EPFL

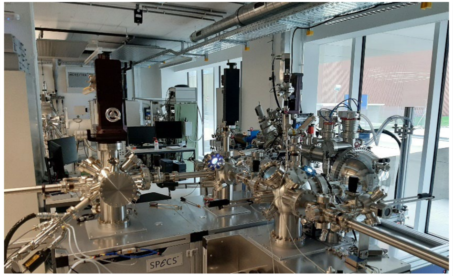
X-ray (and Neutron) Diffraction in Materials Science

Pascal Schouwink
X-Ray Diffraction and Surface Analytics Facility
ISIC-XRDSAP

Labs

Lausanne: BCH 2117, 2118, 1108

EPFL VS Sion: I17 0 I2, I17 – 1 L6+L5



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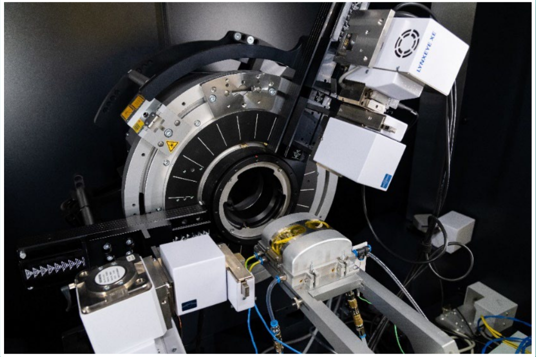

Lausanne campus

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Open to all EPFL users

- 7 diffractometers
- 1 MicroRaman 5 lasers
- 1 XPS/UPS
- 2 AFM
- 1 SAXS lab beamline

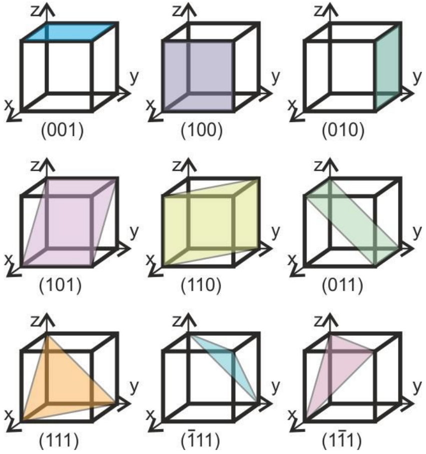
Aim

- Basic understanding of interaction of X-rays (similar for neutrons) with the solid state
- Overview of different common diffraction geometries
- Overview of different methods and applications, what to use when

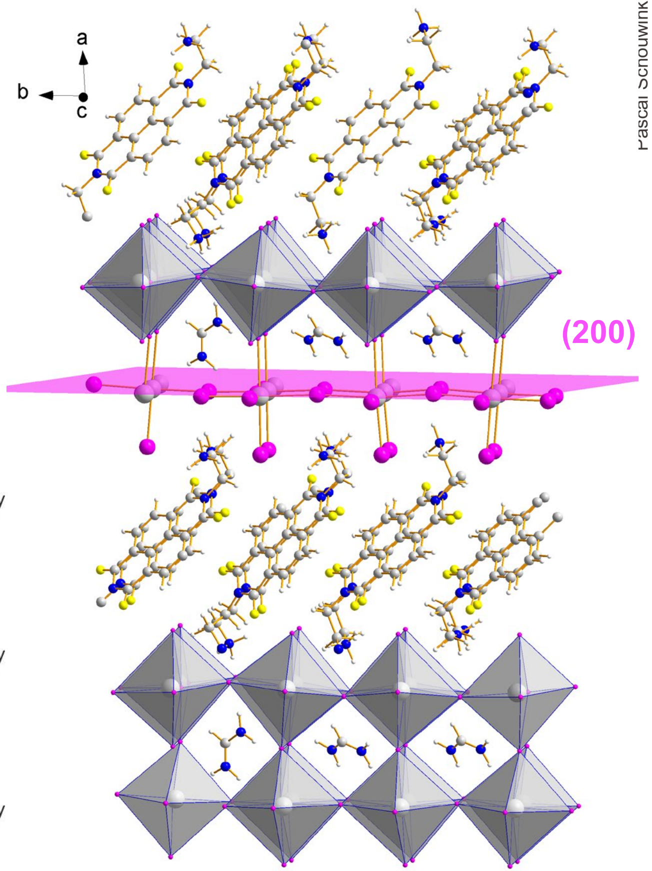
➢ **For more: CH-632, CH-633**

Crystal

- Made up of atoms arranged according to the space group symmetry
- Symmetry (periodic boundary condition) gives rise to what is known as the unit cell (smallest element containing all information and by whose translation 3D space can be tiled)
- Planes hkl can be drawn through any point in the crystal structure, passing through different type and amount of the contained atoms



Source: Naemi Weselnamnn



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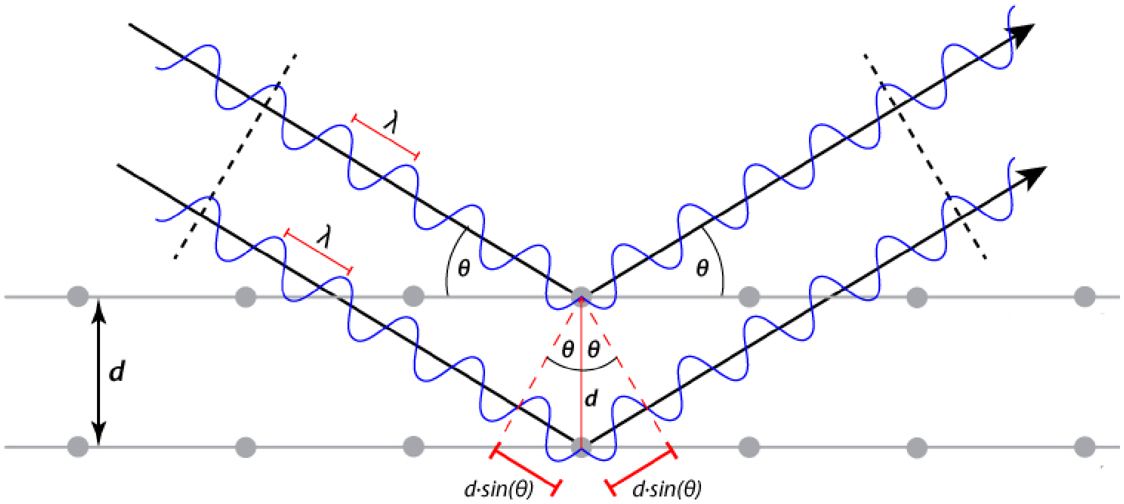
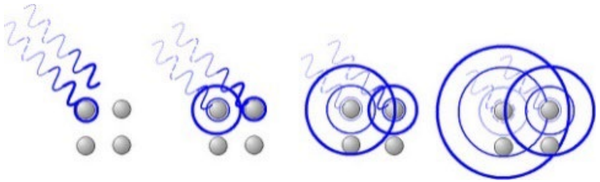
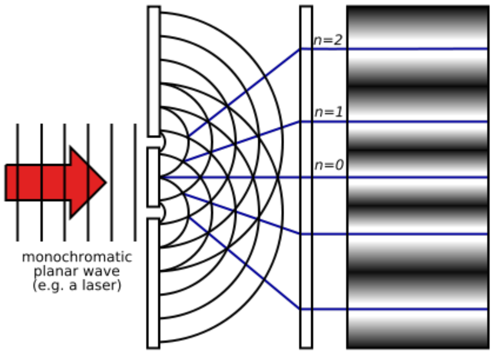
Bragg's law

- (William *Bragg, Nobel Prize Physics, 1915*)
- Geometrical interpretation (!!!) of the diffraction condition.
- Waves "reflected" of lattice planes with a spacing d(hkl) interfer constructively if their phase difference is a multiple of the wavelength.







$2d\sin\theta = n\lambda$ *n*: integer

Bragg's law

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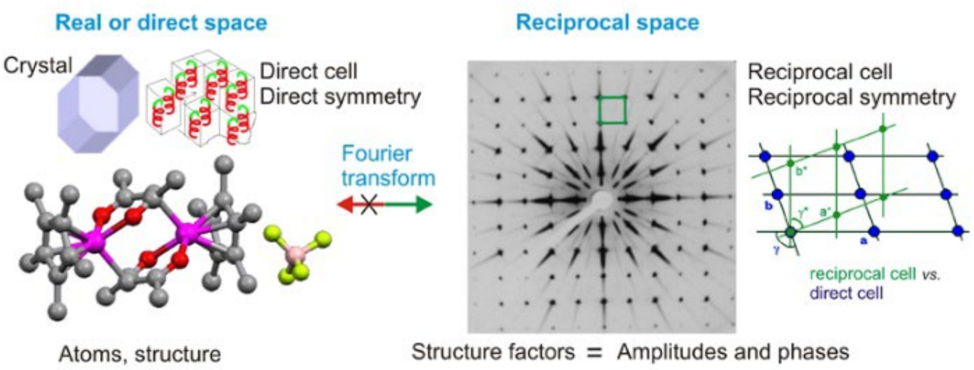
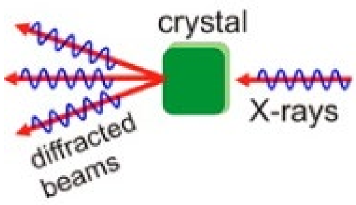
- In reality planes are not occupied by points but atoms (spins), molecules, macromolecules.
- The waves scattered by these objects all interfere simultaneously, giving rise to the diffraction pattern.
- Registered intensities (scattered waves) provide information on the electron density (scatterers) on each plane hkl (atomic structure)





$$\rho(xyz) = \frac{1}{V} \sum_{hkl\,-\infty}^{+\infty} |F(hkl)| \,.\, e^{-2\pi i[hx+ky+lz-\phi(hkl)]}$$

Amplitudes

Phases?

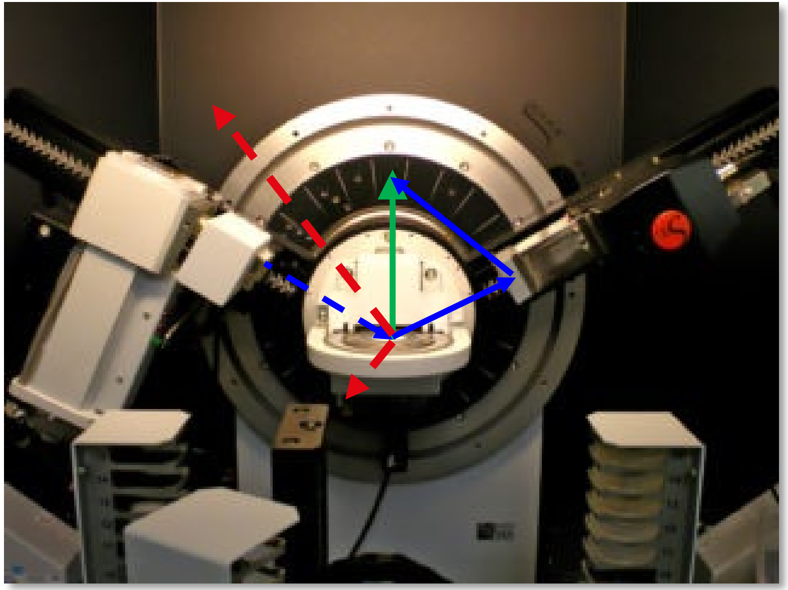
$\rho(r) \rightarrow electron\ density\ \rho(xyz)$
$F(hkl) \rightarrow Scattering\ amplitude: Structure\ Factor$

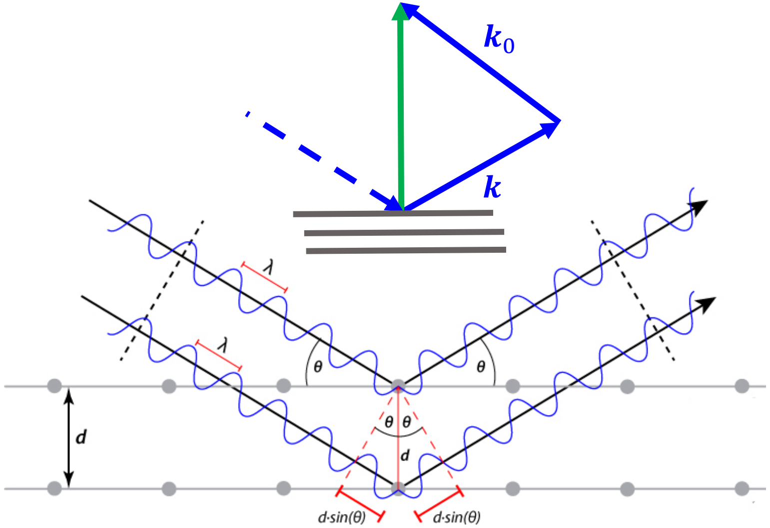
Bragg's law

- Incoming and scattered beam are symmetrical with respect to the lattice plane normal.
- Scattering vector (d^*, Q) is parallel to the lattice plane normal.

➢ Q: How do you measure a scattering vector where this is not the case?

$$\frac{((k - k_0)}{\lambda} = \frac{1}{d} = d^*$$





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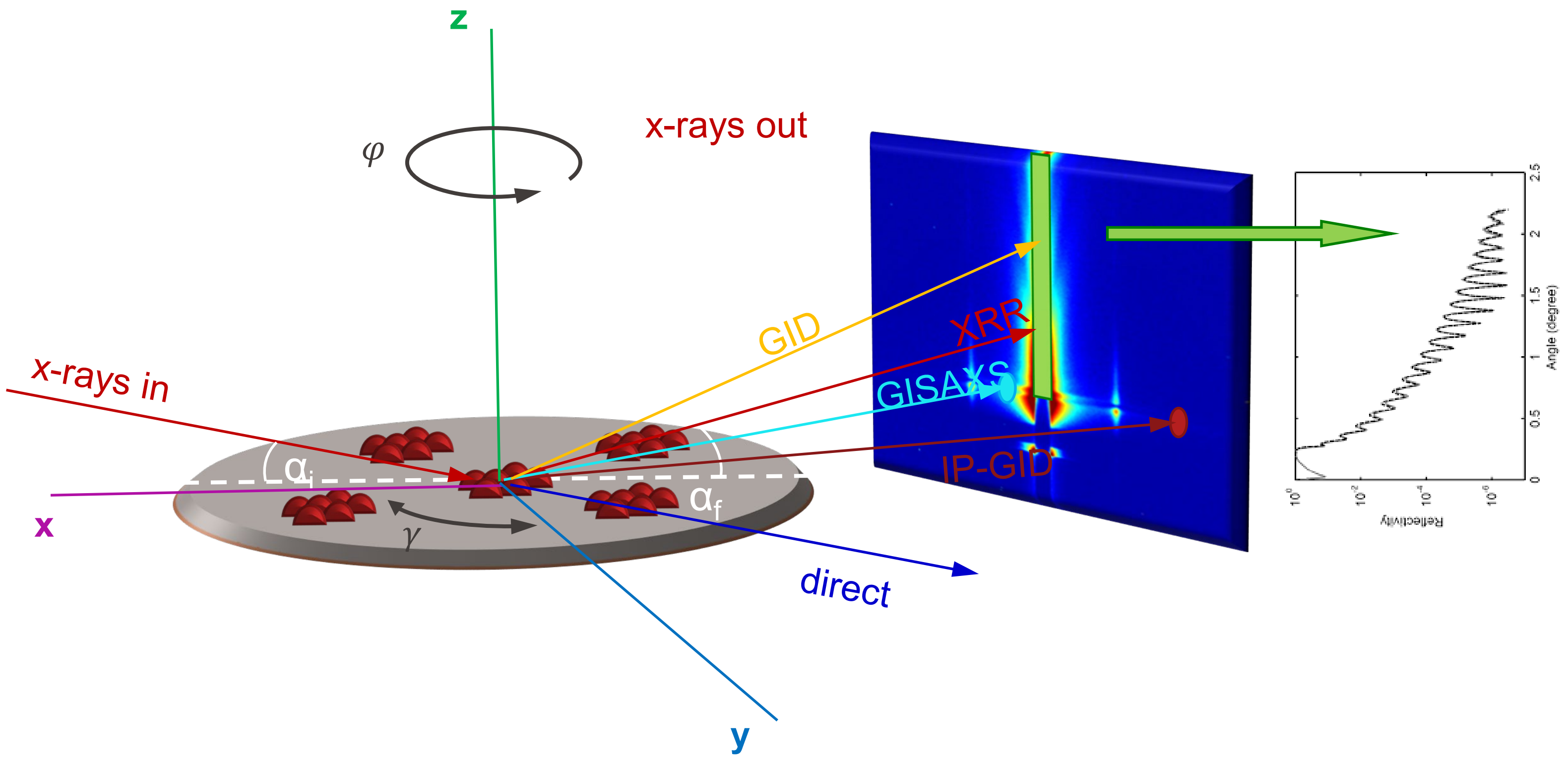
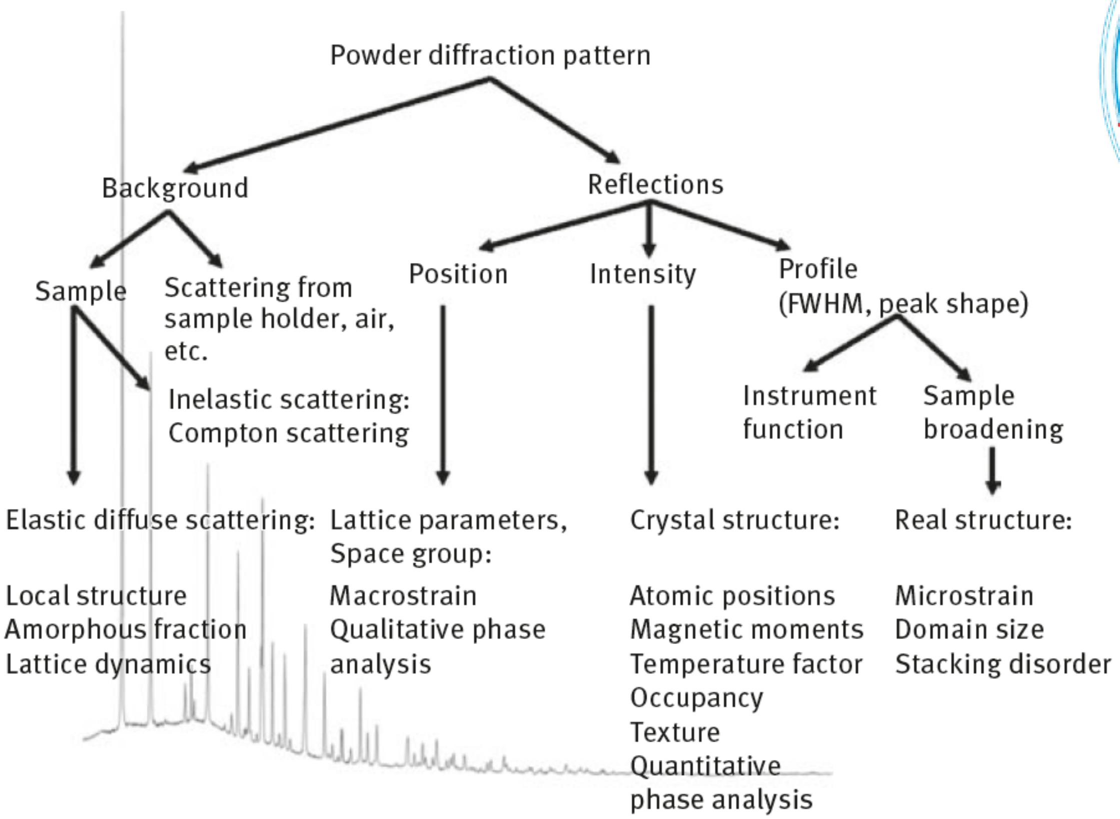
Diffraction geometries

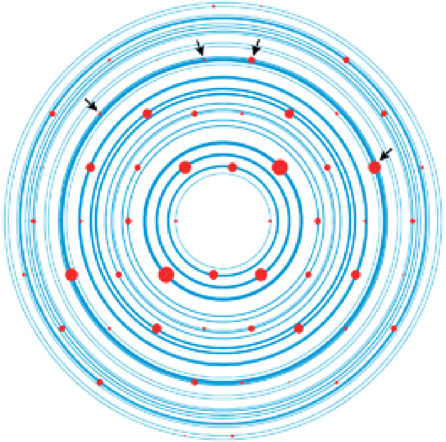


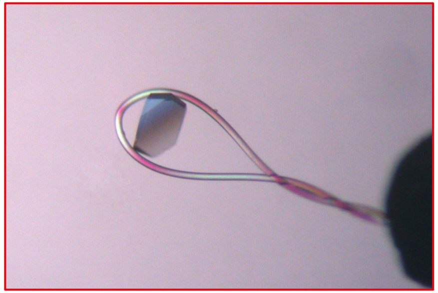
➢ Different optics, motor-movements, geometry, same machine

Diffraction geometries: PXRD

- Information in a diffraction pattern

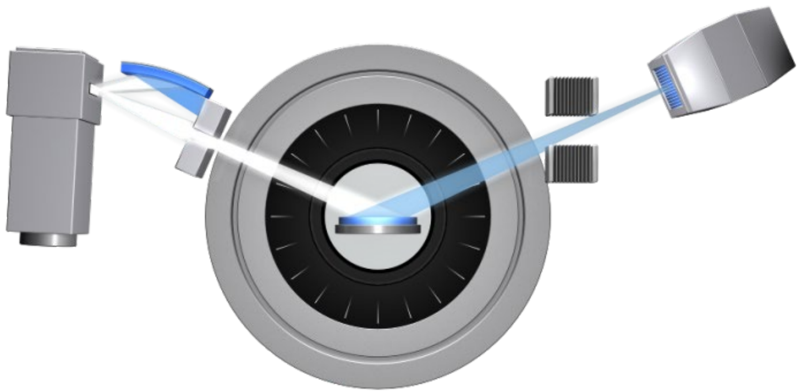


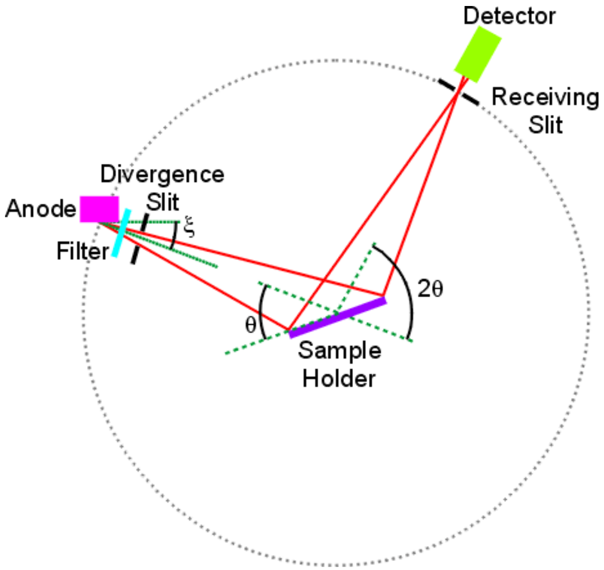




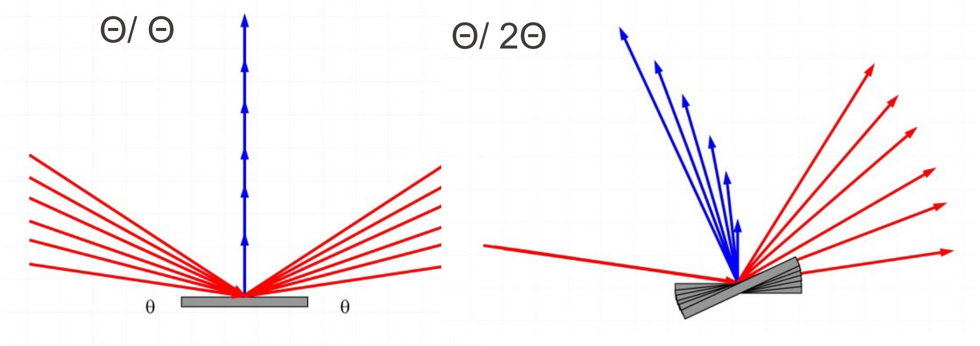
Powder Diffraction: Theory and Practice
Theory and Practice
Robert E. Billinge, S. J. L. Dinnebier

Diffraction geometries: PXRD Bragg Brentano

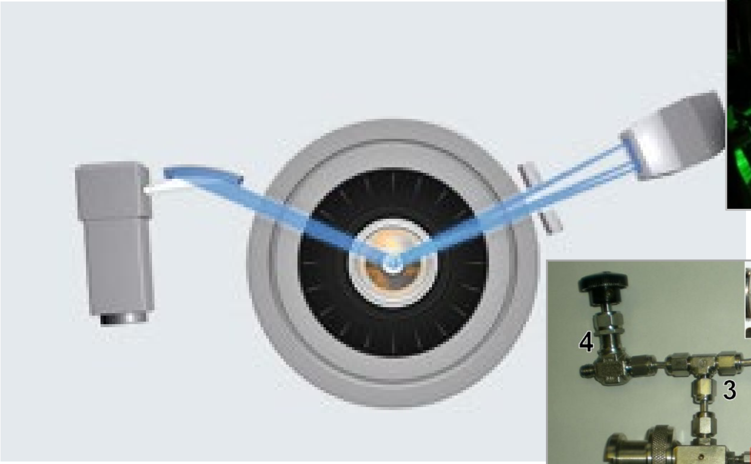


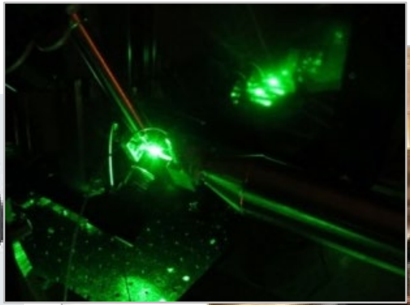


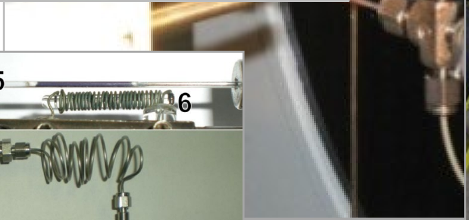
- Reflection geometry.
- Symmetrical scan
- Screening, PXRD

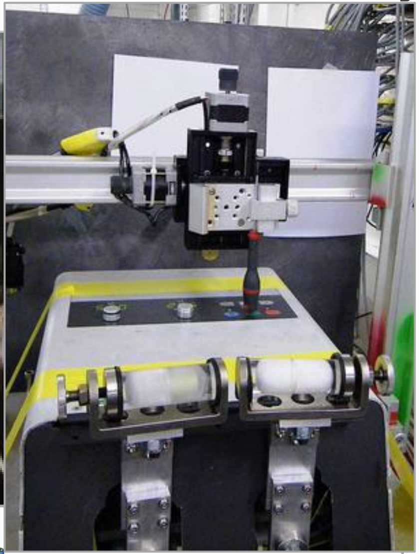


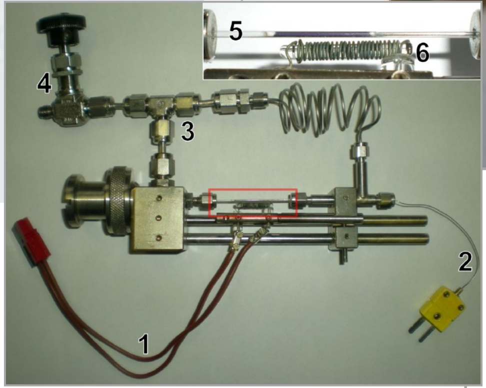
Diffraction geometries: PXRD Debye Scherrer

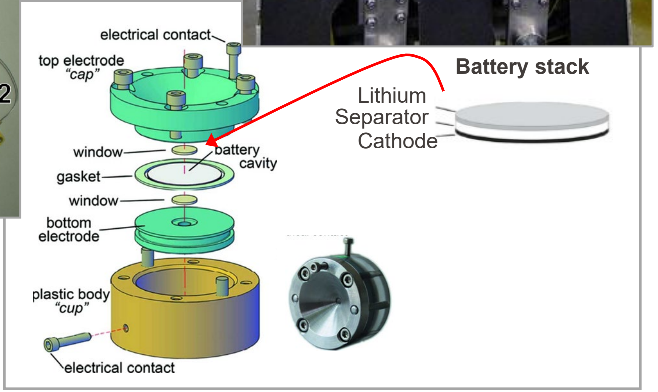












- Transmission geometry
- Detector scan (or 2D image)
- Very flexible (in-situ / in-operando experiments)

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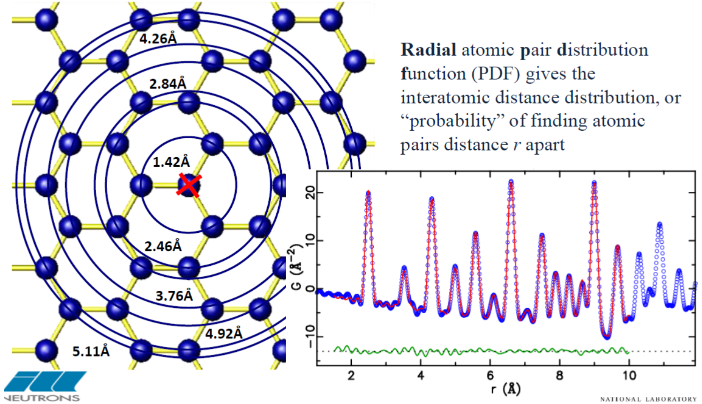
Diffraction geometries: Total Scattering



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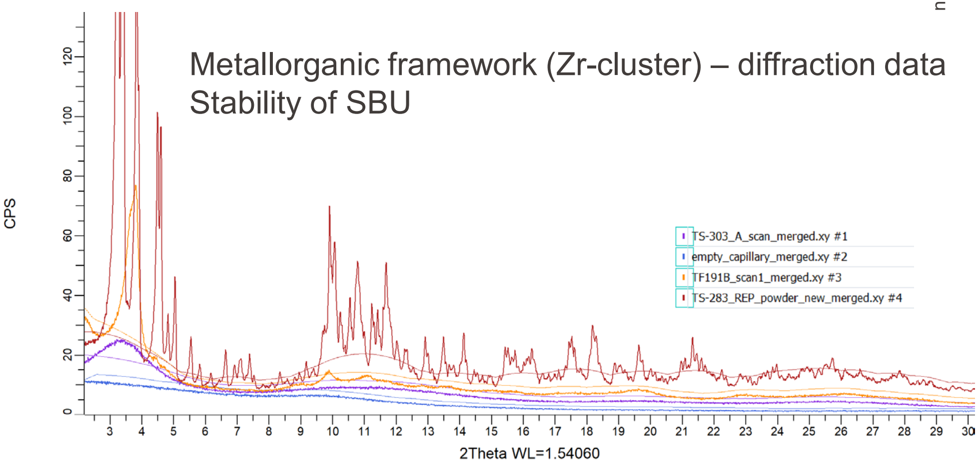
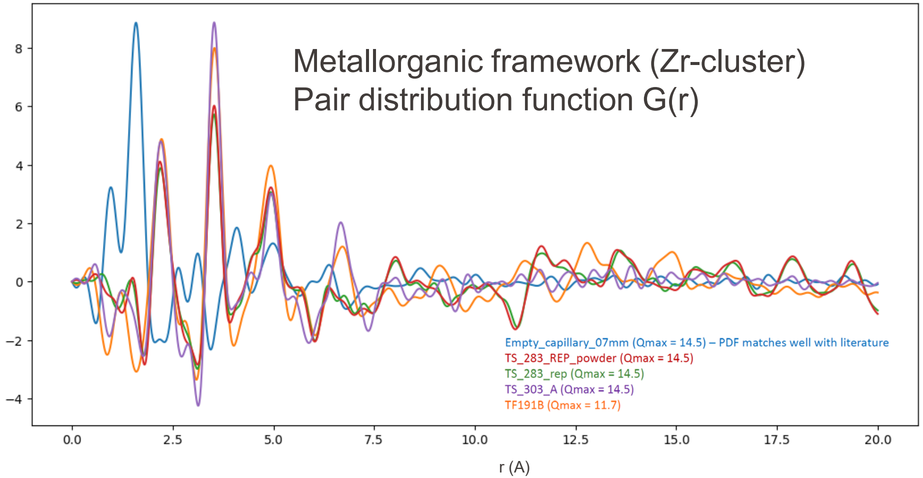
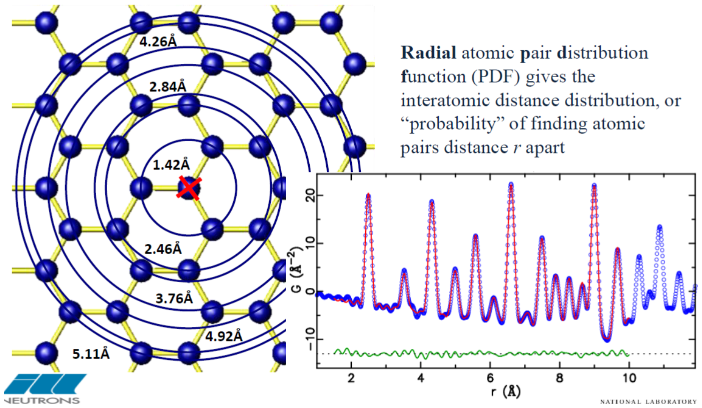


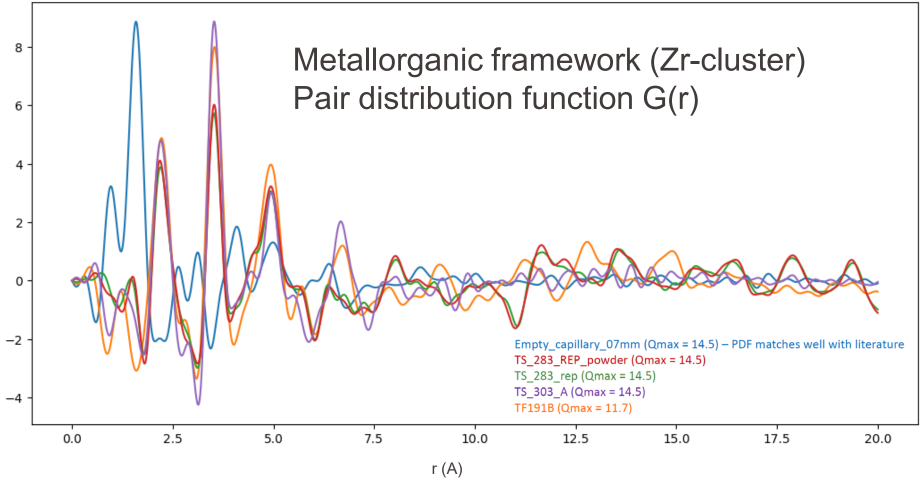


- Transmission geometry as Debye Scherrer
- At least 17 keV! Detector scan (or 2D imag
- Very flexible (in-situ / in-operando experim

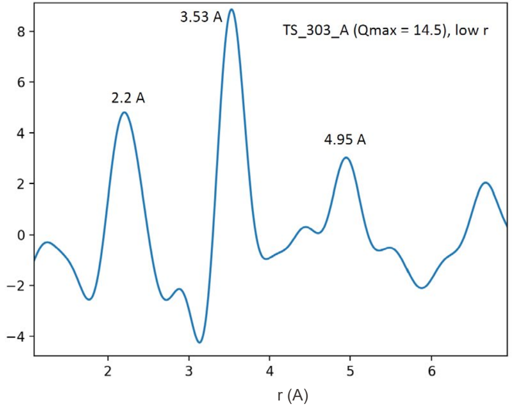
Diffraction geometries: Total Scattering

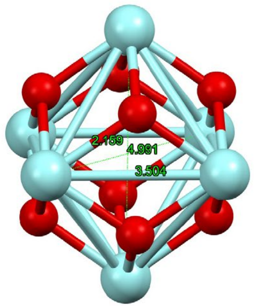


Radial atomic **pair distribution function** (PDF) gives the interatomic distance distribution, or "probability" of finding atomic pairs distance *r* apart

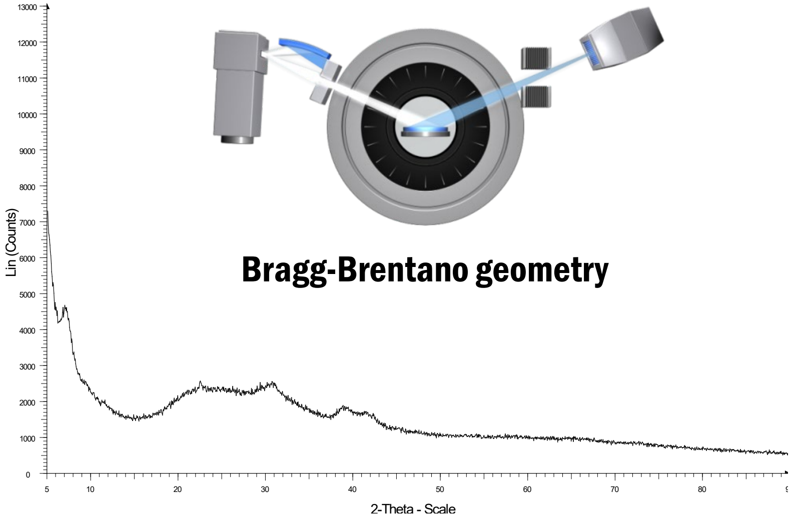


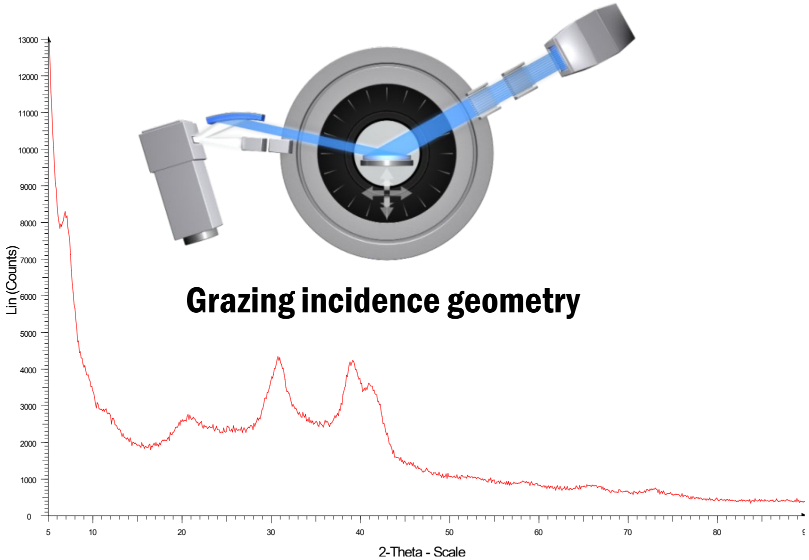
- Transmission geometry as Debye Scherrer
- At least 17 keV! Detector scan (or 2D image)
- Very flexible (in-situ / in-operando experiments)





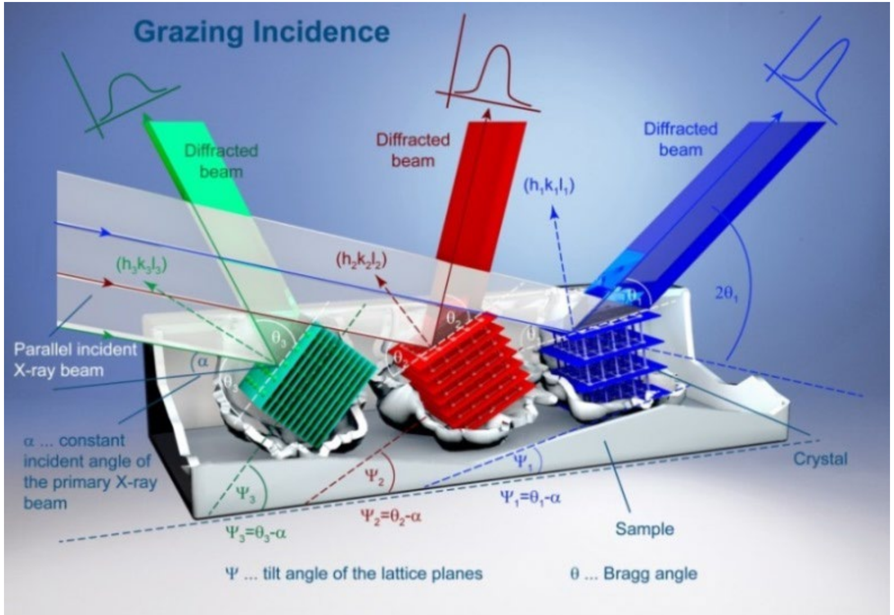
Diffraction geometries: GID
Surface diffraction



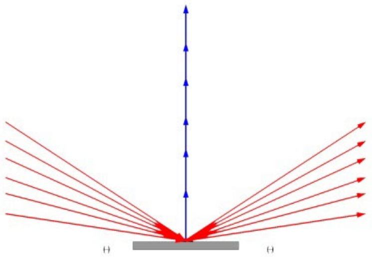


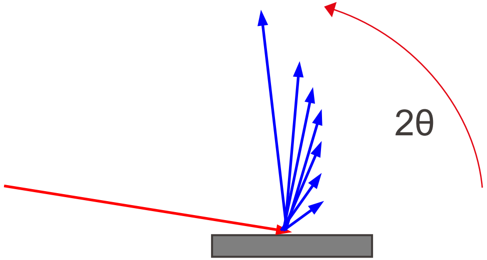
- Thin film geometry
- Constant incident angle
- Surface sensitive
- Depth control
- Scattering vector rotates in scattering plane

Diffraction geometries: GID



Bragg-Brentano



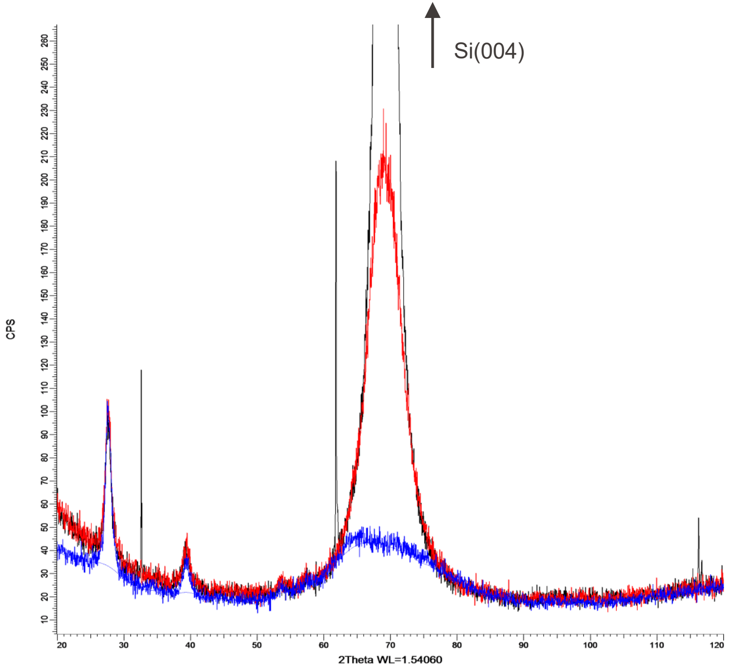


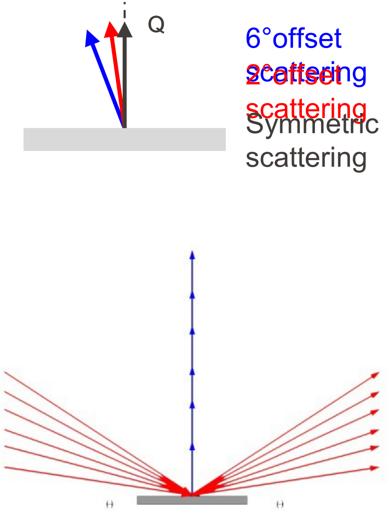
GID

- Thin film geometry
- Constant incident angle
- Surface sensitive
- Depth control
- Scattering vector rotates in scattering plane

Diffraction geometries: GID 14nm RuO_2 on Si(001)

Offset θ/θ scan





- Possible to strongly reduce Si (004) but layer signal still weak

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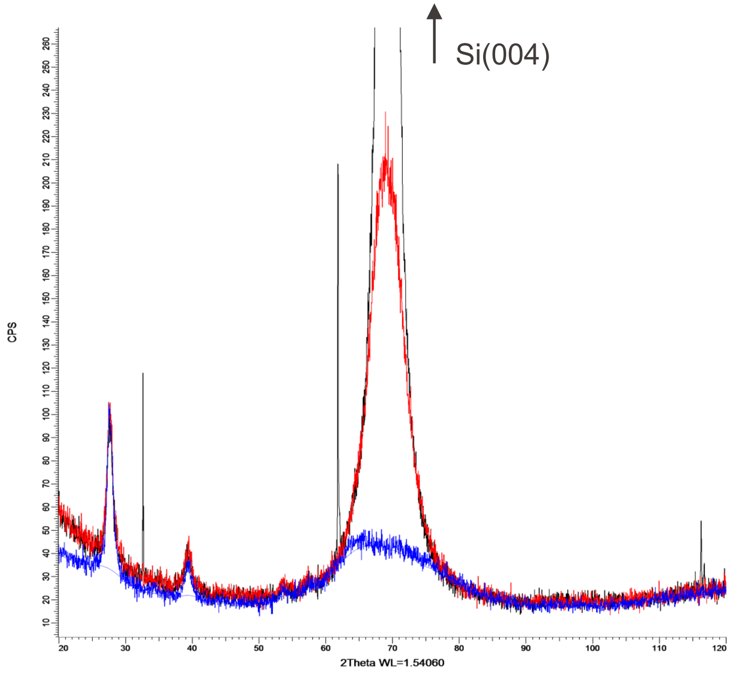
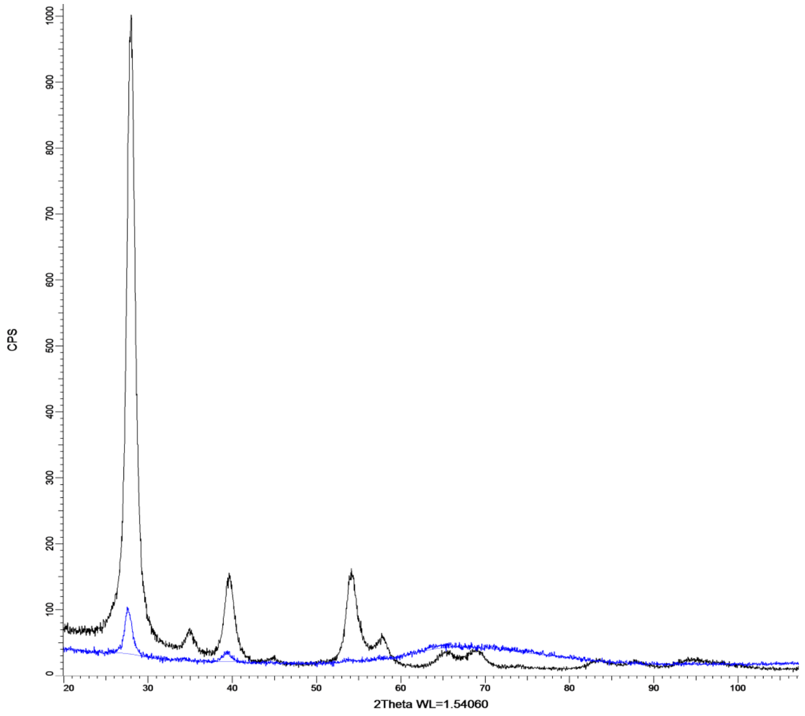
Diffraction geometries: GID 14nm RuO_2 on Si(001)

Offset θ/θ scan



- Possible to strongly reduce Si (004) but layer signal still weak

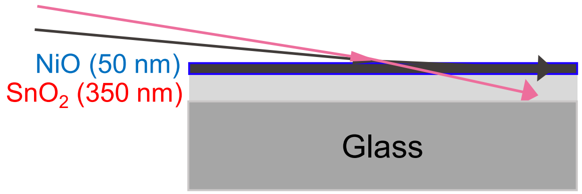
GIXRD *vs* 6° Offset θ/θ scan

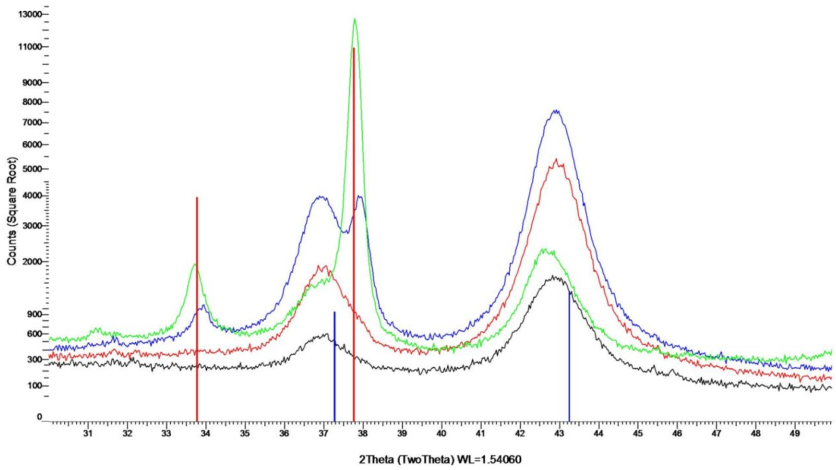


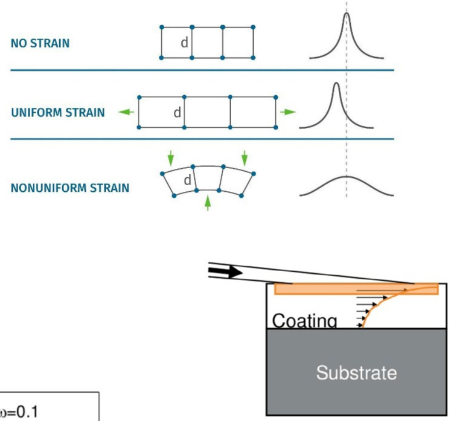
- Possible to remove substrate signal
- Significant gain for layer signal

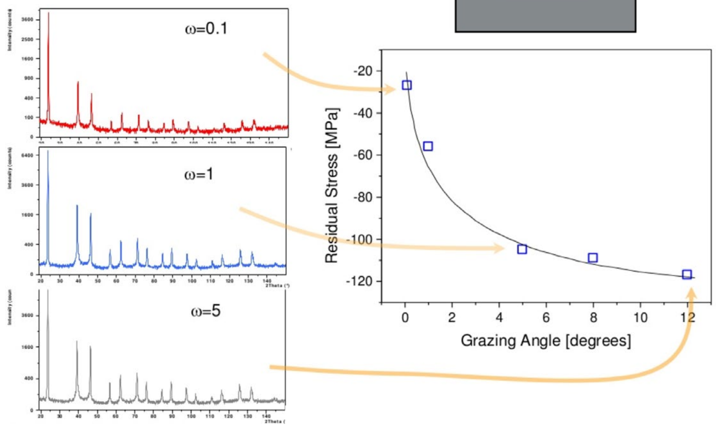
Diffraction geometries: GID

Incident angles: Theta=0.25, 0.3, 0.35, 1.5









- Depth profiling: phase composition and layer sequence
- Depth profiling: stress gradient in CdTe layer of solar cell

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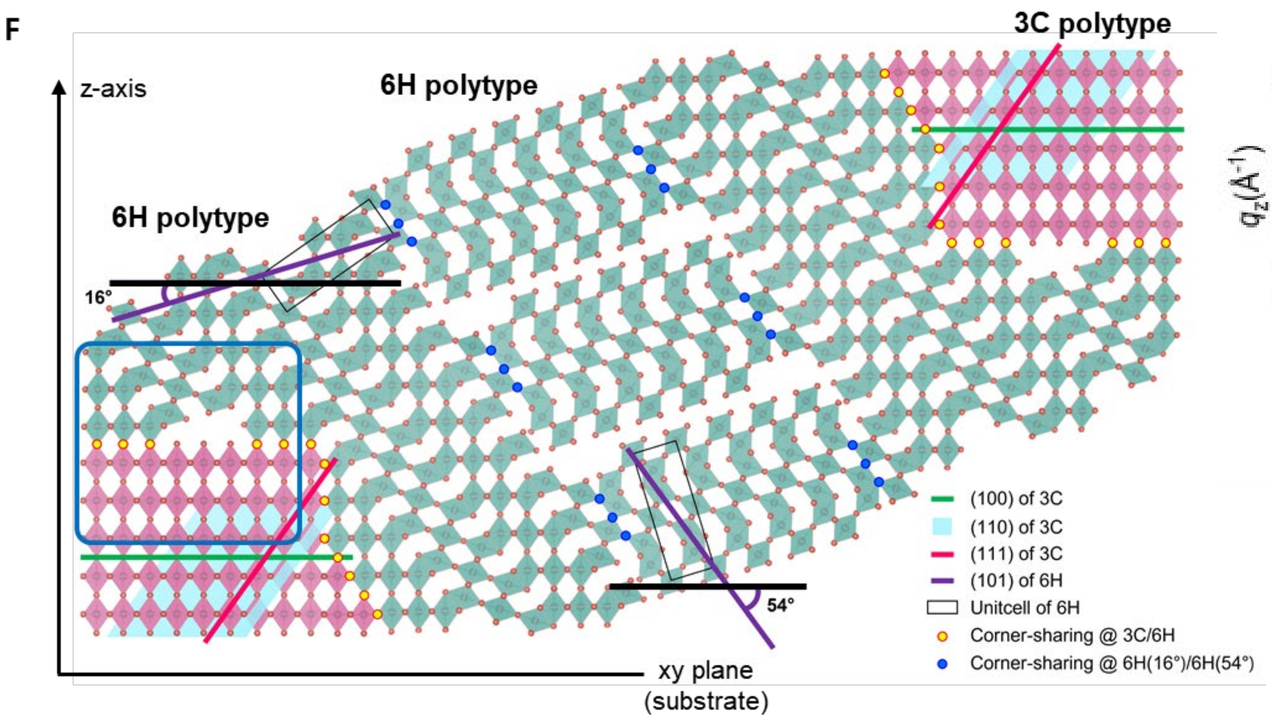
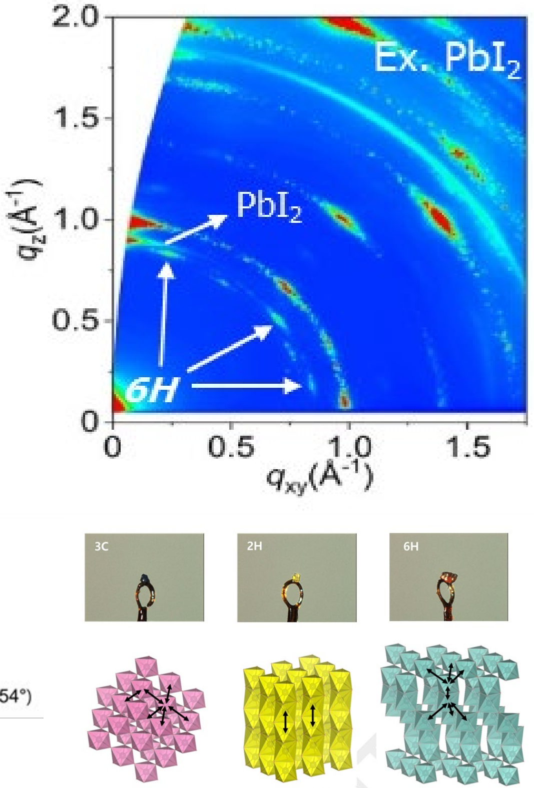
Diffraction geometries: GIWAXS

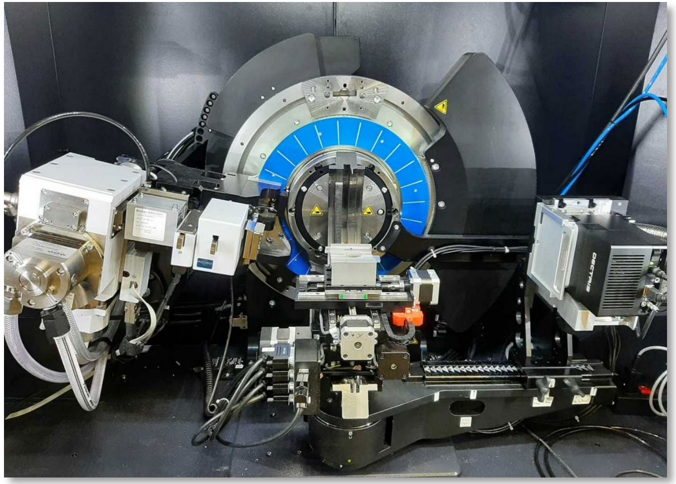
- Texture: reconstruct complex film interfaces (Perovskite PV)



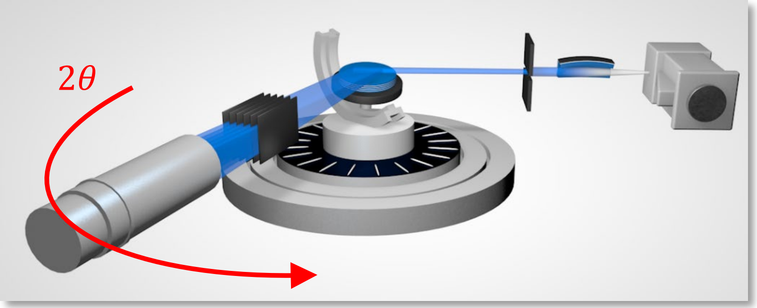


Diffraction geometries: In-plane GID

- Highly oriented films
- In-plane Lattice parameter
- Epitaxial relation
- Domain formation and twist (IP rocking curve)
- In-plane Texture
- Crystallite Size
- Micro Strain



- In-plane detector scan
- Requires special instrumentation



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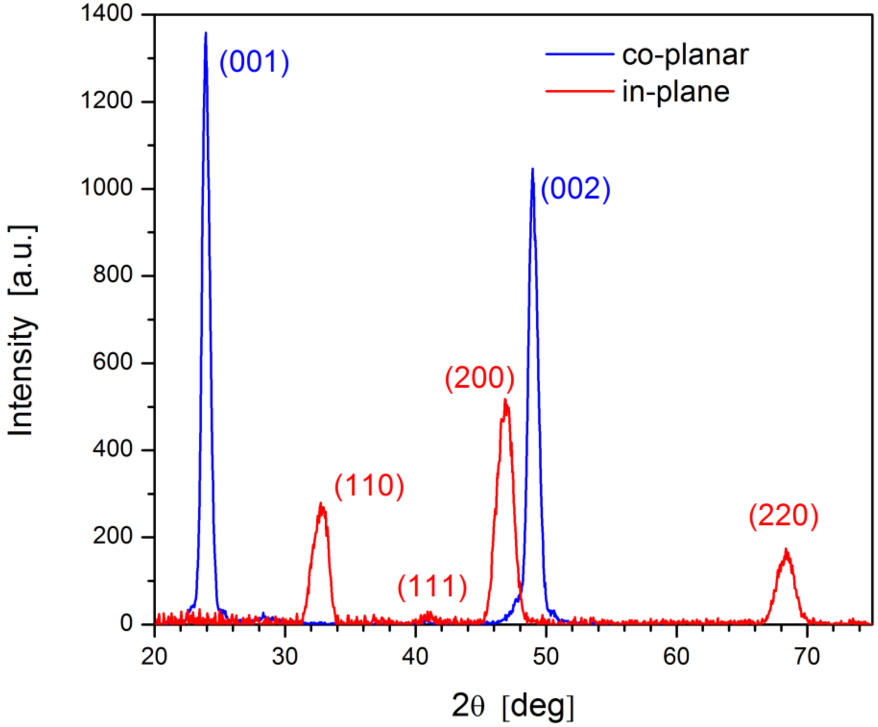
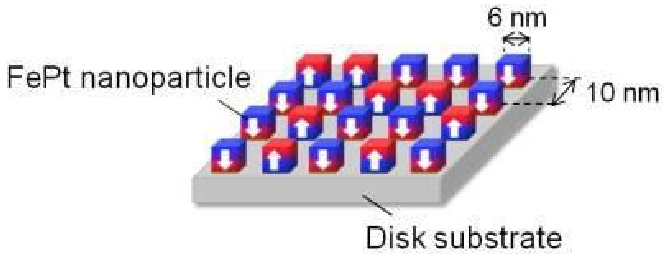
Diffraction geometries: In-plane GID

- FePt thin films of 10 nm (magnetic mass storage)

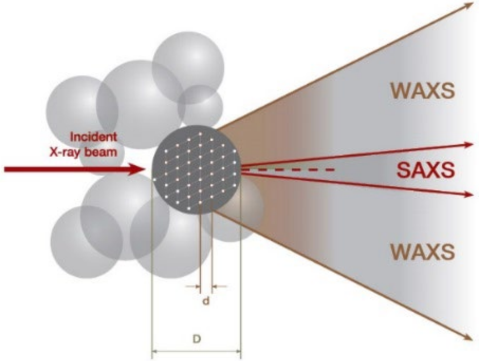




- Crystallite size in the surface normal direction is about the film thickness.
- In-plane crystallite size is about 6.5nm
- In-plane fiber textured around (001)

Diffraction geometries: SAXS

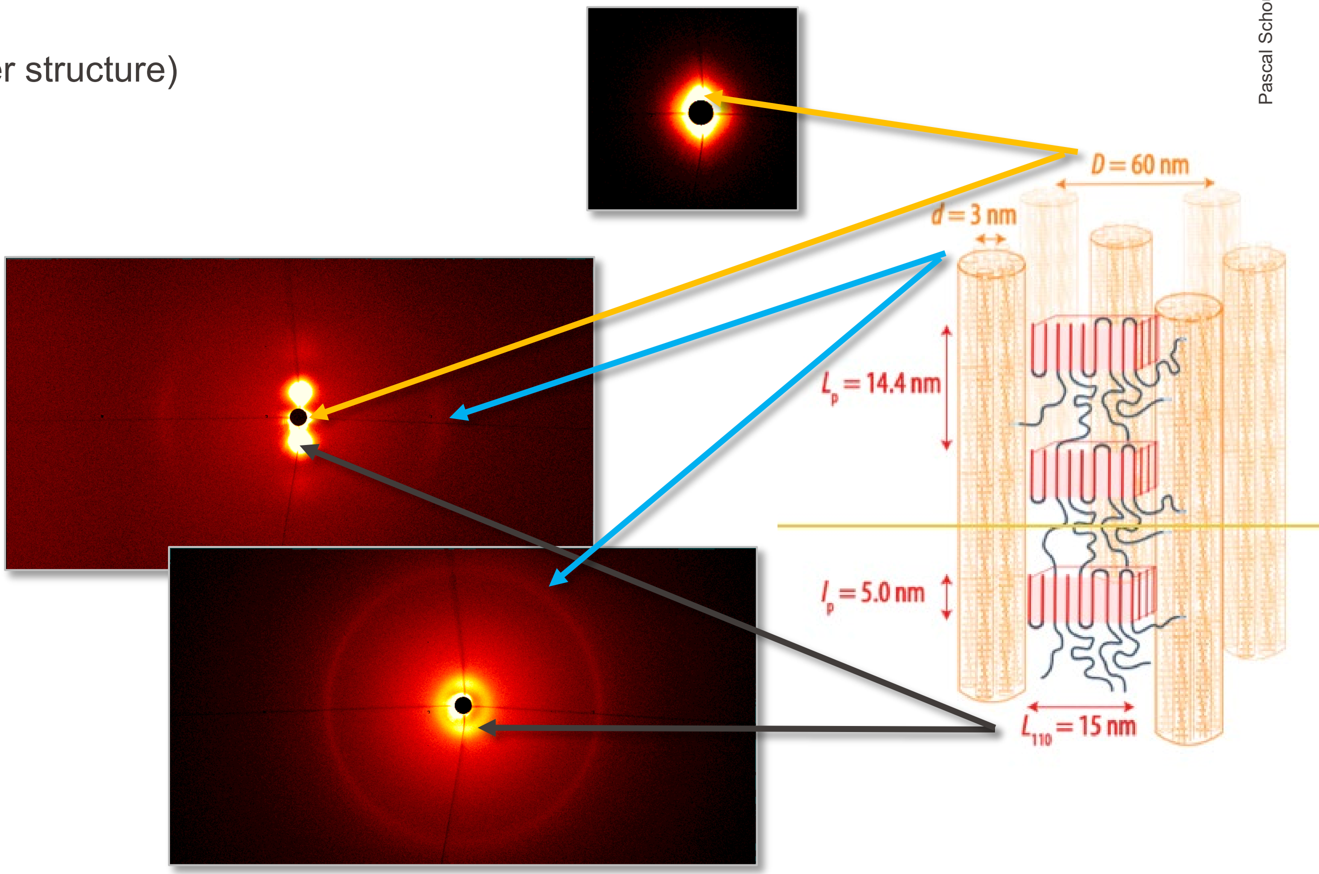
Beam path is evacuated



- X-ray scattering at low angles
- Large distances (nanoscopic order > 1 micron…)
- NP (shape, distribution, core-shell, aggregation, growth…)
- Biomolecules (aggregation, folding…)
- Nanoscopic structures (gratings…)

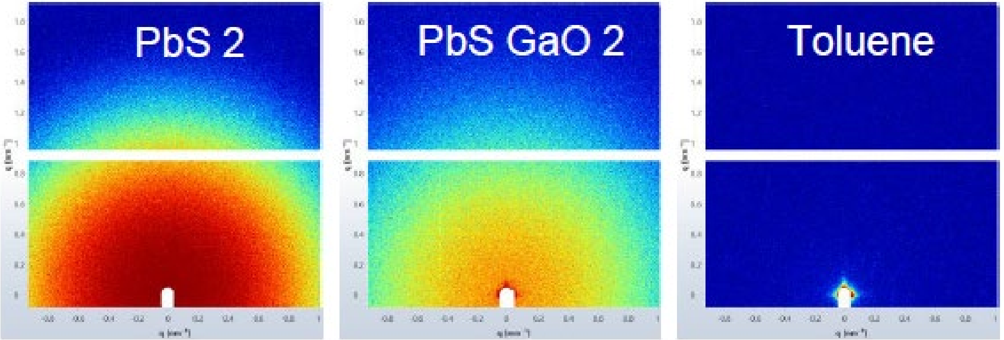
Diffraction geometries: SAXS

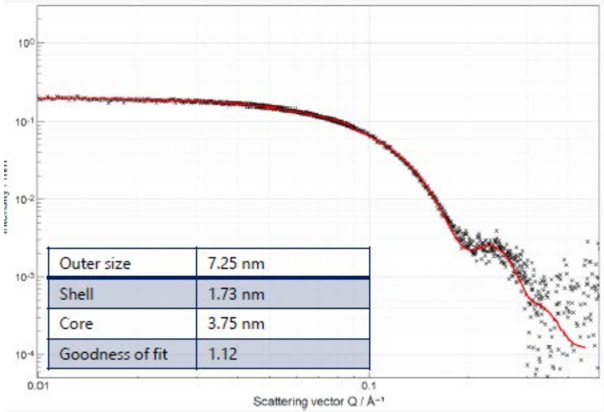
- Large d-spacing (polymer structure)

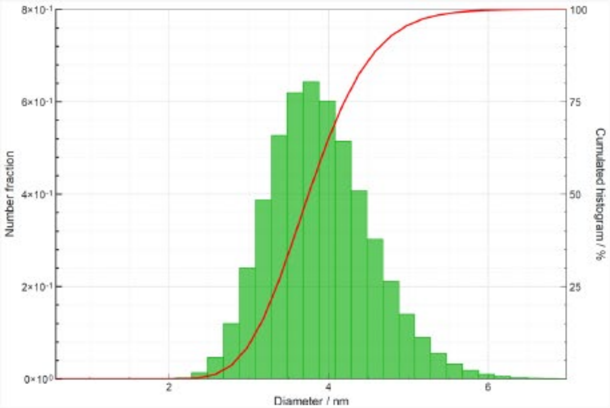


Diffraction geometries: SAXS

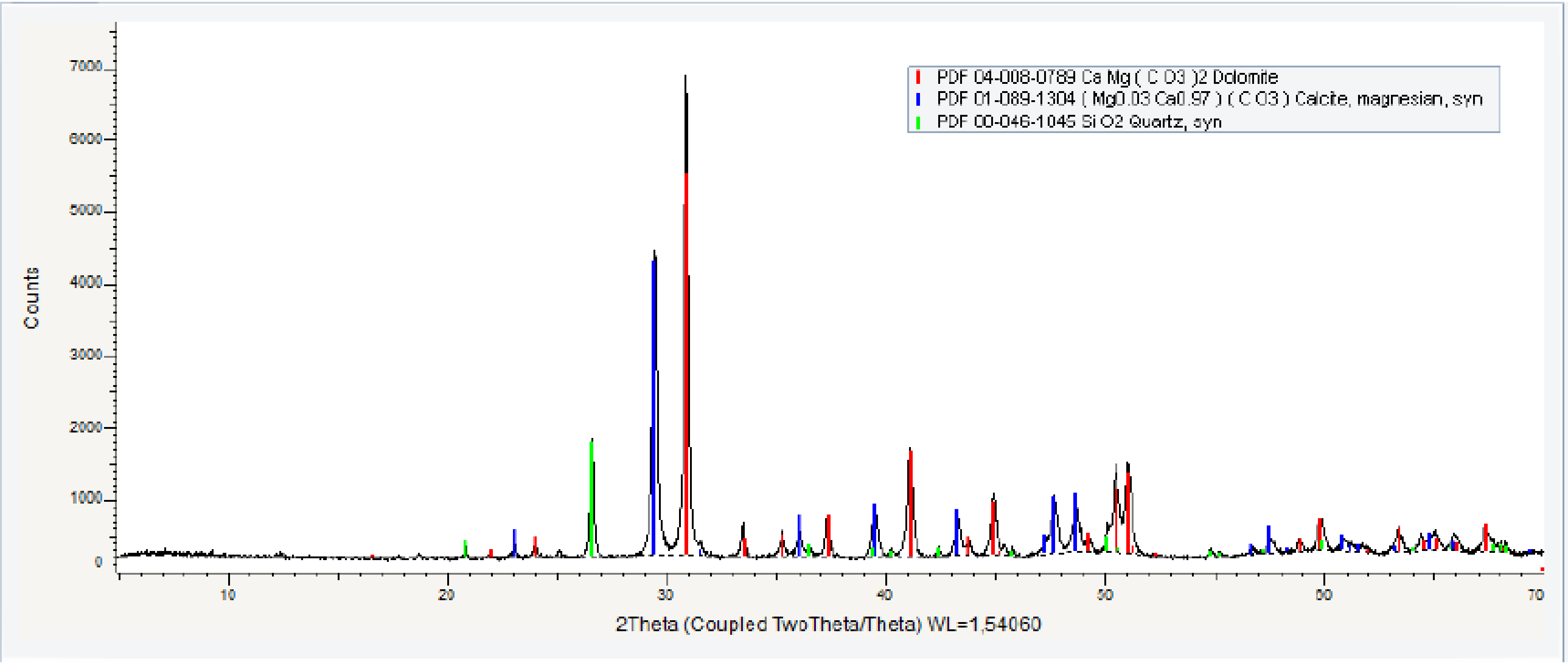
- Particle structure: PbS GaO – core-shell particle





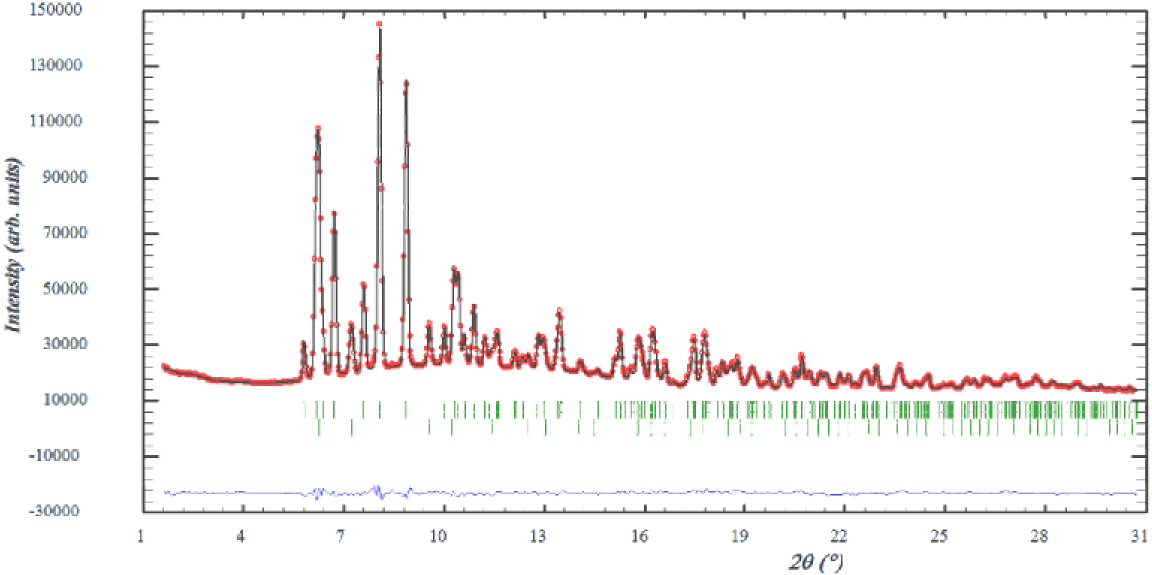


Applications PXRD: Phase identification



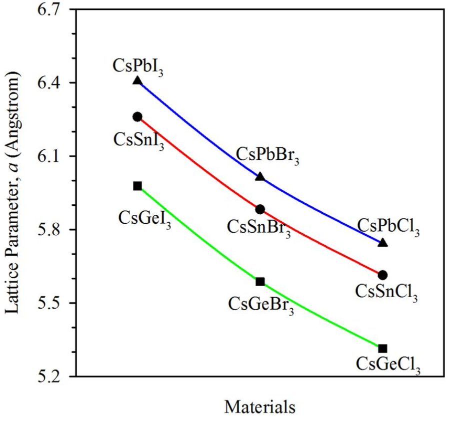
- Requires database

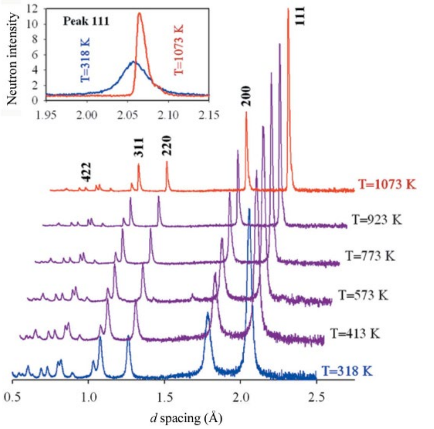
Applications PXRD: Profile fit



- Requires unit cell and space group
- No model (intensities are meaningless)
- Provides all quantities that are not model-based (unit cell parameters, peak shapes….)

Scientific Reports **7**, Article number: 14025





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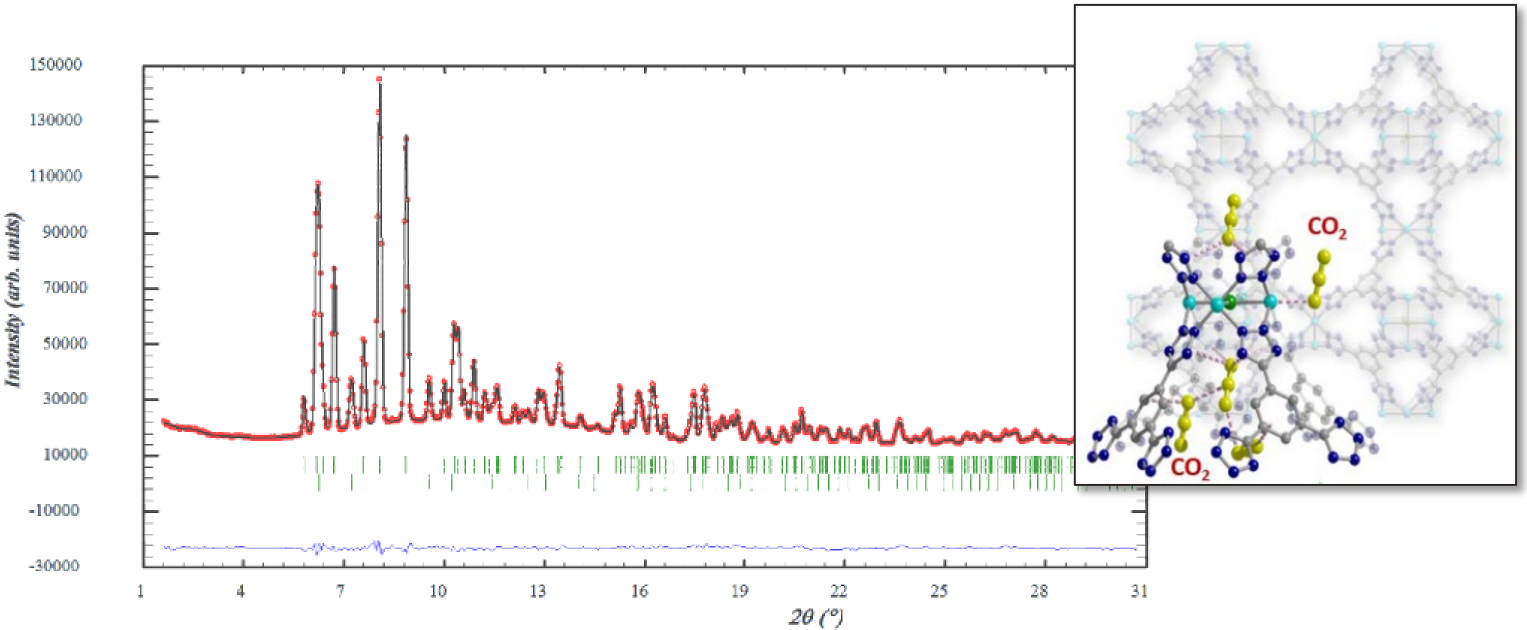
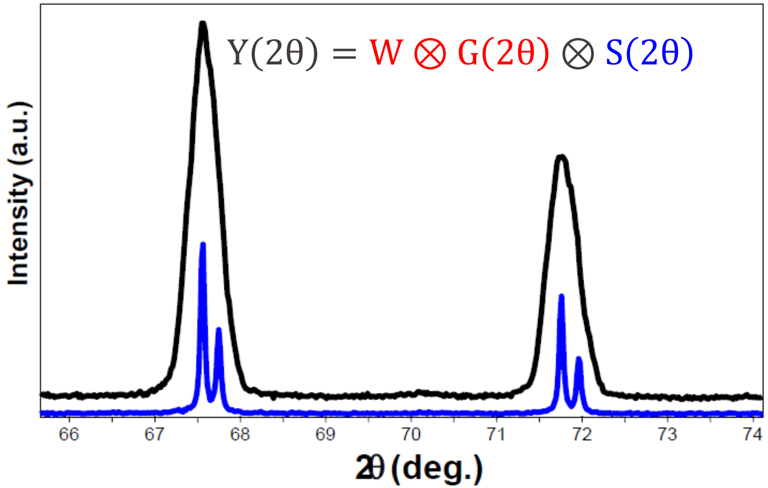
Applications PXRD: Rietveld refinement



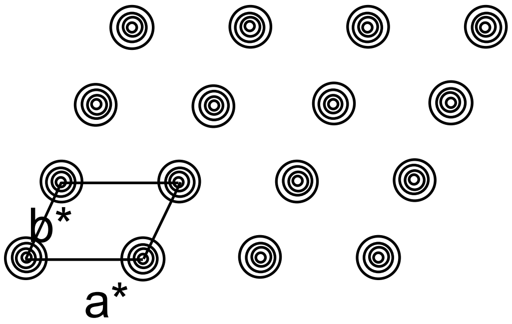
- Requires approximate starting model or CIF files
- Phase quantification
- Structure refinement
- Structure completion (Fourier-difference map analysis)

Applications PXRD: Line broadening

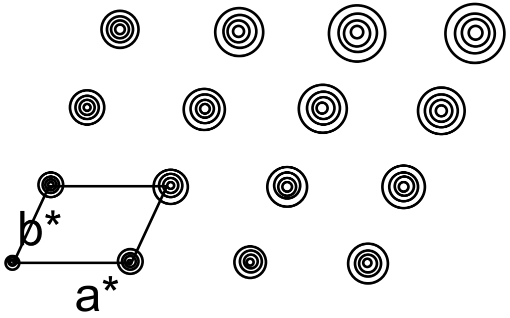
- Diffraction lines broaden due to disruptions of the lattice periodicity
- Peak shapes can be analyzed From profile fit (or Rietveld refinement)



Instrument: measured or calculated (source emission profile W, geometric contribution G = $F_1 \otimes F_1 \otimes F_1 \otimes \ldots$)
Sample



Size broadening

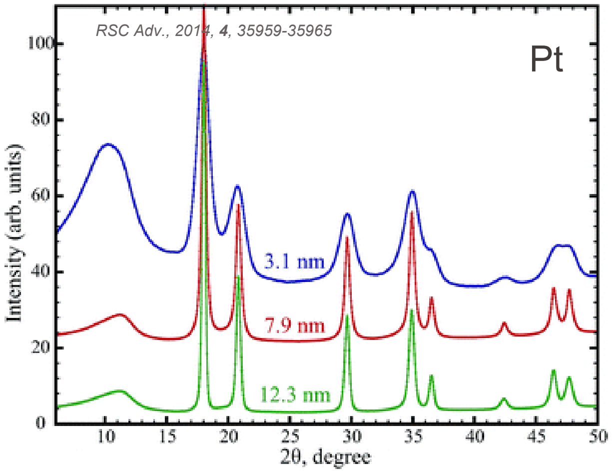


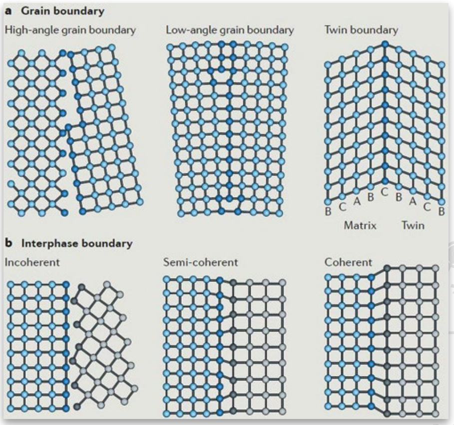
Microstrain broadening

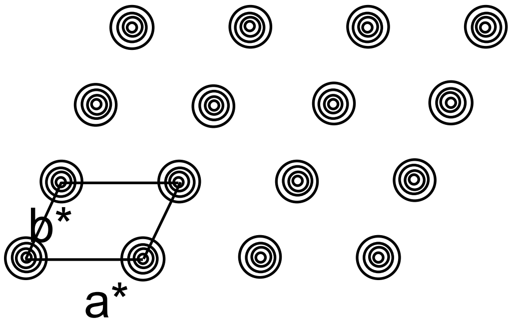
Applications PXRD: Line broadening

- Scherrer equation (over 100 years old)

$$\tau(2\theta) = \frac{K\lambda}{\beta \cdot cos\theta}$$







Size broadening

Microstrain broadening

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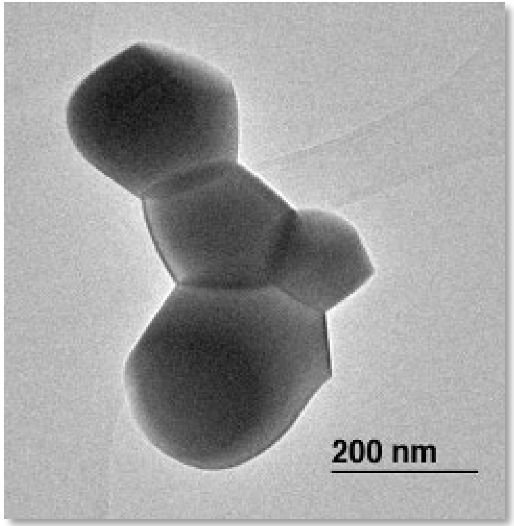
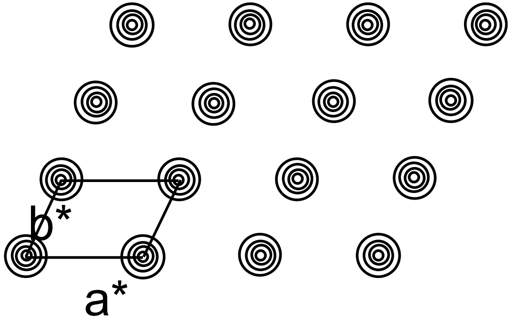
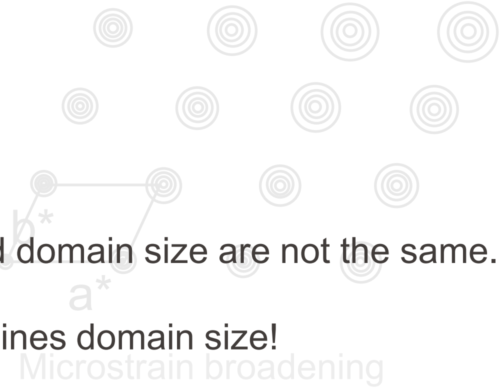




Size broadening



- Particle, crystallite and domain size are not the same.
- XRD (and ND) determines domain size!

Applications PXRD: Line broadening

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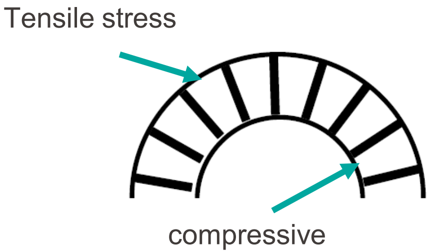
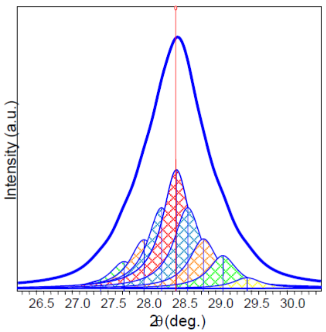
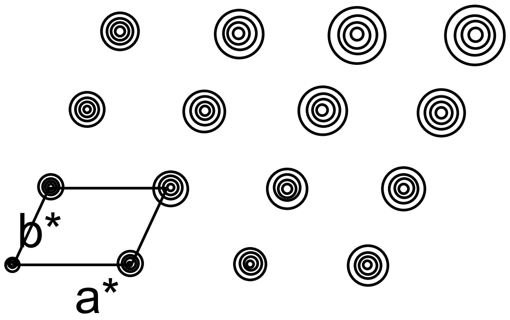
$$\tau(2\theta) = \frac{K\lambda}{\beta \cdot cos\theta}$$





- Distribution of lattice parameters
- Surface tension NP
- 1D, 2D and 0D defects



Microstrain broadening

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Applications PXRD: Line broadening

- Scherrer equation (over 100 years old)

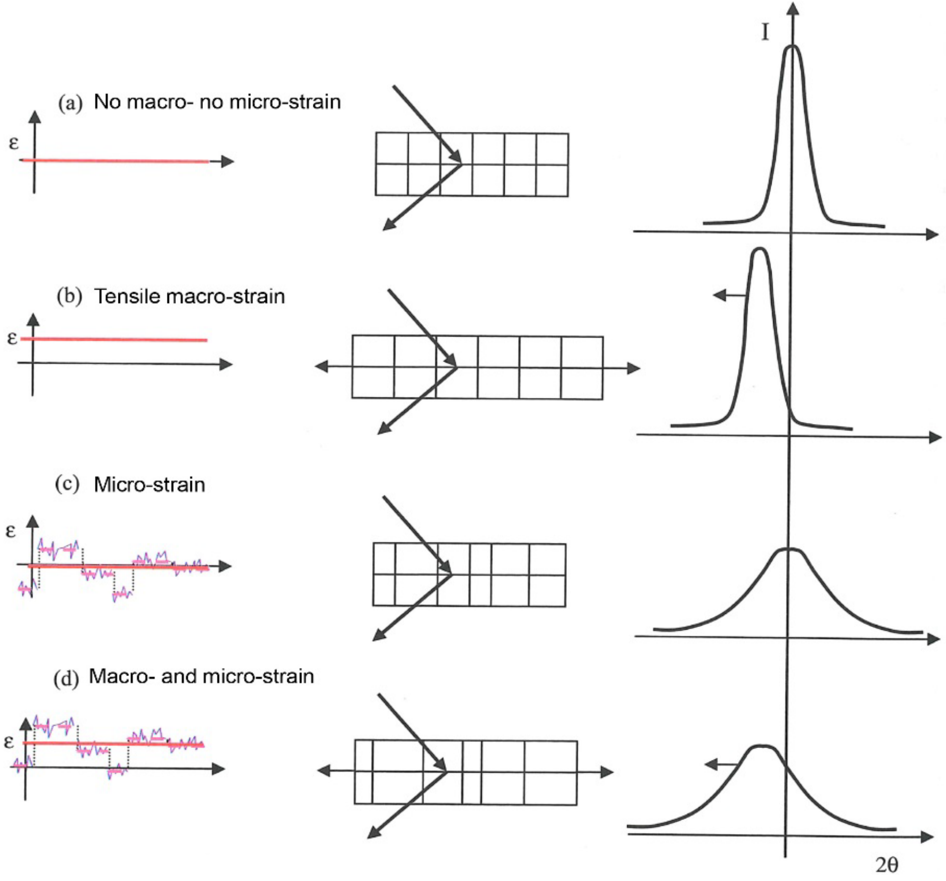
$$\tau(2\theta) = \frac{K\lambda}{\beta \cdot cos\theta}$$

- Macrostrain (residual stress)

$$\varepsilon_{hkl} = \frac{\Delta d_{hkl}}{d_{hkl}}$$

- Microstrain

$$B(2\theta) = C\varepsilon \frac{sin\theta}{cos\theta} = C\varepsilon\, tan\theta$$



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Applications PXRD: Line broadening

- Scherrer equation (over 100 years old)

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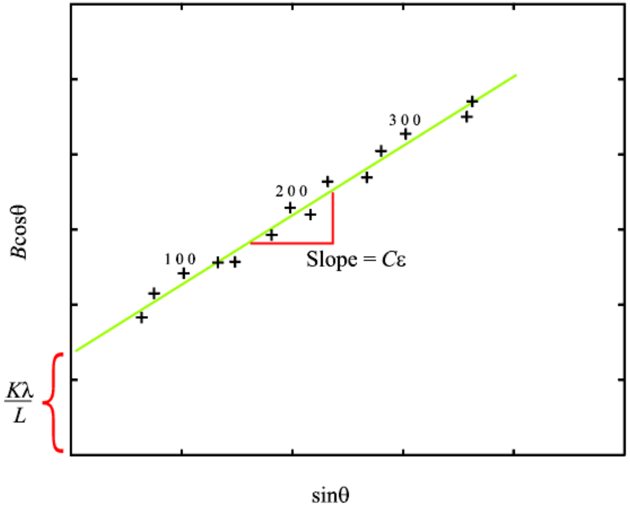
- Microstrain

$$B(2\theta) = C\varepsilon \frac{sin\theta}{cos\theta} = C\varepsilon\, tan\theta$$

Linear relationship: Williamson – Hall plot

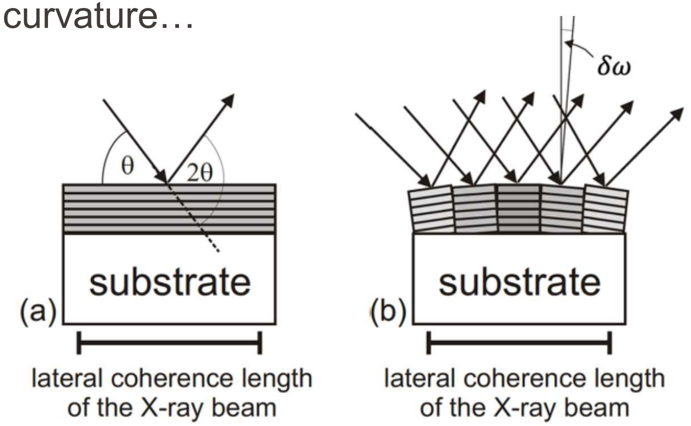
$$\beta_{tot} = B + \tau = C\varepsilon\, tan\theta + \frac{K\lambda}{\beta \cdot cos\theta}$$

$$\beta_{tot} cos\theta = \boldsymbol{C\varepsilon}\, sin\theta + \frac{K\lambda}{\beta}$$

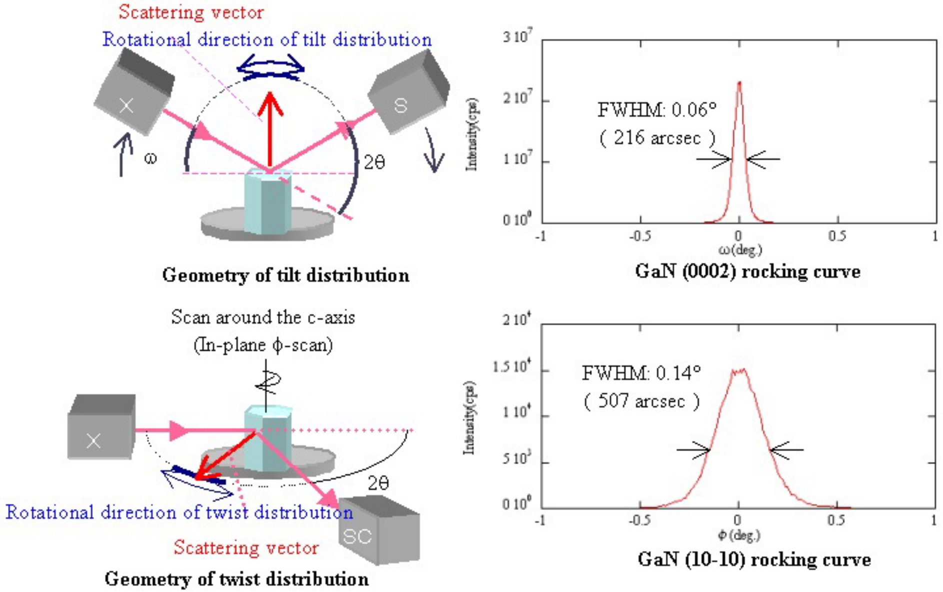


Applications HRXRD: Rocking curves, RSM, Pole figures

- Used to study layer quality and defects: mosaic spread, dislocation density, curvature…



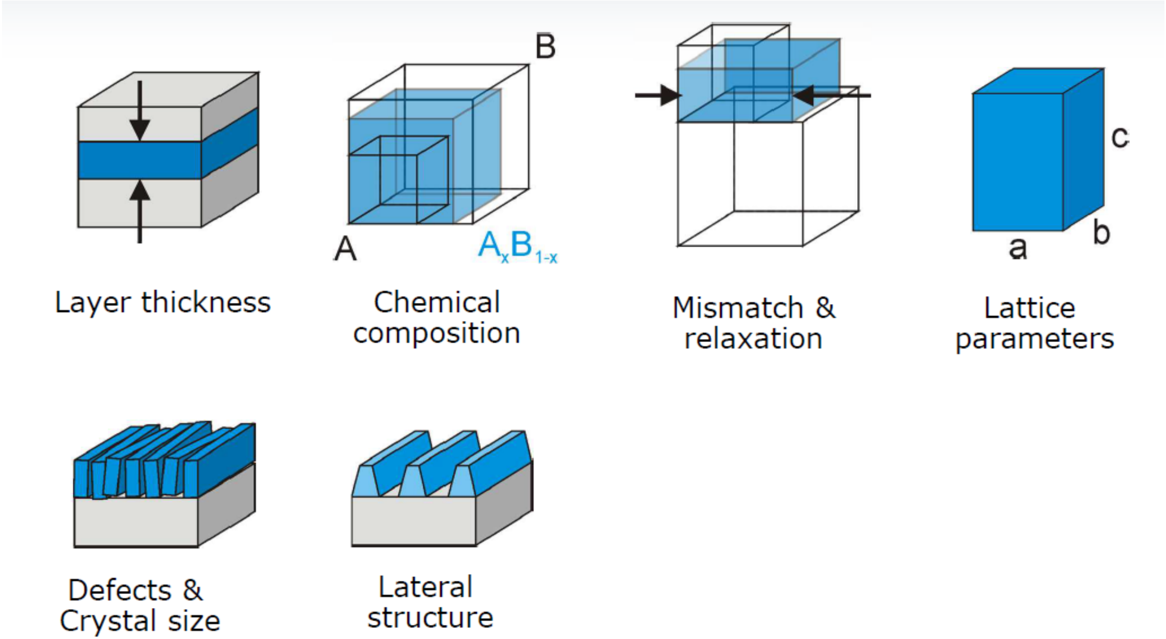
- **Perfect powder:** rocking curve meaningless (flat), detector always in diffraction condition
- **Perfect crystal:** rocking curve produces very sharp peak, only when crystal is properly tilted.



➢ Tilt distribution 0.06°, twist distribution 0.14°.

Applications HRXRD: Rocking curves, RSM, Pole figures

- Reciprocal space maps: used for analysis of epitaxial layers



Applications HRXRD: Rocking curves, RSM, Pole figures

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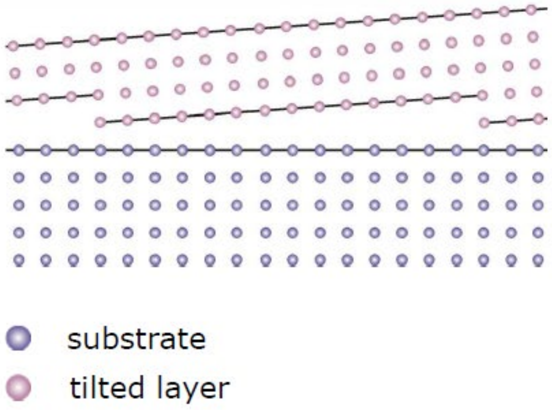

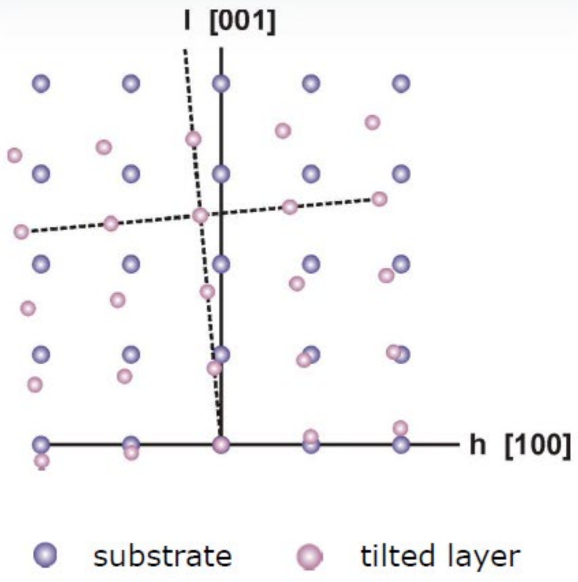

Applications HRXRD: Rocking curves, RSM, Pole figures

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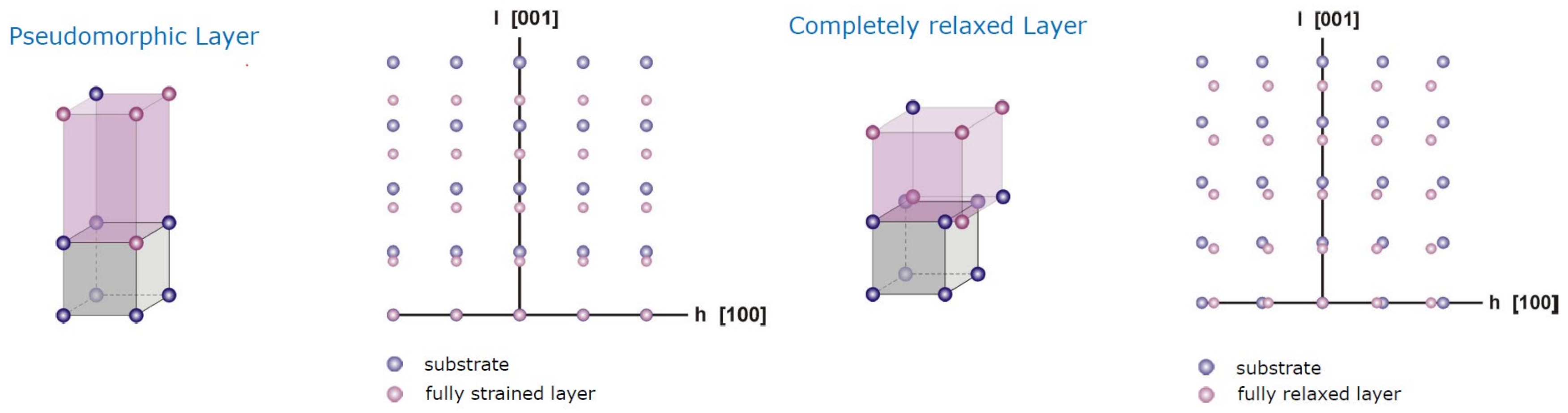
- Reciprocal space maps: used for analysis of epitaxial layers



Applications HRXRD: Rocking curves, RSM, Pole figures

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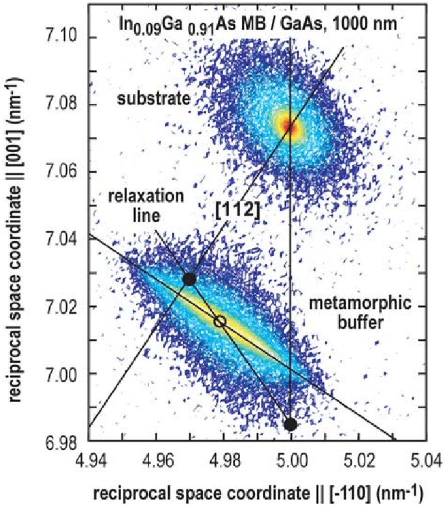
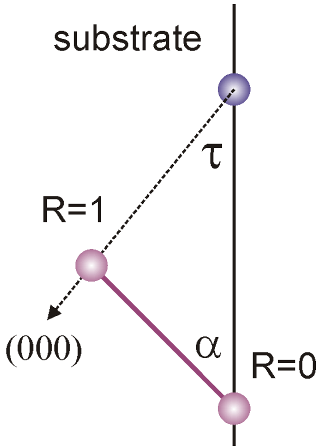
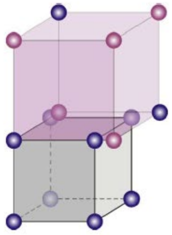
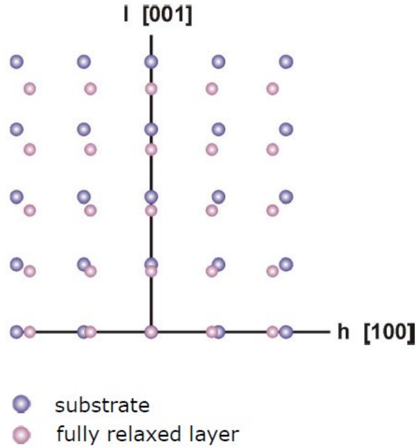




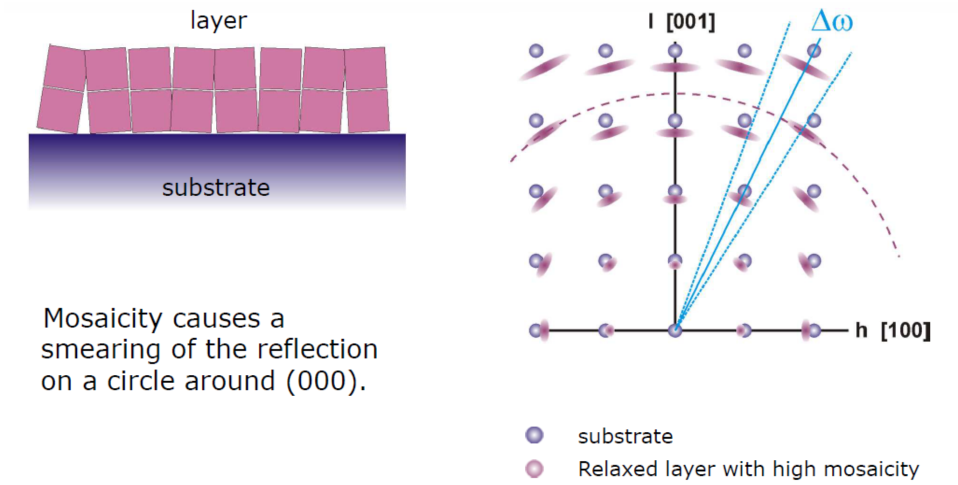


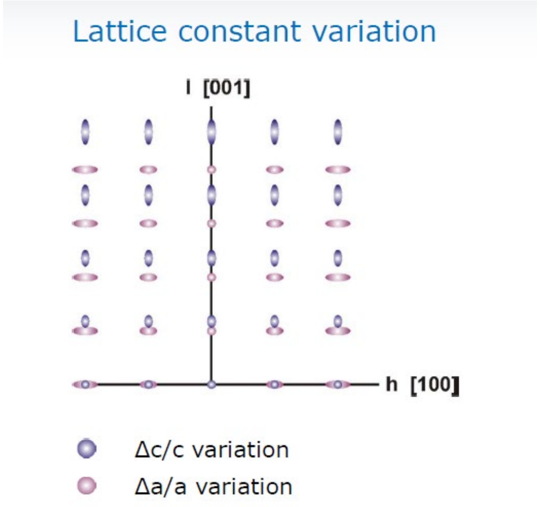


➢ Partially strained metamorphic buffer layer with mosaic broadening

Applications HRXRD: Rocking curves, RSM, Pole figures

- Reciprocal space maps: used for analysis of epitaxial layers





Applications HRXRD: Rocking curves, RSM, Pole figures

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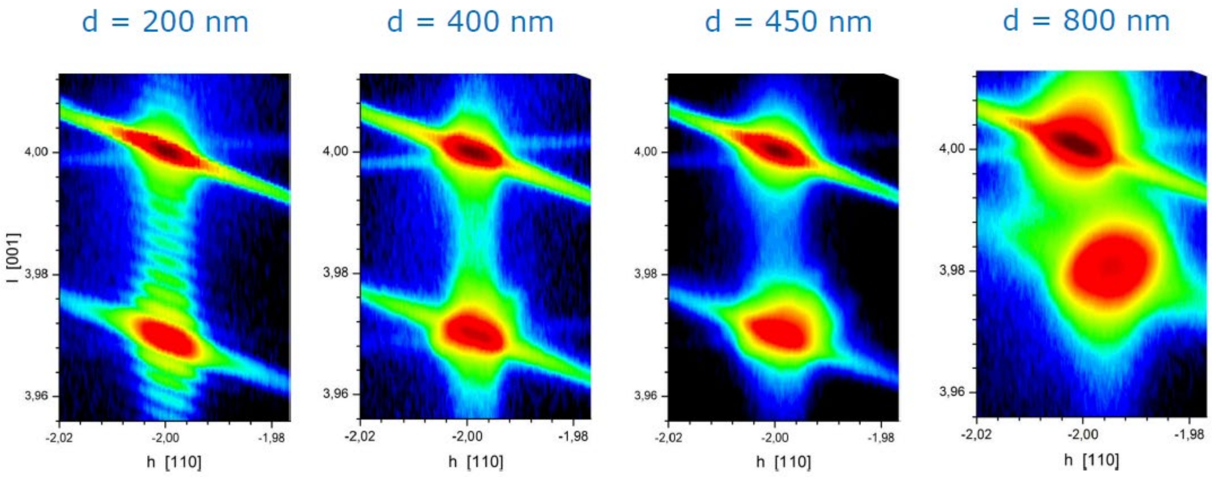
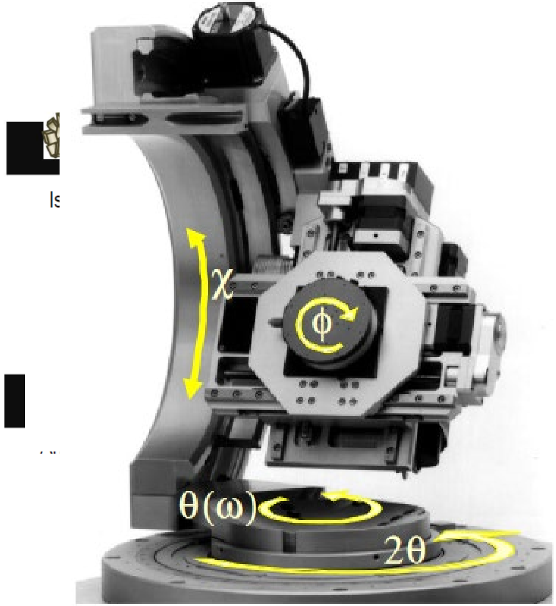


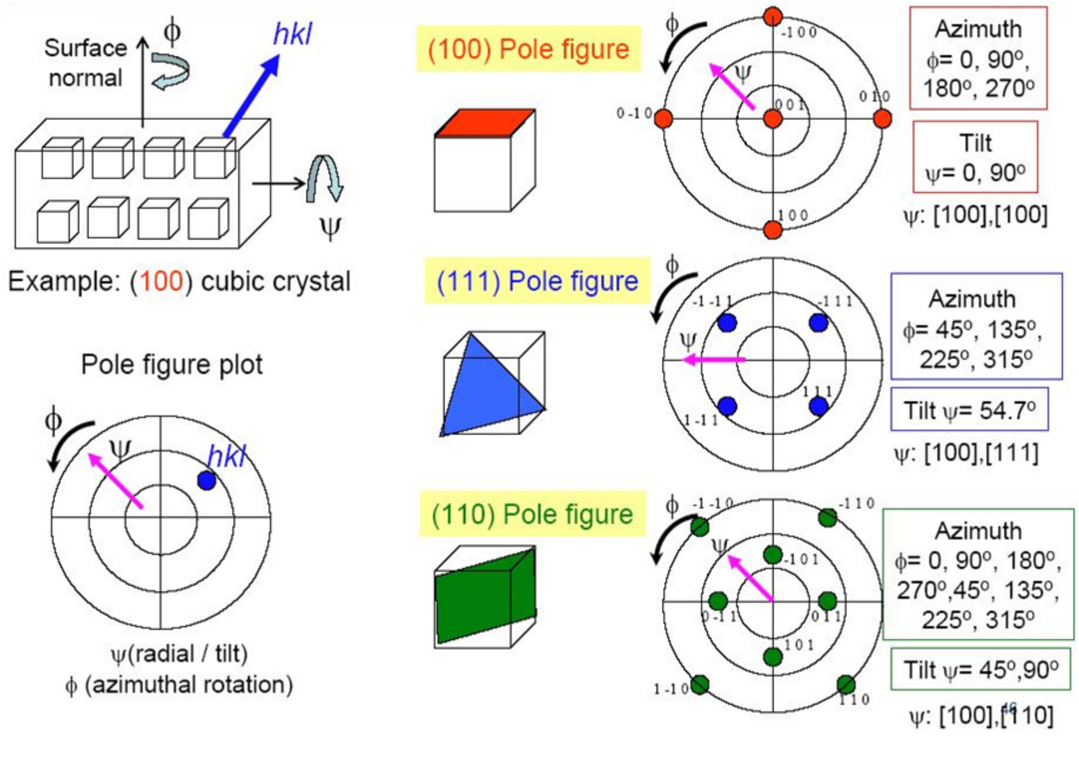
RMS from $In_{0.06}Ga_{0.96}As$ films on GaAs with different layer thickness

Applications HRXRD: Rocking curves, RSM, Pole figures

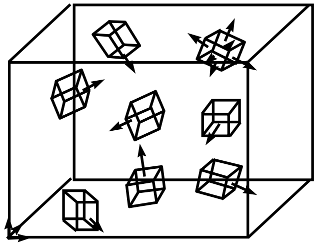
- Pole figure - stereographic projection of a crystal axis down some sample direction
- Pole figures are used to visualize complex texture.
- Access reciprocal lattice points that are not out-of-plane.



Applications HRXRD: Rocking curves, RSM, Pole figures



http://www.ankaanalitik.com.tr



Loose powder

- (100) facet, isotropic powder. What does pole figure look like?

Applications: X-ray reflectometry (XRR)

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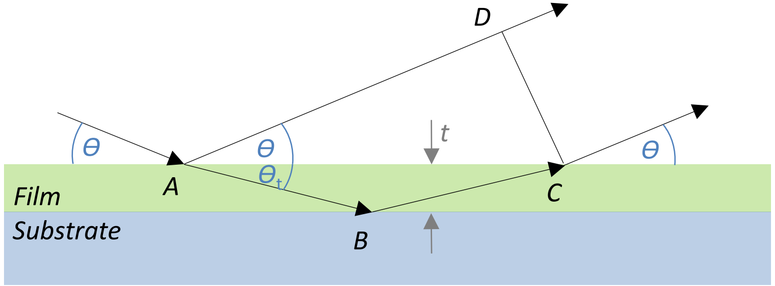
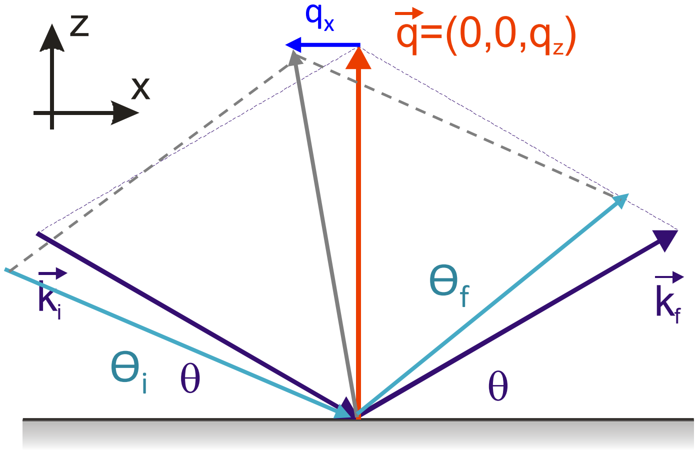
- **Thin film geometry!**
- Not a diffraction method! The specular reflection is measured.
- With XRR we analyze amplitude of **specular** reflection from interfaces

- **Surface sensitive**
  - Measured interference of reflected, not diffracted waves.
  - Works on crystalline and amorphous films.

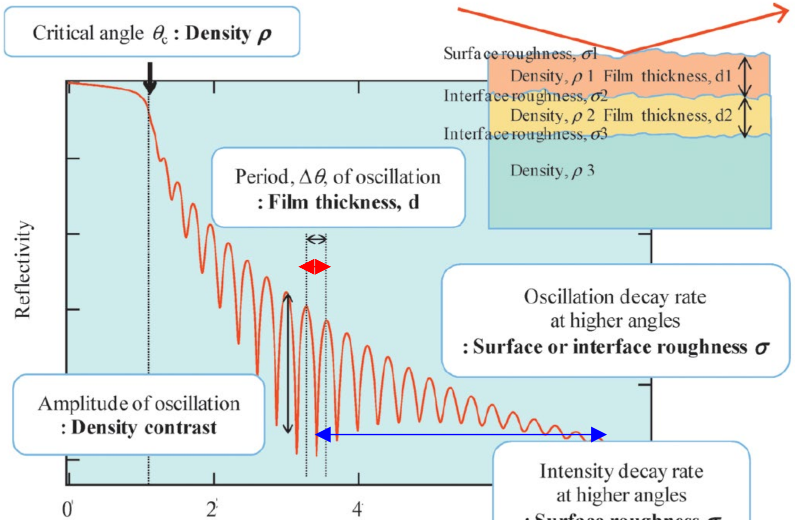
- **Information obtained by XRR**
  - Layer thickness   0.1 nm – 1000 nm
  - Material density < 1-2%
  - Roughness of surfaces and interfaces < 3-5 nm



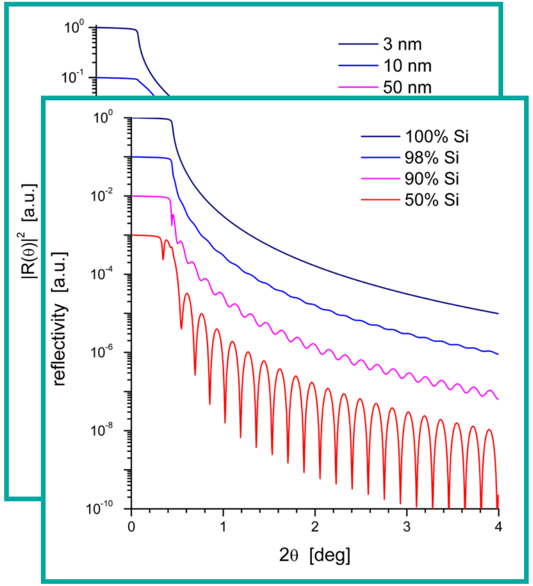


Applications: X-ray reflectometry (XRR)

- Information in XRR curves



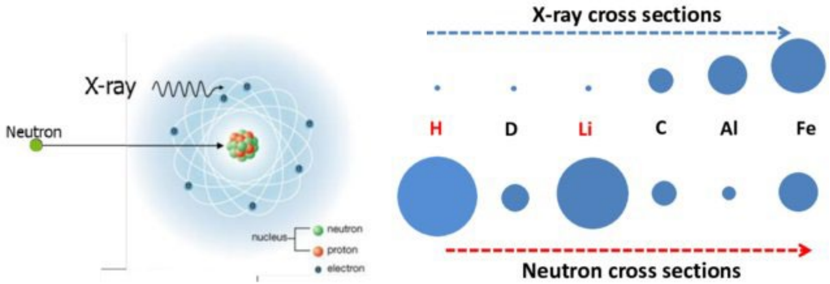
E.g. Si/Ta(20 nm)/TaO_2(1 nm)



- The interference of the waves reflected from the interfaces causes oscillations of period $\Delta q_z = 2\pi/d$
- Minimal observable thickness given by maximal observable range (λ)
- Maximal observable thickness given by instrumental resolution (source, optics, detector)
  - Sample should have thickness observable with diffractometer
- Amplitude of thickness fringes increases with increasing density contrast.
  - Sample should have good contrast in electron density

X-ray vs. Neutron diffraction

- Available methods very similar to X-ray diffraction (measurement + analysis)

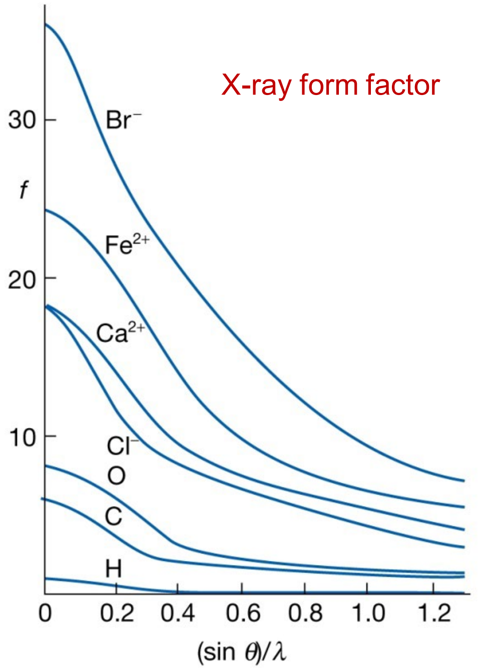


- X-rays interact with electrons, neutrons with the nucleus.

X-ray vs. Neutron diffraction

- Different isotopes might have considerably different cross sections

X-ray form factor



Neutron cross section

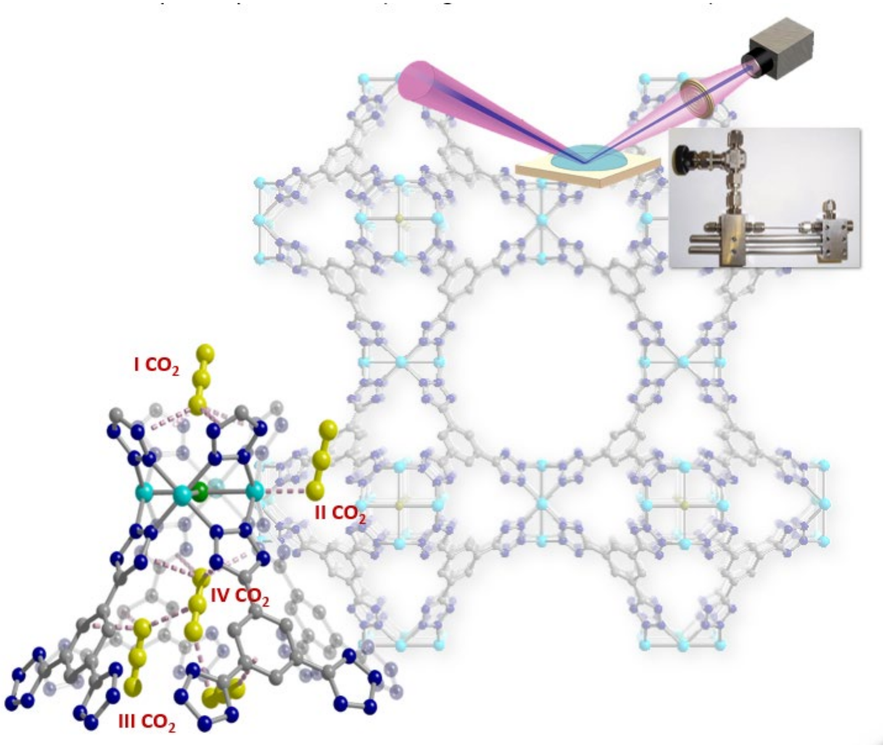
	Mass number	Isotope abundance	b_c (fm)	σ_c (barn)	σ_i (barn)
H	1	99.985	-3.74	1.7583	80.27
	2	**0.015**	**6.671**	**5.592**	**2.05**
C	12	98.9	6.65	5.559	0
	13	1.10	6.19	4.81	0.034
O	16	99.762	5.803	4.232	0
	17	0.038	5.78	4.2	0.004
Al	13	100	3.449	1.495	0.0082
Si	28	92.23	4.107	2.1633	0.0
	29	4.67	4.7	2.12	0.001
	30	3.10	4.58	2.64	0
Mn	55	100	-3.73	1.75	0.4
Fe	54	5.8	4.2	2.2	0
	56	91.7	9.94	12.42	0
Co	59	100	2.49	0.779	4.8

$$I(hkl) = e^{-2B(T)s^2} L_p(\theta)\ A(\theta) y\ PO\ p_{hkl}\ |F(hkl)|^2$$

$$F(hkl) = \sum_N f_N\ e^{2\pi i(hx_N + ky_N + lz_N)}$$

X-ray vs. Neutron diffraction

- Metalorganic framework – gas sorption



X-ray vs. Neutron diffraction

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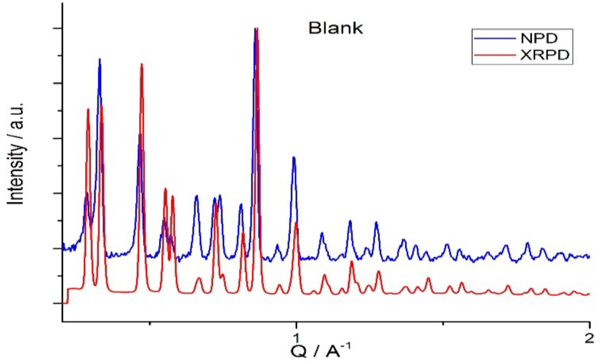

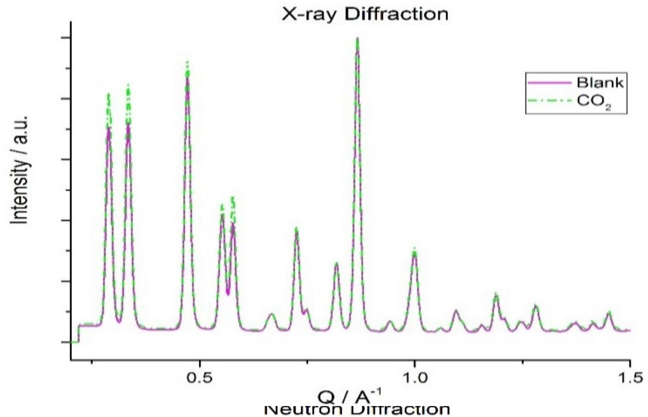

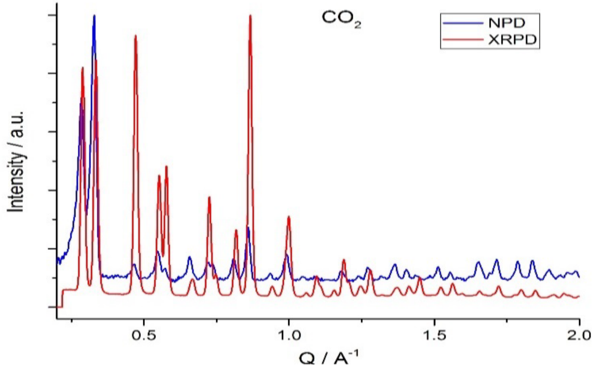

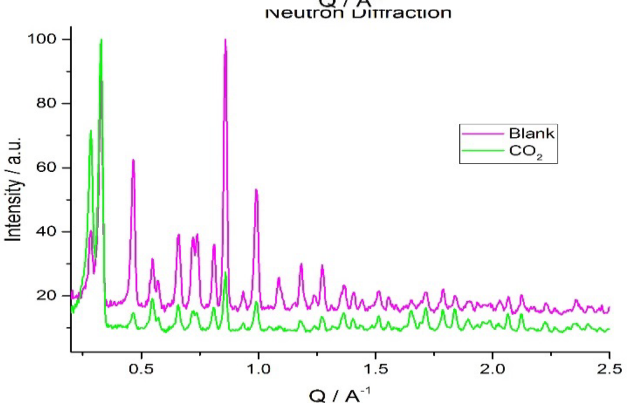

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X-ray vs. Neutron diffraction

➢ Some common cases where it is useful to use neutrons:

- Hydrogen positions (largest scattering cross section of all elements!)
- Oxygen (gases, ordering, vacancies…)
- Transition metal ordering
- Magnetic order
- The n0 is electrically neutral, interaction not with electron cloud but with nucleus: Large penetration depth (devices) + bulk properties.
- The closest neutron sources are at PSI and in Grenoble (ILL)

- You need a rather large sample volume
- Sample will be activated

EPFL

Lab visit

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