenomena (R. Röhlsberger)	**Magnetism and magnetic dynamics** **Fundamentals of resonant light-matter interaction at x-ray energies**
X-ray Nanoscience and X-ray Optics (C. Schroer)	**X-ray imaging: ptychography** **Hard X-ray microscopy** **X-Ray tomography**

Correlation structure / composition with functionality
Watch structure formation
In-situ x-ray diffraction experiments

AND @ University of Hamburg

Centre for Hybrid Nanostructures (CHyN)

Semiconductor Physics

(R. Blick)

Epitaxial Nanostructures

(W. Hansen)

Surface Physics

(H.P. Oepen)

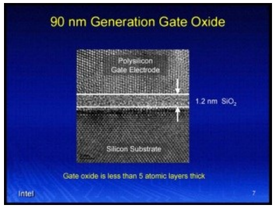
Optics

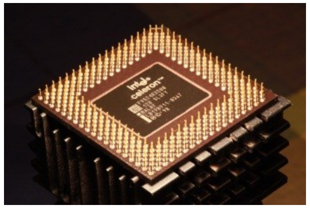
(M. Ruebhausen)

Introduction

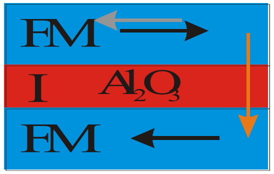
Today's nanotechnology is based on surfaces and interfaces and materials in reduced dimensions

Semiconductor integrated circuits

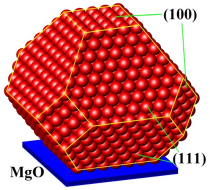




Magnetic sensors (GMR, TMR)



Heterogeneous Catalysis

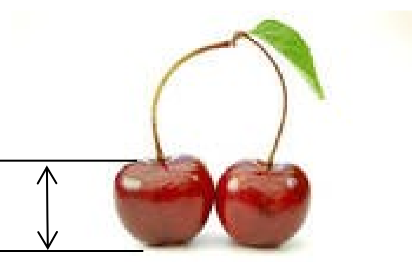


The Nanoworld

Greek νᾶνος (nanos): the dwarf

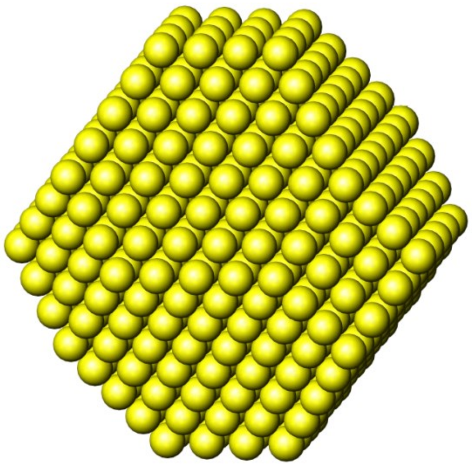
1 nm = 10^{-9} m is with respect to 1 m as

12 mm



12000 km

In the „Dwarf“ World the Rules are Changed



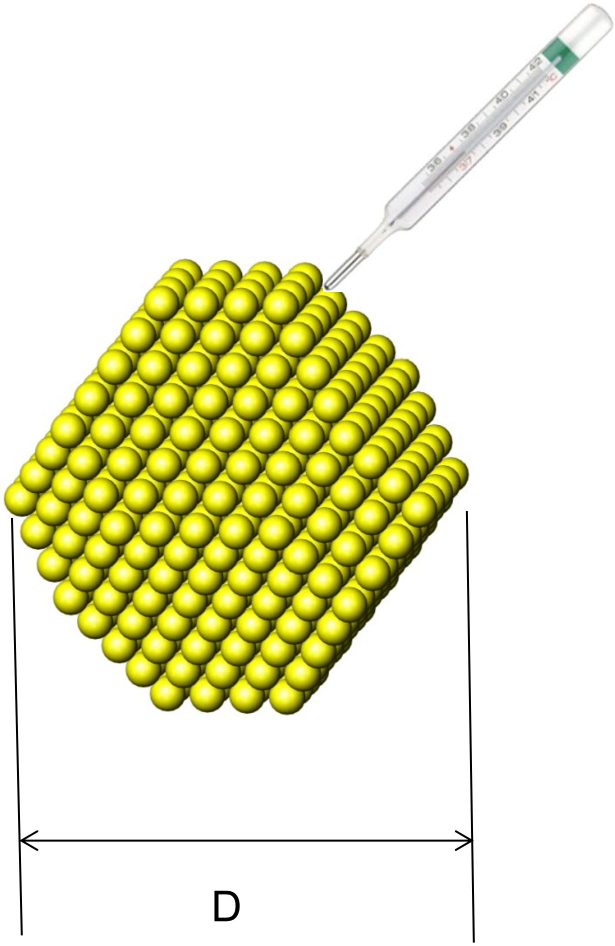
bulk material

Nanoparticle

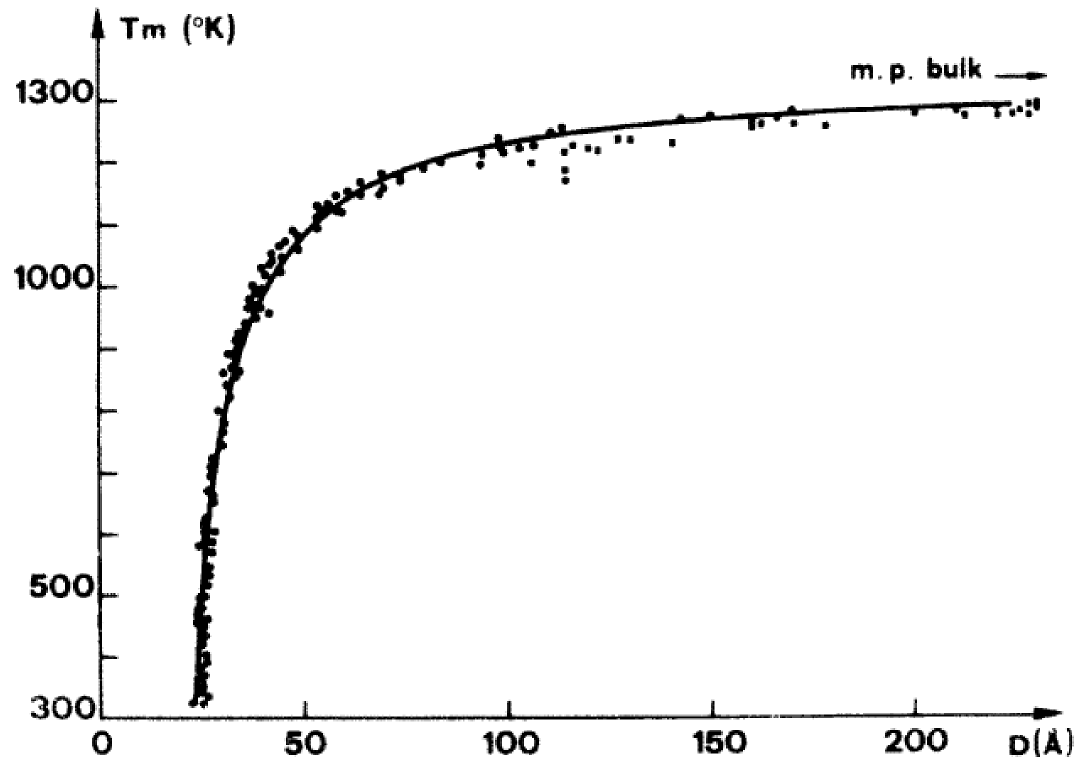
Physical und chemical properties of materials are changed in reduced dimensions

In the „Dwarf“ World the Rules are Changed

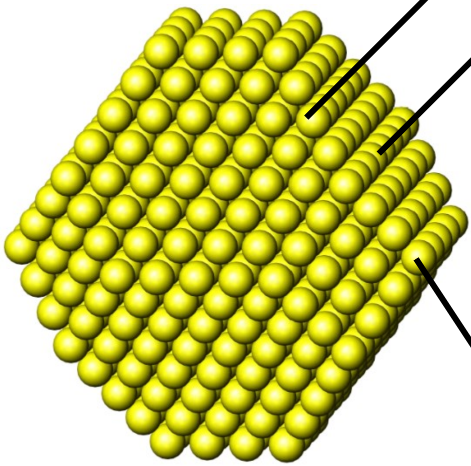
Example: Melting of Gold Nanoparticles



bulk: 1337 K (1064°C)



In the „Dwarf“ World the Rules are Changed



Atoms with reduced coordination:

1: on facets
2: at edges
3: at corners

Relation surface / volume no of atoms

$$\frac{N_O}{N_V} = \frac{3a}{D}$$

Typical Values for spherical particles

D = 3 nm: $N_S/N_V = 0.25$

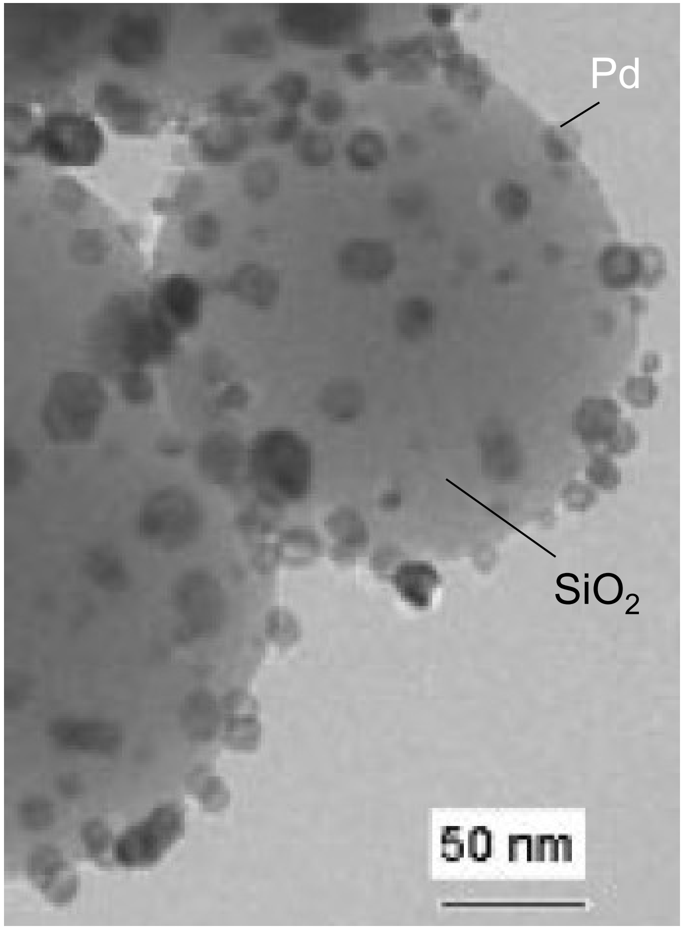
D = 2 nm: $N_S/N_V = 0.375$

D = 1 nm: $N_S/N_V = 0.75$

Reduced dimensions: quantum mechanical effects
box potential for electrons

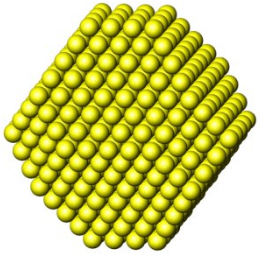
Real Catalysts: The Nanoworld Comes Into Play

„real“ catalyst



A. K. Datye, Topics in Catalysis 13, 131 (2000)

Only surface atoms are „active“



Goal: smaller particles stabilized on an oxide support

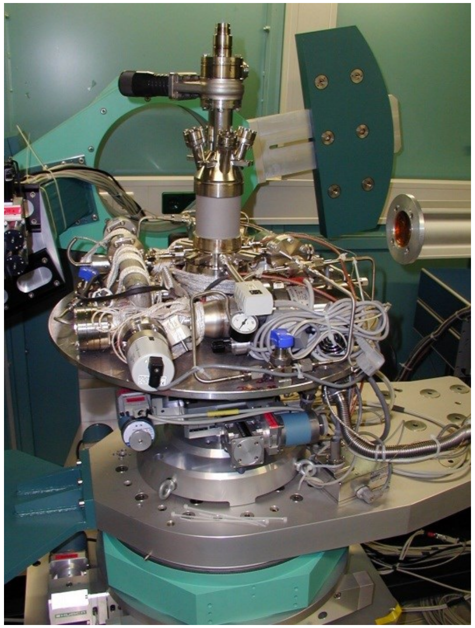
Surface area comparison for 1 kg Pd (expensive !)

Sphere diameter	No of spheres	Surface area
54 mm	1	0.01 m^2
1 mm	159337	0.5 m^2
1 μm	1.58×10^{14}	498 m^2
3 nm	5.85×10^{21}	1.67×10^5 m^2

23 football fields !

Introduction

Characterization on the atomic scale desired



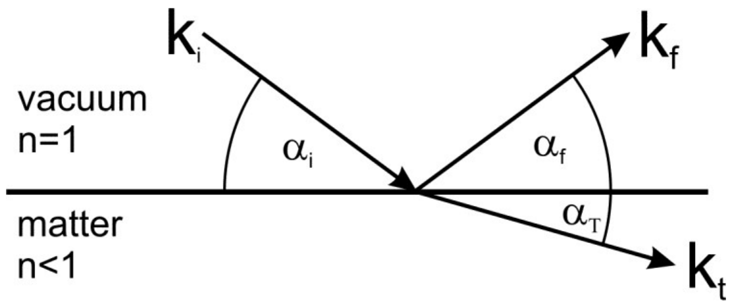
- x-rays: λ=0.1 – 0.01 nm
- non-destructive probe
- sample charging not important (oxides !)
- in-situ measurements (high T, high gas pressure, UHV, electro-magnetic fields, in contact with liquids, .) or during their formation (growth)
- probing statistical information, single objects with nanobeams.
- Quantitative data analysis (relatively) easy: very often single scattering.
- allow studying functionality and microscopic structure of the surface / interface / nano-object in the same experiment !

X-Ray Reflectivity

X-rays: electro-magnetic waves

Fulfill boundary conditions at interfaces

Maxwell's equations are applied
Snell's law:



$$\cos\alpha_i = n\cos\alpha_t$$

For x-rays: refractive index n<1 in matter

Consequence: total external reflection can occur !

X-Ray Reflectivity

$$n = 1 - \delta - i\beta$$

refractive index

$$\delta = \frac{\lambda^2 r_e \rho_e}{2\pi}$$

$$\beta = \frac{\lambda\mu}{4\pi}$$

r_e: classical electron radius (2.82×10^{-15} m)

ρ_e: total electron density

μ: linear mass absorption coefficient

$$\alpha_c = \sqrt{2\delta} = \lambda\sqrt{\frac{r_e \rho_e}{2\pi}}$$

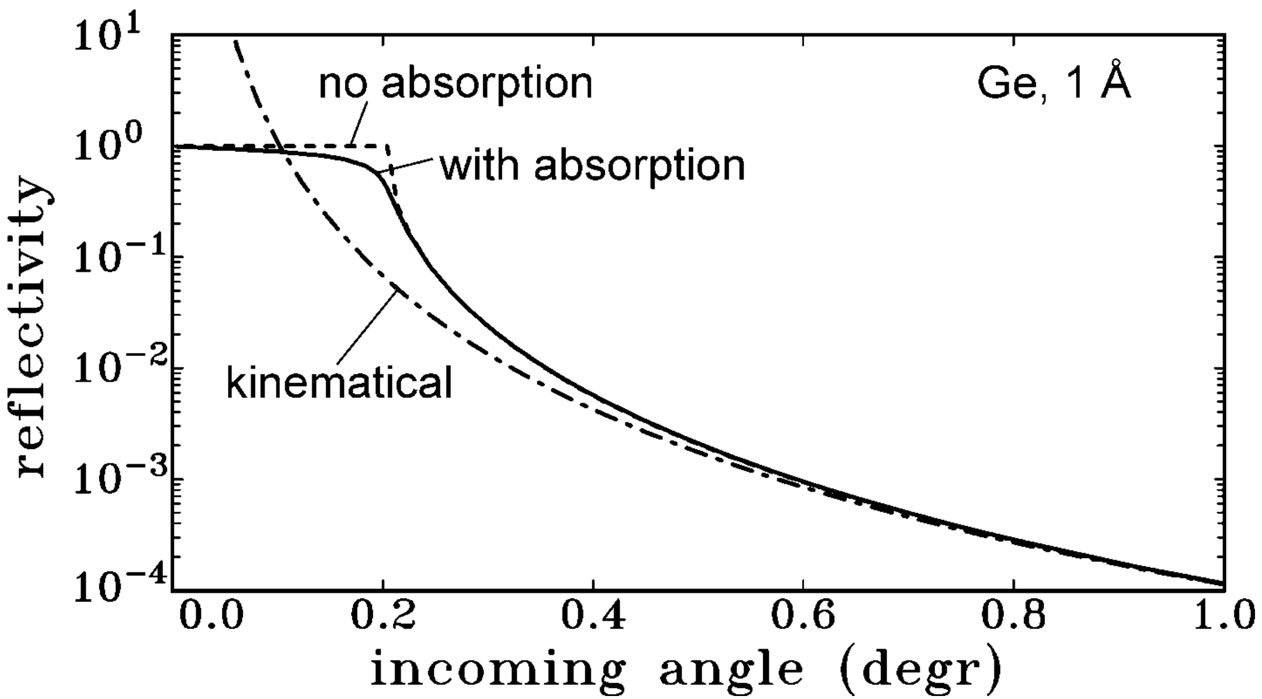
critical angle for total external reflection

X-Ray Reflectivity

Quantitative description:
Fresnel's formulas ($\sin(\alpha) \ll 1$)

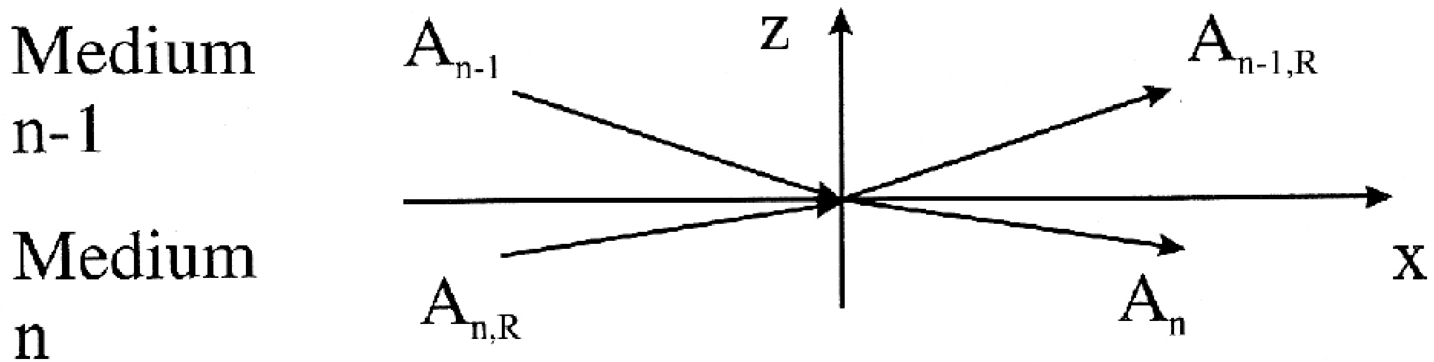
$$T_F = \left| \frac{2\alpha_i}{\alpha_i + \alpha_t} \right|^2 \quad R_F = \left| \frac{\alpha_i - \alpha_t}{\alpha_i + \alpha_t} \right|^2$$

Transmitted (reflected) amplitudes



X-Ray Reflectivity

More complicated case: layered structures



$$R_{n,n-1} = a_{n-1}^4 \frac{R_{n,n+1} + F_{n-1,n}}{R_{n,n+1} F_{n-1,n} + 1} \, .$$

$$F_{n-1,n} = \frac{f_{n-1} - f_n}{f_{n-1} + f_n} \, .$$

$$R_{n,n+1} = a_n^2 \frac{A_n^R}{A_n}$$

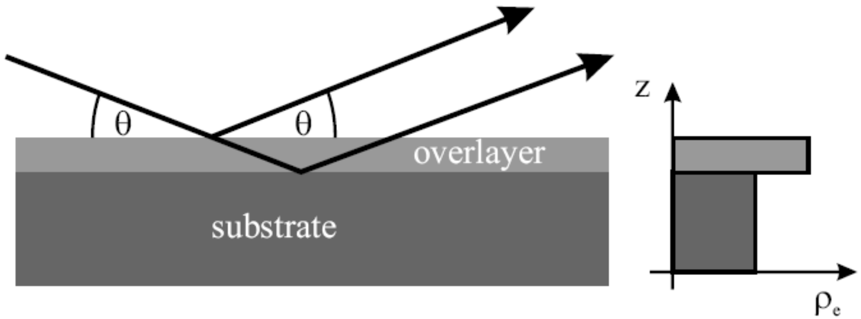
$$f_n = \sqrt{\sin^2 \alpha_i - 2\delta_n - 2i\beta_n} \; , \quad a_n = e^{-iQ_n \frac{d_n}{2}}$$

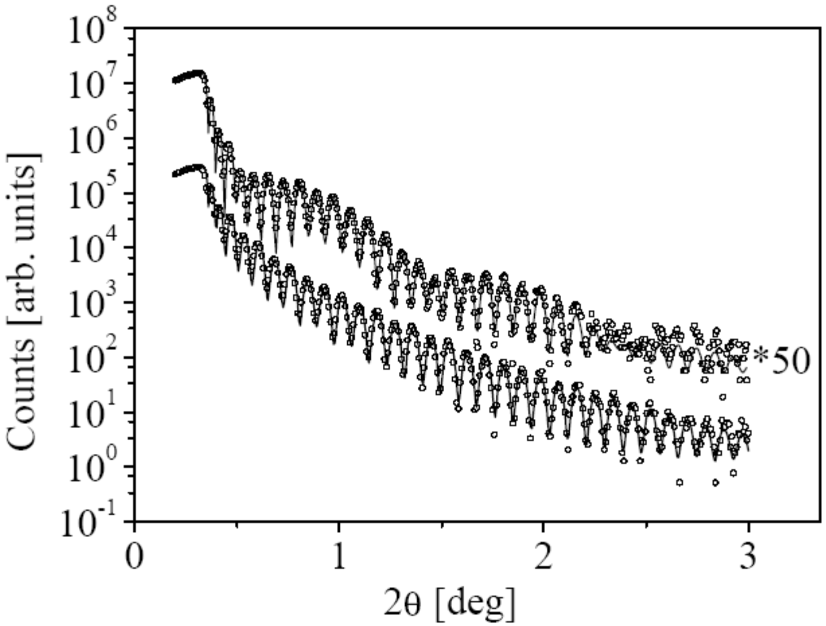
Generalized reflectivity: Parratt formalism

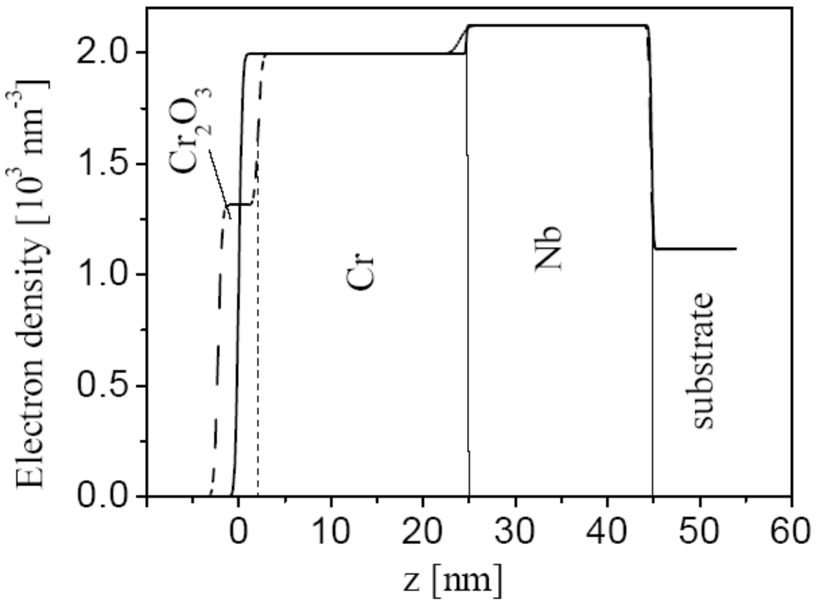
L. G. Parratt, Phys. Rev. 95, 359 (1954)

X-Ray Reflectivity

Example: reflectivity of a Cr film before and after oxidation

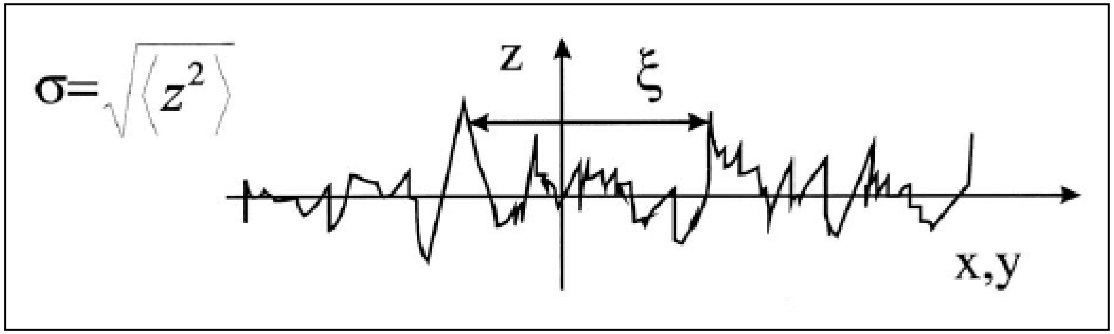






X-Ray Reflectivity

Influence of roughness:



$R=R_F\exp(-\sigma^2 Q_1 Q_2)$

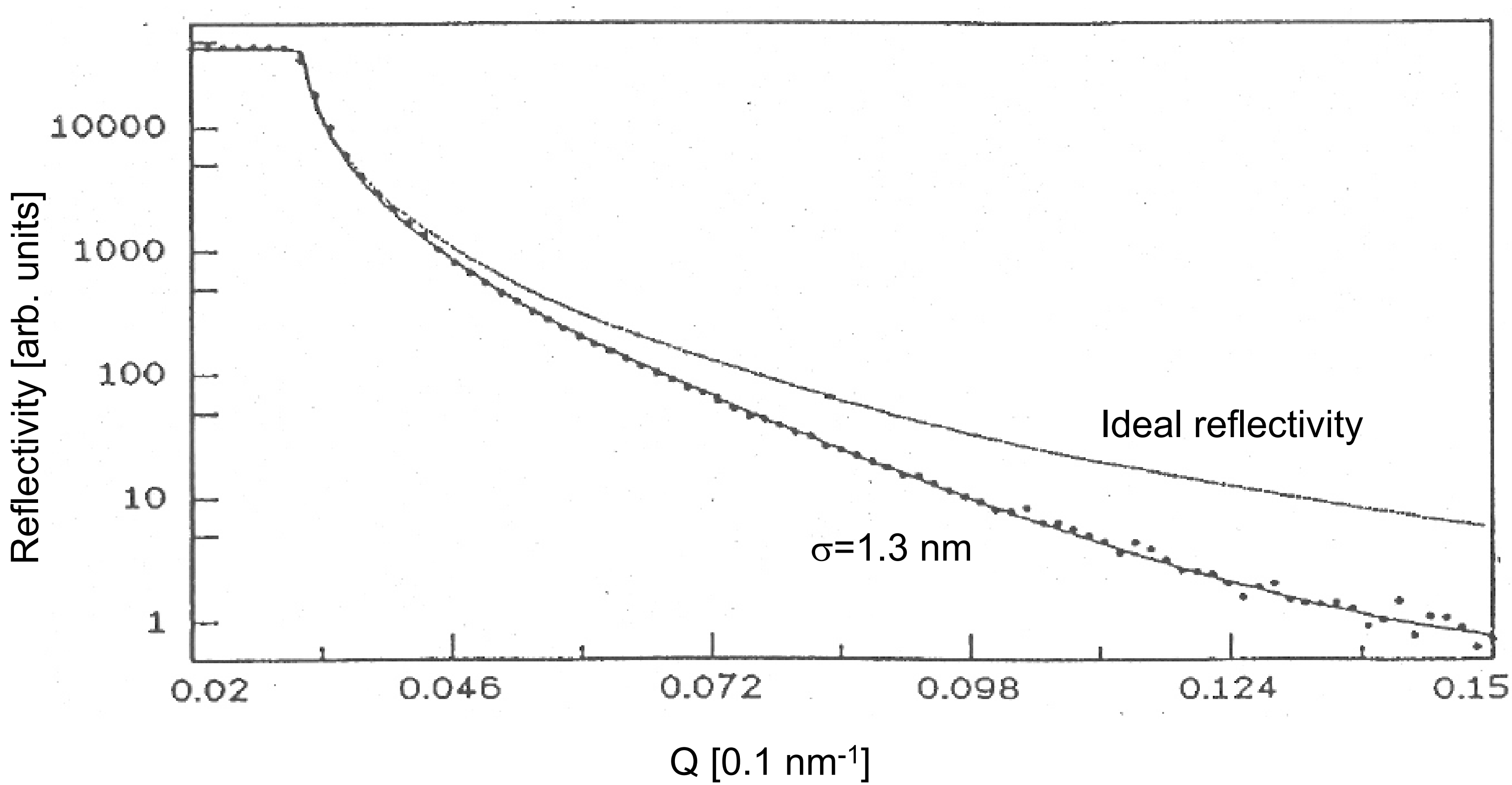
Height fluctuations at an interface

σ: root mean square roughness
from specular reflectivity

ξ: characteristic length to find same height on the surface
from off-specular scattering, Qx,y≠0, not discussed here

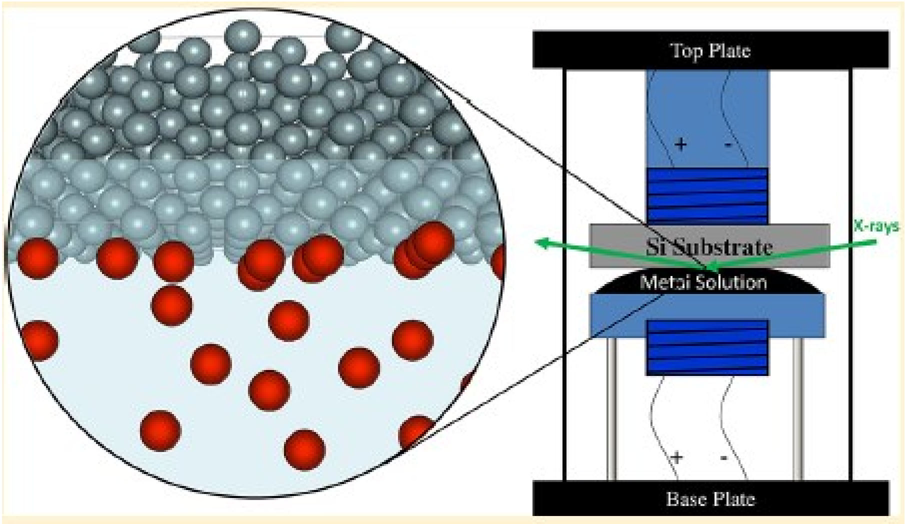
X-Ray Reflectivity

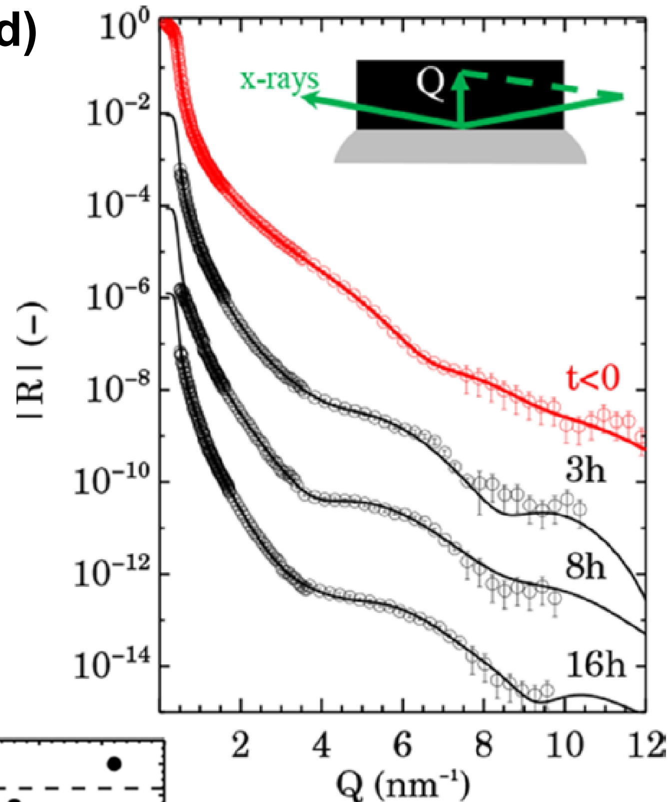
Example: reflectivity from a Si block

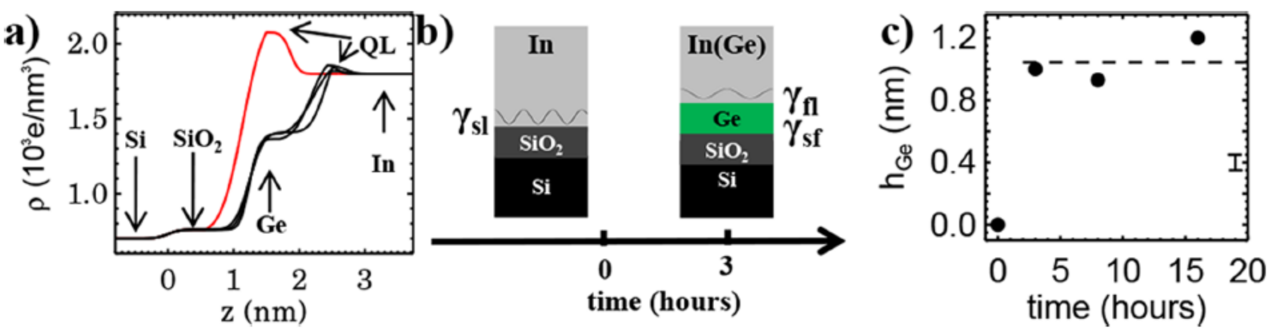


High Energy X-Ray Reflectivity: deeply buried interface

Liquid Phase Epitaxy Ge(In) on Si (undersaturated)



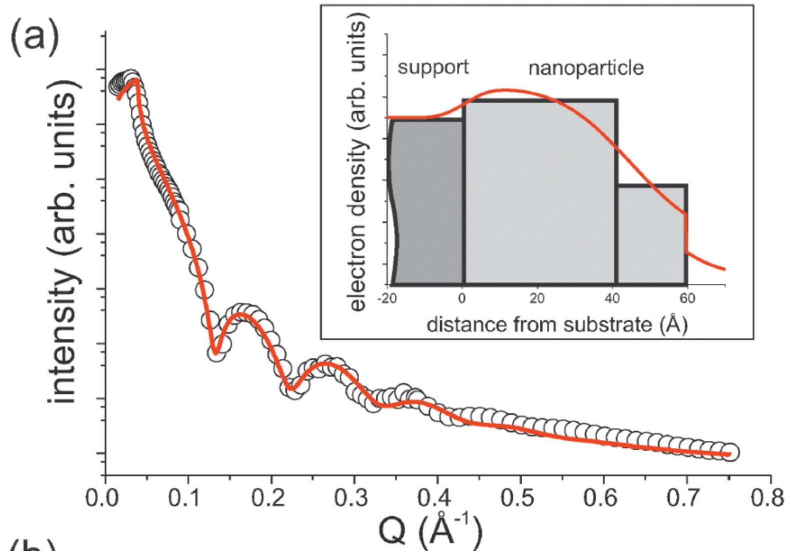


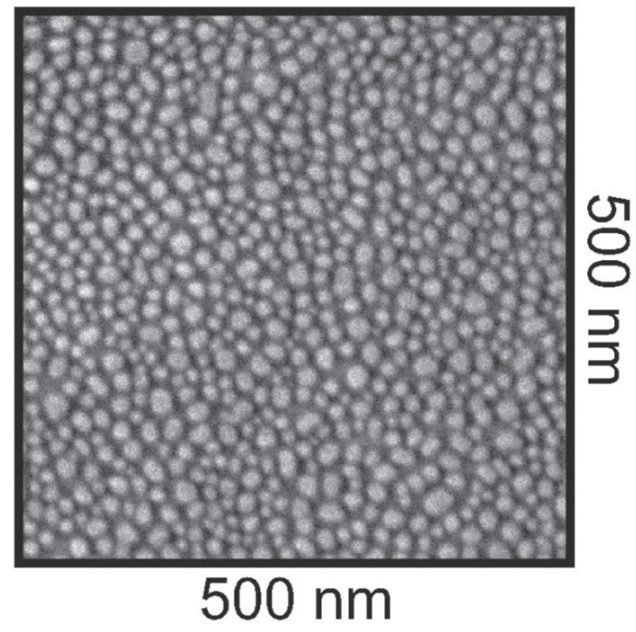


V. Vonk et al., Langmuir 33, 814 (2017).

Coverage Determination for Nanoparticles

PdRh nanoparticles on MgAl2O4





SEM after oxidation

Height: 6 nm
Coverage: 36%

P. Müller, et al. *Phys. Chem. Chem. Phys.*, 2014, **16**, 13866–13874

X-Ray Reflectivity

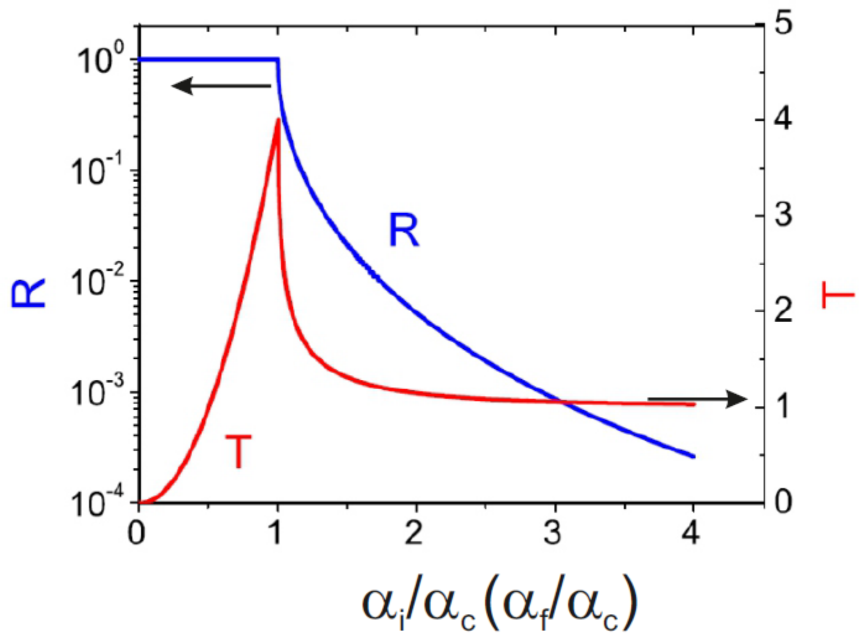
Summary x-ray reflectivity:

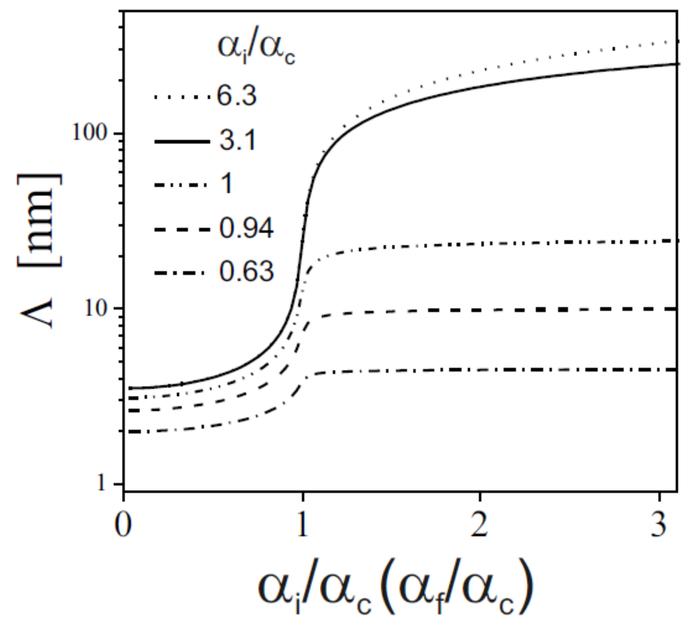
Obtainable Parameters (with sub-nm resolution)

- layer thicknesses
- statistical information on interfacial roughness
- layer density profiles
- limited to stratified media, flat substrate
- independent of crystalline state

Grazing Incidence X-ray Diffraction

Remember: total external reflection induces evanescent wave traveling parallel to the surface.



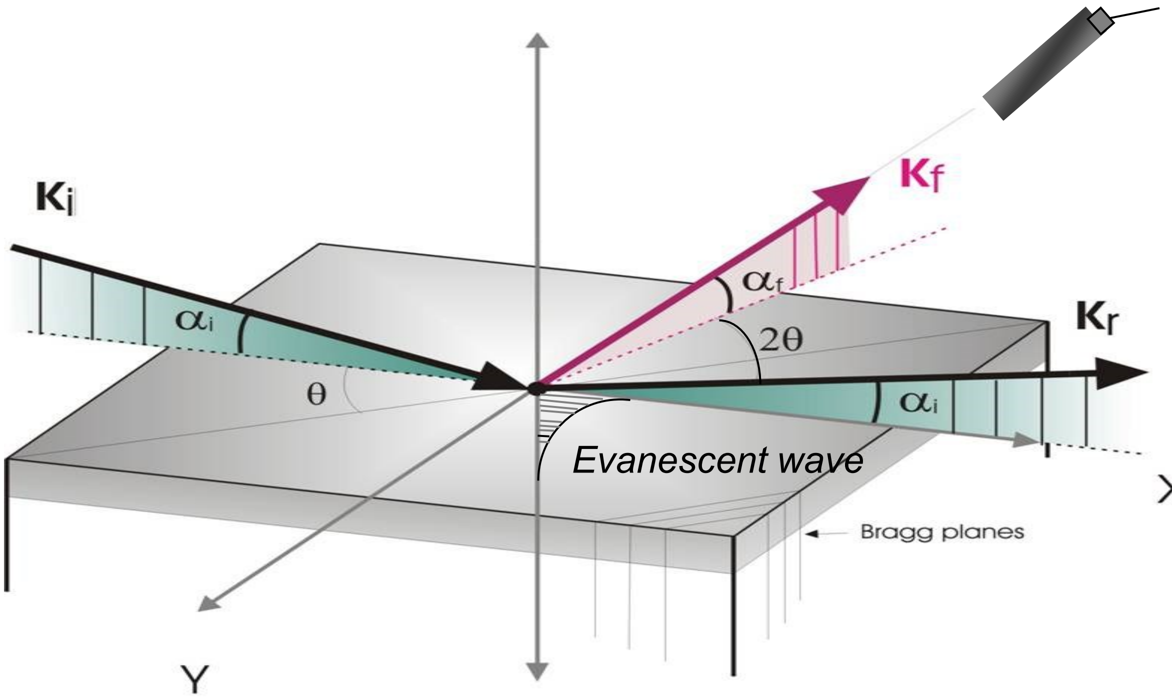


$$I(q) \sim |T(\alpha_i)|^2\, S(q')\, |T(\alpha_f)|^2$$

S: any type of diffraction / absorption process
q': scattering vector inside material

Grazing Incidence X-ray Diffraction

Example: evanescent Bragg scattering

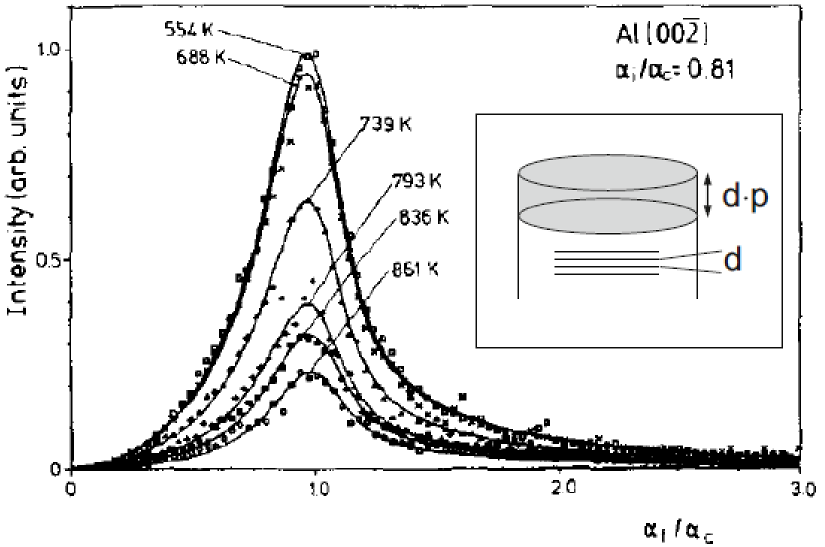


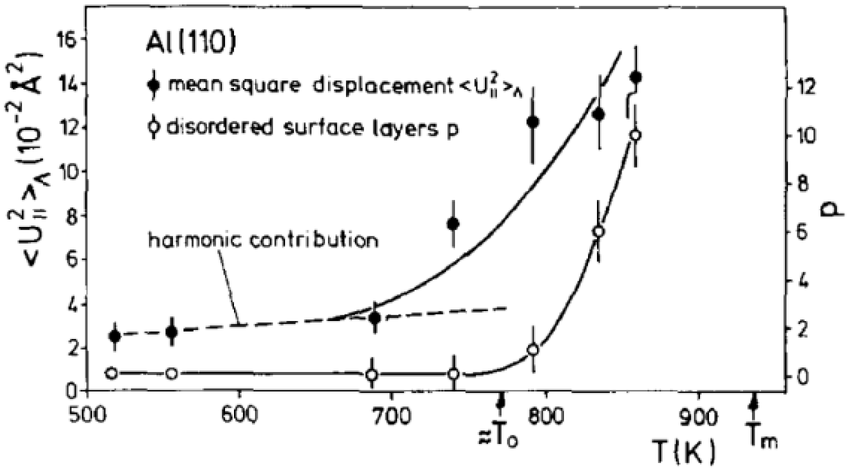
$$S(q') = |F_{hkl}|^2 \, \delta(\mathbf{q}_{\parallel} - \mathbf{G}_{hkl}) \, |1 - \exp(i q'_z a_{\perp})|^{-2}$$

evanescent Bragg scattering law

H. Dosch, Springer Tracts in Mod. Phys. (Springer), Berlin, 1992, p. 126.

Example: surface melting of Al(110)

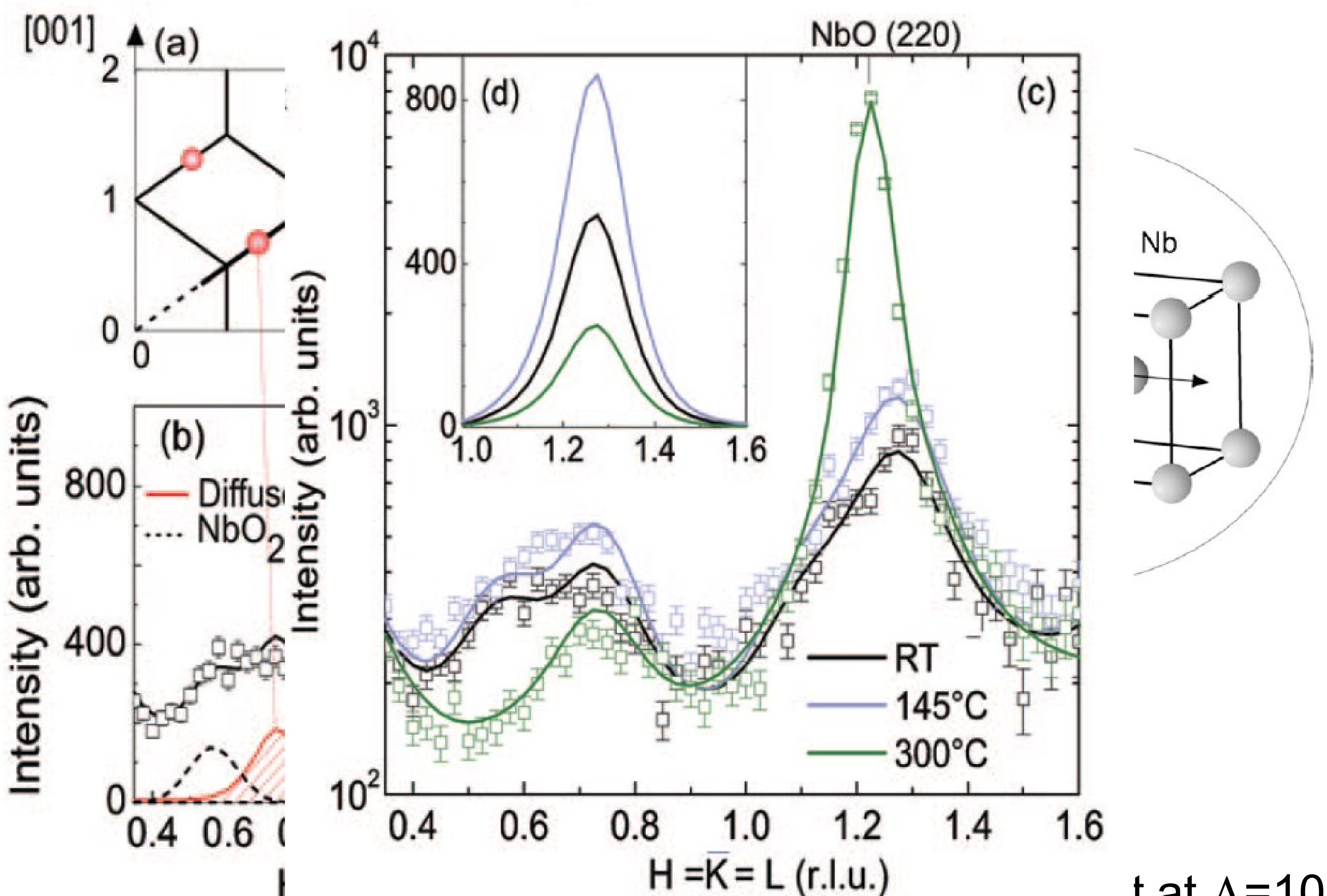




H. Dosch, Physica B 198 78 (1994)

Grazing Incidence X-ray Diffraction

Example: oxidation of Nb(110)



t at Λ=10 nm

M. Delheusy, et al., Appl. Phys. Lett . 92, 101911 (2008)

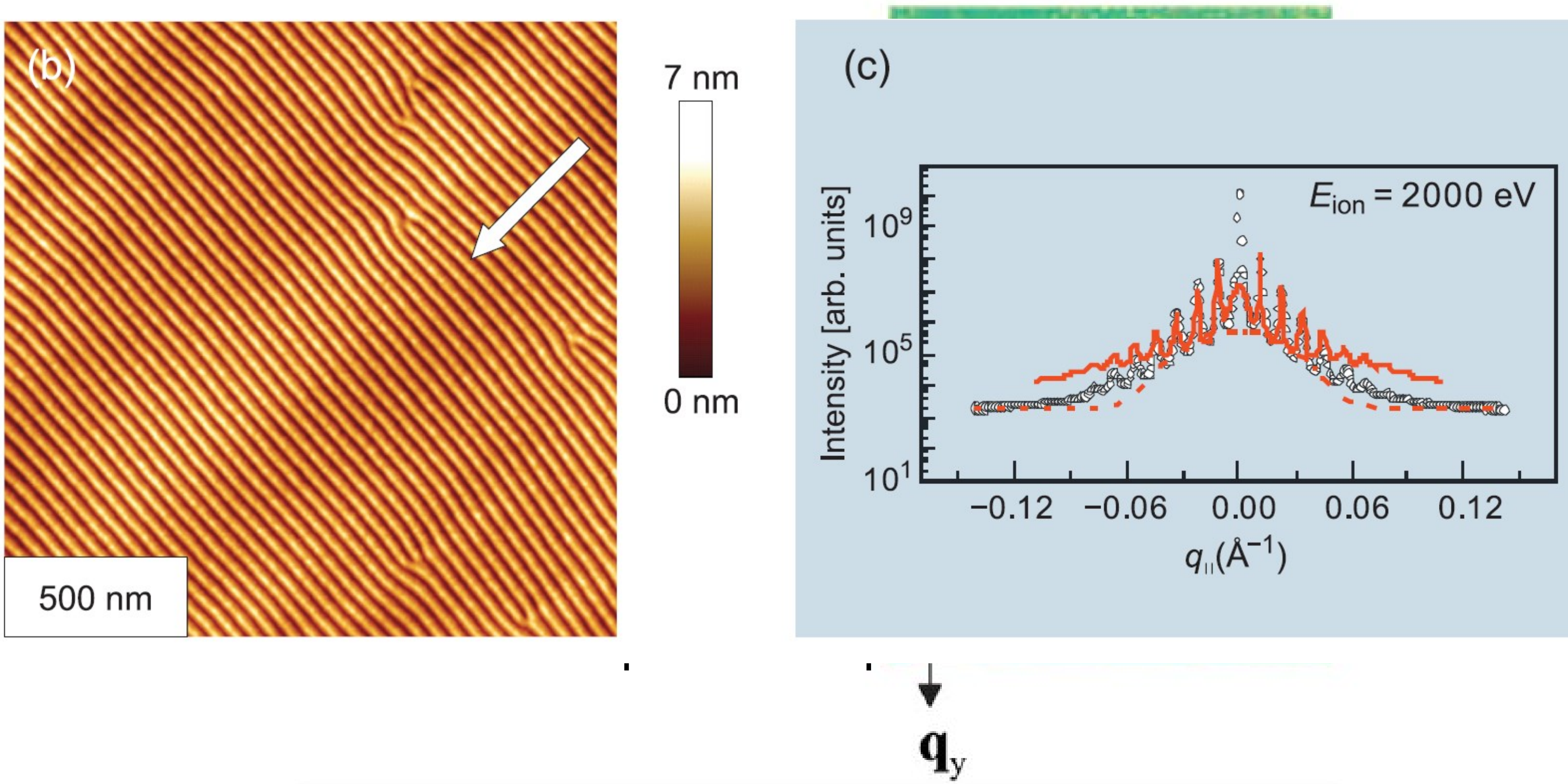
Grazing Incidence X-ray Diffraction

Summary grazing incidence x-ray diffraction:

Obtainable Parameters (with nm resolution)

- all structural parameters and chemical composition with variable information depth, e.g. lattice and order parameters, crystallinity, mosaicity, interstitials,…

Grazing incidence small angle scattering (GISAXS)



J. Oleander, et al., Phys. Rev. B B 76, 075409 (2007)
D. Carbone et al., J. Phys. Cond. Matt. 21 224007 (2009)
G. Renaud, et al., Surface Science Reports 64 255 (2009)

PETRAIII, P03, S. Roth

Grazing incidence small angle scattering (GISAXS)

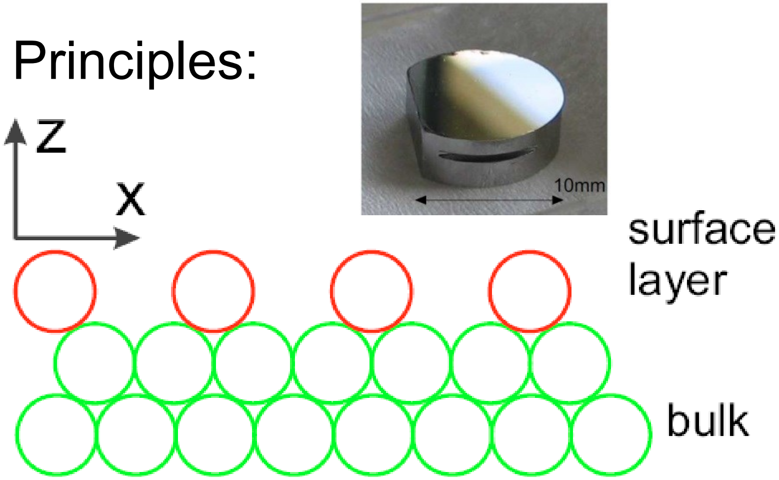
Summary GISAXS

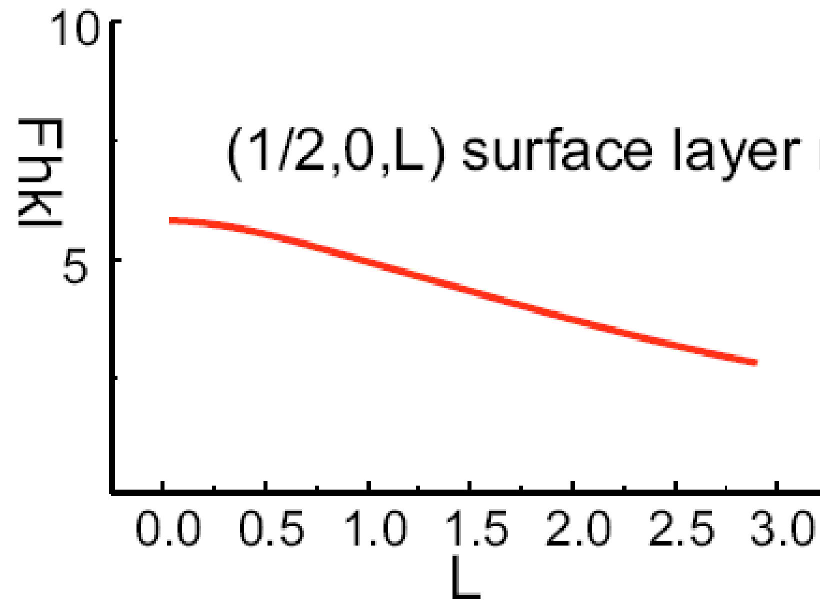
Obtainable Parameters (with nm resolution)

- average nanoparticle / nanostructure size, distance, shape
- lateral morphological information
- independent of crystalline state

Surface X-ray Diffraction

Principles:





$$F_{CTR} = A(\vec{q}) \sum_{n_3=0}^{\infty} e^{i\, q_z n_3 a_3} = \frac{A(\vec{q})}{1 - e^{i\, q_z a_3}} = \frac{A(\vec{q})}{1 - e^{i\, 2\pi\, l}}$$

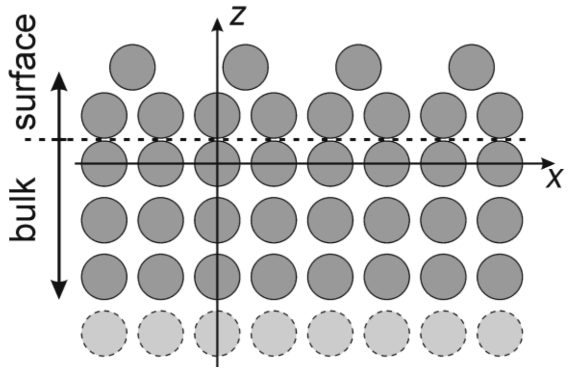
Crystal Truncation Rods

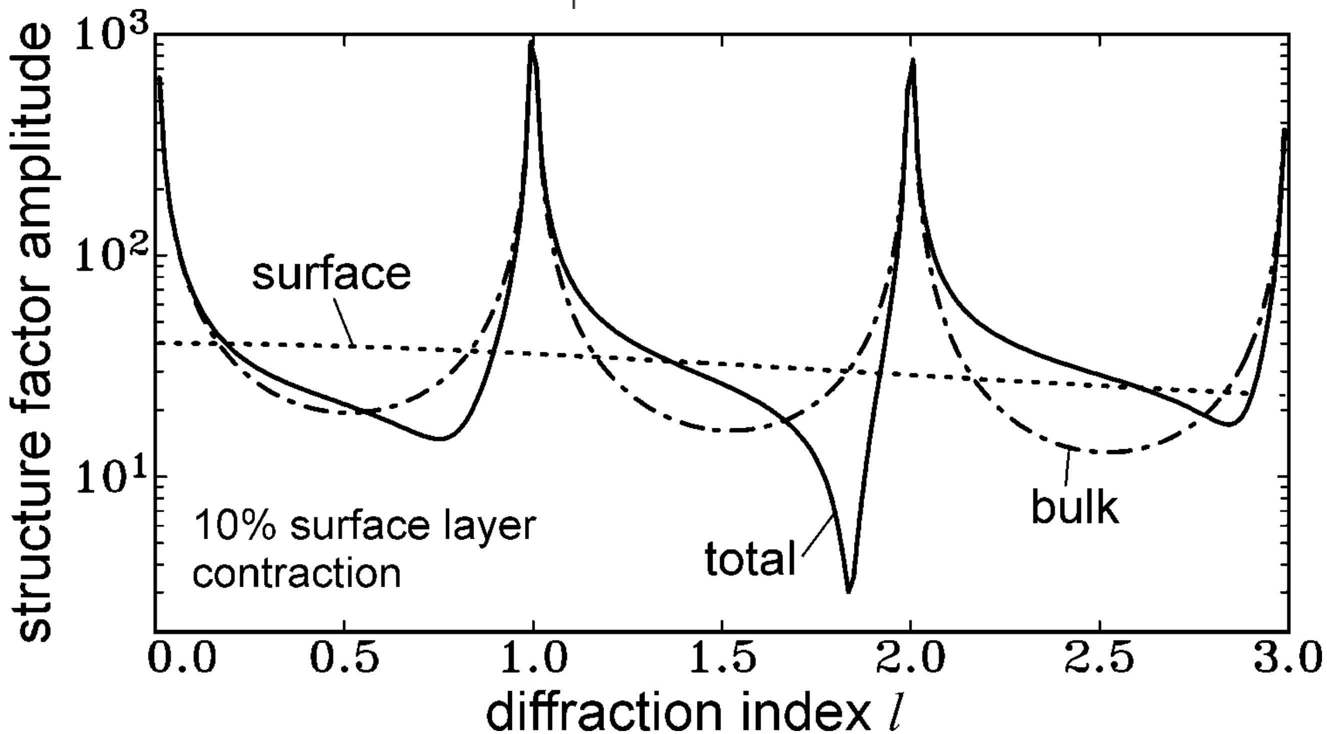
$$I_{CTR}(\vec{q}) = \left| \frac{r_0}{R} A_0 F(\vec{q}) N_1 N_2 \right|^2 \frac{1}{4 \sin^2(\pi l)}$$

E. Vlieg, J. Appl. Cryst. 33, 401 (2000)
R. Feidenhans'l, Surf. Sci. Rep. 10, 105 (1989)
I. K. Robinsion, D. J. Tweet, Rep. Prog. Phys. 55, 599 (1992)

Surface X-ray Diffraction

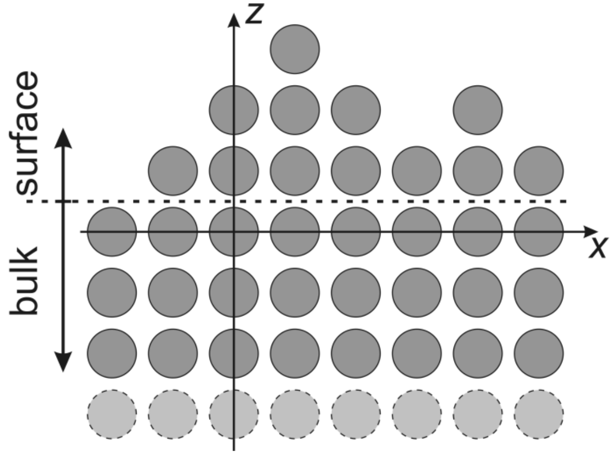
Influence of relaxations:

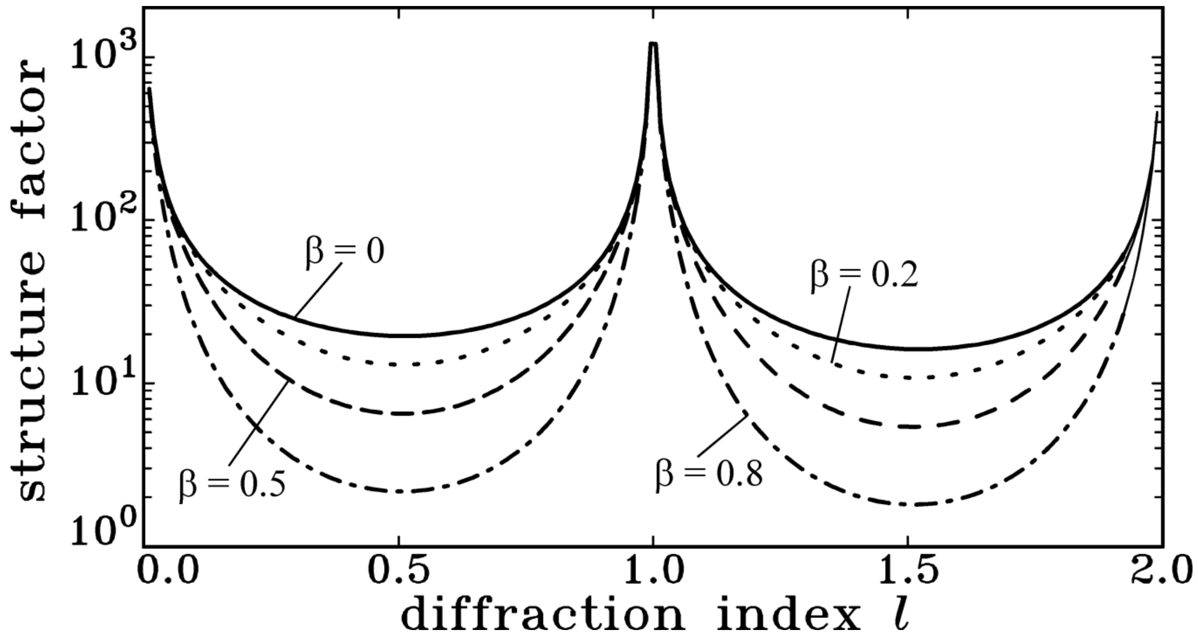




Surface X-ray Diffraction

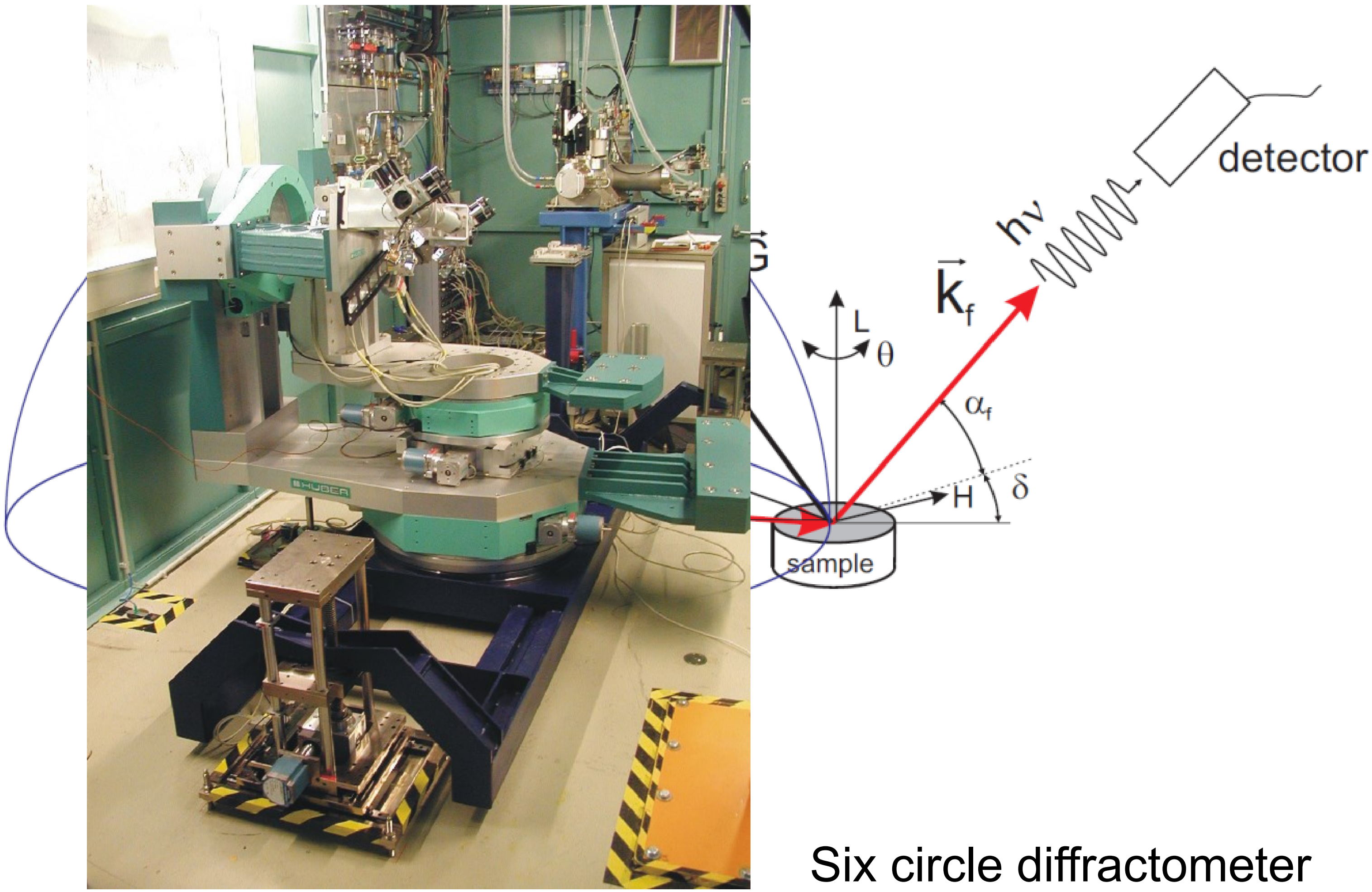
Influence of roughness:





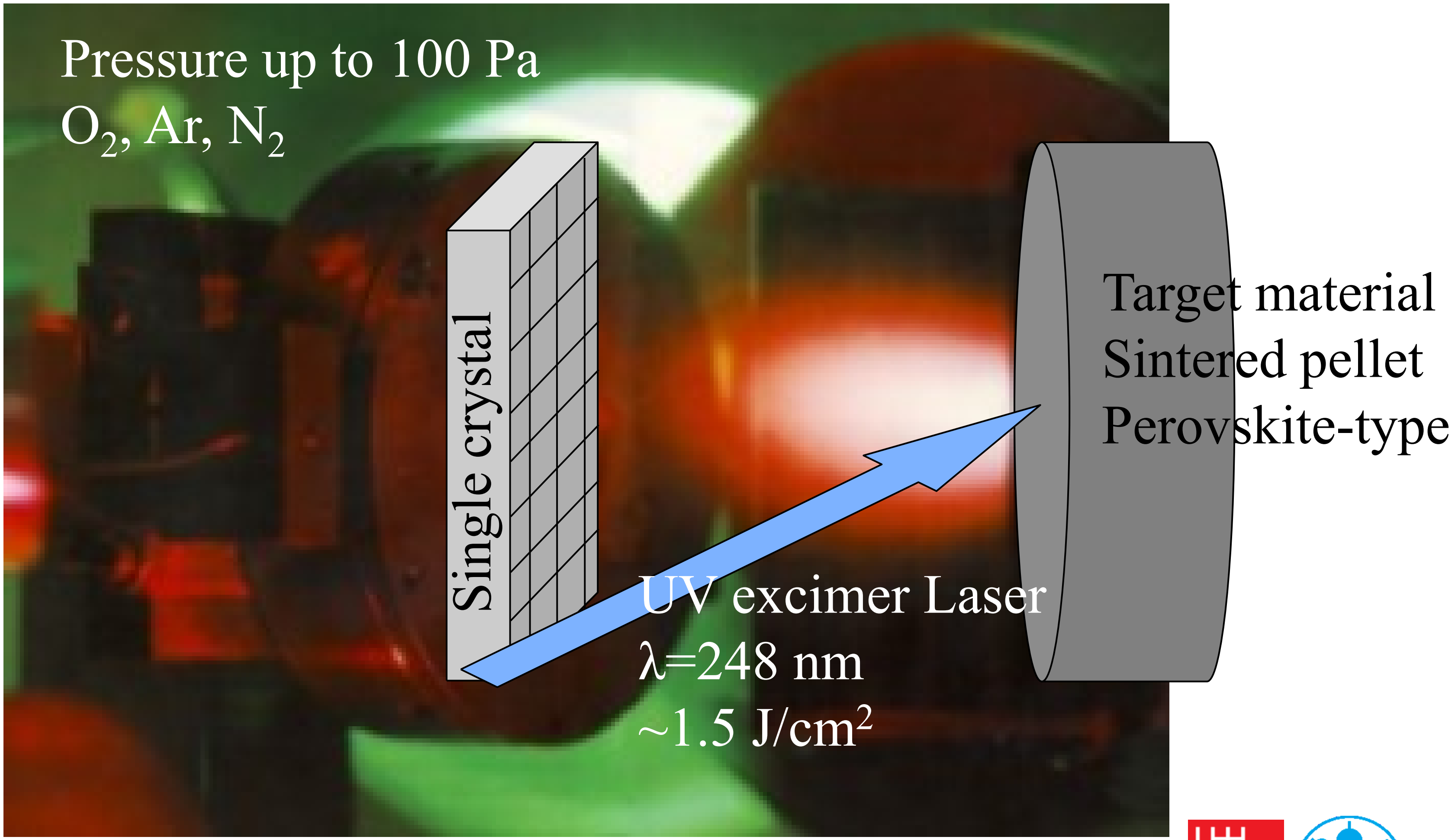
β model: occupation of layer n: β^n

Experimental realization:

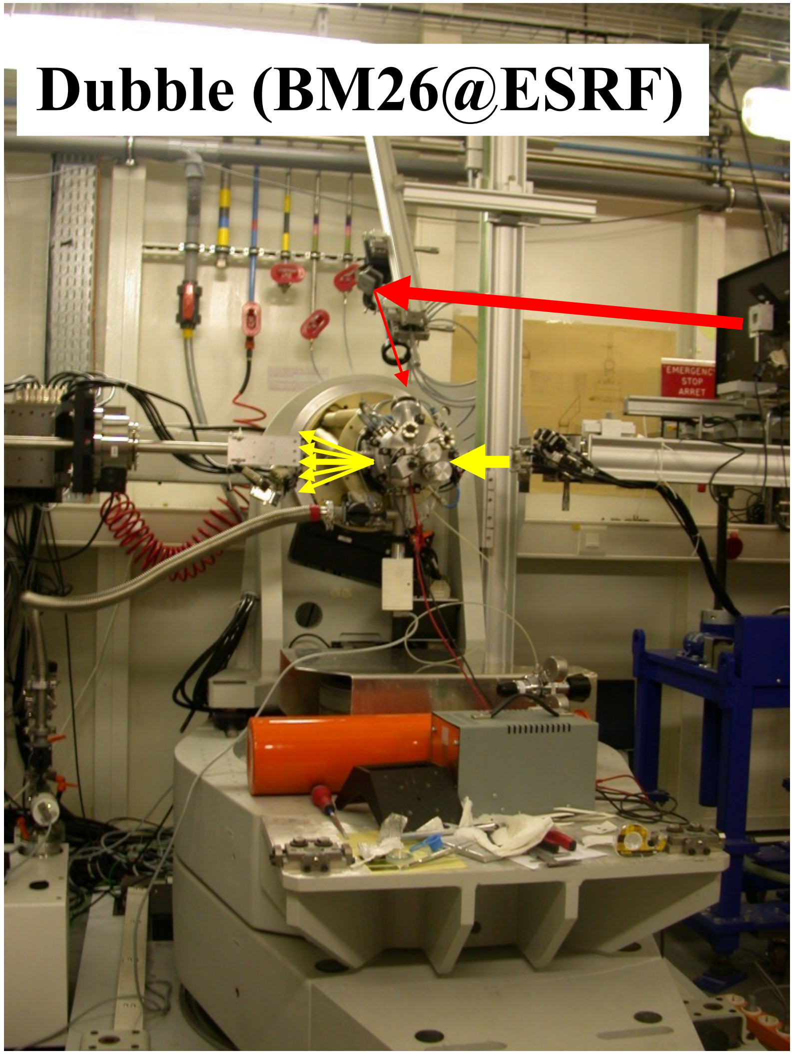


Six circle diffractometer

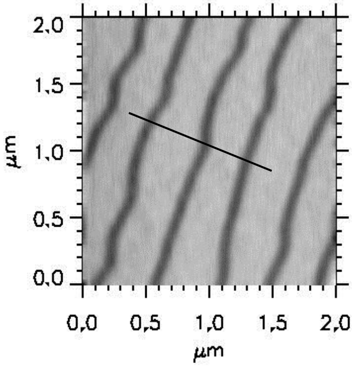
Surface X-ray Diffraction during Pulsed Laser Deposition

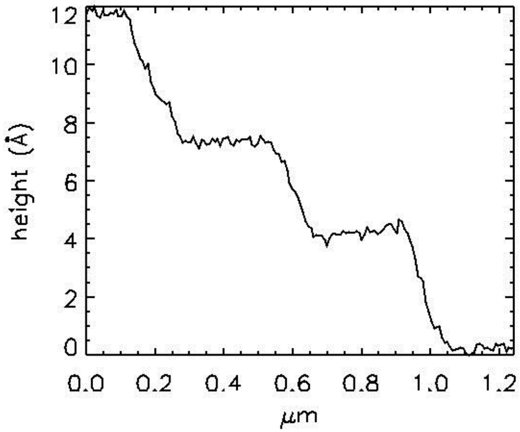


Setup and principle



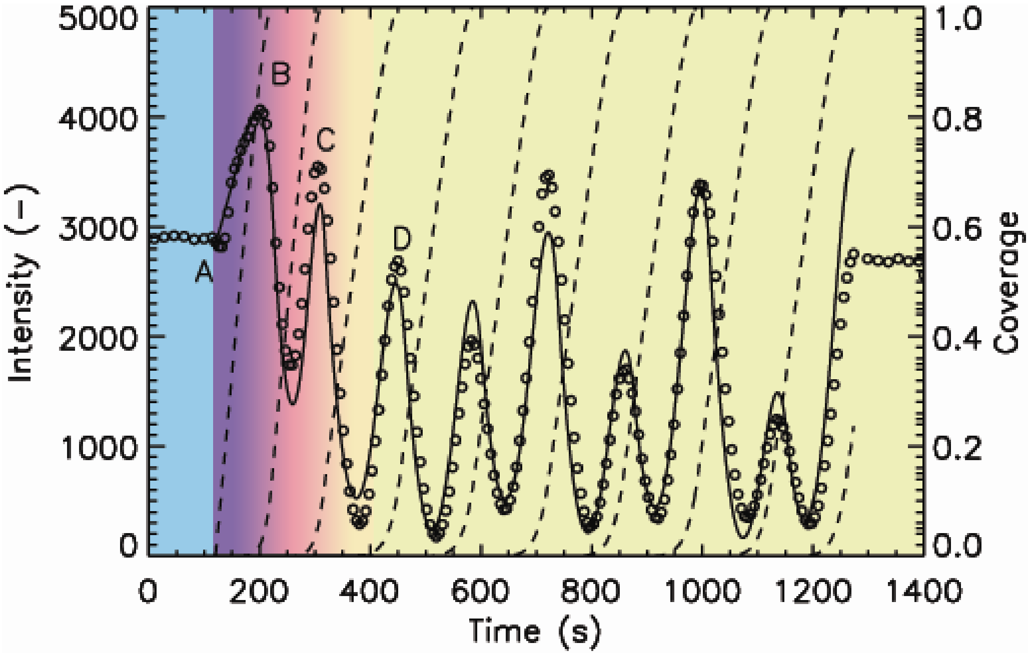
SrTiO3 Substrate: atomically flat + terraces

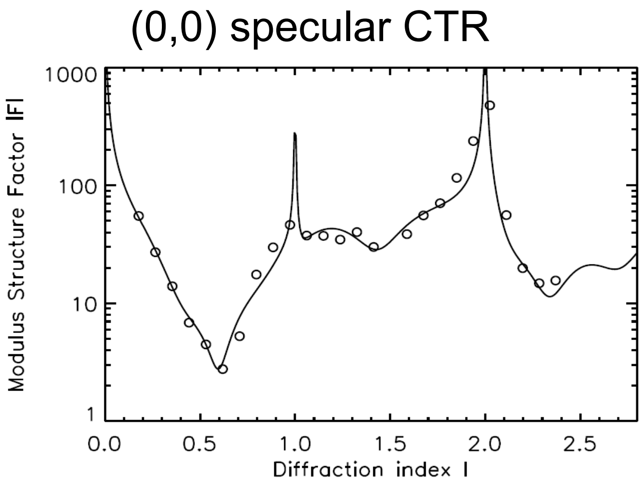


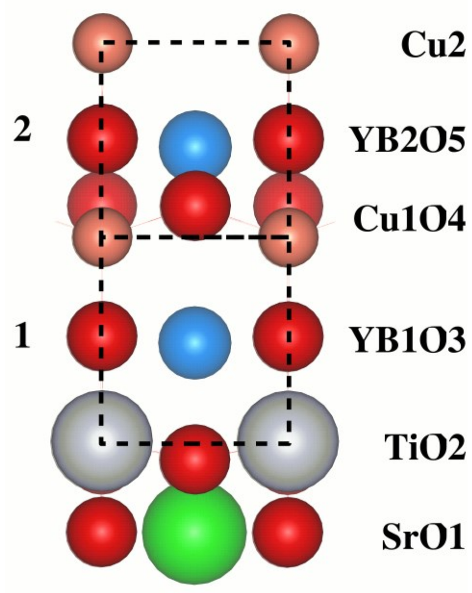


Layer-by-layer vs. step-flow growth modes

Heteroepitaxy: $YBa_2Cu_3O_{7-x}$ on $SrTiO_3$ substrate



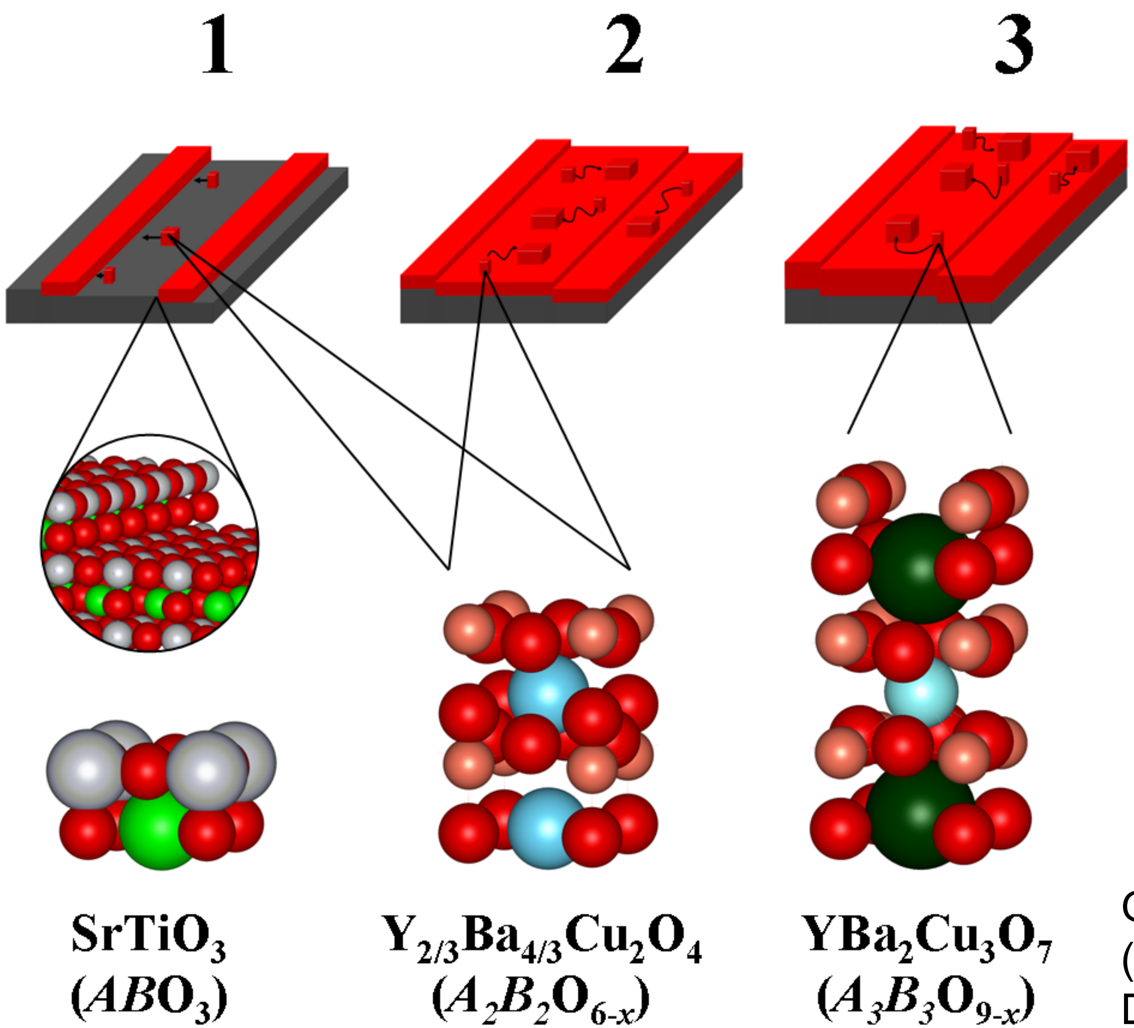




Kinematic scattering: $I \sim |F(hkl)|^2$

One can calculate the scattered intensity and compare with atomic scale models.

Heteroepitaxy: YBa2Cu3O7-x on SrTiO3 substrate

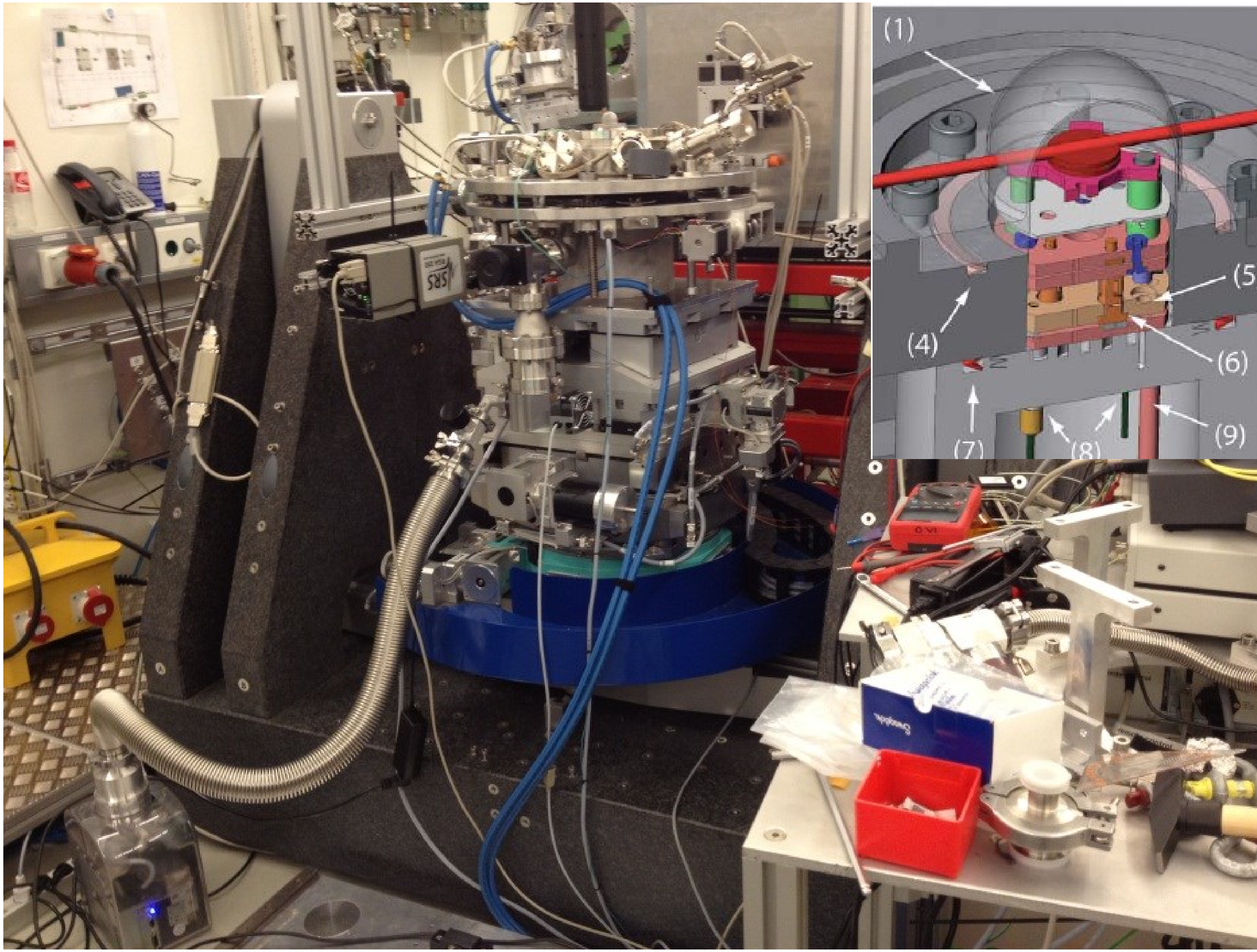


Growth starts with a (Metastable) Double perovskite

V. Vonk, et al., Phys. Rev. Lett . 99, 196106 (2007)

In-situ Studies of Chemically Active Nanomaterials

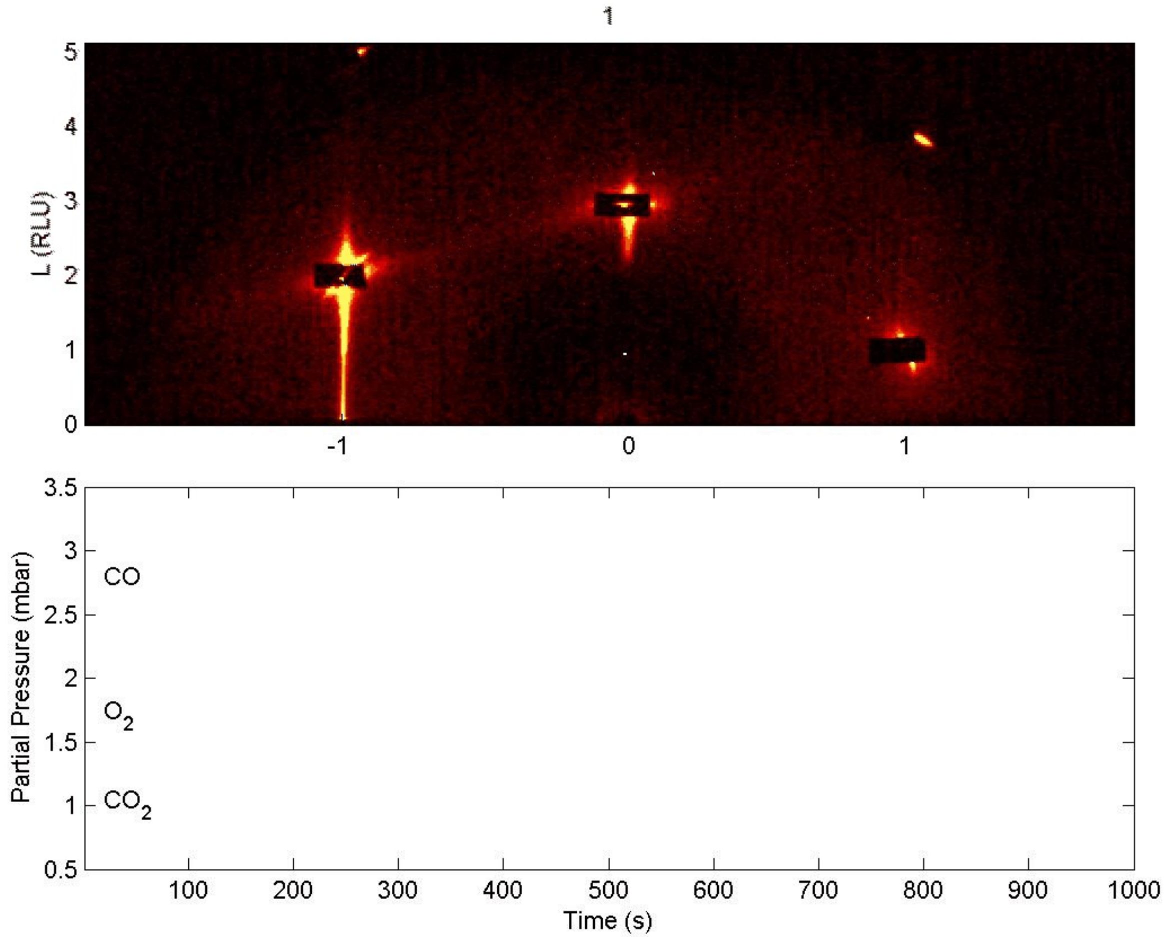
Method: In-situ high energy x-ray reciprocal space mapping (E=85 keV)



P07
PETRAIII

In-situ Studies of Chemically Active Nanomaterials

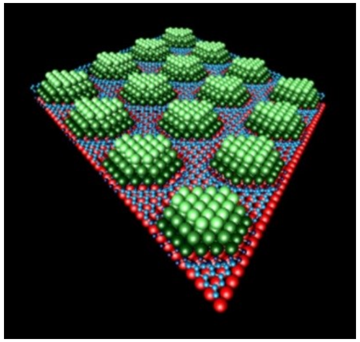
X-ray movie of Rh(111) surface during CO Oxidation (P07, PETRA III)



2D Detector
40 cm x 40 cm

RA Kollaboration: Uni Lund (Sweden) and Desy

Surface X-ray Diffraction



Summary surface x-ray diffraction

fit: kinematical diffraction theory

parameters:

overlayer structure+registry, thickness,

relaxations, roughness

Structure of ultrasmall nanoparticles

near surface composition

thermal vibrations

In-situ observation of surface processes

Surface Sensitive X-ray Diffraction

Surface Sensitive X-Ray Diffraction Methods

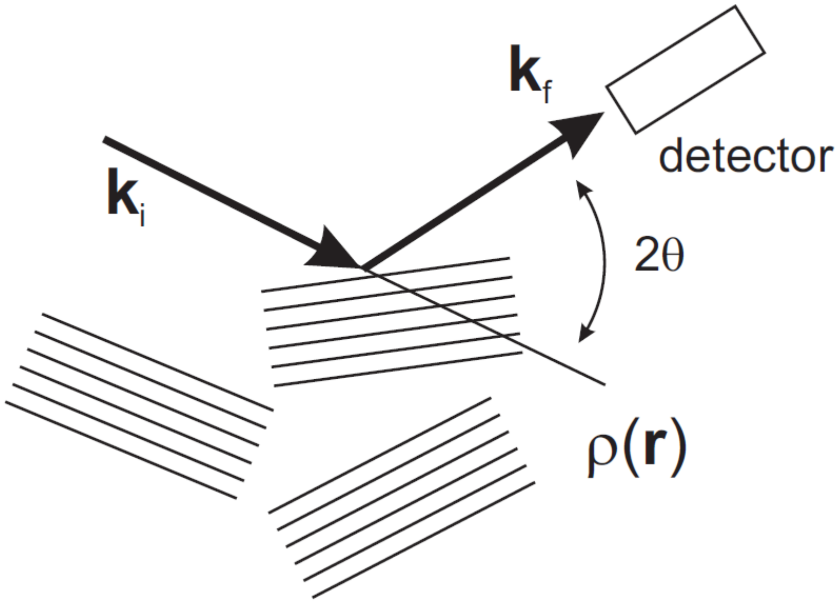
Andreas Stierle, University of Siegen, Germany; Elias Vlieg, Radboud University Nijmegen, The Netherlands

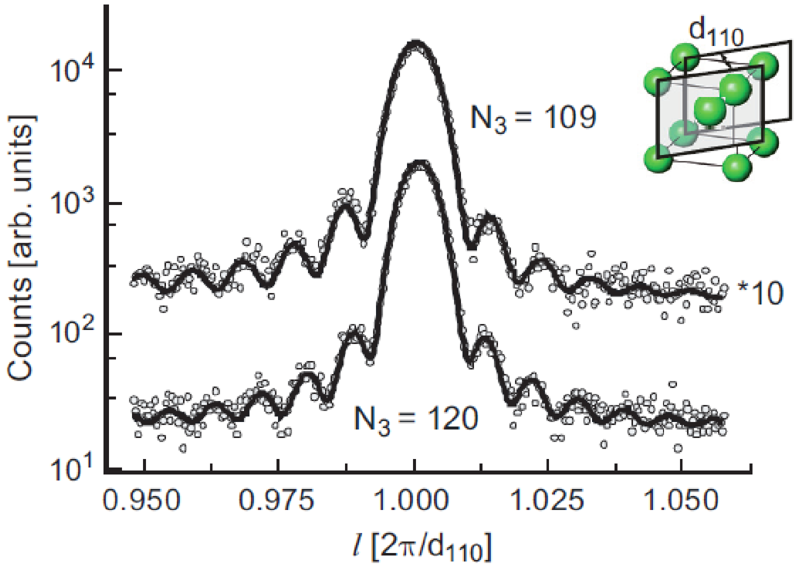
1 Introduction

Since the first demonstration in 1912 [1], X-ray diffraction (XRD) has become the dominant technique to determine the bulk structure of crystals. In fact, many crystals are grown with the sole purpose of determining the structure of their building blocks. This is especially relevant for

A. Stierle, E. Vlieg, in *Modern Diffraction Methods*, edited by E. J. Mittemeijer and U. Welzel, Wiley VHC Weinheim, 2012.

Nanoparticle Structural Analysis





$q = 4\pi/\lambda \sin(\theta)$: scattering vector

epitaxial film diffraction

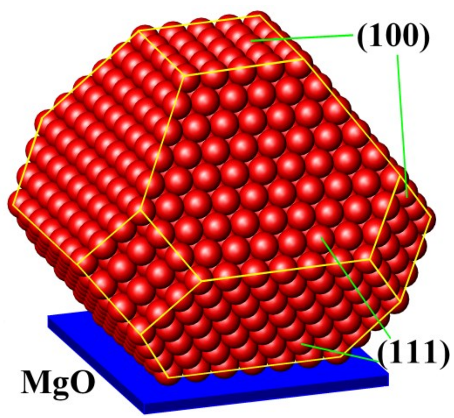
$$\propto |F(\boldsymbol{q})|^2 \prod_{j=1}^{3} \frac{\sin^2\left(\frac{1}{2} N_j \boldsymbol{q}\cdot\boldsymbol{a}_j\right)}{\sin^2\left(\frac{1}{2}\boldsymbol{q}\cdot\boldsymbol{a}_j\right)}$$

- Surface information lost for powder diffraction
- Small particles produce broad peaks in reciprocal space

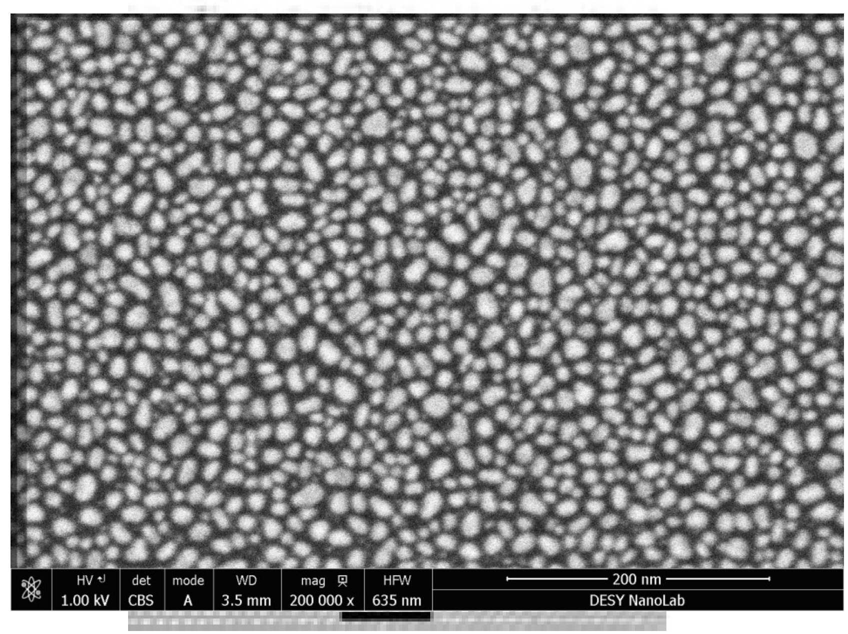
Interference function for single crystalline film

Our Approach: Epitaxial Nanoparticles

Model system: epitaxial nanoparticles supported by oxide single crystals



Pd, Rh, Pt/MgO(100)
PtRh, PdRh /$MgAl_2O_4$(100)
cube-on-cube epitaxy



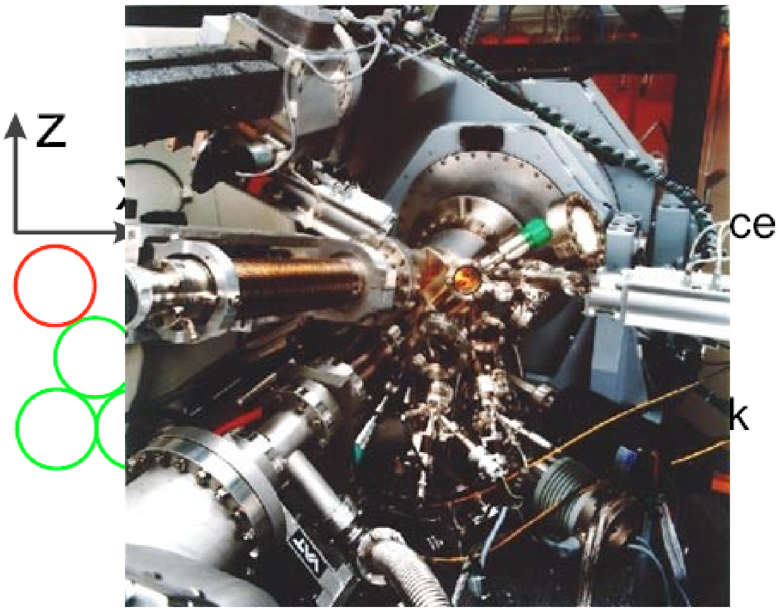
FEI Nova Nano, E= 1 keV
HRTEM, ARM 1.2 MeV

Sample preparation by MBE growth at T=400°C
Size distribution: 30-60%

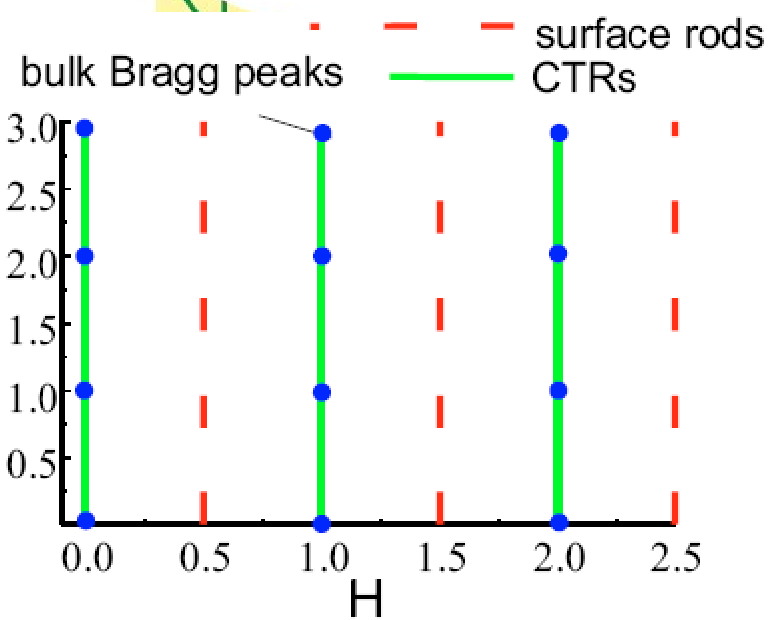
Shape Change of Pd and Rh Nanoparticles on MgO(100)

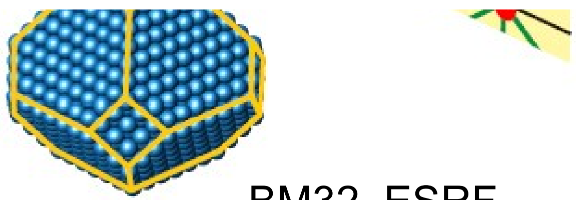
High resolution reciprocal space mapping

Experimental set-up at BM32, ESRF



UHV surface x-ray diffraction and GISAXS chamber



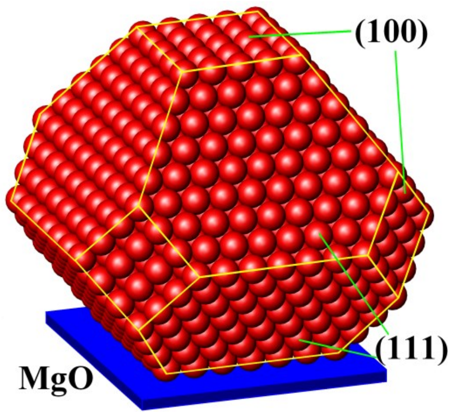


BM32, ESRF
E_p=12 keV

G. Renaud, et al. Nuc. Inst. Meth. B 95, 422 (1995)

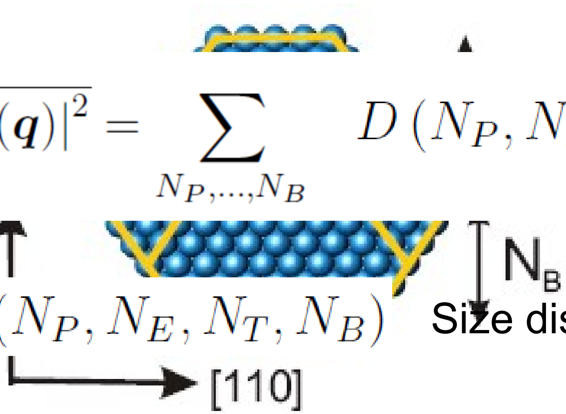
Shape Change of Pd and Rh Nanoparticles on MgO(100)

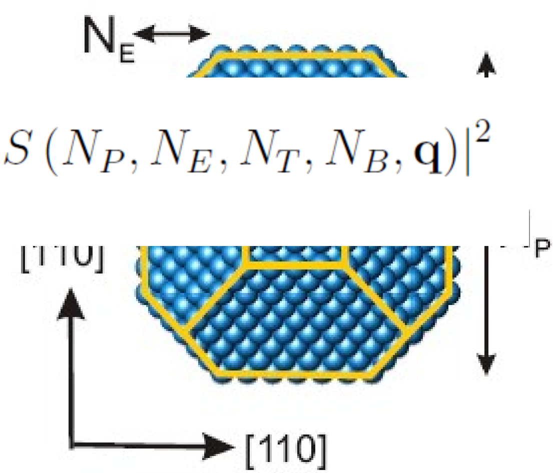
Particle Size & Shape Variation:



4 parameters for x-ray structure factor calculation

$\{N\} \equiv \{N_P, N_E, N_T, N_B\}$





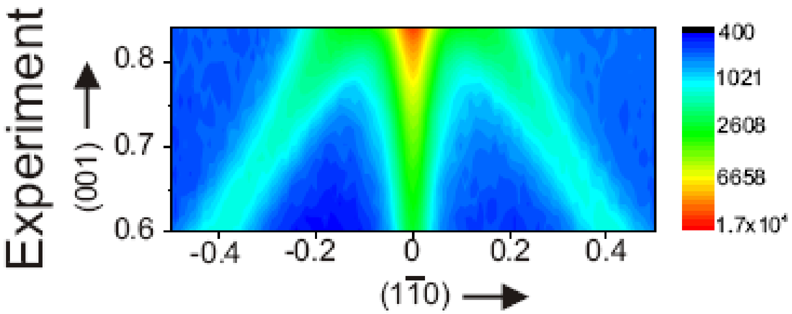
$$\overline{|S(\mathbf{q})|^2} = \sum_{N_P,\ldots,N_B} D\left(N_P, N_E, N_T, N_B\right) \left|S\left(N_P, N_E, N_T, N_B, \mathbf{q}\right)\right|^2$$

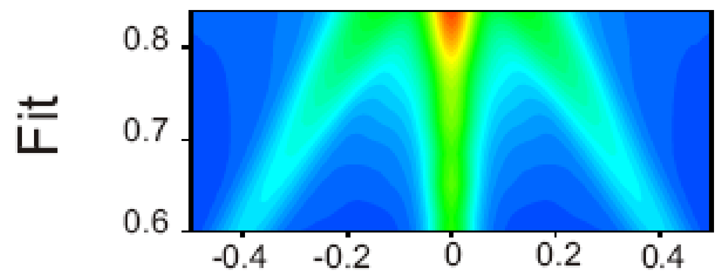
$D\left(N_P, N_E, N_T, N_B\right)$ Size distribution

N. Kasper, et al., Surf. Sci. 600, 2860 (2006)

Shape Change of Rh Nanoparticles on MgO(100)

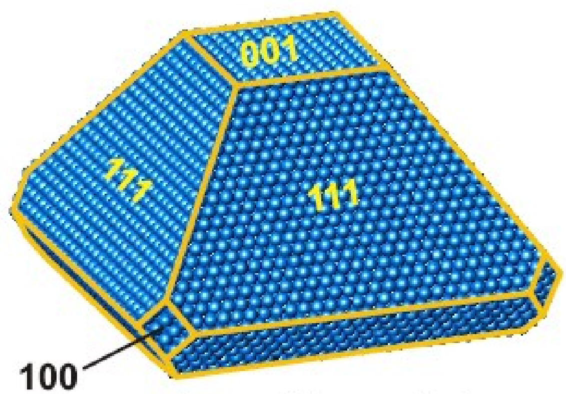
Clean Rh nanoparticles SXRD reciprocal space maps at T=600 K





Fit Results:
NP=31±1,
NT=20±1,
NB=5±1
NE=3±1

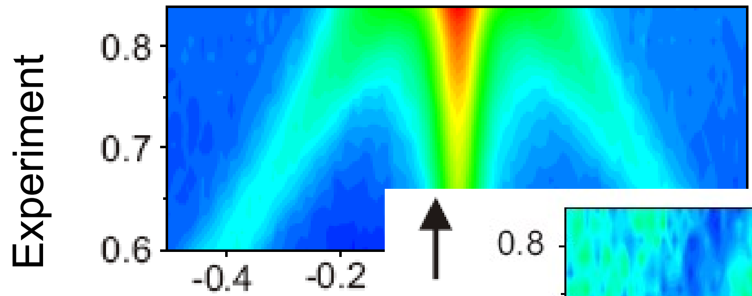
average diameter: 8.3 nm
average height: 4.8 nm

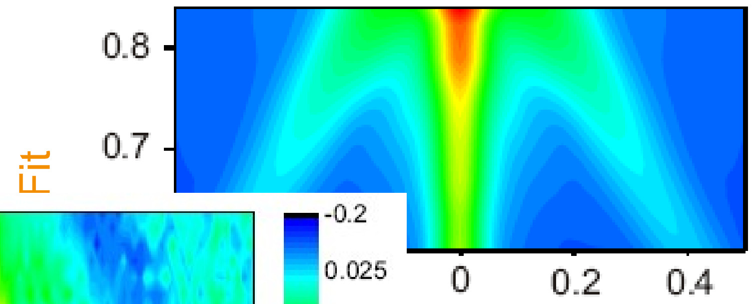


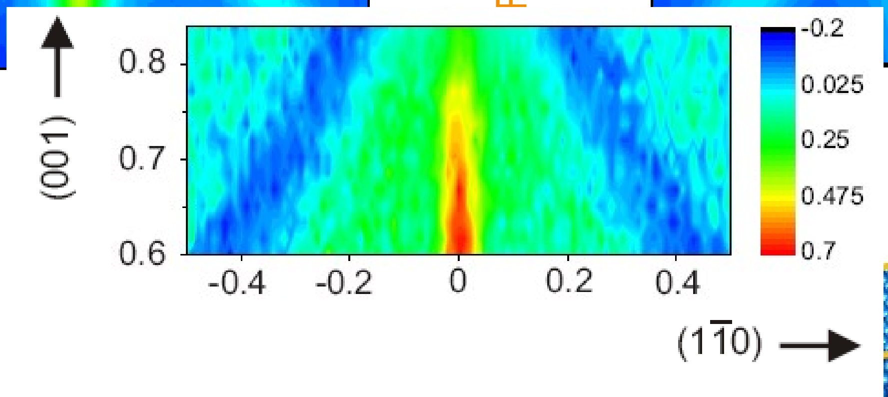
clean Rh particle

Shape Change of Rh Nanoparticles on MgO(100)

Oxidation at T=600 K, $p(O_2)=3x10^{-5}$ mbar

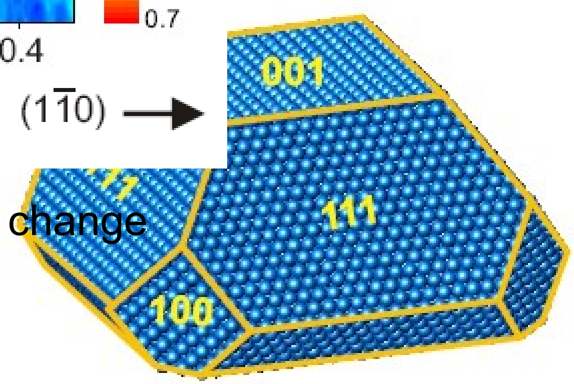






Fit Results:
NP=31±1,
NT=16±1,
NB=5±1
NE=7±1

Oxygen adsorption induced signal change

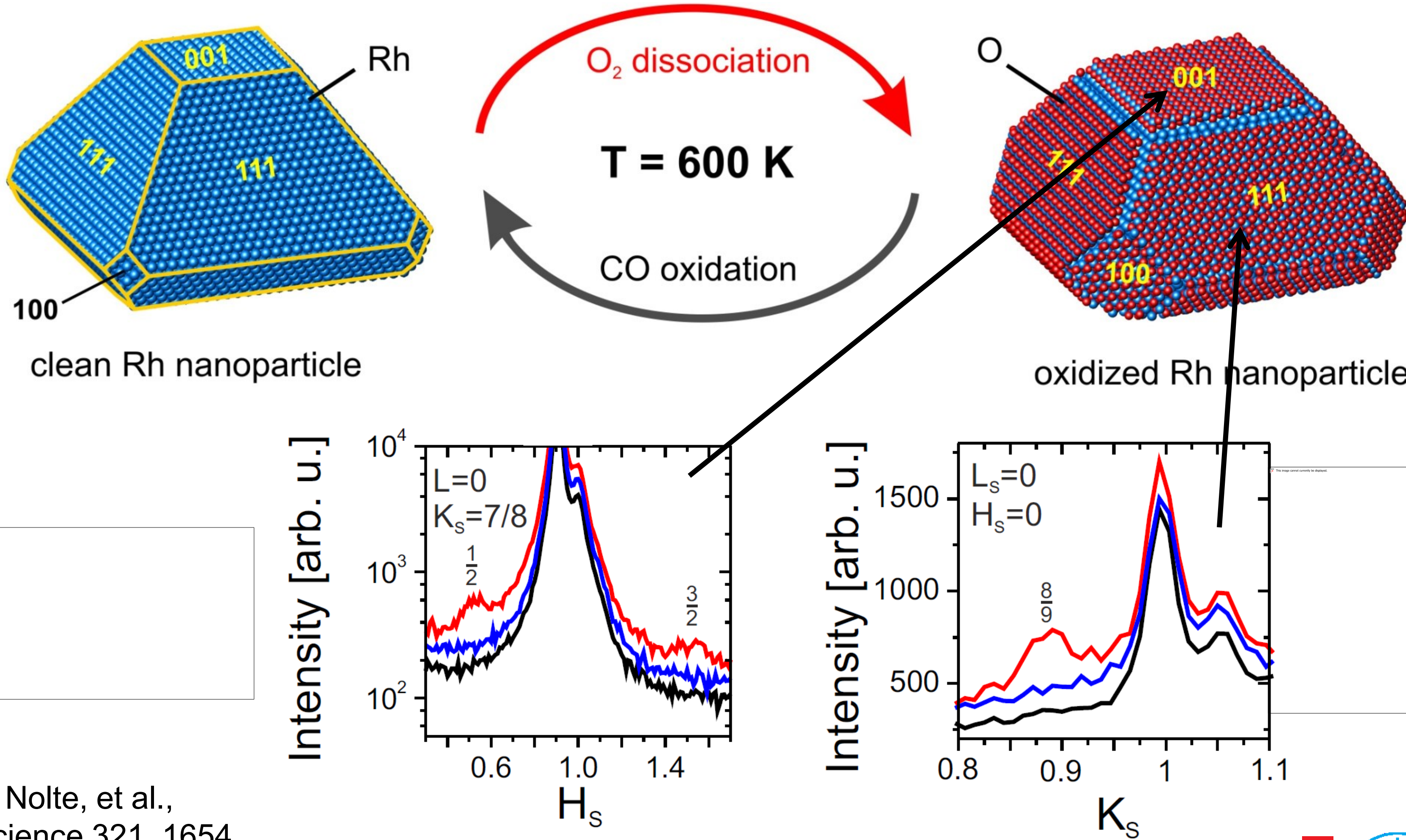


oxidized Rh particle (core)

average diameter: 8.3 nm
Average height: 4.0 nm

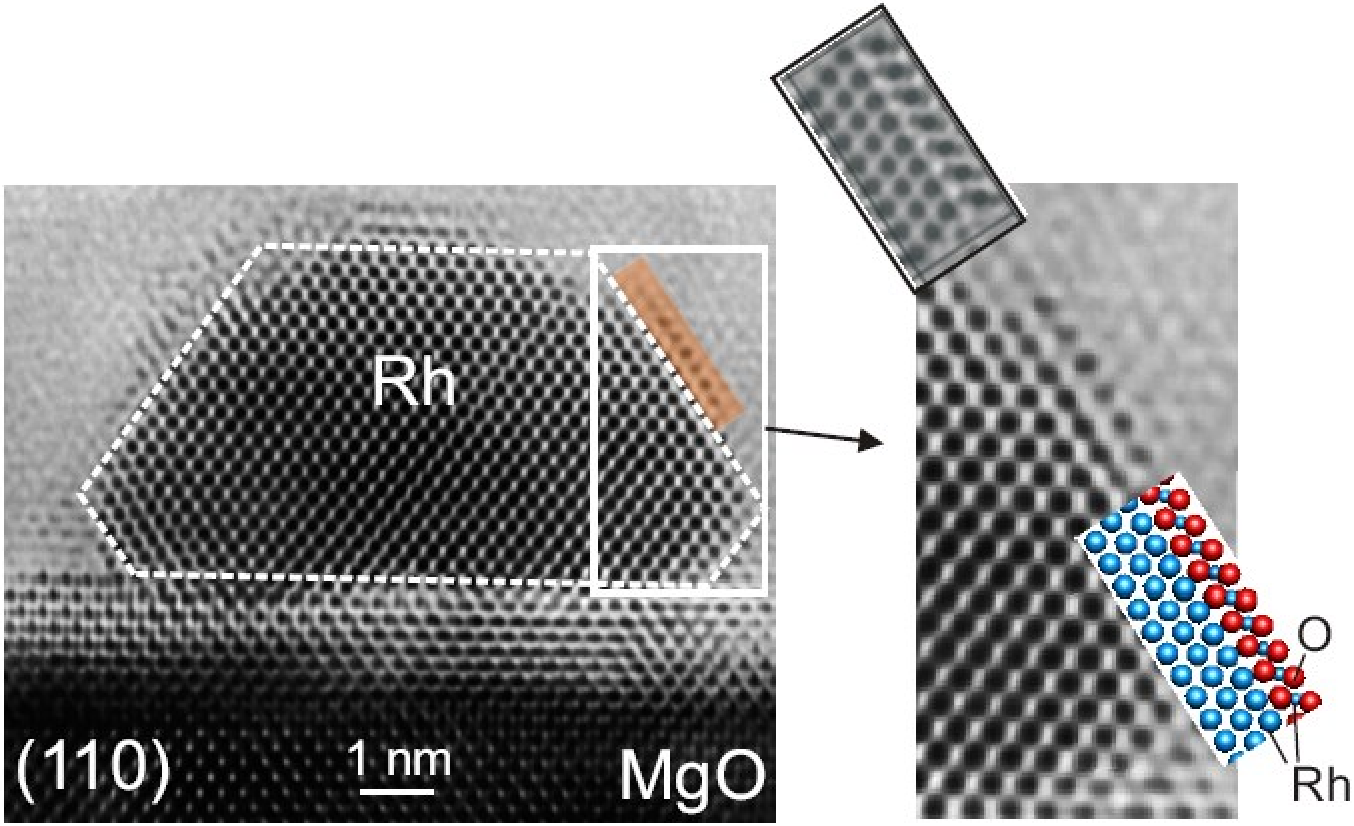
Shape Change of Rh Nanoparticles on MgO(100)

CO Reduction and Reversible Shape Change
T=600 K, p(CO)=3×10^{-5} mbar



P. Nolte, et al.,
Science 321, 1654
(2008)

Ex-Situ Cross-Section TEM Characterization

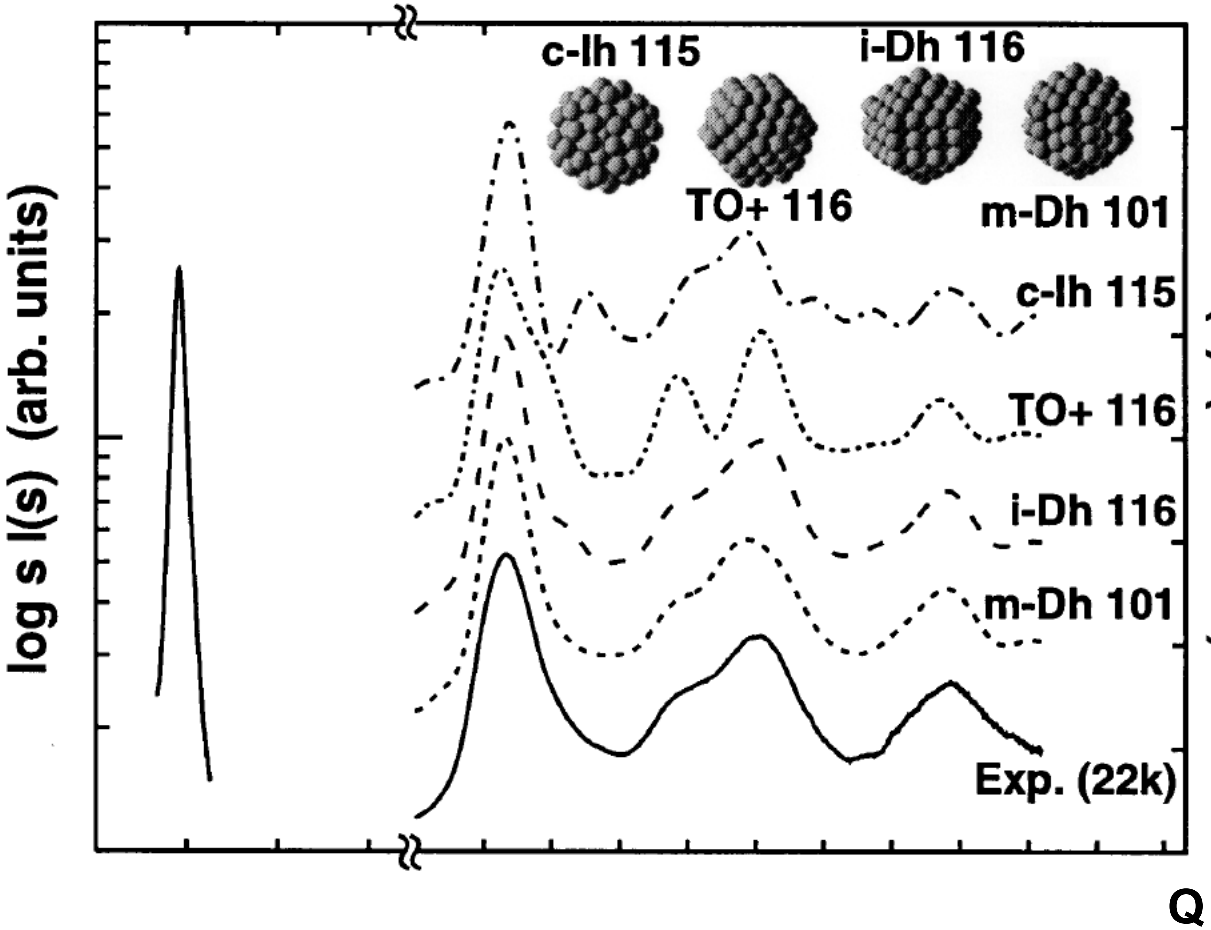


Surface oxide formation, stable in air

HR-TEM MPI IS (MPI-MF) Stuttgart

N.Y. Jin-Phillipp, et al., Surf. Sci. 603, 2551 (2009)

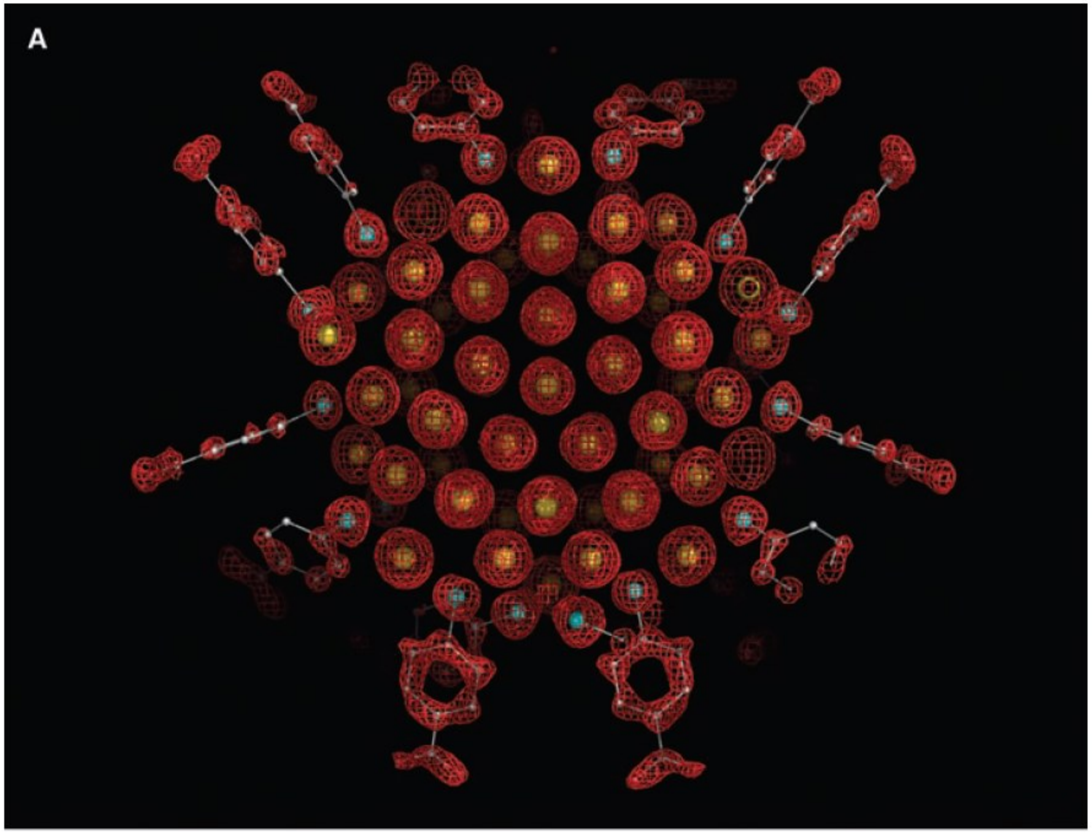
Pair Distribution Function Analysis



Au nanoparticles with different shape

Cleveland, et al. Phys. Rev. Lett. 79, 1873 (1997)

Single crystal XRD



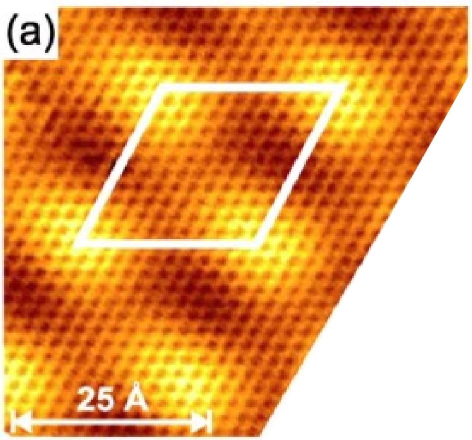
Electron density map of Au_{102} Np.

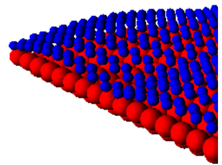
Thiol stabilized Au nanoparticles grown into a single crystal

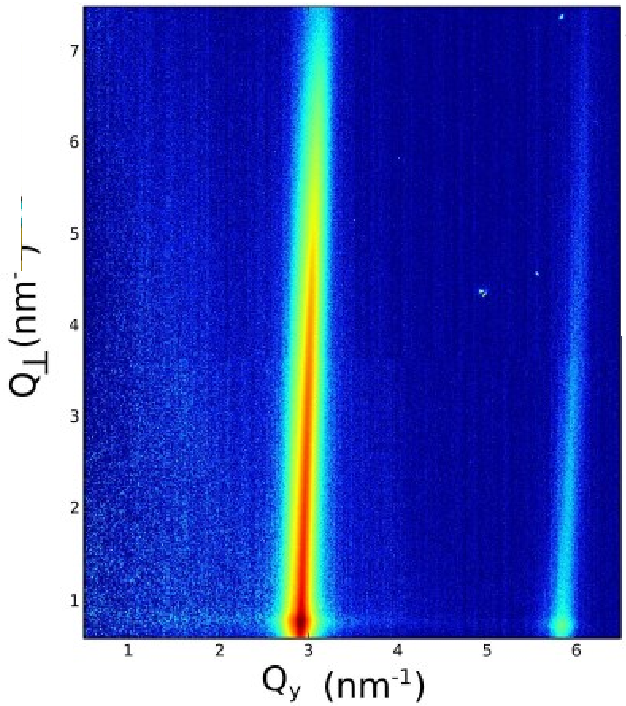
Jadzinsky, et al. Science 318, 430 (2007)

Atomic Structure of Ultra

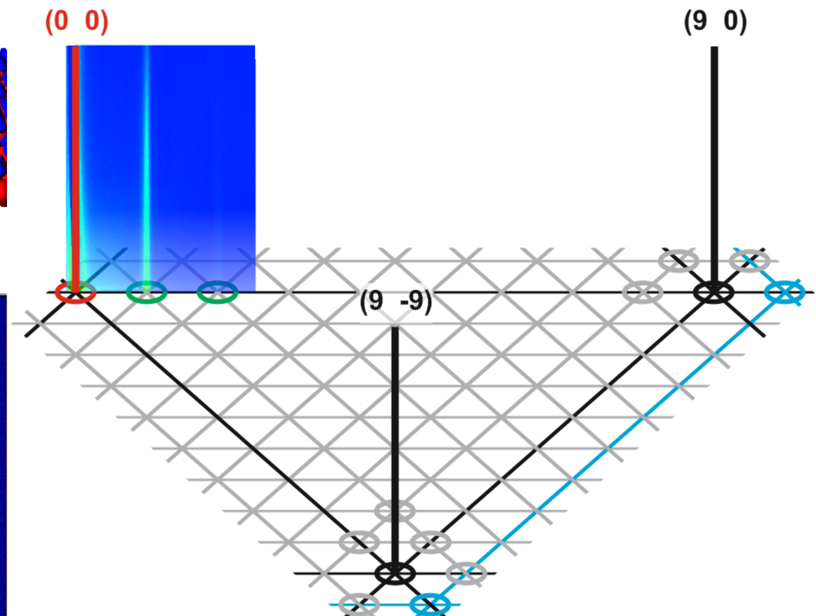
Nanoparticles: Pt, Ir, Pd(Ir), Fe(Ir), Au(Ir), Rh
Support: graphene







GISAXS 0.1 ML Pt



Reciprocal space

T. Michely, Uni Köln

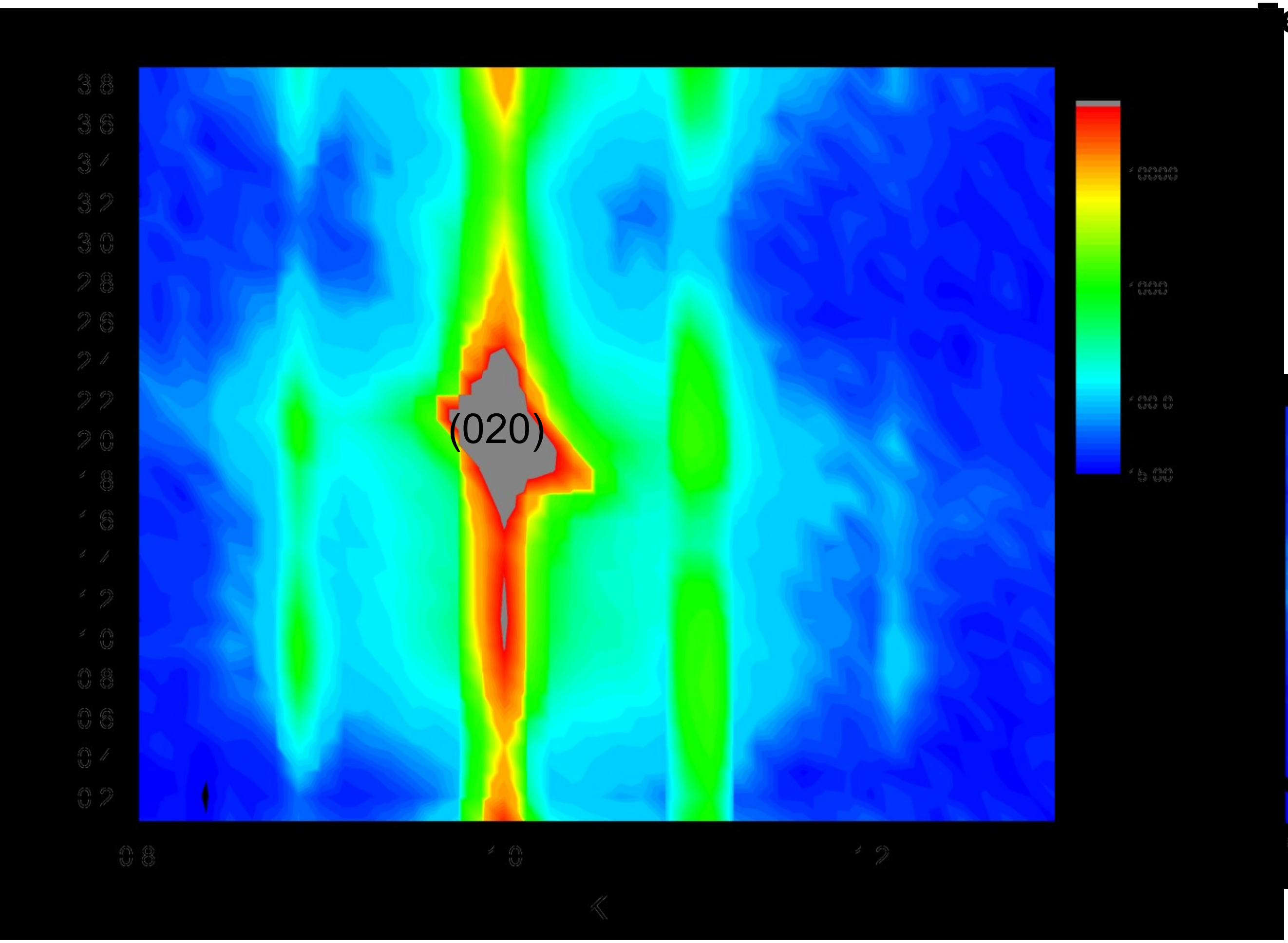
A. T. N'Diaye, S. Bleikamp, P. J. Feibelman, T. Michely, Phys. Rev. Lett. 97, 215501, (2006)

Ultrasmall Particles Supported by Graphene

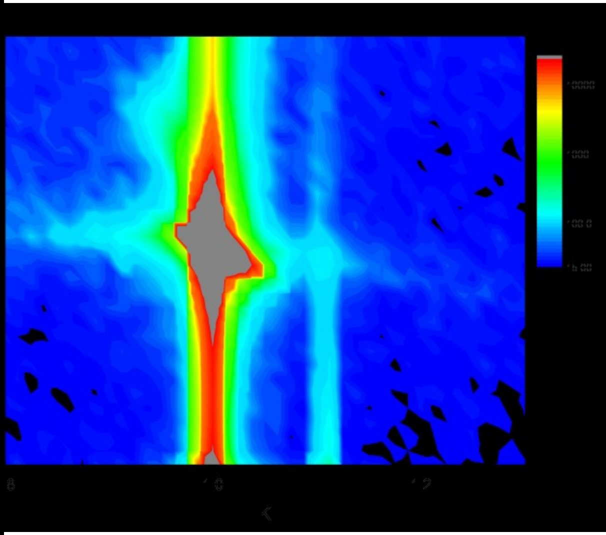
Ir nanoparticle superlattice enhanced x-ray diffraction

Features of map:

- (0 1) CTR,(0 1) SR
- (0 2 0) Bragg-Peak
- superstructure rods
- oscillation of rods (crystalline NP, well defined height)

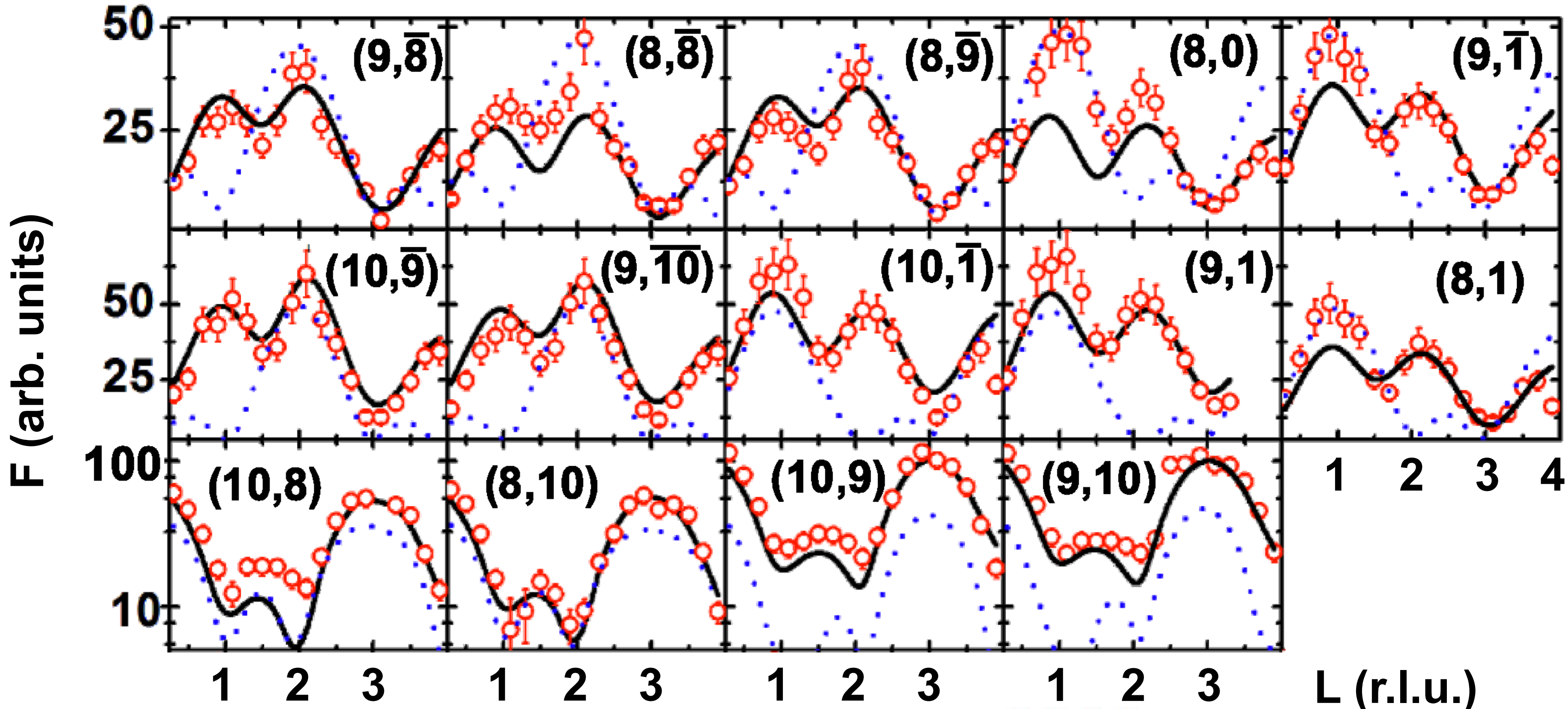


(0KL) map – sample with NP (~1ML)



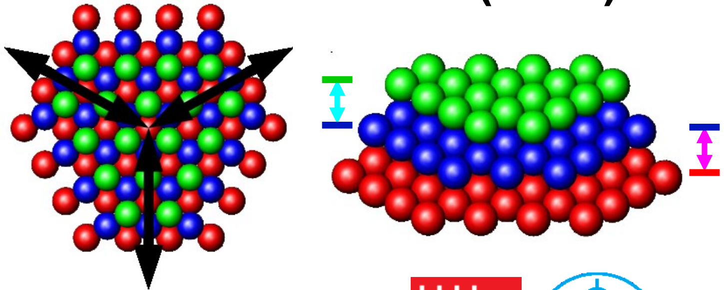
(0KL) map – clean sample

Ultrasmall Particles Supported by Graphene



Fit-Results:

- three/four layered cluster with ABC and ACB stacking
- occupancies (b, 2nd , t-layer): **53 %** , **49 %**, **45 %**
- strain (b, 2nd, t -layer): **2.5 %**, **2.3 %**, **3.6 %**
- z - displacement: **-4.8 %** (2nd-layer), **+3.9 %** (3rd-layer)



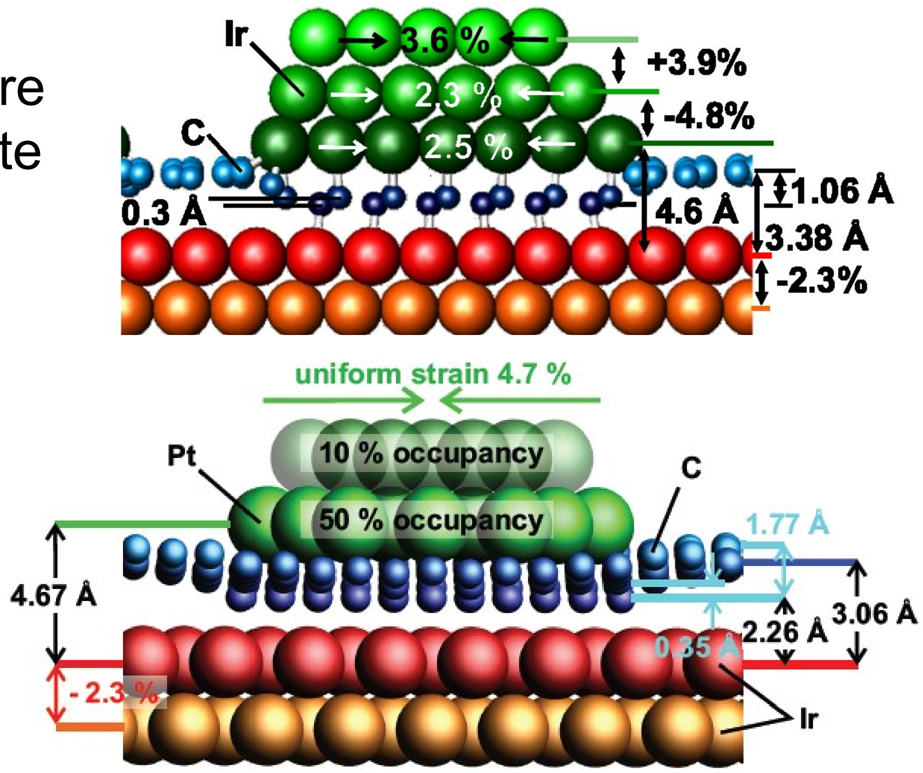
Ultrasmall Particles Supported by Graphene

- SXRD together with graphene moire templated growth is a possible route of metal cluster structure analysis

➢ Gas adsorption experiments (suitable metals, reactions)

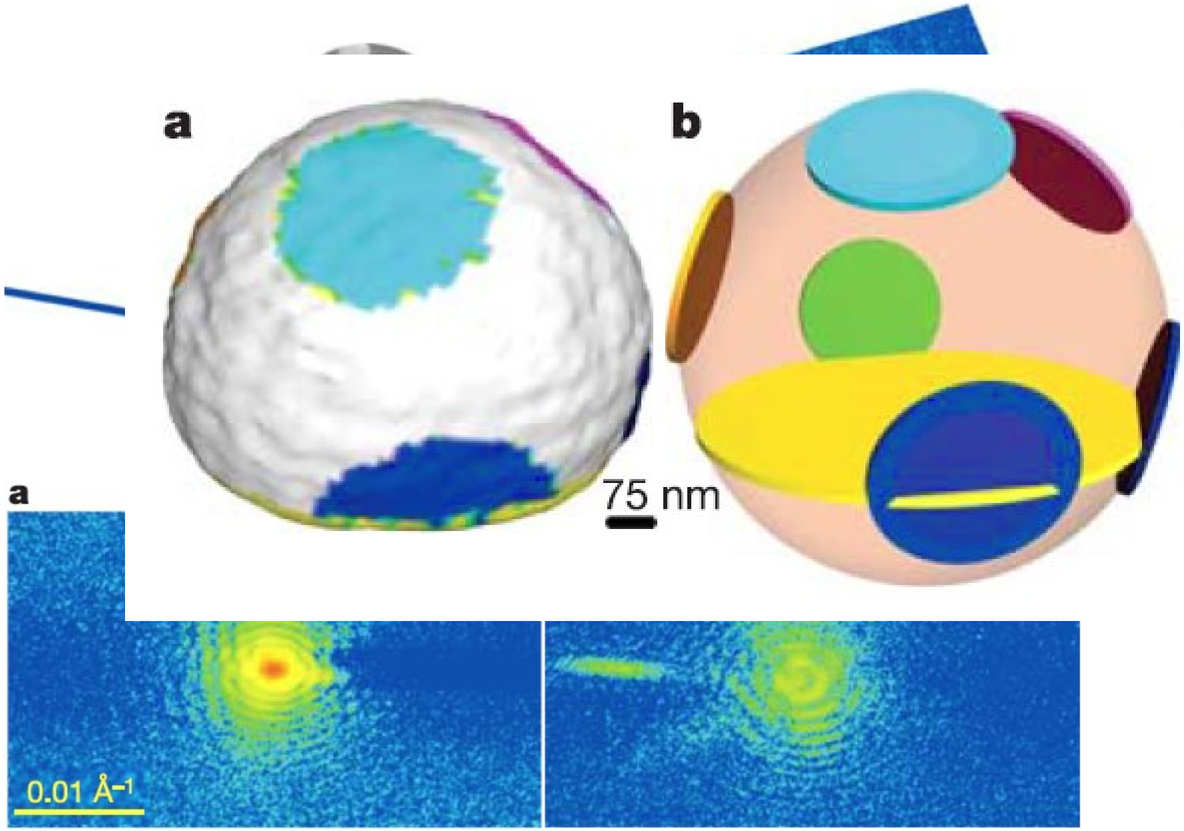
➢ Alloy nanoparticles in confinement

➢ Magnetism



D. Franz, S. Runte, C. Busse, S. Schumacher, T. Gerber, T. Michely, M. Mantilla, V. Kilic, J. Zegenhagen, A. Stierle, Phys. Rev. Lett. 110, 065503 (2013).
S. Billinge, Nature 495, 453 (2013)
PhD work Dirk Franz

Coherent Diffraction X-Ray Imaging



Single particle diffraction with <u>coherent</u> x-ray beam

M. A. Pfeifer, et al., Nature 442, 63 (2006).

Nanoparticle Structural Analysis

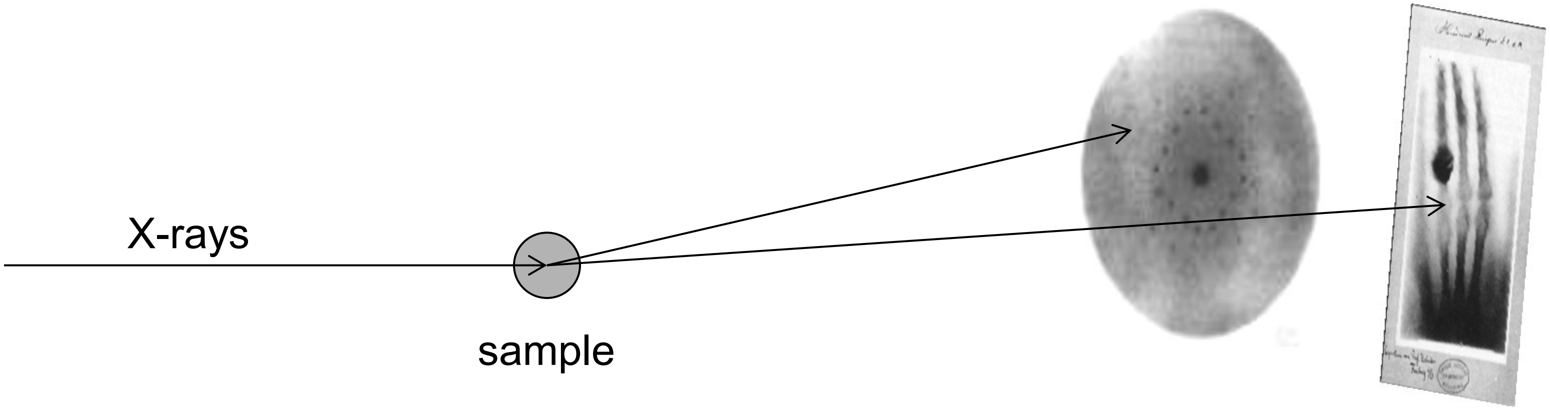
Summary nanoparticle structural analysis

- **Atomic structure of nanoparticles: size, shape**
- **Model systems (=large single crystals) needed to address nanoparticle surface**
- **Analysis complicated by broad Bragg reflections, random particle orientation and size distribution**
- **Protein crystallography approach allows to get atomic scale information**

Take-home message

Synchrotron X-ray based methods for nanostructure investigation:

X-ray Reflectivity (XRR)
Grazing incidence X-ray Diffraction (GIXRD)
Surface X-ray Diffraction (SXRD)
Grazing Incidence Small Angle X-ray Scattering (GISAXS)
Coherent Diffraction Imaging (CDI)



What you see depends on the sample AND the diffraction geometry