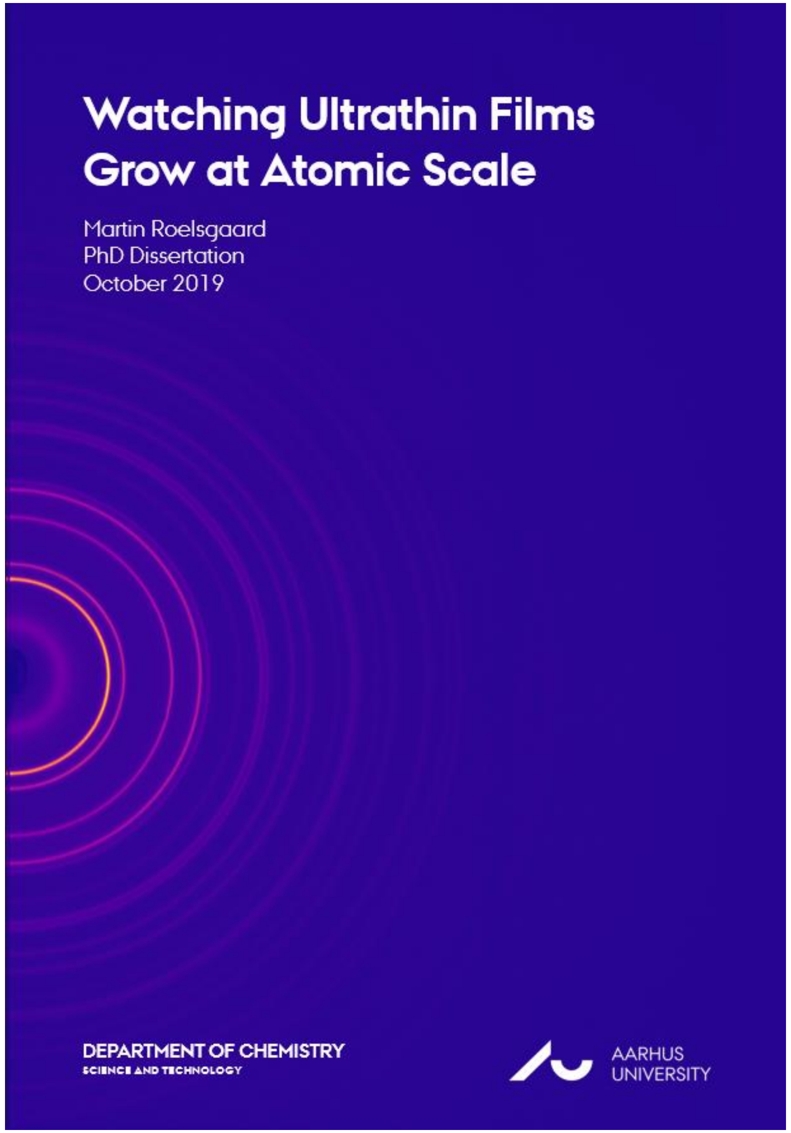
Watching ultrathin films grow at atomic scale

AARHUS UNIVERSITY
DEPARTMENT OF CHEMISTRY

DESY SCIENCE DAY
2 DECEMBER 2020

MARTIN ROELSGAARD
POSTDOC

… based on my PhD dissertation



PhD programme at Dept. of Chemistry, Aarhus University in collaboration with PETRA III

"observing atomic evolution during thin film depositon"
"with total scattering techniques…"

Total scattering from ultrathin films at grazing incidence and *in-situ* magnetron sputter deposition unit

Other topics:
- High-resolution powder x-ray diffraction
- *Operando* module for thermoelectric materials
- Nanoparticle nucleation and growth studies

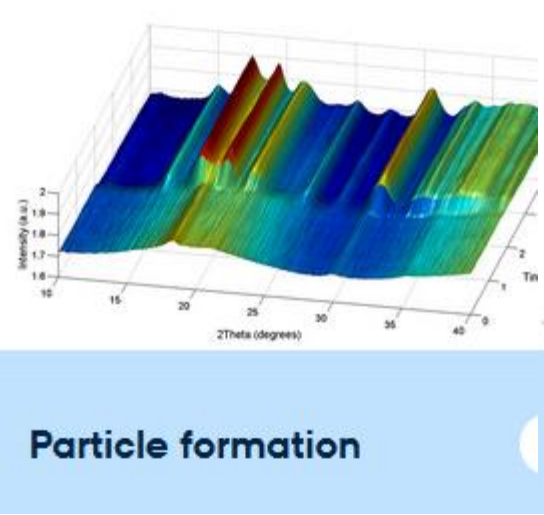
Center for Materials Crystallography – BBI
Who are we?

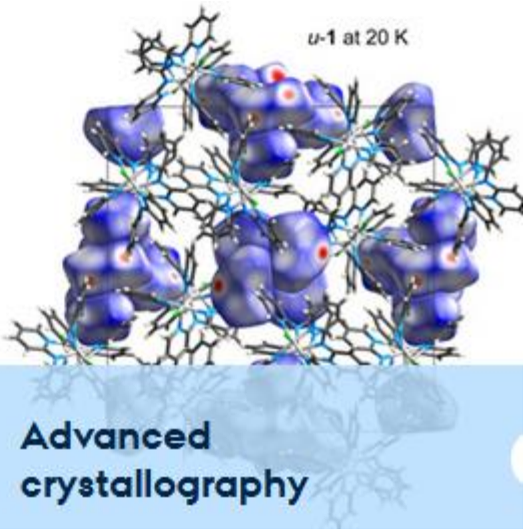
Prof. Bo Brummerstedt Iversen group @ AU:
***Many** activities by …*
- 6 B.Sc. & M.Sc. Students
- 16 PhD students
- 14 PostDocs

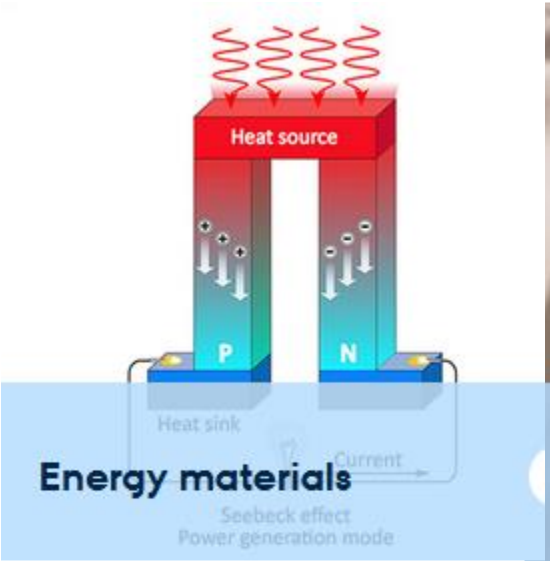
New techniques at synchrotron & neutron facilities

Powder X-ray diffraction, single-crystal X-ray diffraction,
In- and out- of house (such as **PETRA III**)

Directions from Dept. of Chemistry to DESY:
Turn left on Ringgaden,
Turn right on HJ Plads and Marselisborg Blvd,
Stay on E45 and exit at Bahrenfeld (3 hours or so)
Turn right on Notkestraße



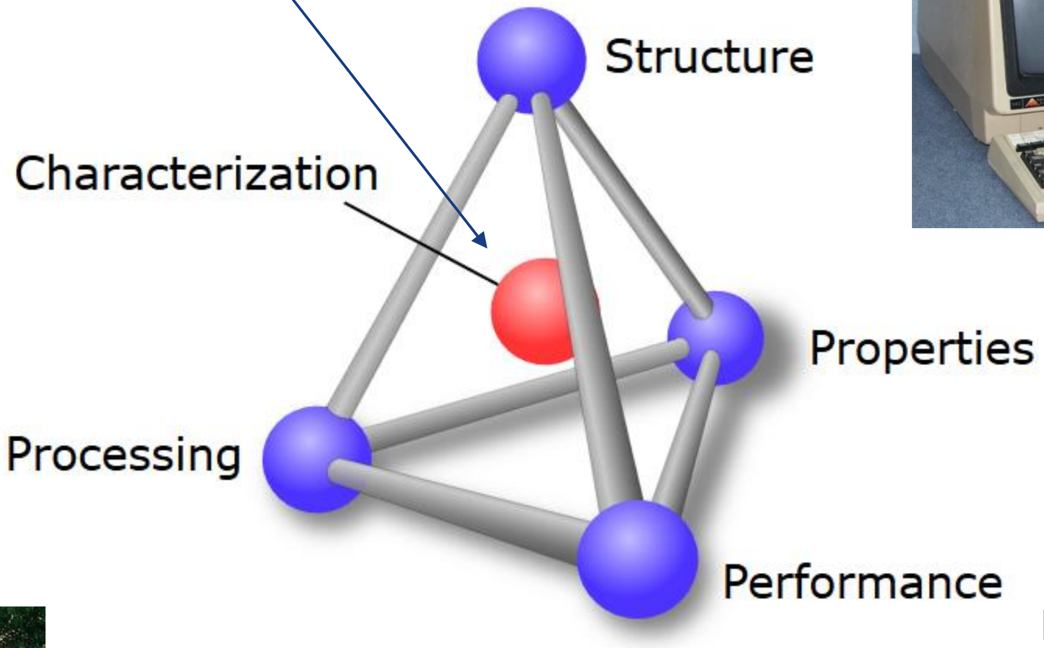




Materials Science
Materials Chemistry / Crystallography

Energy

CRYSTALLOGRAPHY



Computing

Telecommunications

Parking sensors

Batteries

Electric cars

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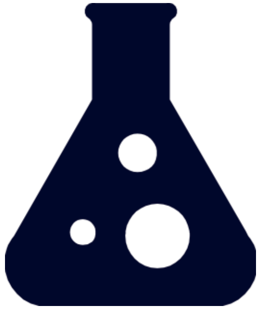
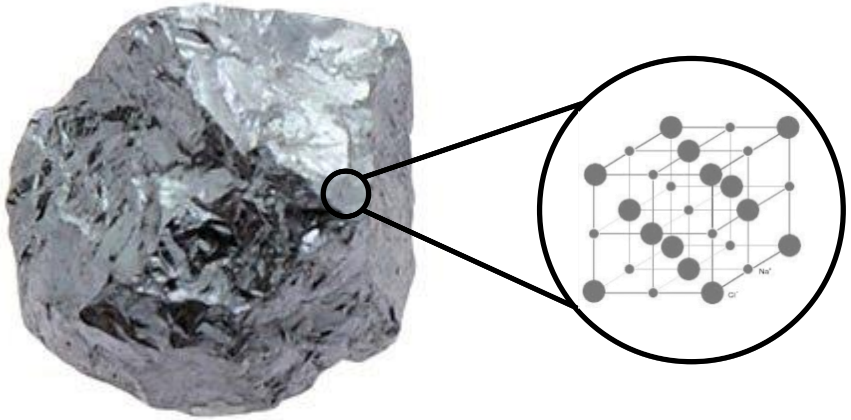
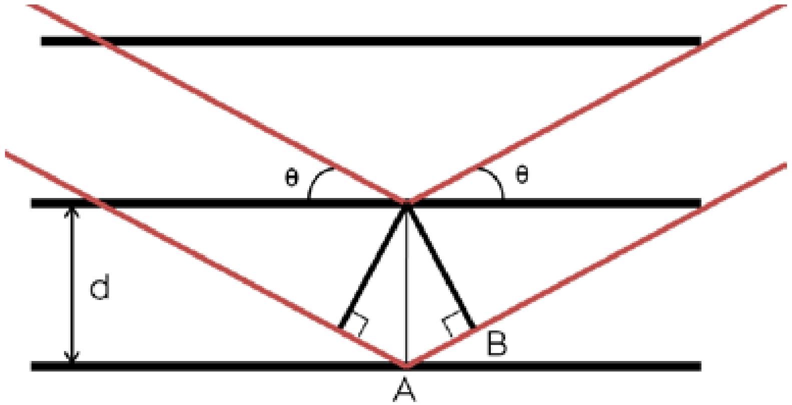
MS tetrahedron from Wikipedia. Photos from google photos.

Crystallography and photon science





'healing crystal'



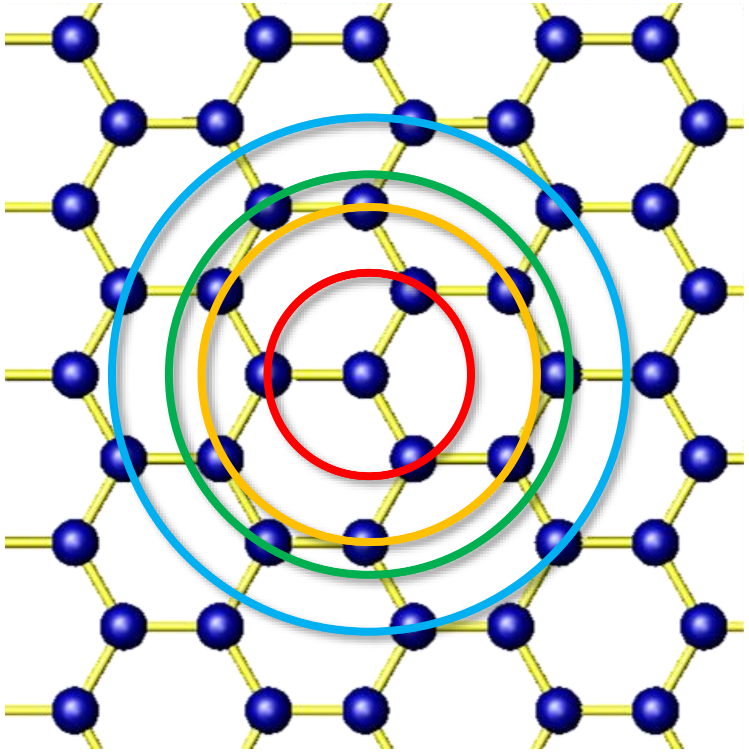
Bragg's law: $n \cdot \lambda = 2d \cdot sin\theta$

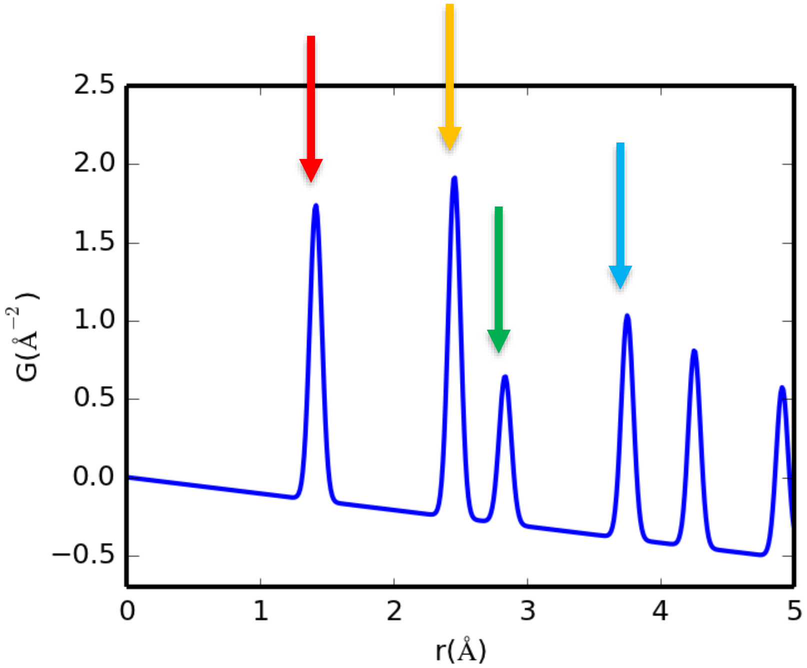
'Scattering angle': $Q = 4\pi sin\theta/\lambda$

Atomic pair distribution function (PDF)

<u>Definition</u>

The PDF is a histogram of interatomic distances in real space i.e. describes the probability of finding a pair of atoms at distance *r*.





Relatively easy to obtain!

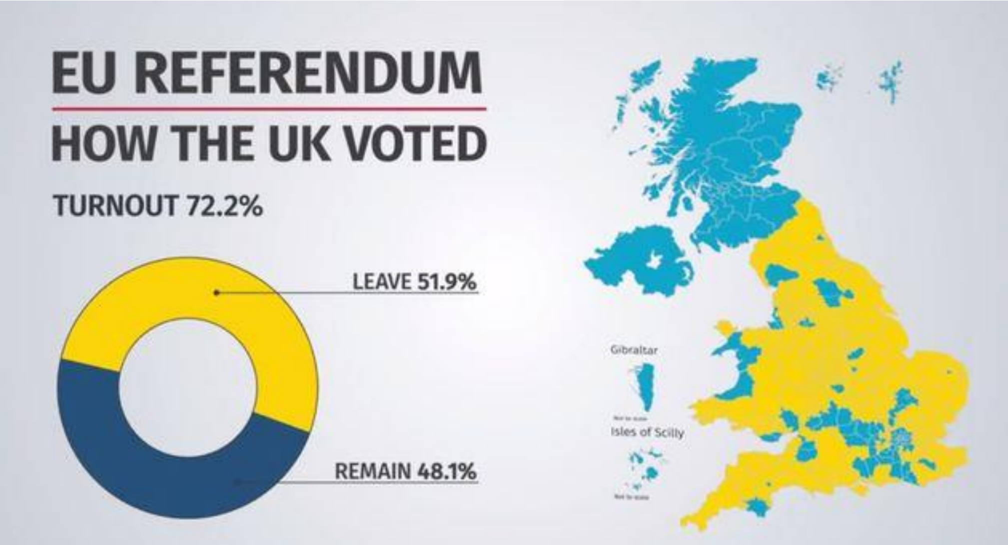
Intuitive, real-space information directly accessible!

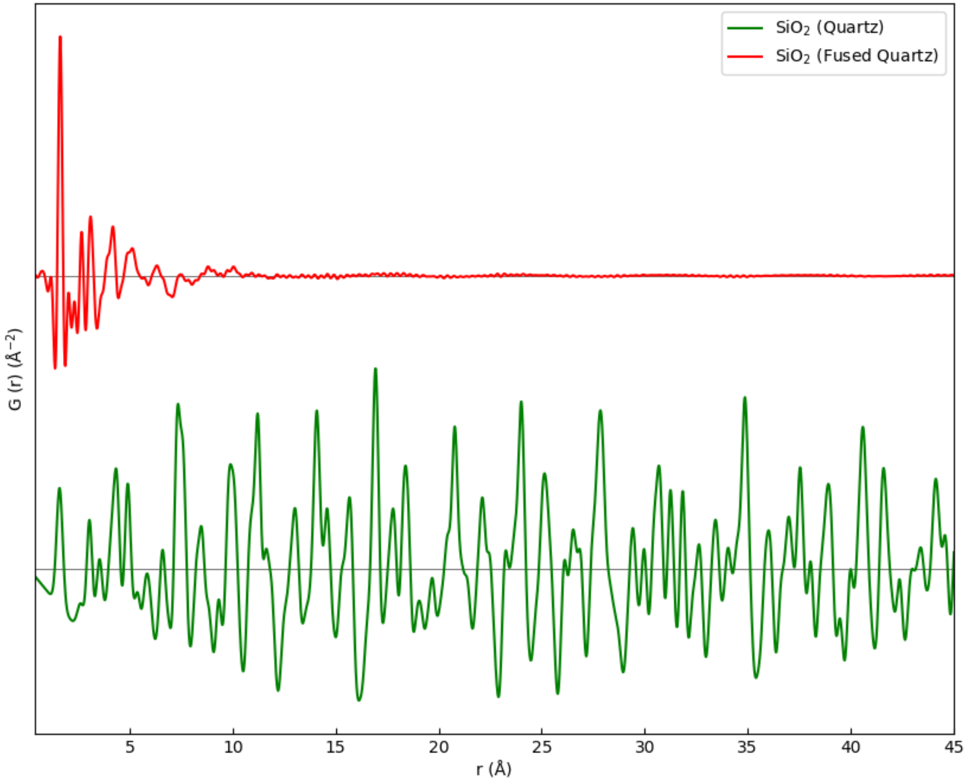
Why bother with the short-range order?

Crystallography is not always enough to understand atomic structure.

Macroscopic properties dependent *not only* on long range order!

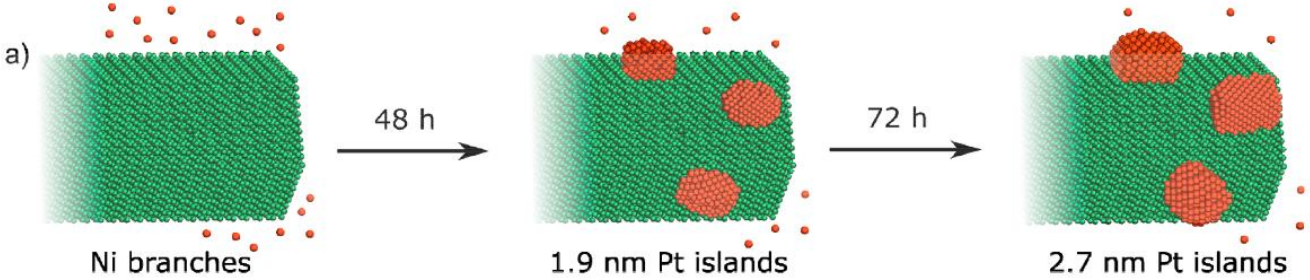
Chemical bonds are dictated by chemistry.

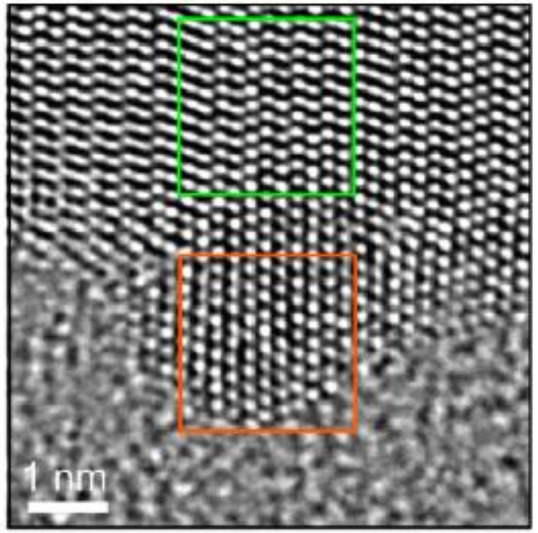


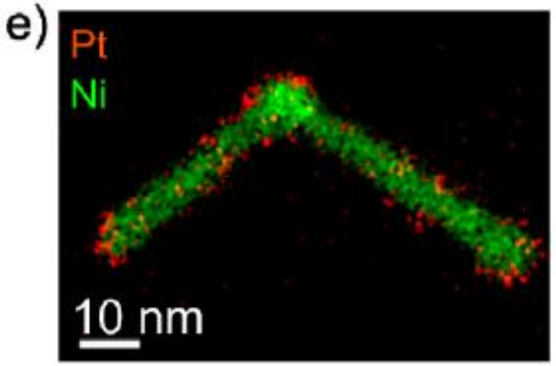


ex: strained Pt on branched Ni nanoparticles

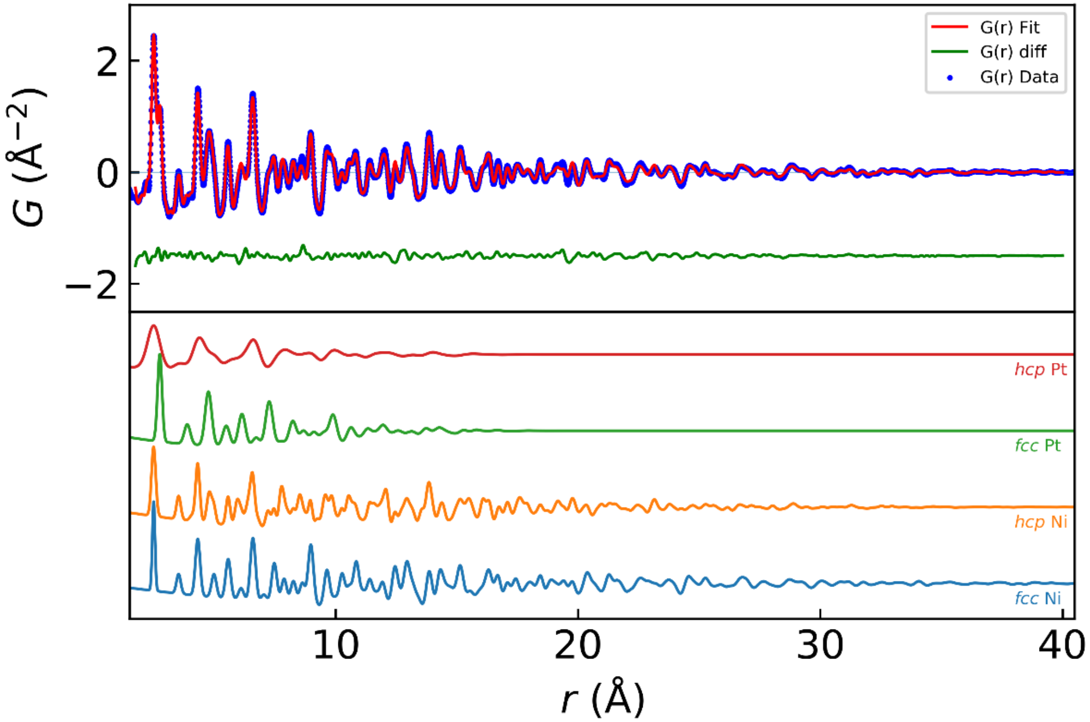
Theory: Strained Pt@Ni(hcp) would be highly beneficial to ORR catalysis. Colleagues at UNSW can synthesize it, but are the imaging observations global?







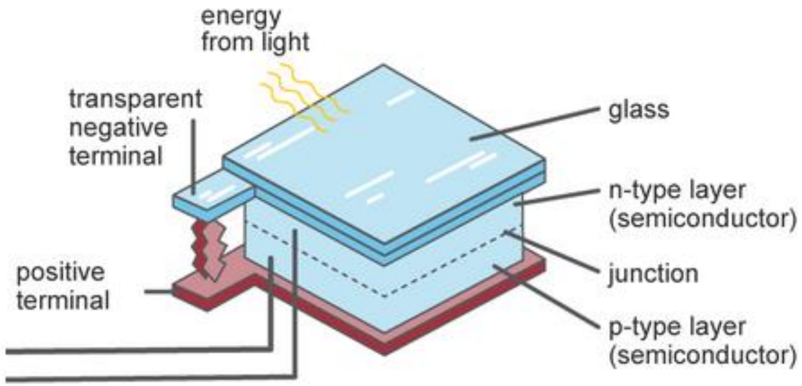
Example from dissertation chapter 6
HR-TEM (Pt on Ni):
DOI: 10.1021/jacs.9b07659



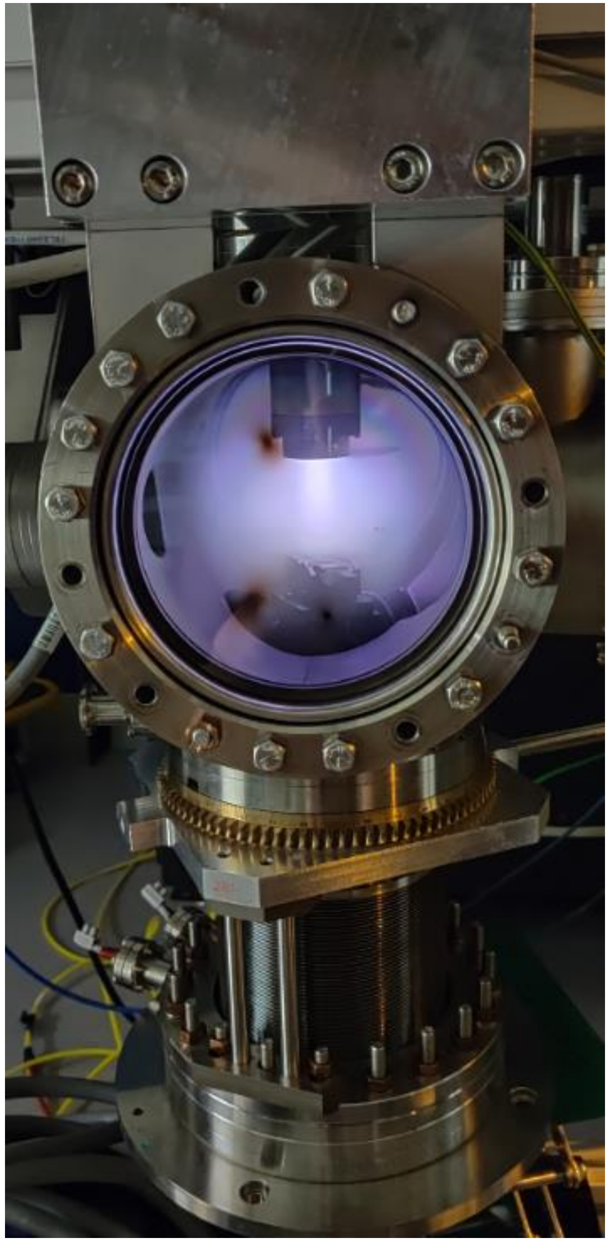
Fcc-Pt highly strained (2.75 Å),
hcp-Pt highly disordered (2.59 Å)
at.w% Pt-Pt at 2.64 Å (5% relative to bulk-Pt)

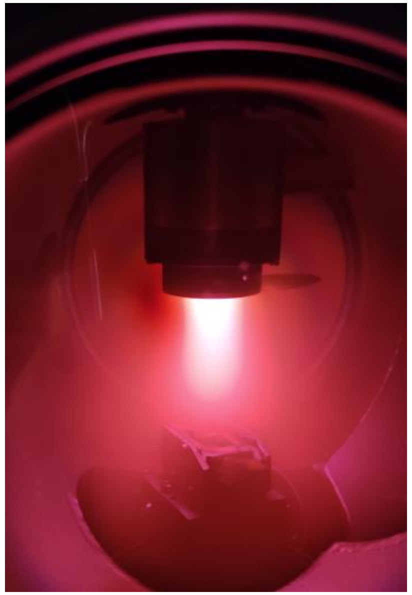
Thin film deposition

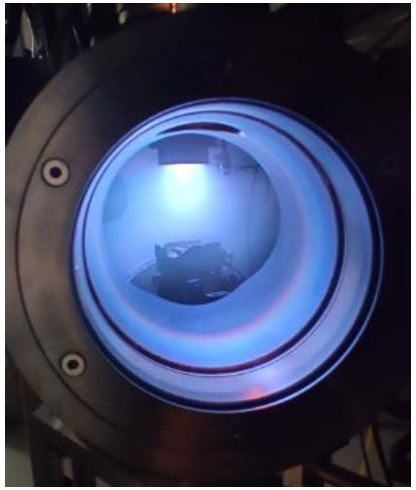
Titanium nitride hardcoat



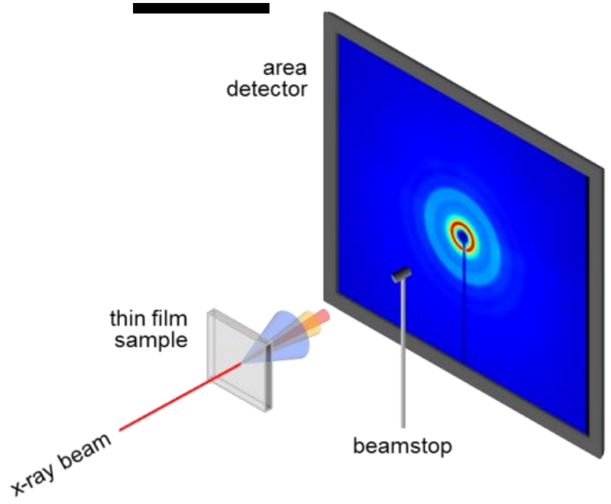
Sputter coating line for glass panels can be yours for 1M $!







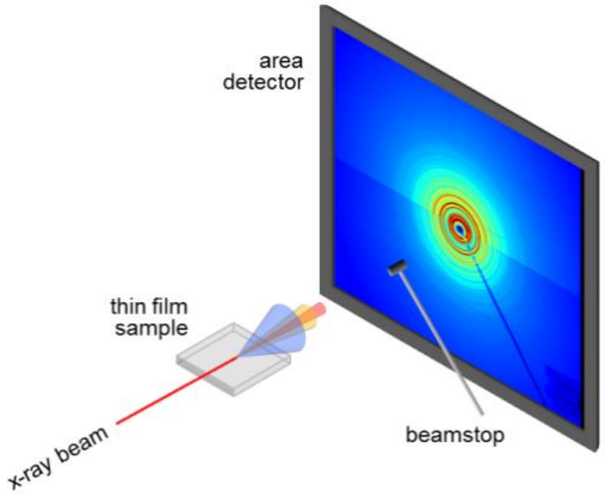
Thin films are hard



Simple experiment – difficult data reduction

360 nm Fe-Sb thin films
Jensen *et al.* (2015)
DOI: 10.1107/S2052252515012221

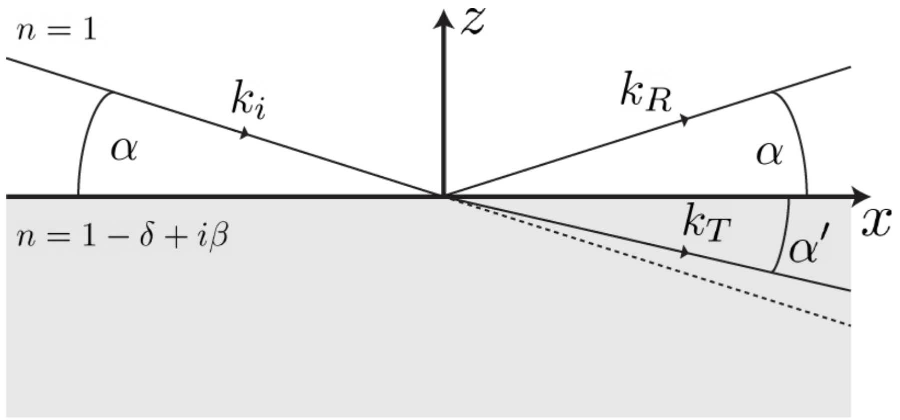
Since then:
transmission mode: 40-50 nm tfPDF (unpublished)

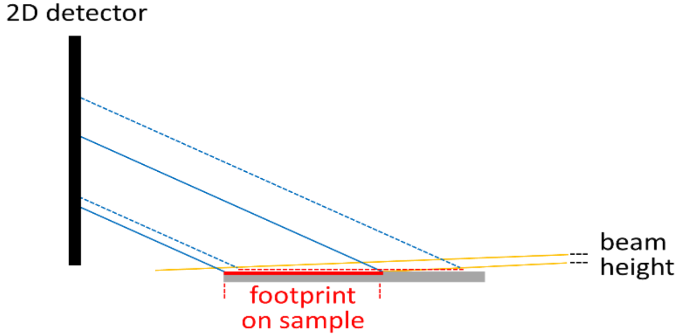


Difficult experiment – simple(r) data reduction

Requires high-precision surface diffractometer, micron-focused high-energy photon beam

3 nm Pt
Roelsgaard *et al.* (2019)
DOI: 10.1107/S2052252519000514





Real-world-numbers:

X-ray focus: 2.5 x 25 μm^2 (H x V FWHM) 100 keV
α in milliradians ~**0.015-0.048** deg. in solids

Beam footprint is thus 3-10 mm.
Sample-surface 10x10 mm^2

Tolerances are about 1 μm and 0.001 degree.

From data to PDF

a $I(Q)$ is measured to high Q

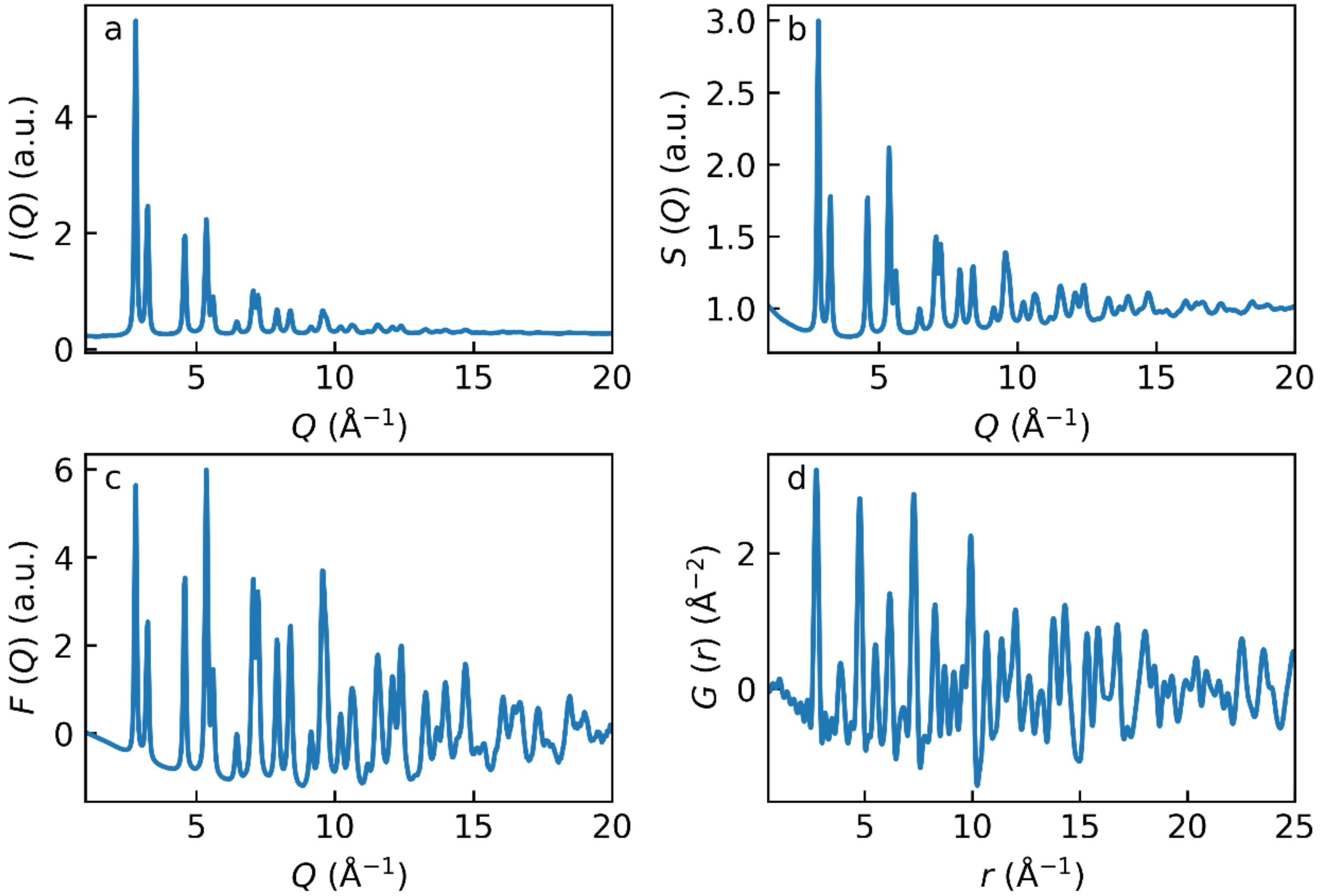
b Normalized according to X-ray scattering factors

c Structure function $S(Q)$ is fitted with a polynomial *ad hoc* to remove incoherent contributions.

$$F(Q) = Q \cdot [S(Q) - 1]$$

d And transformed to real space:

$$G(r) = 2/\pi \cdot \int_{Q_{min}}^{Q_{max}} F(Q) \cdot \sin(Qr)\, dr$$



Magnetron sputtering at a beamline

High or Ultrahigh Vacuum with active stabilization for process gasses

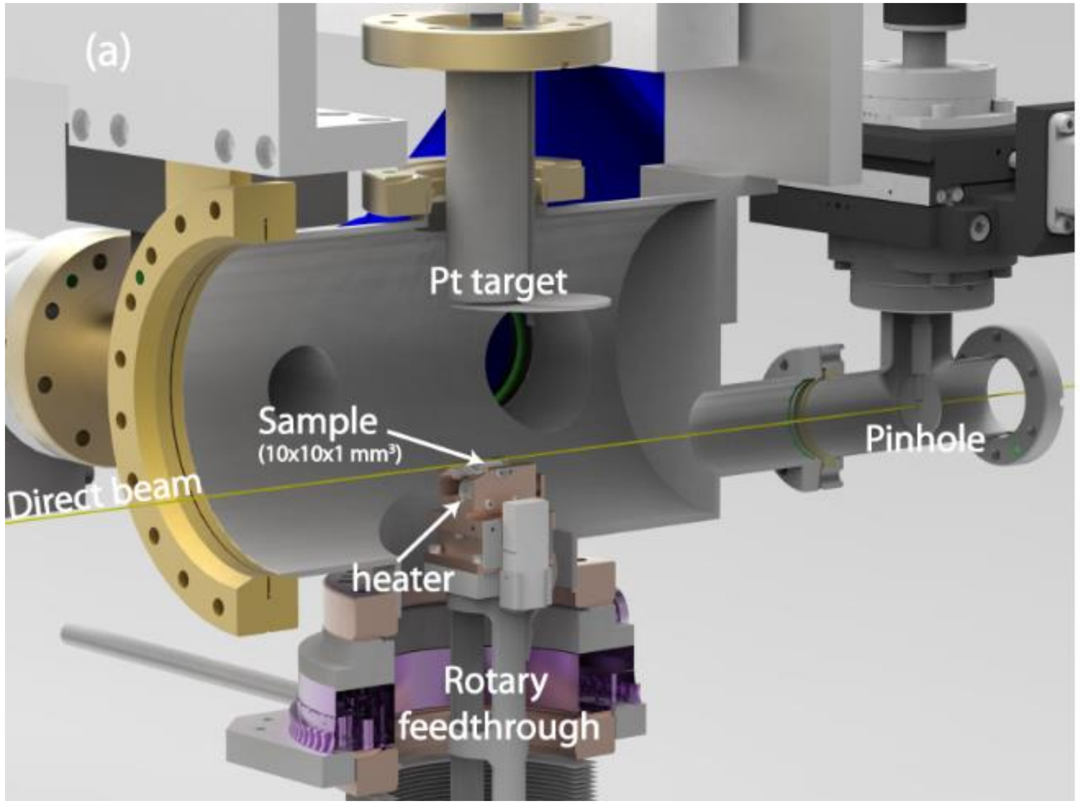
Uninterrupted view downstream of sample up to minimum 23 degrees

Isothermal substrate heating 700 °C

1-inch RF or DC power source 4-12 cm from sample

In-vacuum pinhole system

Full remote control outside experimental hutch



Roelsgaard *et al.* IUCrJ (2019)
DOI: 10.1107/S2052252519000514

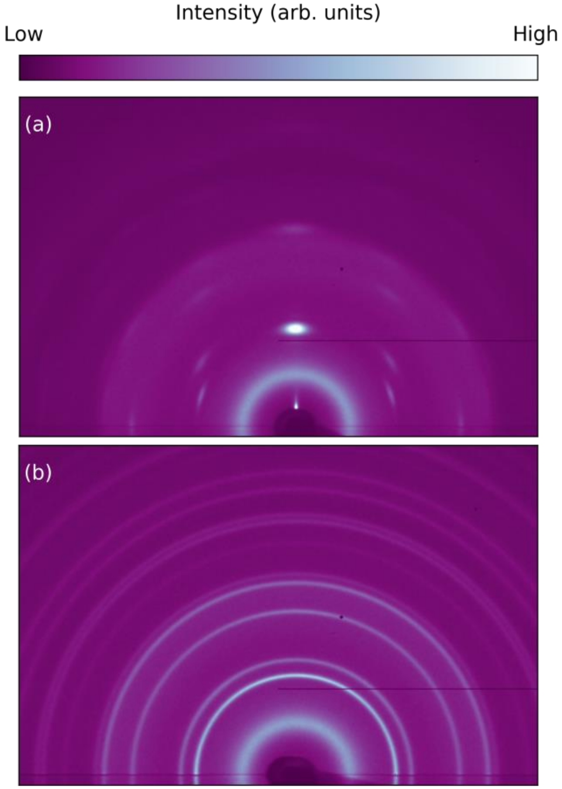
Polycrystalline Platinum – the benchmark

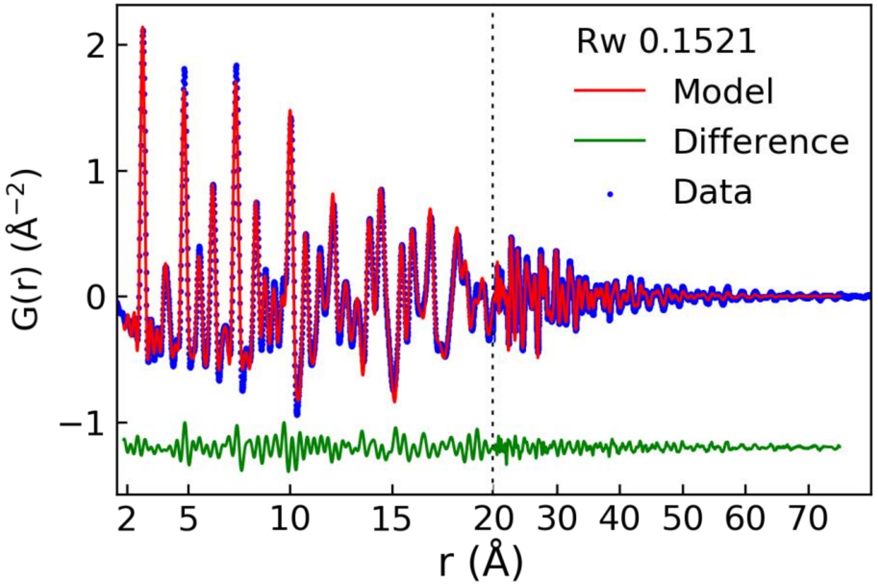
(a) Is about 4.5 nm Pt film with (111) planes parallel to substrate surface (fibertexture)

(b) Is 25.4 nm Pt film with random orientation

The direction of **Q** is important if crystallite orientation is not random! (in solution, N.P. *etc.* is most often random in PDF)

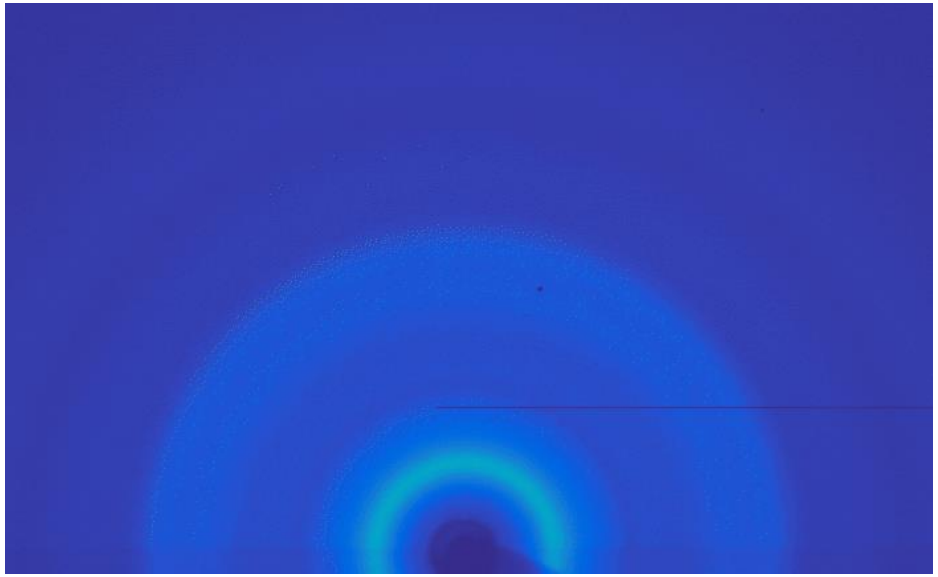
Our best transmission-tfPDF: 50 nm Pt





… in (double) real time!

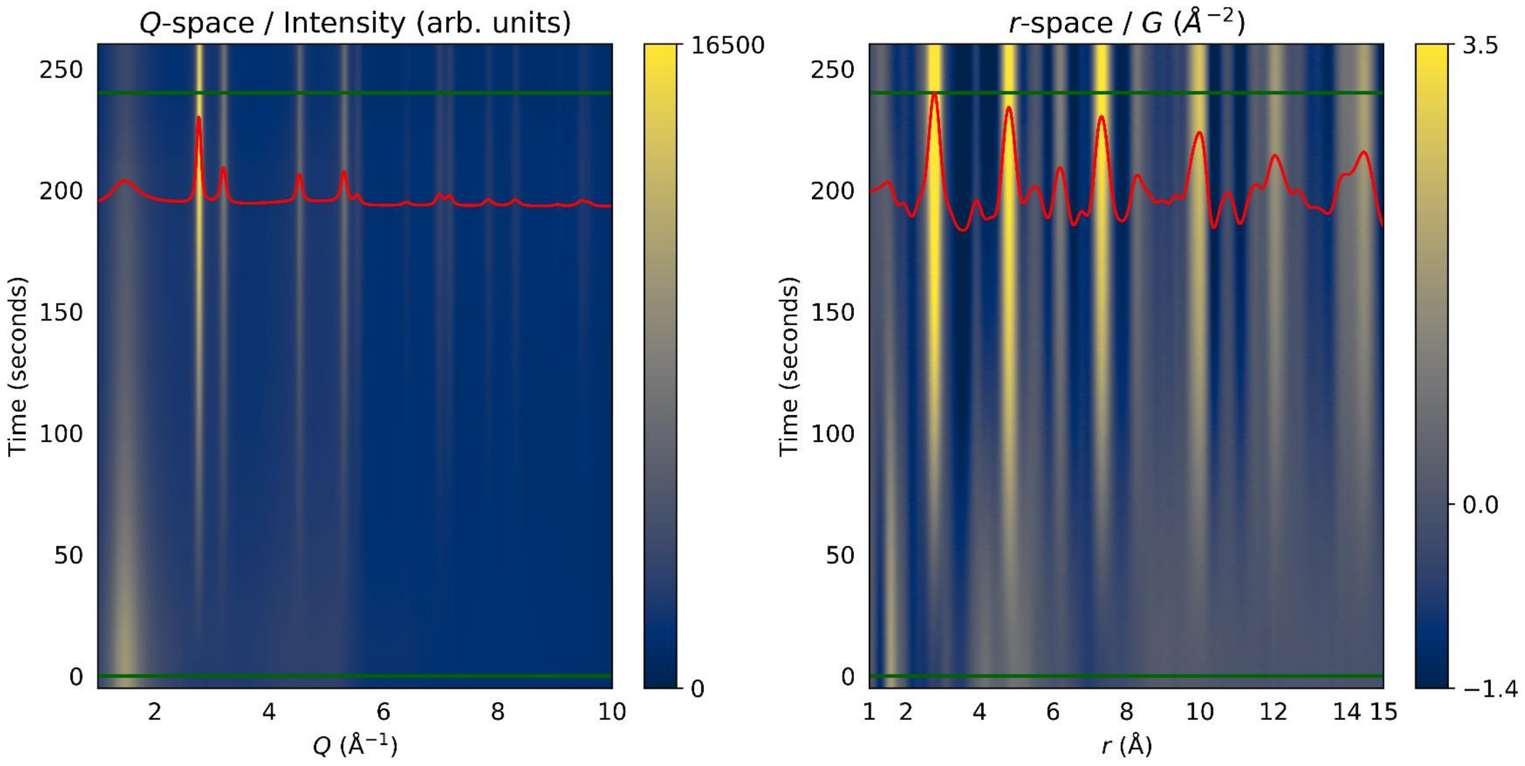
60 seconds of deposition in 30 seconds.



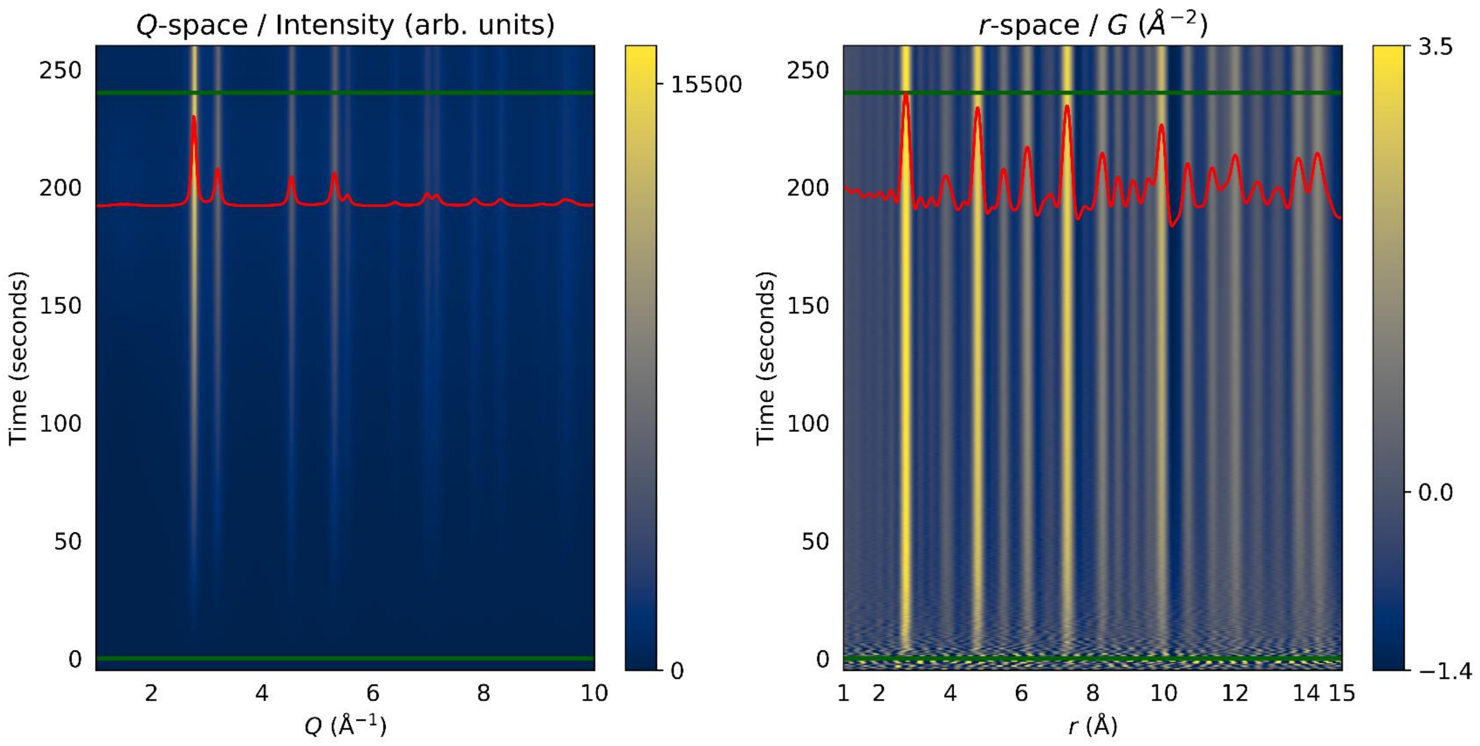
Polycrystalline film without preferred orientation

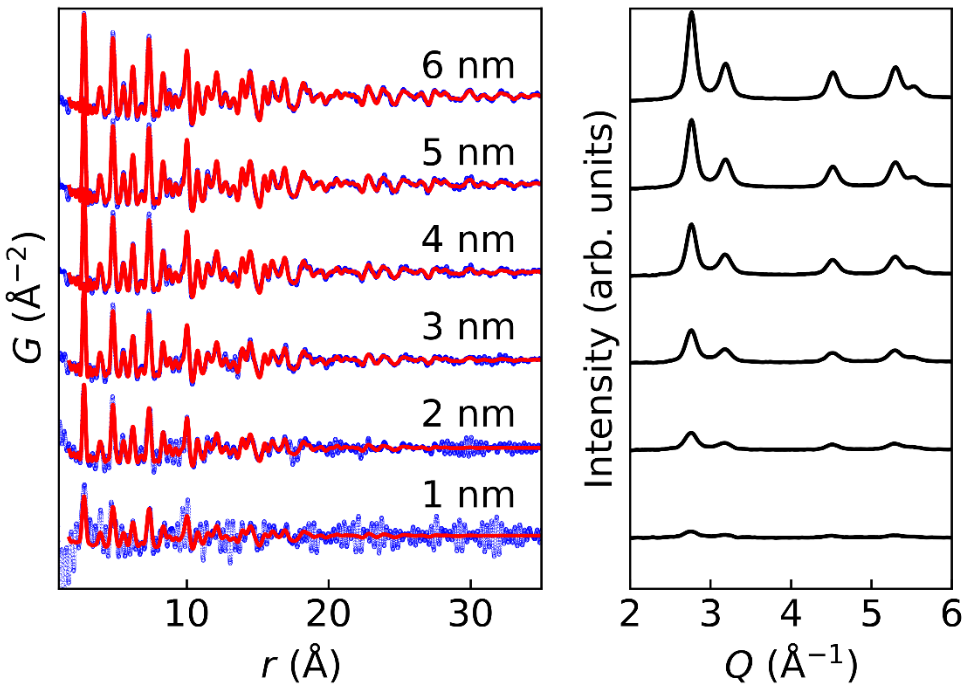
Background changes frame-by-frame due to penetration depth at grazing incidence!

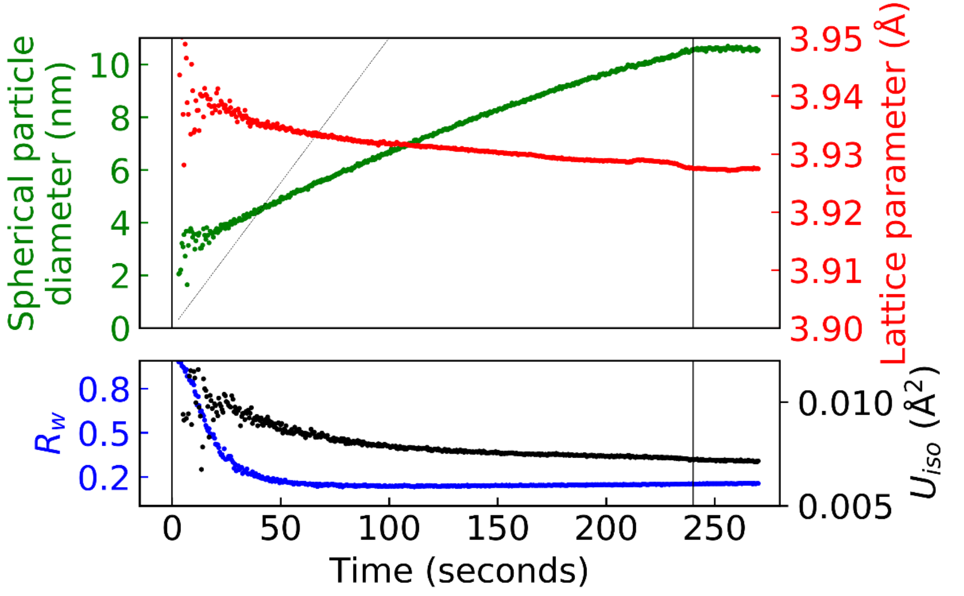
Solved by multivariate curve-resolution alternating least squares method for the *concentration* of background (model-independent)



Time-resolved modelling







Conclusions

1. Total scattering and Pair Distribution Function analysis is gaining traction – also for true, **thin** films

2. GIPDF enables studies of ultrathin films!

3. In real-time during for ex. thin film deposition or temperature treatment

Acknowledgements

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CMC Center for Materials Crystallography

DESY.

DanScatt

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THE VELUX FOUNDATIONS
VILLUM FONDEN VELUX FONDEN

Thank you for your attention.

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