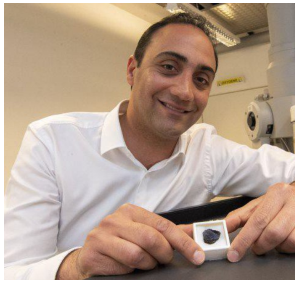
Advanced Solid State and Surface Characterization

CH-633 Chemistry and Chemical Engineering (edoc)

Mounir Mensi, Emad Oveisi, Pascal Schouwink

2025


https://www.epfl.ch/schools/sb/research/isic/platforms/x-ray-diffraction-and-surface-analytics
https://www.epfl.ch/research/facilities/cime/

EPFL

EPFL

14/14	Nom Prénom	Sciper	Genre	Section	Courriel
1	Ameres Marie-Gabrielle	397033	Féminin	EDMX	✉
2	Fabbiano Marco	383203	Masculin	EDCH	✉
3	Gupta Riya	390573	Féminin	EDCH	✉
4	Liu Wai Kwan	390681	Féminin	EDCH	✉
5	Meoli Matthieu	282576	Masculin	EDCH	✉
6	Naderasli Pardis	377802	Féminin	EDCH	✉
7	Ouyang Boyu	366580	Masculin	EDCH	✉
8	Prakash Vivek	371567	Masculin	EDCH	✉
9	Salehi Rozveh Zahra	397220	Féminin	EDCH_ECH	✉
10	Smith Olivier Thomas	372870	Masculin	EDCH	✉
11	Tritschler Moritz	390743	Masculin	EDCH	✉
12	Venkatachalam Sanjay	323482	Masculin	EDCH	✉
13	Wang Shaoyu	371652	Masculin	EDCH	✉
14	Warkentin Hugh Andrew	398693	Masculin	EDCH	✉

Dates

- Wednesdays 10:15 – 12:00, 12.02. – 30.04.2024 (exception: 19.03. session moved to 18.03.)

- https://epfl.zoom.us/s/62989985578

Content

- 1 session intro + 3 X-ray scattering methods (Surface XRD,HRXRD,SAXS,PDF)
- 2 session electron microscopy
- 6 sessions surface spectroscopy/microscopy

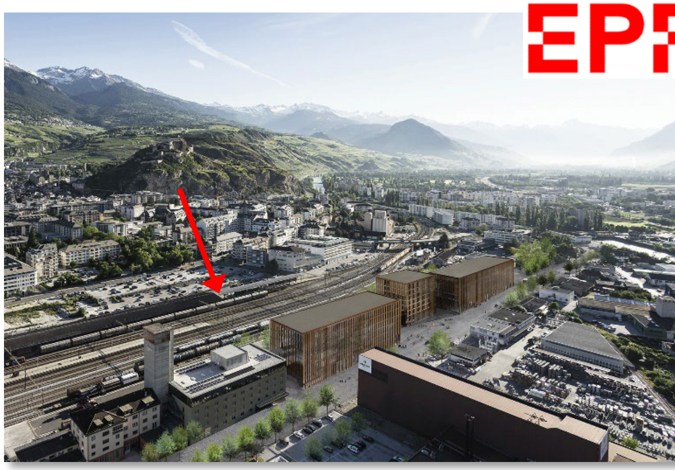
- Lecture notes + miscellaneous on moodle

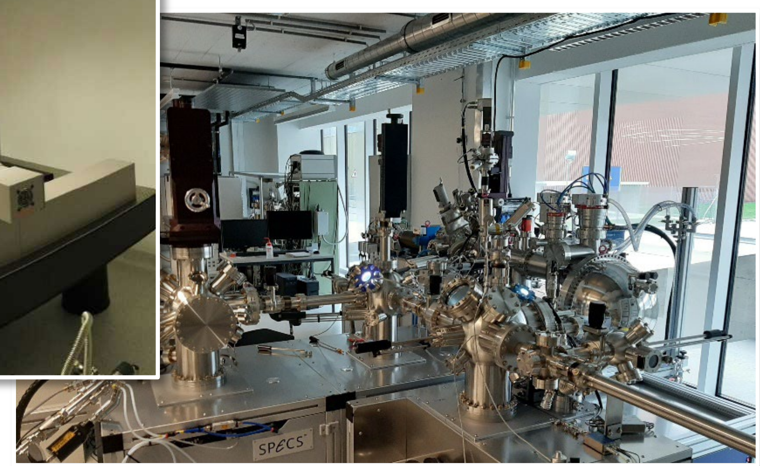
Exam

- Written, questions + exercises, date tbd

EPFL X-ray diffraction and Surface Analytics XRDSAP

EPFL Valais Wallis

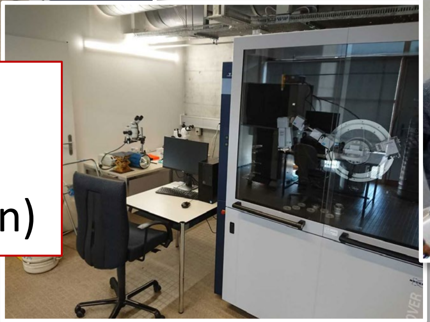




- 3 diffractometers
- 1 MicroRaman 4 lasers
- 1 XPS/UPS
- 1 AFM

X-ray diffraction and Surface Analytics XRDSAP

Lausanne campus



- 5 diffractometers
- SAXS beamline
- Multipurpose AFM (soon)

Contents

- Aim of the course: know your way around basic concepts of state-of-the art methods and when to use which.
  - Long range vs. short range order
  - Length scale
  - Resolution of experiment, resolution given by data
  - Bulk vs. surface
  - Phase sensitive?
  - Oxidation state sensitive?
  - Chemical composition
  - Detection limit, impurities?
  - …
  - ..
  - This course does not include instrument training on any method!
  - But: training on most discussed methods is done at our facilities.

- In-depth theory and analysis of XRD, SCD and EM are taught in CH-632 and CIME courses

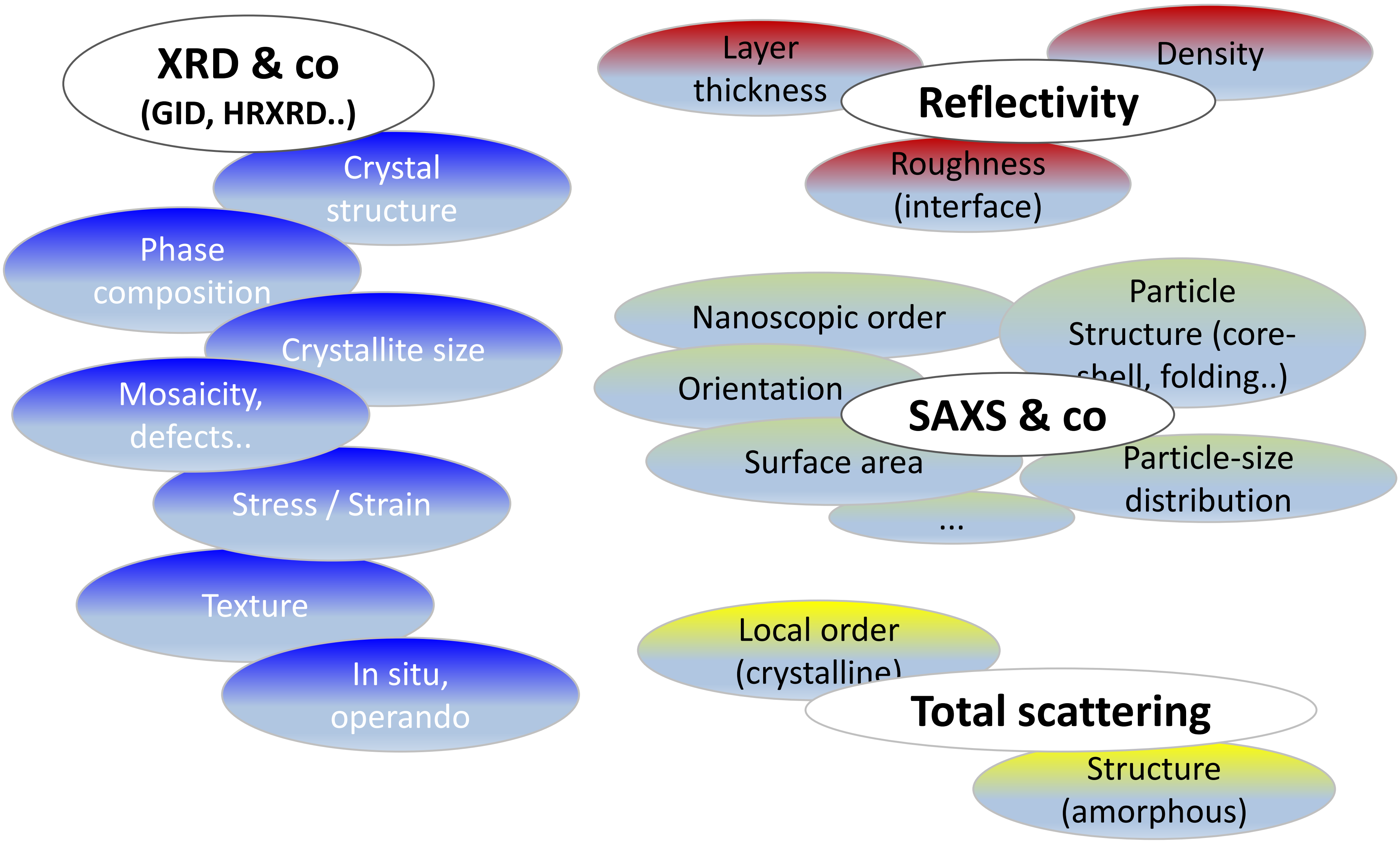
Contents

➢ CH-633 – my part:

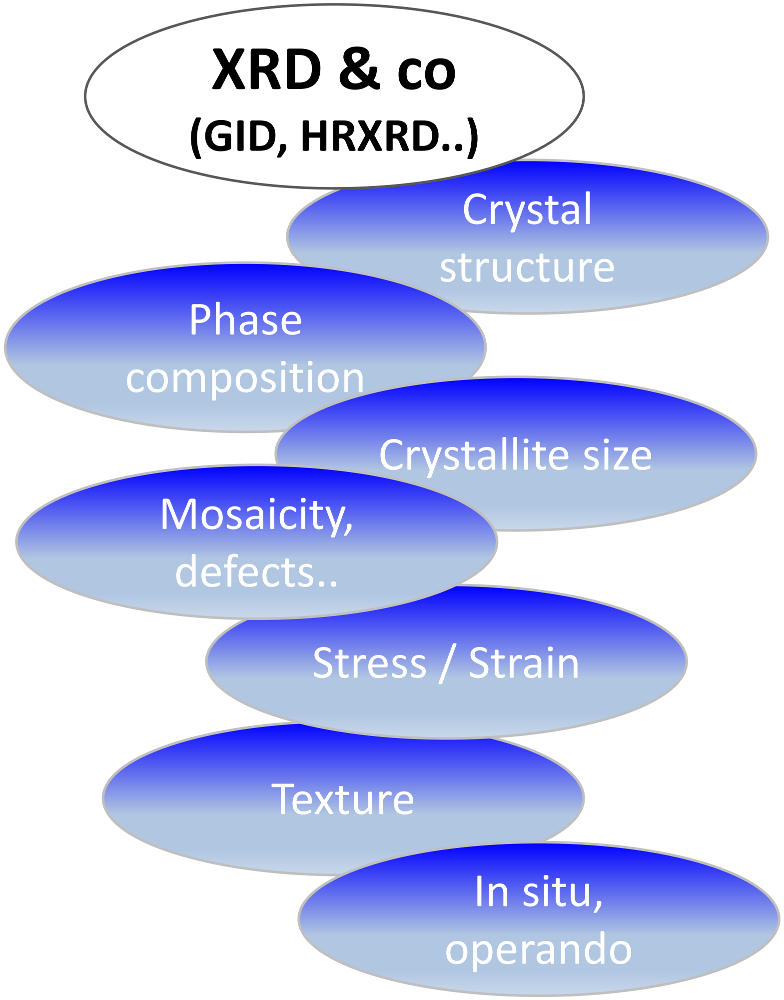
1. Introduction and XRD recap, surface diffraction
   - Condensed matter: atomic structure, periodicity and symmetry
   - Interaction of X-rays with solids
   - From bulk (CH-632) to surface diffraction

2. Thin film diffraction and reflectometry
3. Small angle X-ray scattering
4. Total scattering

Contents: session 1 – 4



Contents: session 1



➢ Some relevant XRD methods possible in XRDSAP labs

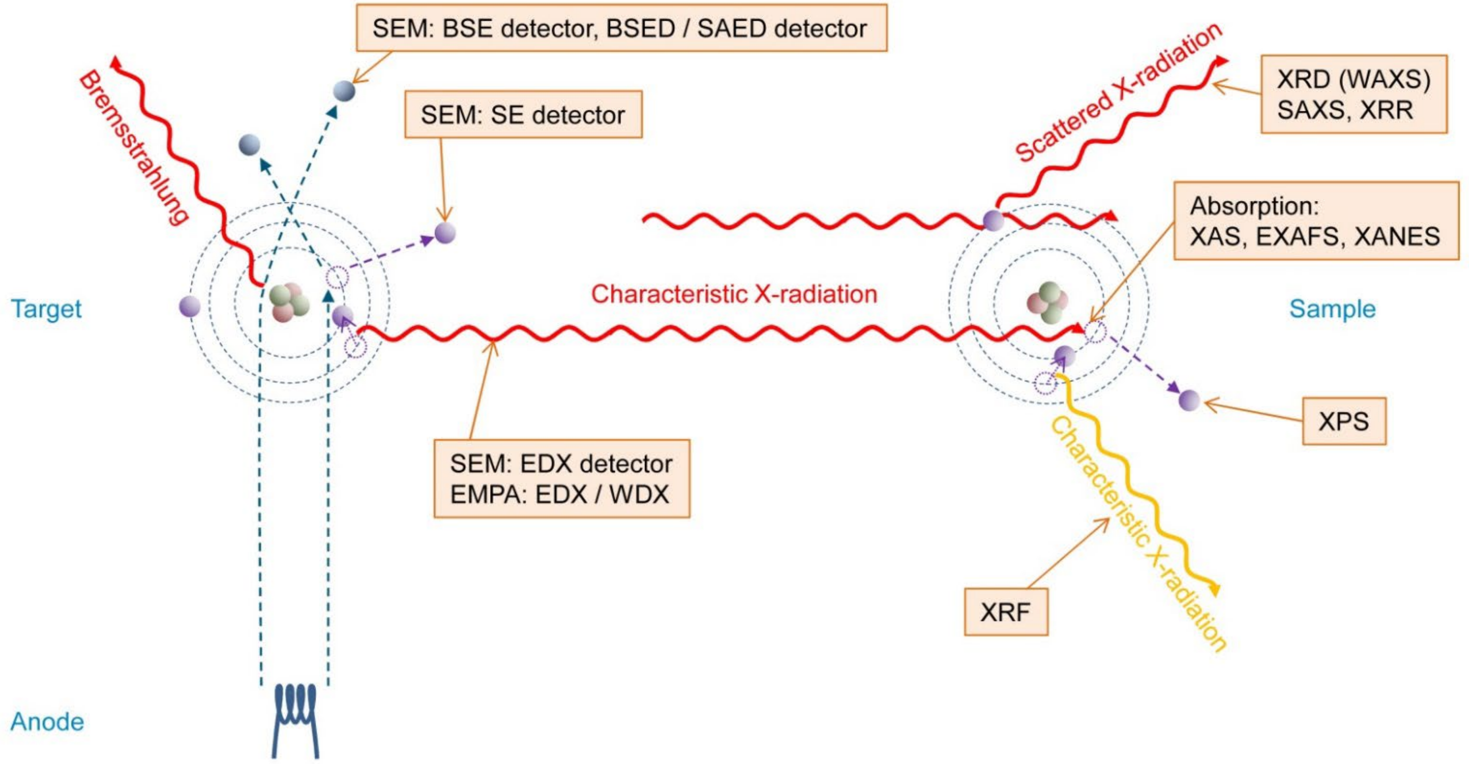
- Grazing incidence diffraction geometries
  - GID, IP-GID, GIWAXS and derivatives
- Texture methods
  - Pole figures, ODF, GIWAXS
- High Resolution Diffraction HRXRD
  - Reciprocal space maps, RC
- X-ray reflectometry
  - Not a diffraction method

EPFL Introduction

- Feasibility often depends on sample type
    - Not all techniques are possible in reflection AND transmission geometries
    - Grazing incidence-experiments require flat surfaces
    - Texture methods (usually) require mechanically stable sample
    - Transmission methods depend on sample absorption and/or thickness
    - X-ray reflectometry requires extremely flat surface

    - Transmission: PDF, SAXS, WAXS (texture)
    - Reflection: GID, GIWAXS, GISAXS, HRXRD, XRR (PDF at specialised beamlines)
    - Multi-method: SAXS-WAXS, PDF-PXRD, PDF-XRD-XAS, XRD-Raman…..

Introduction

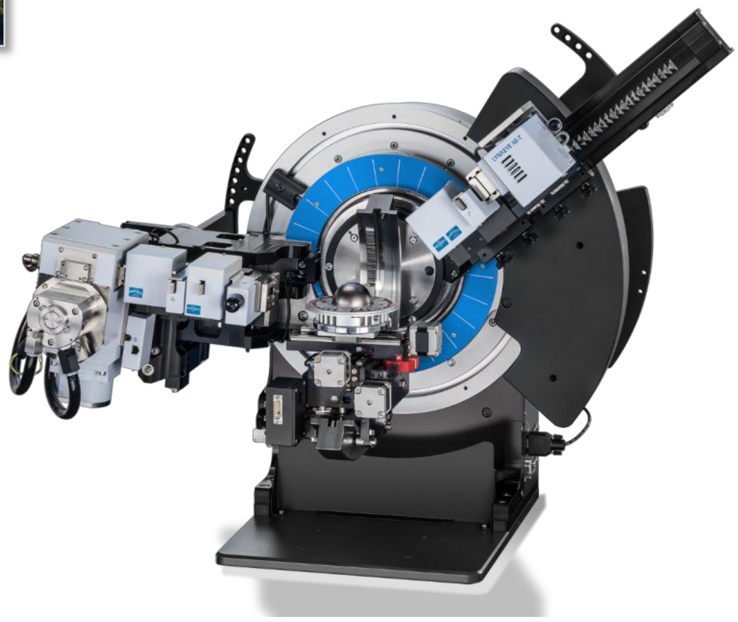


- Similar setups
- Very different analytical tools

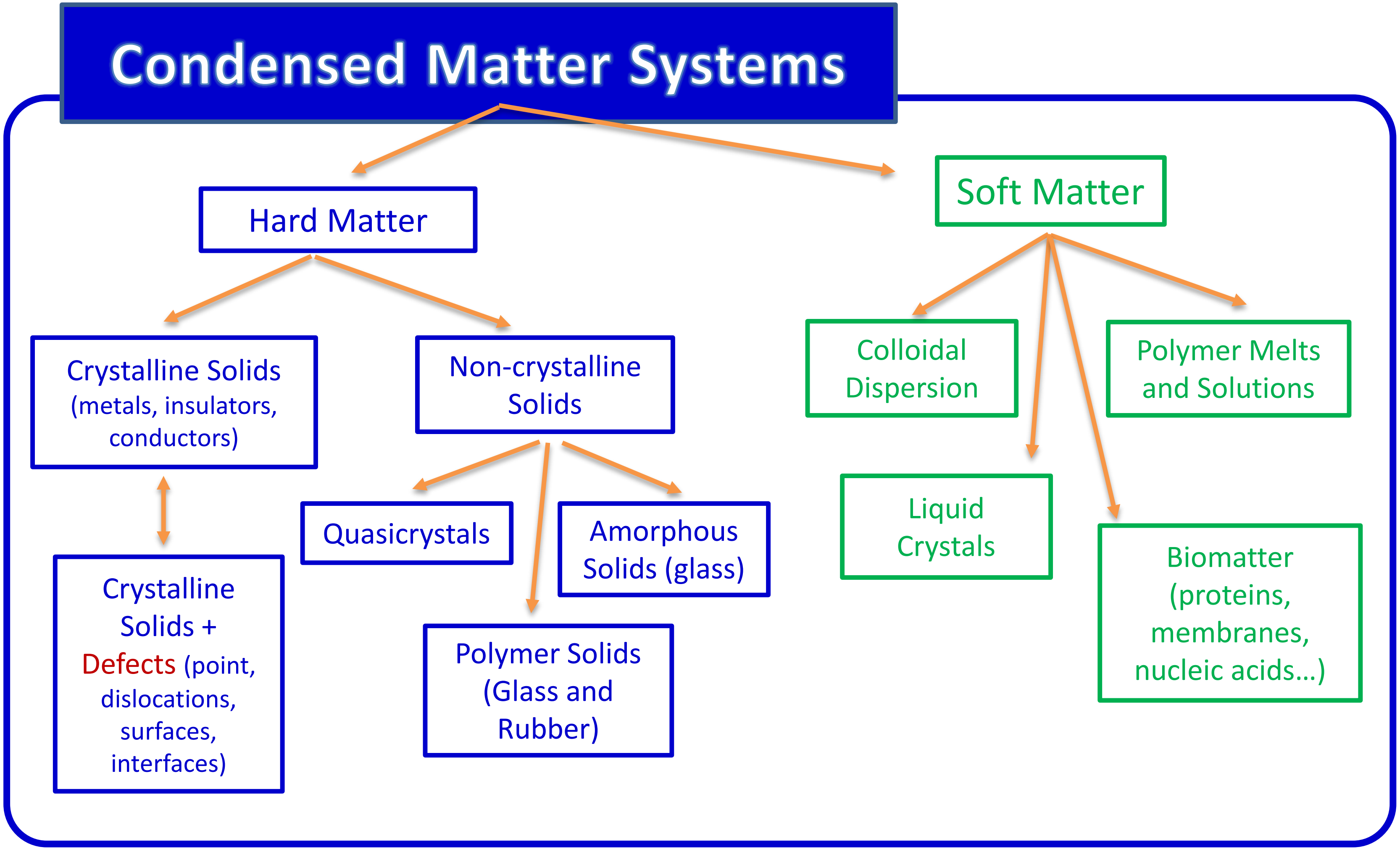
- Beam energy
- Beam shape
- Beam flux
- Machine geometry

EPFL

Introduction



Introduction

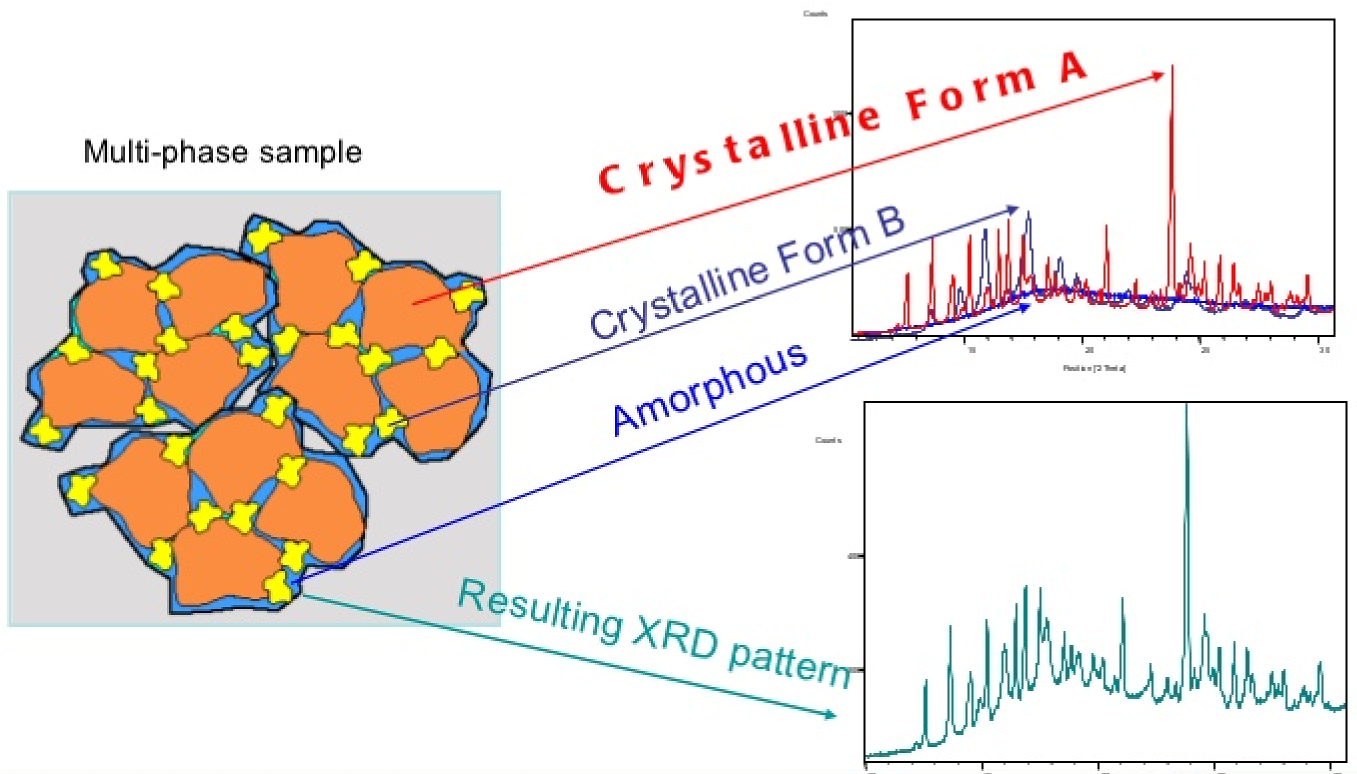


Introduction

A crystallographer's definition of solids:

Crystal: A material **is a crystal** if it has essentially a sharp diffraction pattern (IUCr). This arises from the periodicity of the lattice.

The **amorphous solid** lacks this because it lacks long range order.



➢ Patterns are additive, you see everything in your data.

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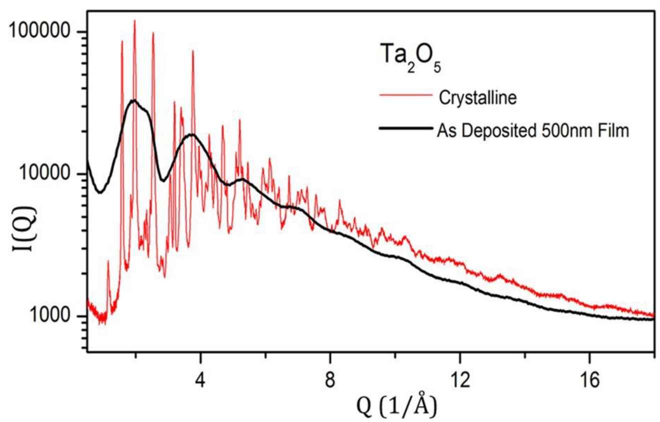
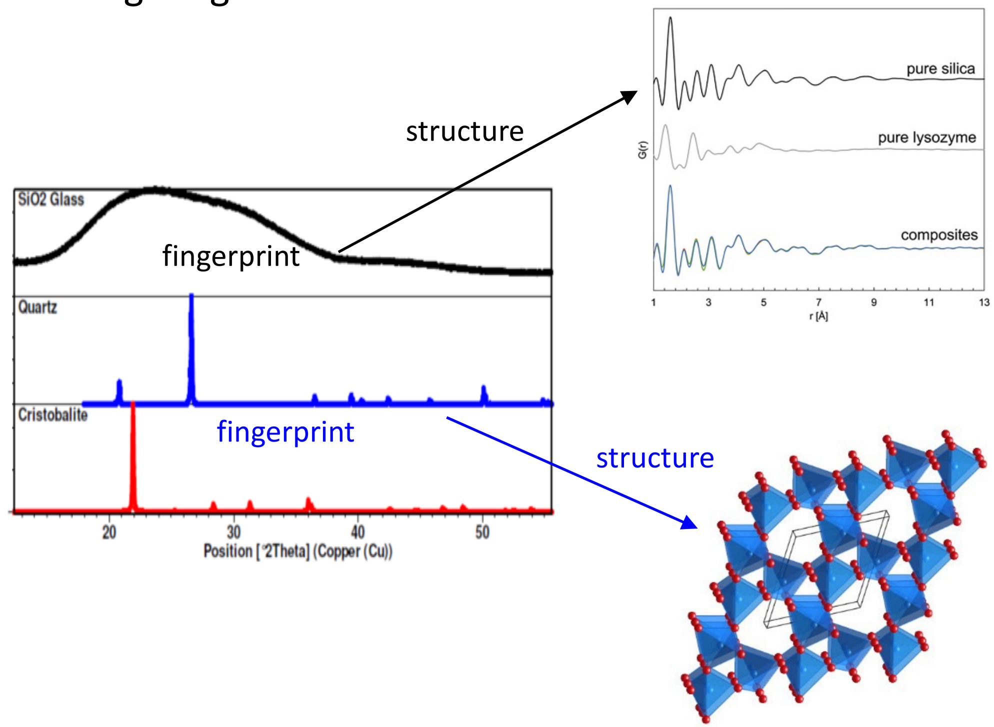


Scientific Reports ***volume 6****, Article number: 32170*

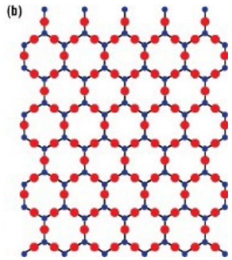


Introduction

Crystalline solid

Constituents are arranged in periodic manner on the Å length scale (several to 10s of Å). A crystal lattice is formed in 3D.

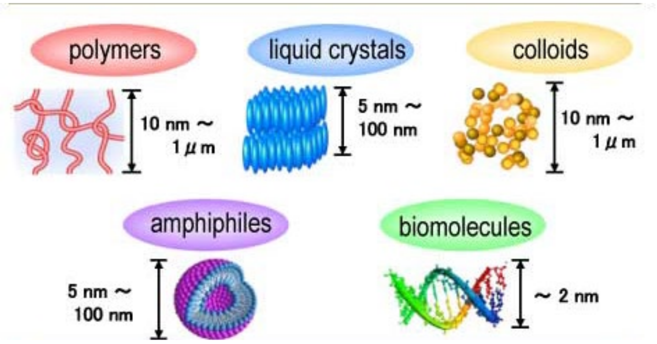
Q: How do we measure atomic structure?



Soft matter:

Intermediate legth scales between atomic and macroscopic sizes (10s to 100s of nm).

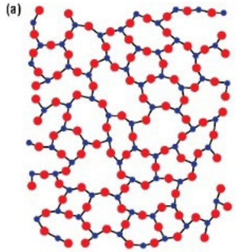
Q: How do we measure atomic structure?



Amorphous solid:

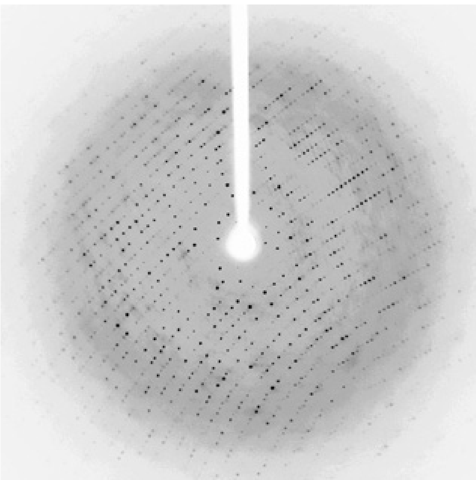
No long range order, no sharp melting point.

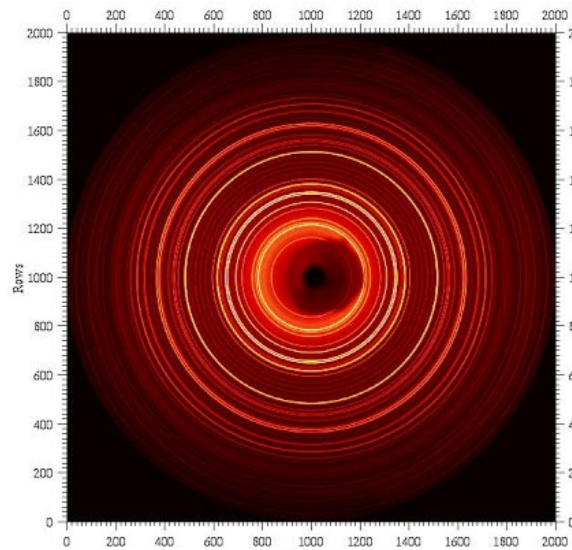
Q: How do we measure atomic structure?

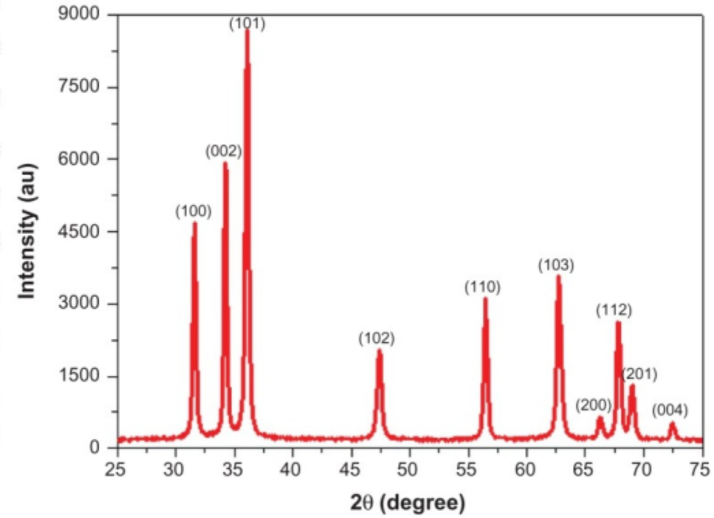


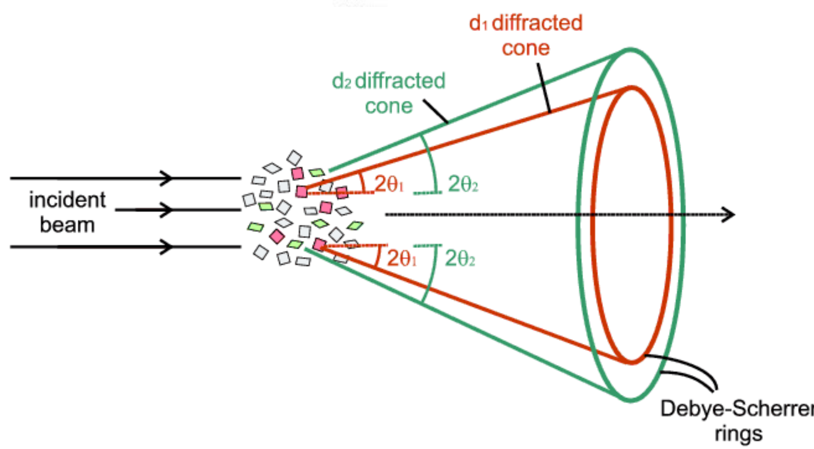
Introduction

$$I_i^{calc} = S_F \sum_k e^{-2B(T)s^2} L_k(\theta) P_k(\theta) A(\theta) y\, PO\, p_k\, S(2\theta_i - 2\theta_k) |F_k|^2 + bkg_i$$









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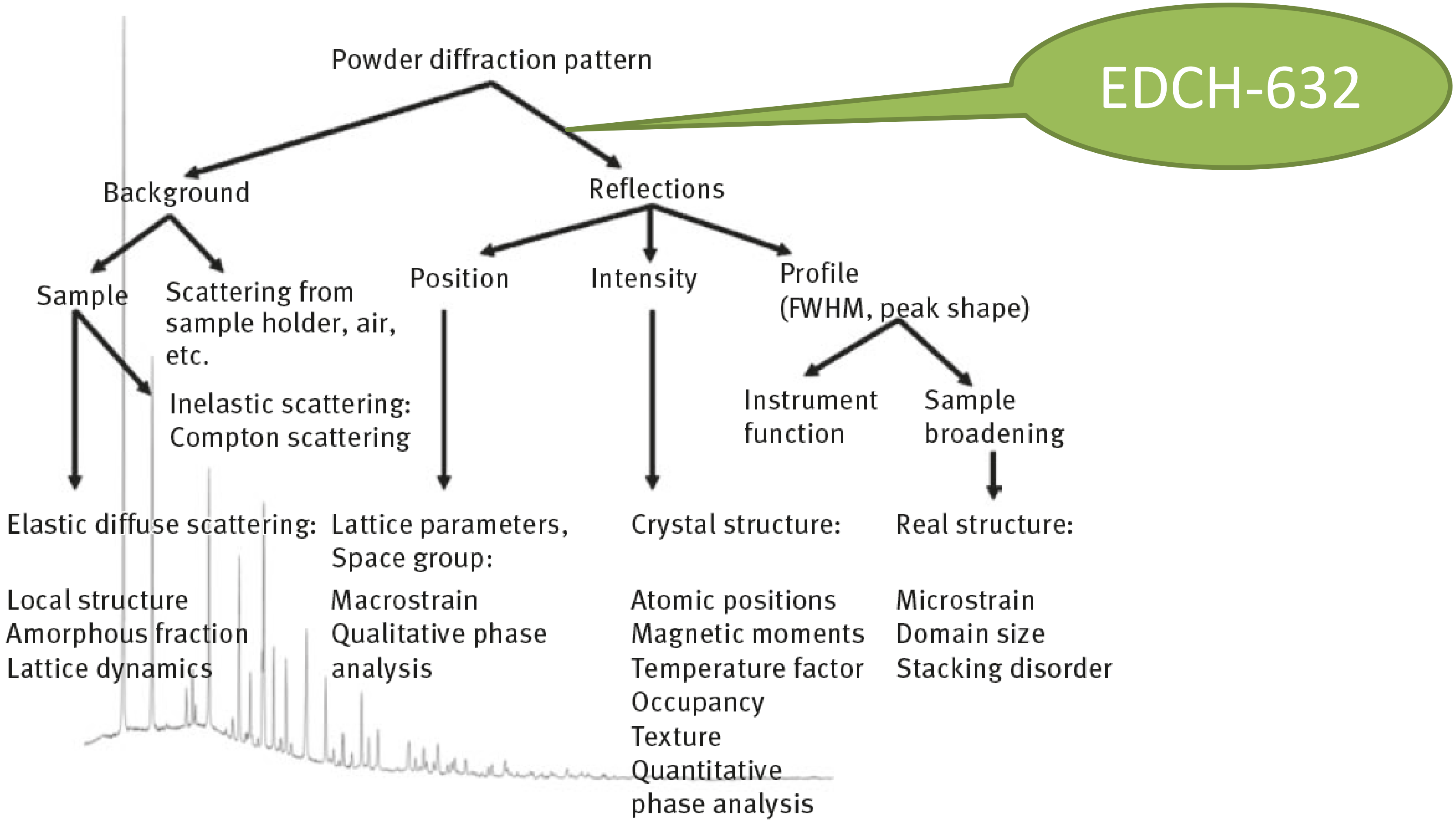

EPFL Introduction

$$I_i^{calc} = S_F \sum_k e^{-2B(T)s^2} L_k(\theta) P_k(\theta) A(\theta) y \; PO \; p_k \; S(2\theta_i - 2\theta_k) |F_k|^2 + bkg_i$$

Related to actual structure

- Debye-Waller factor
- Lorentz-Polarization correction
- Absorption correction $A(\theta)$, extinction *y* (SCD only)
- Preferred orientation (PXRD only)
- Multiplicity (PXRD only)
- Profile shape function (line broadening)
- ***Squared*** structure factor (atomic form factor, unit cell + content)
- *k*: scattering vector

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

F(hkl) is the structure factor of the reflection hkl of the unit cell, f_N is the atomic scattering factor (form factor) for each of the *N* planes

- Electronic property – information about atom types in structure (Amplitude)
- Structural property – information about atom position in the unit cell (Phase)

Introduction

$$I_i^{calc} = S_F \sum_k e^{-2B(T)s^2} L_k(\theta) P_k(\theta) A(\theta) y \; PO \; p_k \; S(2\theta_i - 2\theta_k) |F_k|^2 + bkg_i$$

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

$$I(q) = P(Q)S(Q)$$

SAXS

$$I(q) = \sum_n \sum_m f_m, f_n, \frac{sinqr_{mn}}{qr_{mn}}$$

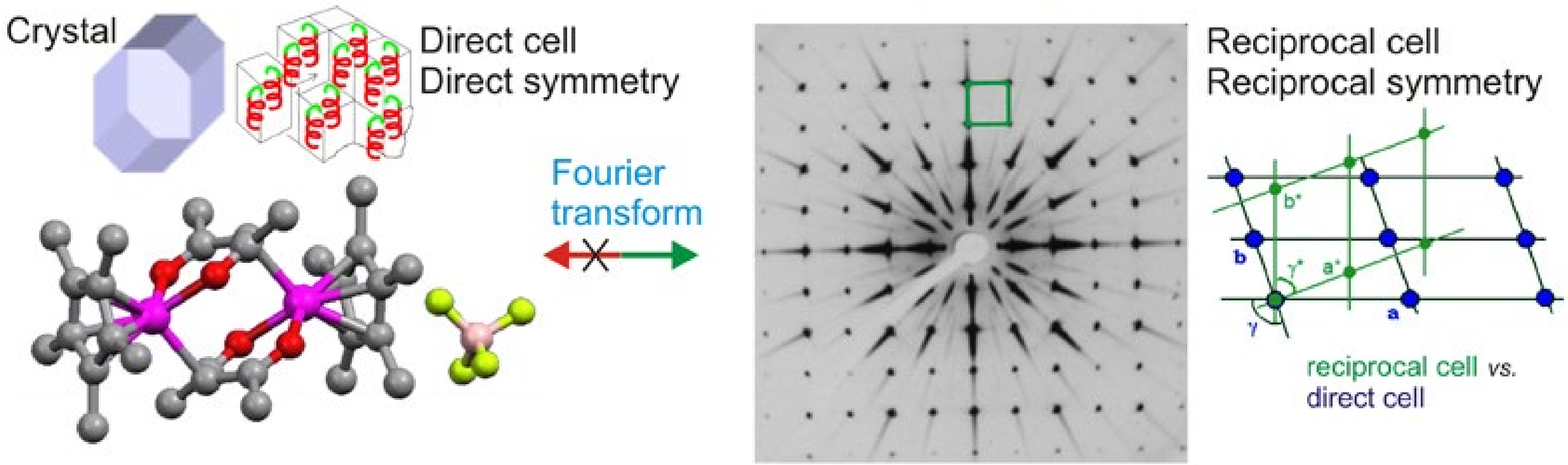
Total scattering (PDF)

EPFL Introduction

$$I_i^{calc} = S_F \sum_k e^{-2B(T)s^2} L_k(\theta) P_k(\theta) A(\theta) y \; PO \; p_k \; S(2\theta_i - 2\theta_k)|F_k|^2 + bkg_i$$

Real or direct space

Reciprocal space



Atoms, structure

Structure factors = Amplitudes and phases

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

Amplitudes

Phases?

Introduction

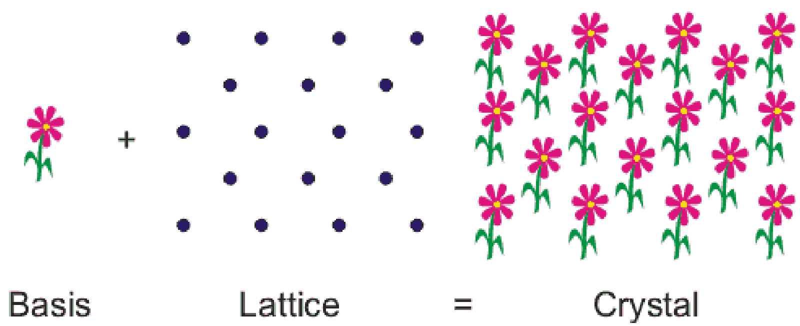
Some necessary basics:

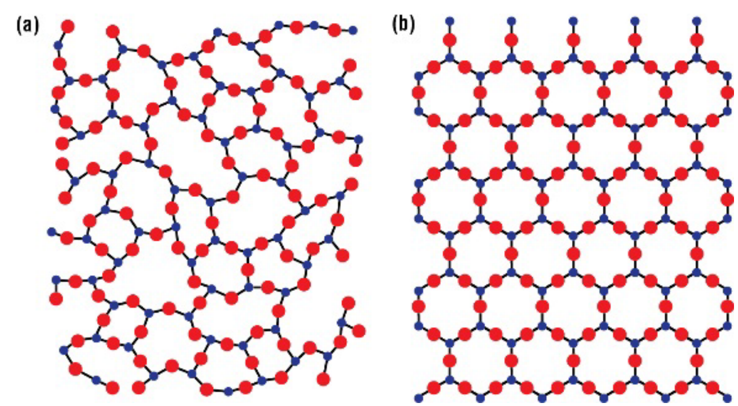
- **Symmetry**
- Diffraction condition
- Structure factor and extinctions

Symmetry

The crystal lattice

- Periodicity gives rise to discrete signals in the diffraction pattern
- A solid lacking long range order does not “diffract”
- **Bravais lattice:** regular arrangement of points generated by translation
  - $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$
- **Periodicity gives rise to the unit cell:** smallest repetitive unit of a lattice that contains all the information - defines the symmetry and structure of the entire crystal lattice.





amorphous (no unit cell)

crystalline (unit cell)

The crystal lattice

- **Bravais lattice:** regular arrangement of points generated by translation
  - $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$
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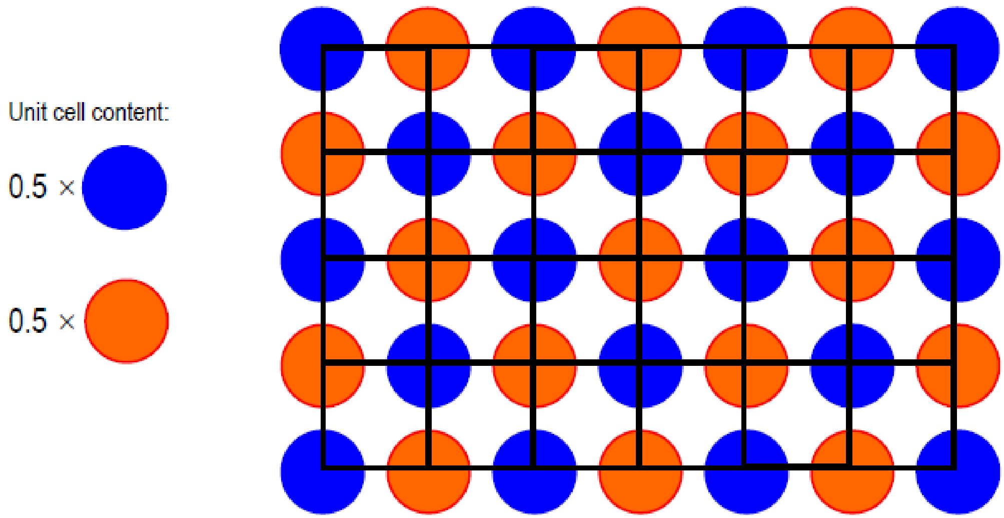

Wrong selection

Symmetry

The crystal lattice

- **Bravais lattice:** regular arrangement of points generated by translation
  - $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$
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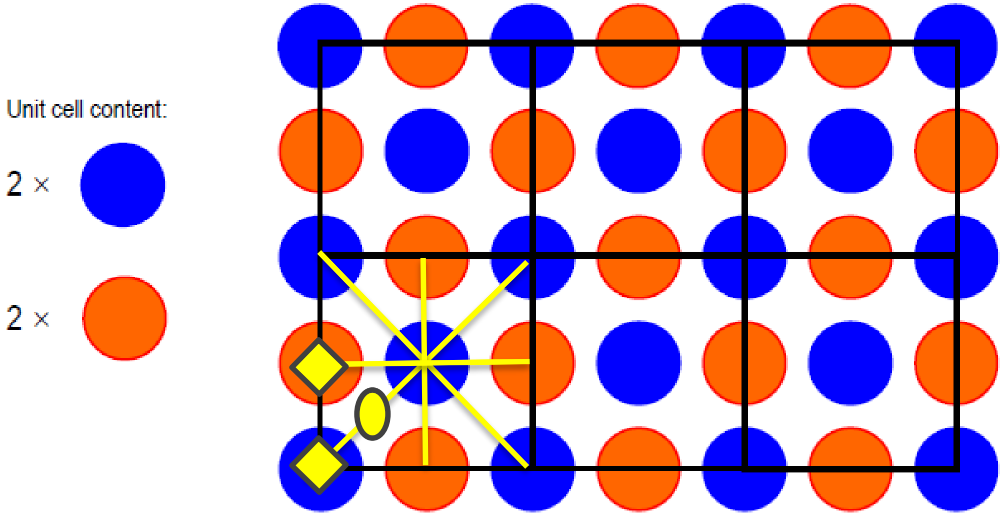
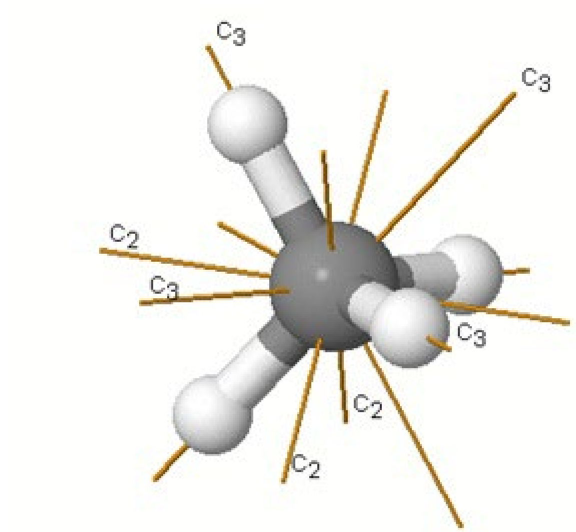


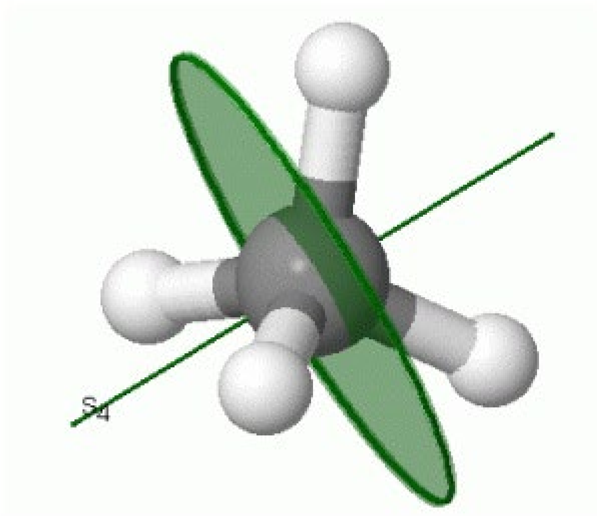
➢ Periodicity gives rise to symmetry in the lattice

Symmetry

A closer look at symmetry (more detailed treatment CH 632)

- How do you describe the symmtrey of a molecule (gas, liquid..)





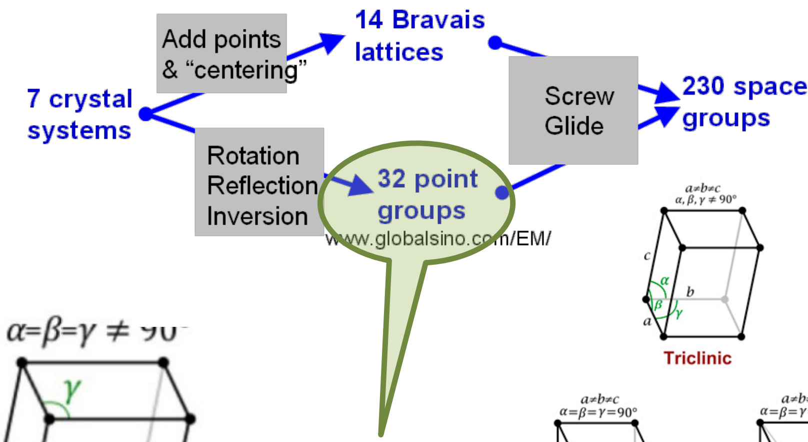
T_d – tetrahedral group (point group)

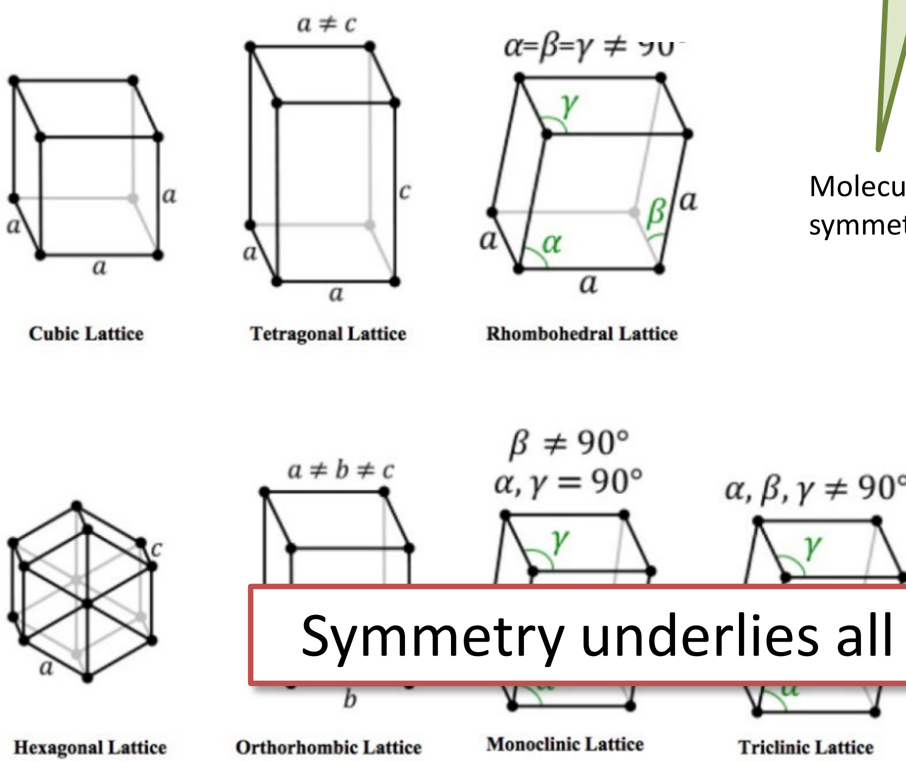
Schoenfliss notation: point symmetry, used to describe molecular symmetry (point groups)

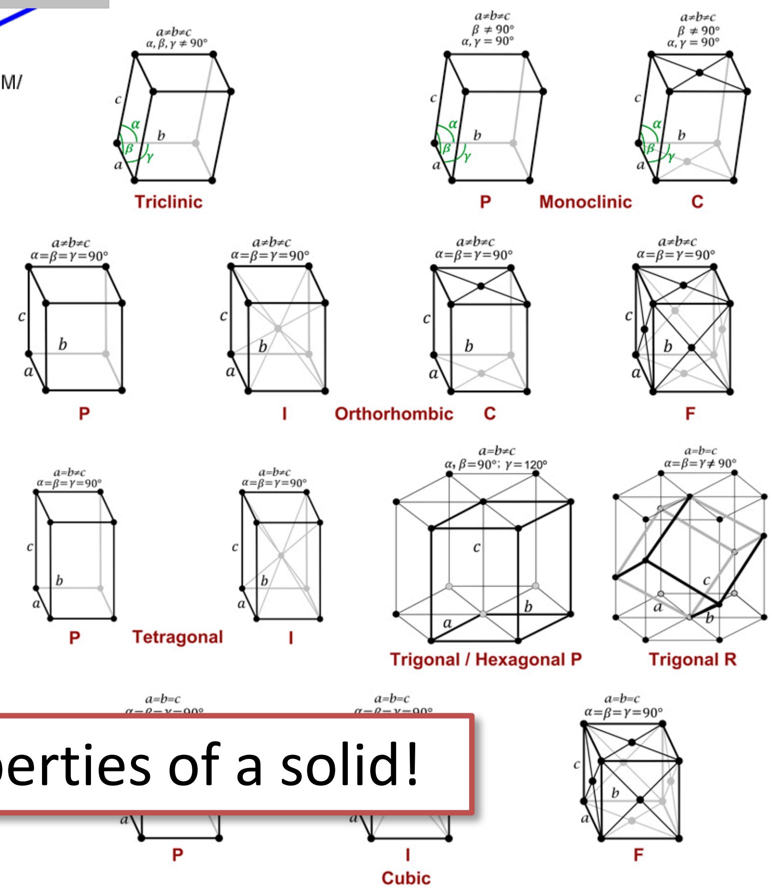
Hermann-Mauguin notation: used to describe to describe translational symmetry (space groups)

A crystal is an extended solid!

Space group symmetry







Symmetry underlies all properties of a solid!

Symmetry

Space group symmetry

- PG symmetry (32 groups) + translation results in SG symmetry (230 groups).
- SG symmetry defines which peaks you see for a given unit cell!

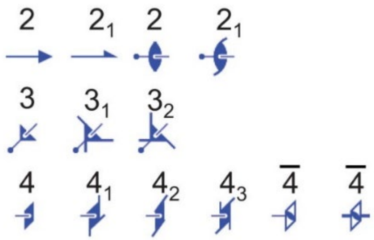
7 crystallographic systems and their symmetry point groups							
triclinic	C_1	$\mathbf{C_i}$					
	1	$\bar{1}$					
monoclinic	C_2	C_s	$\mathbf{C_{2h}}$				
	2	m	**2/m**				
ortorhombic	D_2	C_{2v}	$\mathbf{D_{2h}}$				
	222	mm2	**mmm**				
tetragonal	C_4	S_{4i}	C_{4h}	D_4	C_{4v}	D_{2d}	$\mathbf{D_{4h}}$
	4	$\bar{4}$	4/m	442	4mm	$\bar{4}2m$	**4/mmm**
trigonal (rhombohedral)	C_3	C_{3i}	D_3	C_{3v}	$\mathbf{D_{3d}}$		
	3	$\bar{3}$	32(1)	3m	$\bar{3}$**m**		
hexagonal	C_6	C_{3h}	C_{6h}	D_6	C_{6v}	D_{3h}	$\mathbf{D_{6h}}$
	6	$\bar{6}$	6/m	622	6mm	$\bar{6}m2$	**6/mmm**
cubic	T	T_4	O	T_d	$\mathbf{O_h}$		
	23	$m\bar{3}$	432	$\bar{4}3m$	**m3m**		

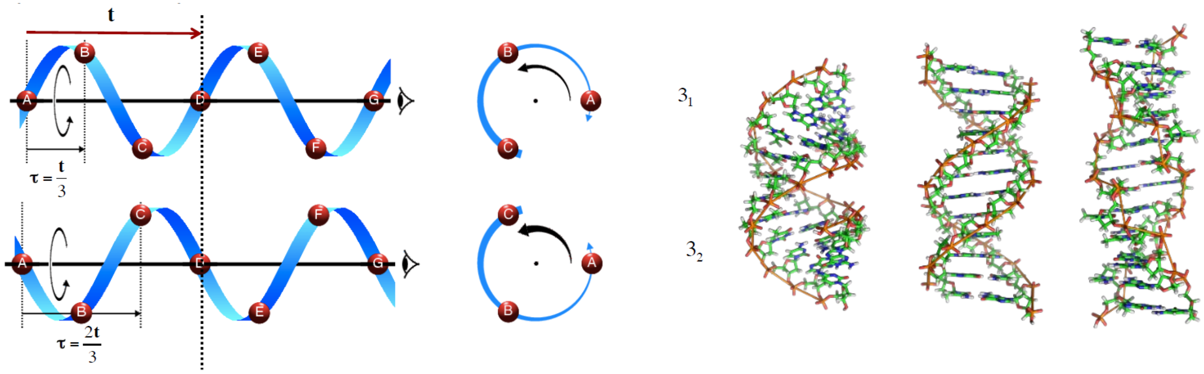
Space group symmetry

- PG symmetry (32 groups) + translation results in SG symmetry (230 groups).
- SG symmetry defines which peaks you see for a given unit cell, as well as the crystal structure!

Screw axis 3_1

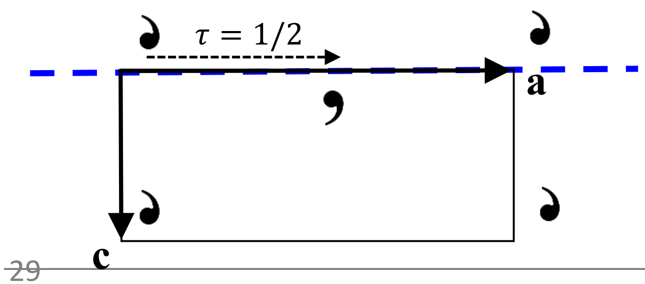
- 3 equivalent positions
- 3 symmetry operations (order)

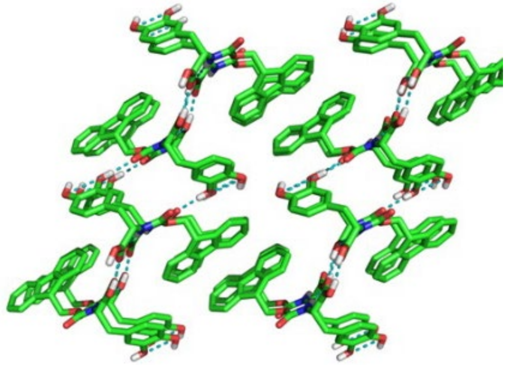




c glide plane

- 2 equivalent positions
- 2 symmetry operations (order)





EPFL Symmetry

Space group symmetry

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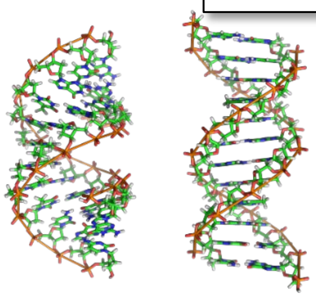
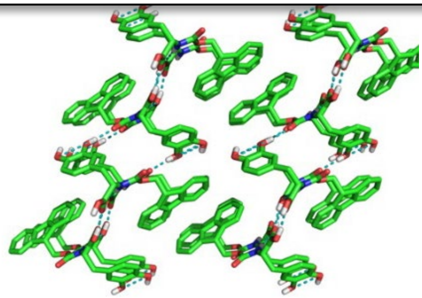
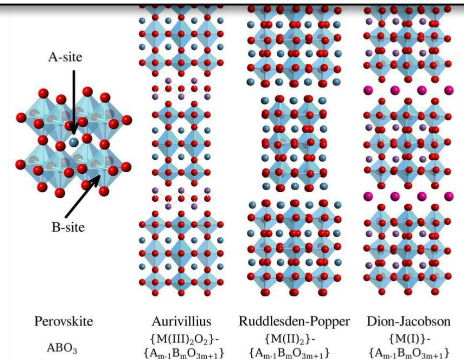
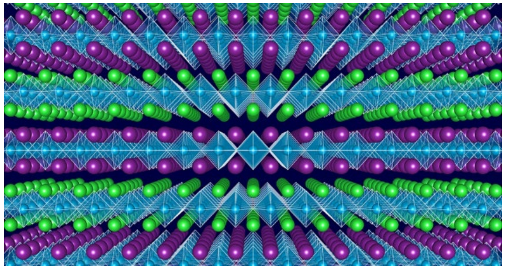
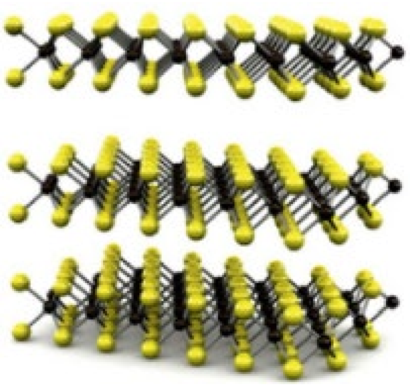
➢Different types of material "like" different types of symmetry

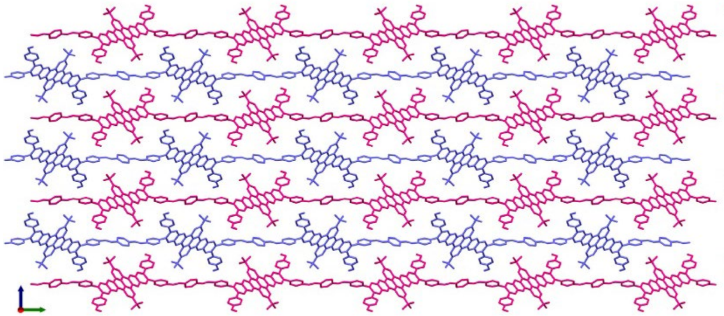


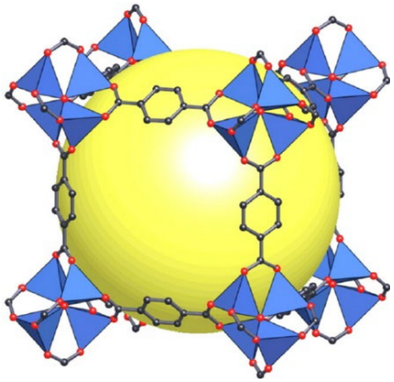












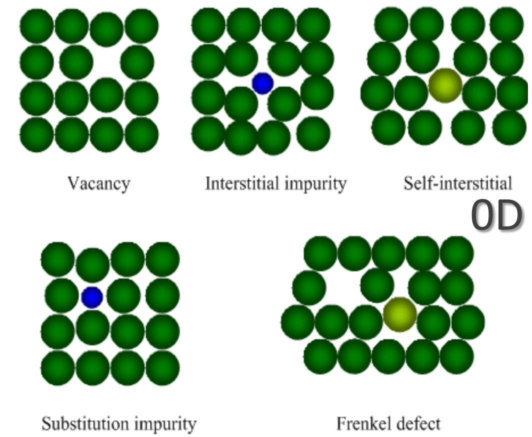
Symmetry

Real solids contain defects at finite temperature.

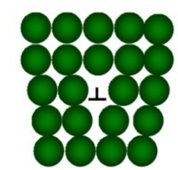
- Conventional 0D, 1D, 2D
- Missing linkers or non-periodic sorption sites (MOFs)
- Structural disorder (polymers)
- …

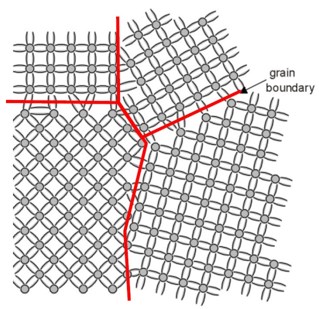
➢ What type, is defined by processing, topology, symmetry, bonding…

➢ Hard to quantify, but have different signatures (EM, XRD, XPS…)

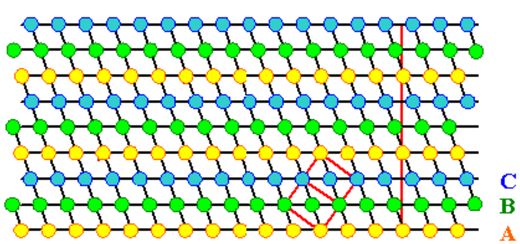


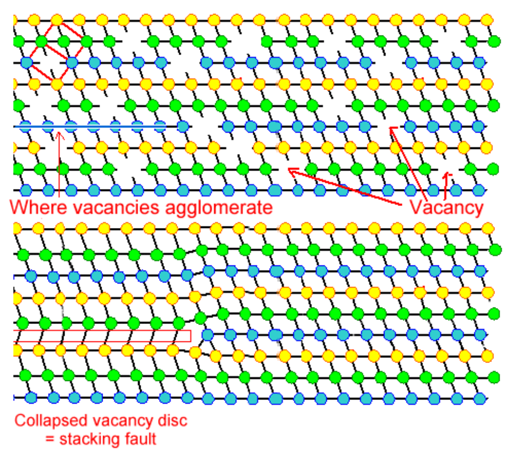
1D

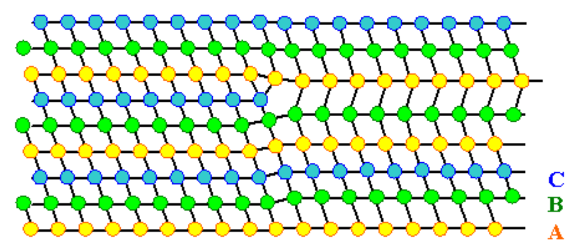




2D







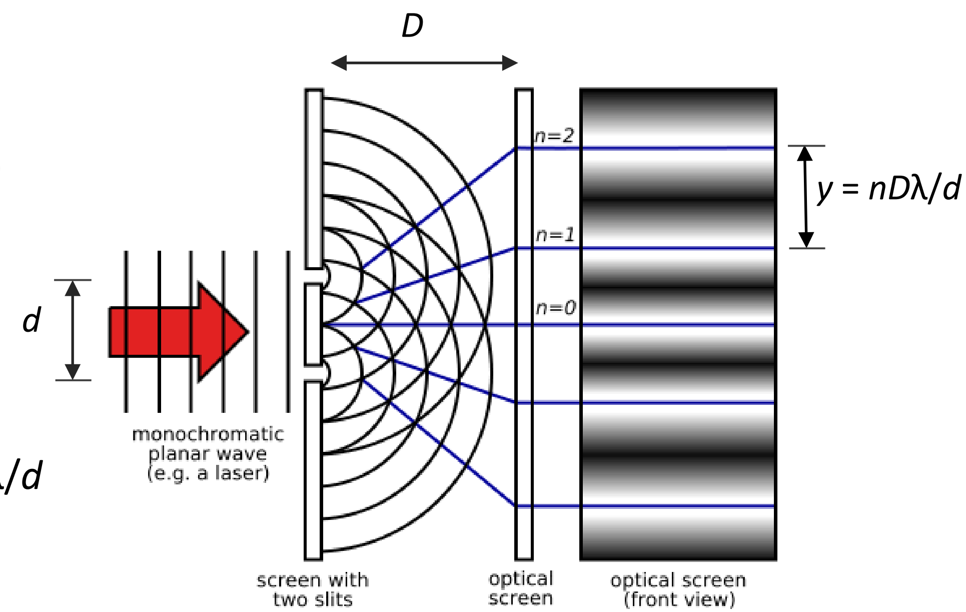
Diffraction

Some necessary basics:

- Symmetry
- **Diffraction condition**
- Structure factor and extinctions

Double – slit experiment:

- Maxima are registered due to interference.
- Periodicity
- Spacing between detected maxima: $y = nD\lambda/d$

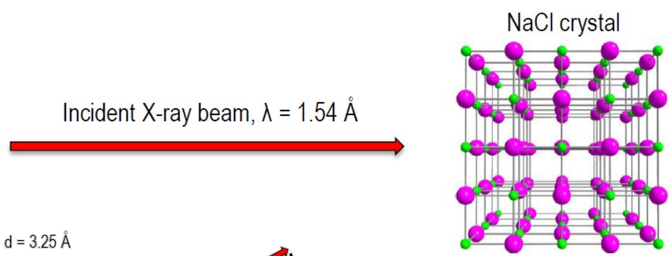


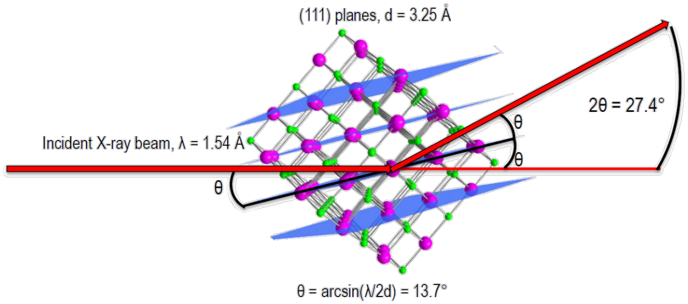
- ➢ Crystal is a 3D diffraction grating
- ➢ With XRD we measure the reciprocal lattice

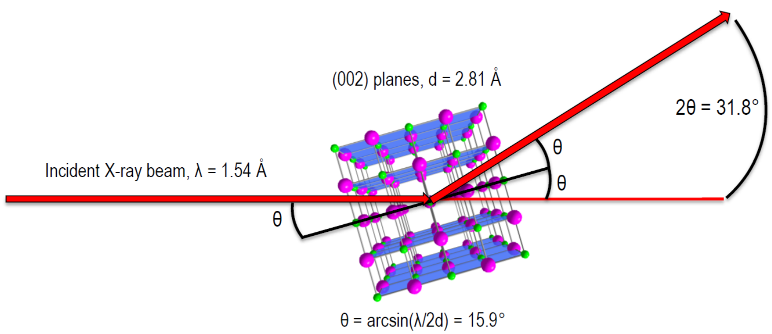
Q: Why do we use X-rays?
Q: When do X-rays interfere constructively?
Q: How do we get the direct lattice (atomic structure)?

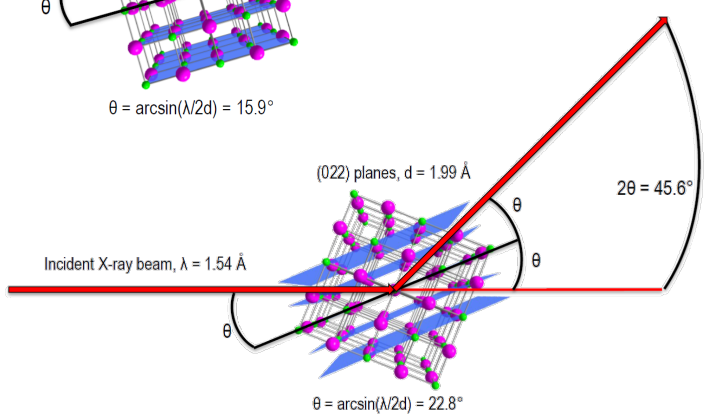
Diffraction

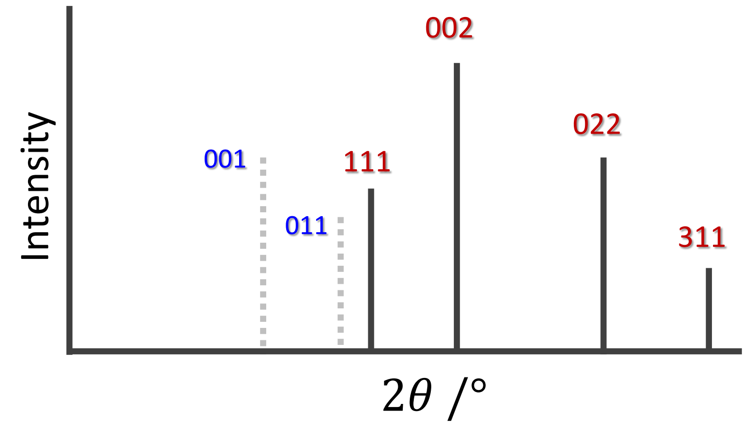
NaCl, *Fm*-3*m*:







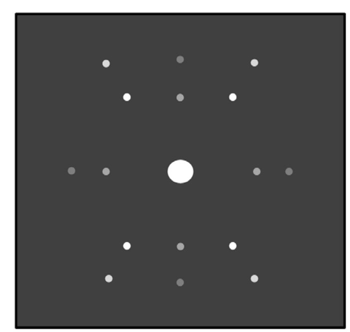


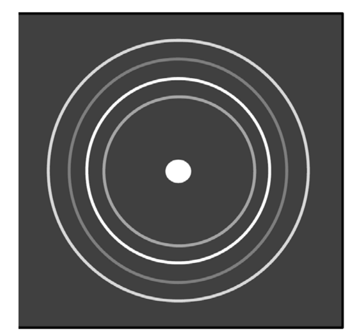


Bragg law: $2d sin\theta = n\lambda$

Q:

- Where is (200)?
- Where are (001), (011)…



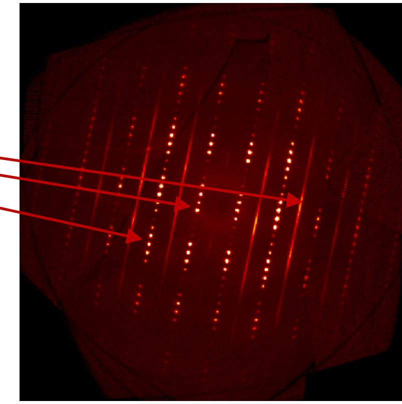


The reciprocal lattice

Direct and reciprocal lattice:

$$\mathcal{L}(\mathbf{r}) = \sum_{UVW} \delta[\mathbf{r} - (U\mathbf{a} + V\mathbf{b} + W\mathbf{c})] \quad \xrightarrow{FT} \quad R(\mathbf{Q}) = \sum_{hkl} \delta[\mathbf{Q} - (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)]$$

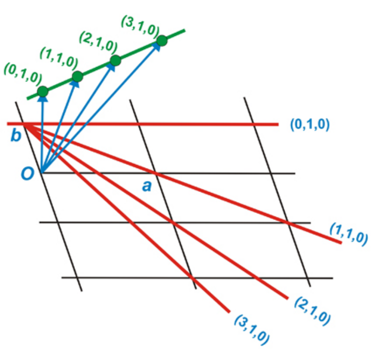
FT^{-1}

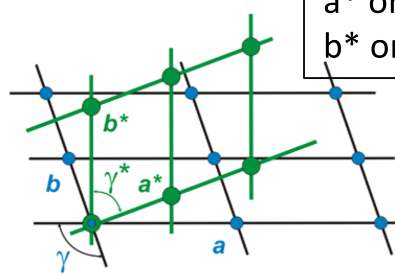


- Construct reciprocal:
- Vectors **r*** normal to planes in lattice with distance *d* from origin

Miller indices:

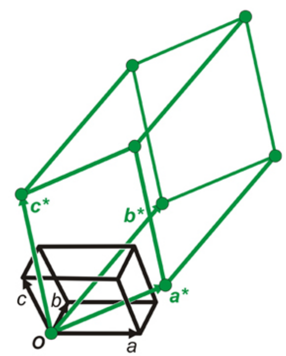
Notation to describe reciprocal lattice points $\mathbf{r}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$





a* orthogonal to b
b* orthogonal to a

3D →



$$\mathrm{a}^* = 2\pi \frac{\mathrm{b} \times \mathrm{c}}{\mathrm{a} \cdot (\mathrm{b} \times \mathrm{c})}, \qquad \mathrm{b}^* = 2\pi \frac{\mathrm{c} \times \mathrm{a}}{\mathrm{b} \cdot (\mathrm{c} \times \mathrm{a})}, \qquad \mathrm{c}^* = 2\pi \frac{\mathrm{a} \times \mathrm{b}}{\mathrm{c} \cdot (\mathrm{a} \times \mathrm{b})}$$

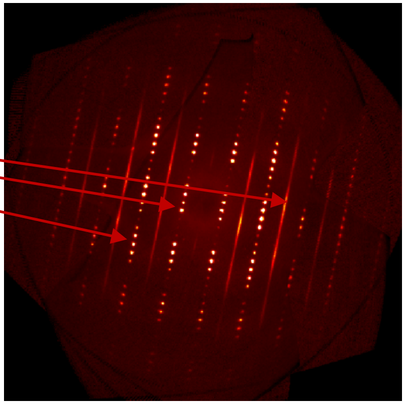
$$Q = \frac{2\pi}{d} = \frac{4\pi \sin\theta}{\lambda} \quad / \ \text{Å}^{-1}$$

The reciprocal lattice

Direct and reciprocal lattice:

$$\mathcal{L}(\mathbf{r}) = \sum_{UVW} \delta[\mathbf{r} - (U\mathbf{a} + V\mathbf{b} + W\mathbf{c})] \quad \xrightarrow{FT} \quad R(\mathbf{Q}) = \sum_{hkl} \delta[\mathbf{Q} - (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)]$$

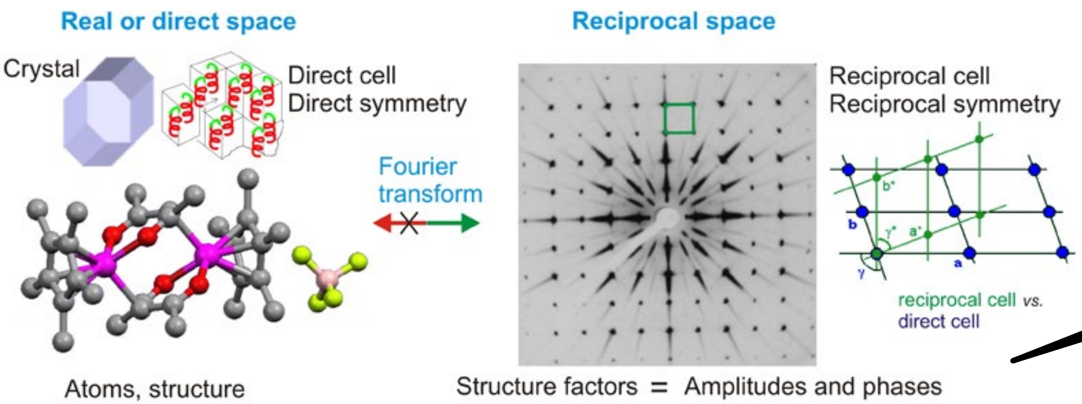
FT^{-1}



- Construct reciprocal:
- Vectors **r*** normal to planes in lattice with distance *d* from origin

Miller indices:

Notation to describe reciprocal lattice points $\mathbf{r}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$



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

Amplitudes

Phases?

Structure solution: FT^{-1}

Q: Why is this different from electron microscopy?

Recap – intensity equation

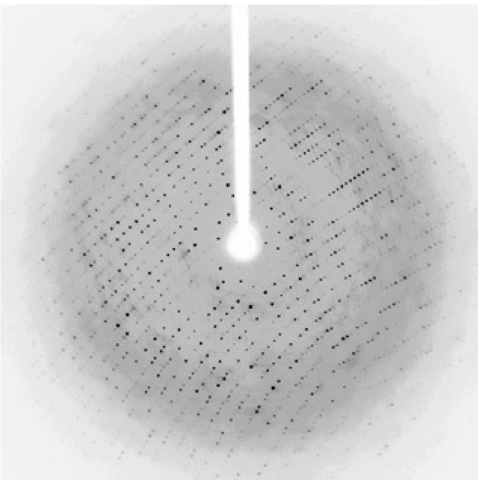
Some necessary basics:

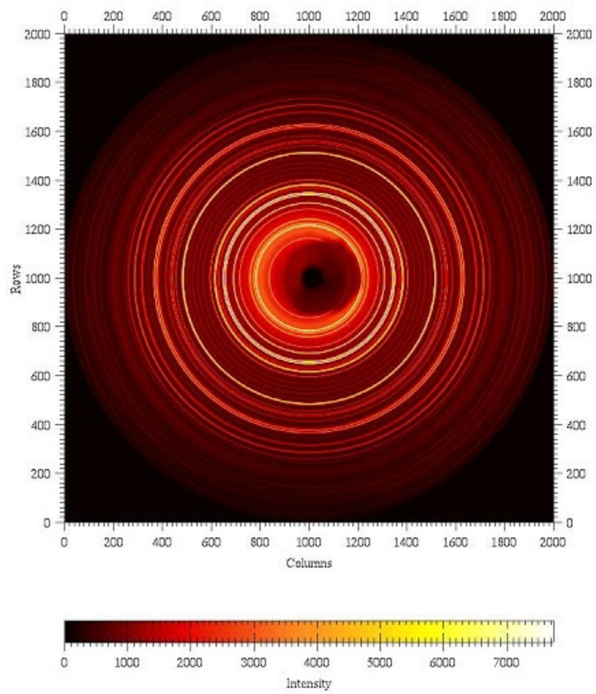
- Symmetry
- Diffraction condition
- **Structure factor and extinctions**

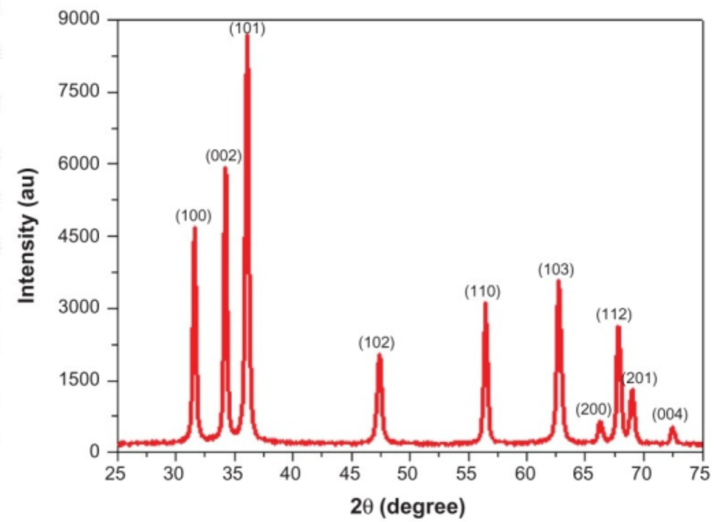
Recap – intensity equation

$$I_i^{calc} = S_F \sum_k e^{-2B(T)s^2} L_k(\theta) P_k(\theta) A(\theta) y \, PO \, p_k \, S(2\theta_i - 2\theta_k) |F_k|^2 + bkg_i$$

Related to actual structure – Structure Factor





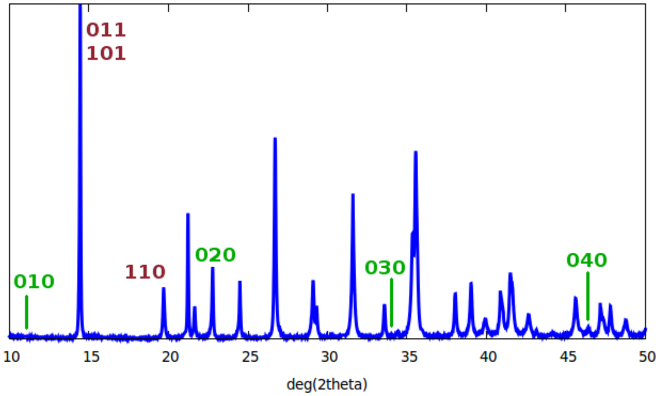


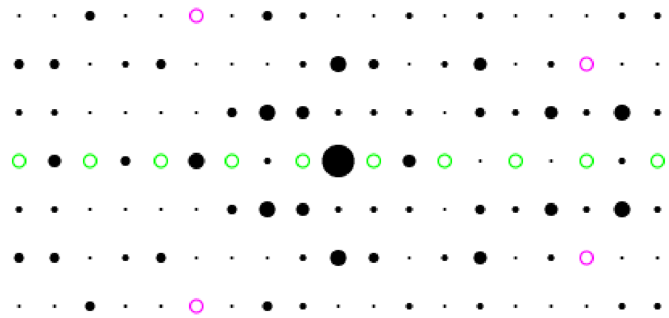
Space group symmetry

- Space group symmetry symmetry defines which peaks you see for a given unit cell!
- When are Bragg peaks “allowed/forbidden”?

The structure factor

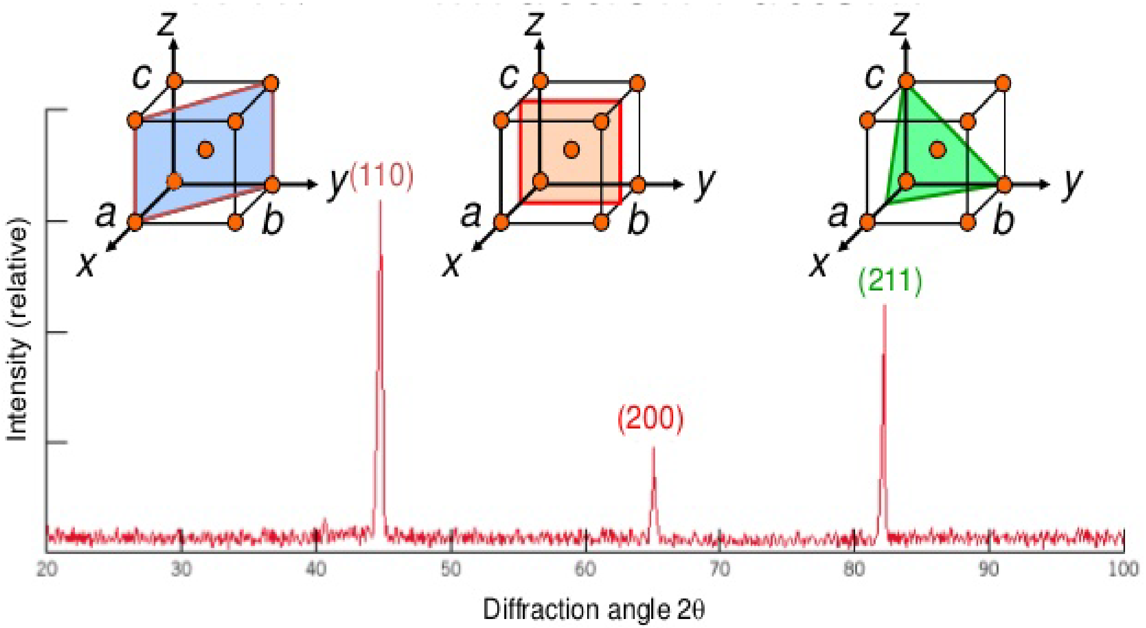
Systematic absences / extinctions





α – Fe (bcc), *Im*-3*m*

Q: Where is 100, 210..



The structure factor

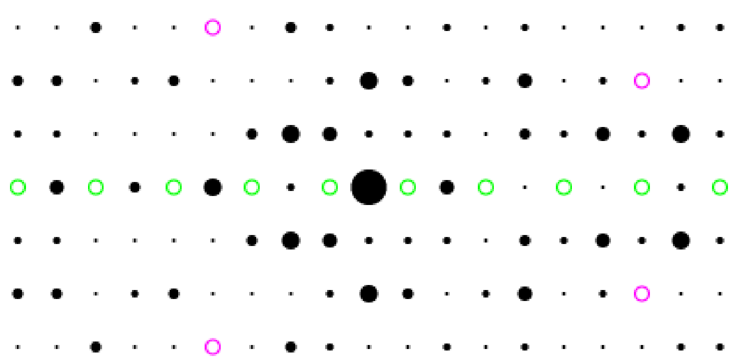
Systematic absences / extinctions

- Translational symmetry (screw, glide, centering) generates extinction conditions, where Bragg intensity is = 0 due to destructive interference of scattered waves.

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

F(hkl) is the structure factor of the reflection hkl of the unit cell, f_N is the atomic scattering factor (form factor) for each of the N planes

- Electronic property – information about atom types in structure (Amplitude)
- Structural property – information about atom position in the unit cell (Phase)



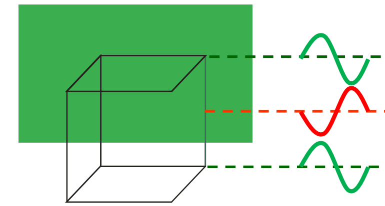
b^*

- 010, 030, 050… no intensity

The structure factor

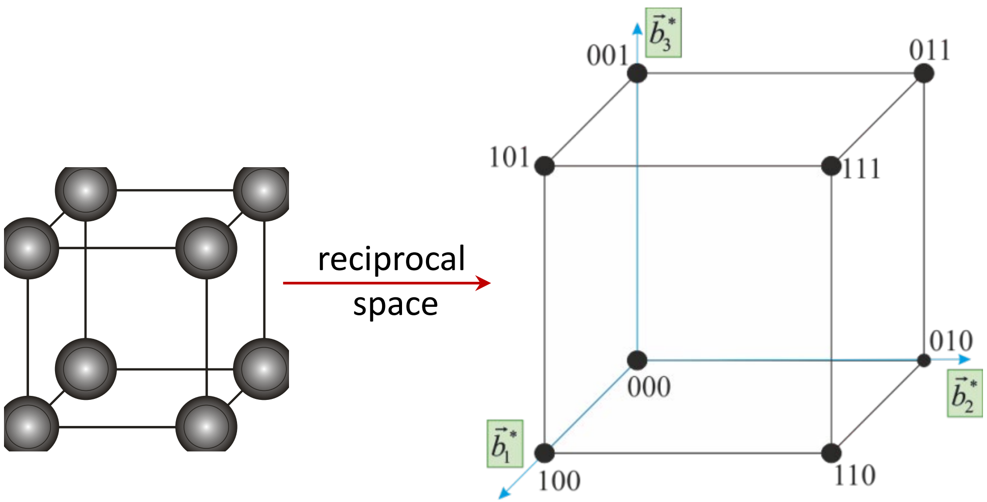
$$F(hkl) = \sum_N f_N \, e^{2\pi i (h x_N + k y_N + l z_N)}$$

Systematic absences / extinctions



Example: Cubic primitive lattice, 1 atom at (0,0,0) and equivalent.
Space group *Pm*-3*m*.

$$e^{ni\pi} = (-1)^n$$



$$F^{hkl} = f_j e^{i\varphi_j} = f_j e^{i[2\pi(h x_j' + k y_j' + l z_j')]}$$

$$F = f e^{i[2\pi(h0+k0+l0)]} = f e^0 = f$$

$$F^2 = f^2$$

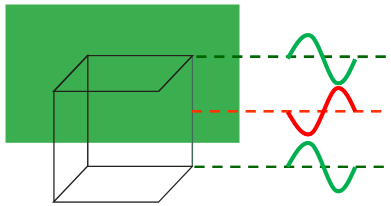
Structure factor calculation

The structure factor of a plane (hkl) is weighted by the contributing atomic form factors f_j
Perform summation of $f$exp($i\varphi$)

The structure factor

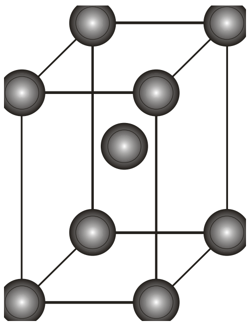
$$F(hkl) = \sum_N f_N \, e^{2\pi i (h x_N + k y_N + l z_N)}$$

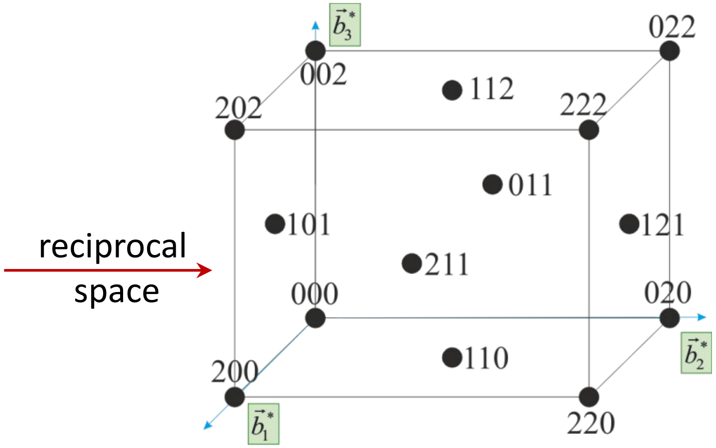
Systematic absences / extinctions



Example: Orthorhombic body-centred, 2 atoms at (0,0,0) and ($^1/_2$, $^1/_2$, $^1/_2$) and equivalent. Space group *Immm*.

$$e^{n i \pi} = (-1)^n$$





$$F^{hkl} = f_j e^{i\varphi_j} = f_j e^{i[2\pi(h x_j' + k y_j' + l z_j')]}$$

$$F = f e^{i[2\pi(h\,0 + k\,0 + l\,0)]} + f e^{i\left[2\pi\left(h\frac{1}{2} + k\frac{1}{2} + l\frac{1}{2}\right)\right]}$$

$$= f e^0 + f e^{i\left[2\pi\left(\frac{h+k+l}{2}\right)\right]} = f\left[1 + e^{i\pi(\mathbf{h+k+l})}\right]$$

$$(h+k+l) = 2n \rightarrow F = 2f \rightarrow F^2 = 4f^2$$

$$(h+k+l) \neq 2n \rightarrow F = 0 \rightarrow F^2 = 0$$

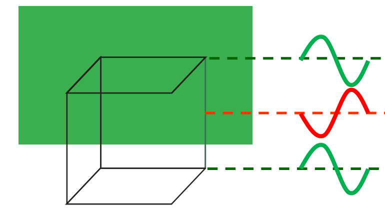
- (110), (200), (211)… observed; (100), (001), (111)… extinct
- Lattice centring is an integral extinction, valid for all Bravais lattices. hkl: h+k+l = 2n

The structure factor

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

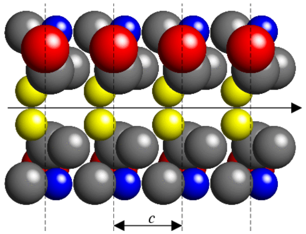
Systematic absences / extinctions

Example: Screw axis 2_1 II c, operation $(-x, -y, z + {}^1/_2)$

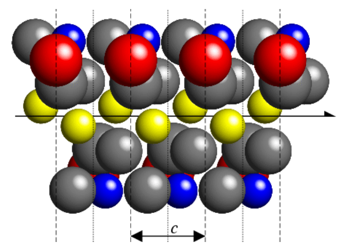


$$e^{ni\pi} = (-1)^n$$

2



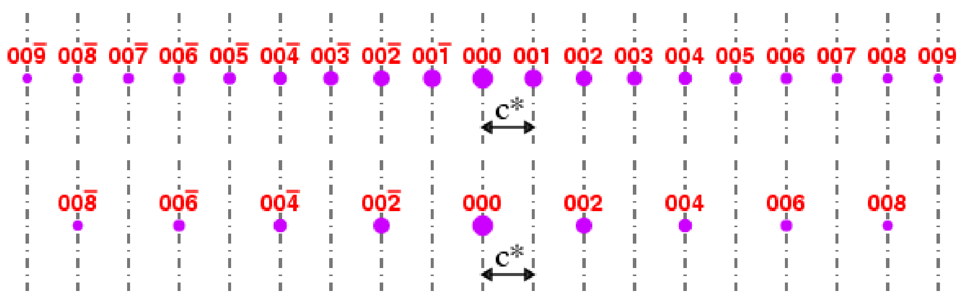
2_1



$$F^{hkl} = f_j e^{i\varphi_j} = f_j e^{i[2\pi(hx_j' + ky_j' + lz_j')]}$$

$$F = fe^{i[2\pi(h\,0 + k\,0 + l\,0)]} + fe^{i\left[2\pi(-h\,-k + l\frac{1}{2})\right]}$$

$$F^{00l} = fe^0 + fe^{i\left[2\pi\left(\frac{l}{2}\right)\right]} = f\left[1 + e^{i\pi(l)}\right]$$



$l = 2n \rightarrow F = 2f \rightarrow F^2 = 4f^2$

$l \neq 2n \rightarrow F = 0 \rightarrow F^2 = 0$

- Serial extinction – affects one direction
- For (00l): (002), (004), (006)… observed; (001), (003), (005)… extinct. 00l: l = 2n

Introduction & Recap: Summary

- Perodicity of a crystalline solid gives rise to the unit cell, which allows to fully describe an atomic structure.
- Periodicity gives rise to translational symmetry (space group symmetry).
- Periodicity is at the origin of the diffraction condition.
- The diffraction experiment "takes place" in reciprocal space, which is related to real space by Fourier transform.
- The intensity registered on the detector is proportional to the amplitude of the structure factor.
- Translational symmetry leads to extinctions conditions of the observable structure factor.

Orbitals and periodicity…

- ## Chemical bonding

Chemist's picture: chemical bonding in molecules based on concept of orbitals

LCAO method: usual approximations of **molecular orbitals** (no translational symmetry!)

Molecular orbitals: The more atoms in the molecule the more MO (**n_{tot}(MO) = n(valence AO**) used to make them).

Solid: huge, but **finite** number of MO ("crystal orbitals", with **small energy spacing** (wavenumber *k* is quasi-continuous) – formation of "bands"

Shape of the bands can be derived using LCAO or the free electron model – what is the form of the wave function of an electron moving along a row of atoms?

Periodic boundary conditions (crystal) mean that Values of *k* outside $-\frac{\pi}{a} \leq k < \frac{\pi}{a}$ do provide are repetitions of already generated orbitals.

Orbitals and periodicity…

▪ Band structure

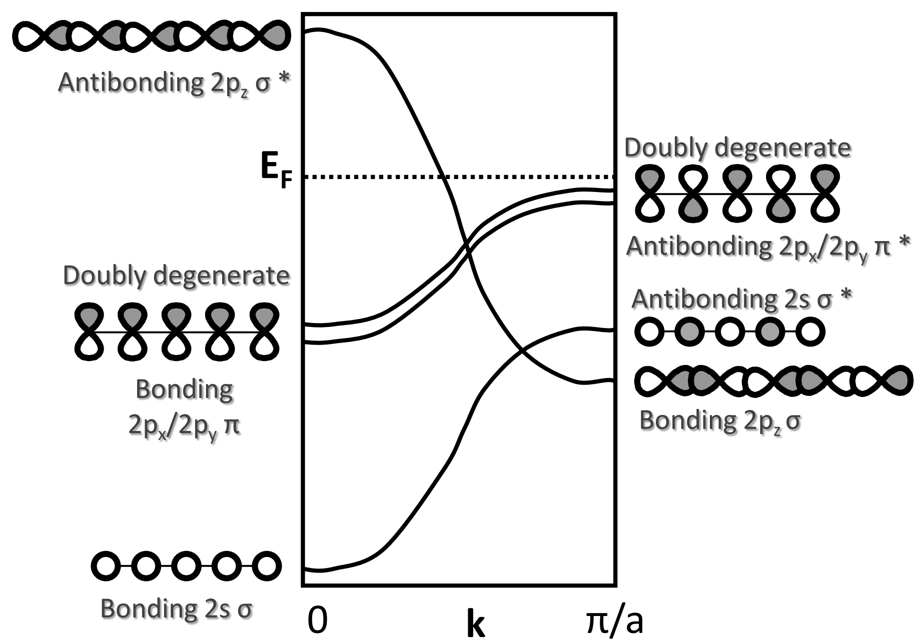
➢ Increasing density of orbitals leads to non-uniform distribution within allowed bands:
Density of states *N*(*E*)d*E* (number of allowed energy levels per unit volume of solid in *E*..E + d*E*)

- $N(E) = 0$ in band gap E_g.

- **Width** of a band depends on degree of interaction and separation, lattice parameter.
- Width < 0.1 eV (no contribution to bonding, e.g. core levels)….several eV
- **E_g range** (top-filled to bottom empty band): E_g >12 eV (ionic solids) … 0.1 eV semiconductors

- LCAO theory

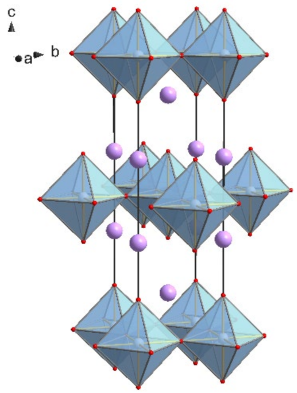
➢ Example: monatomic chain

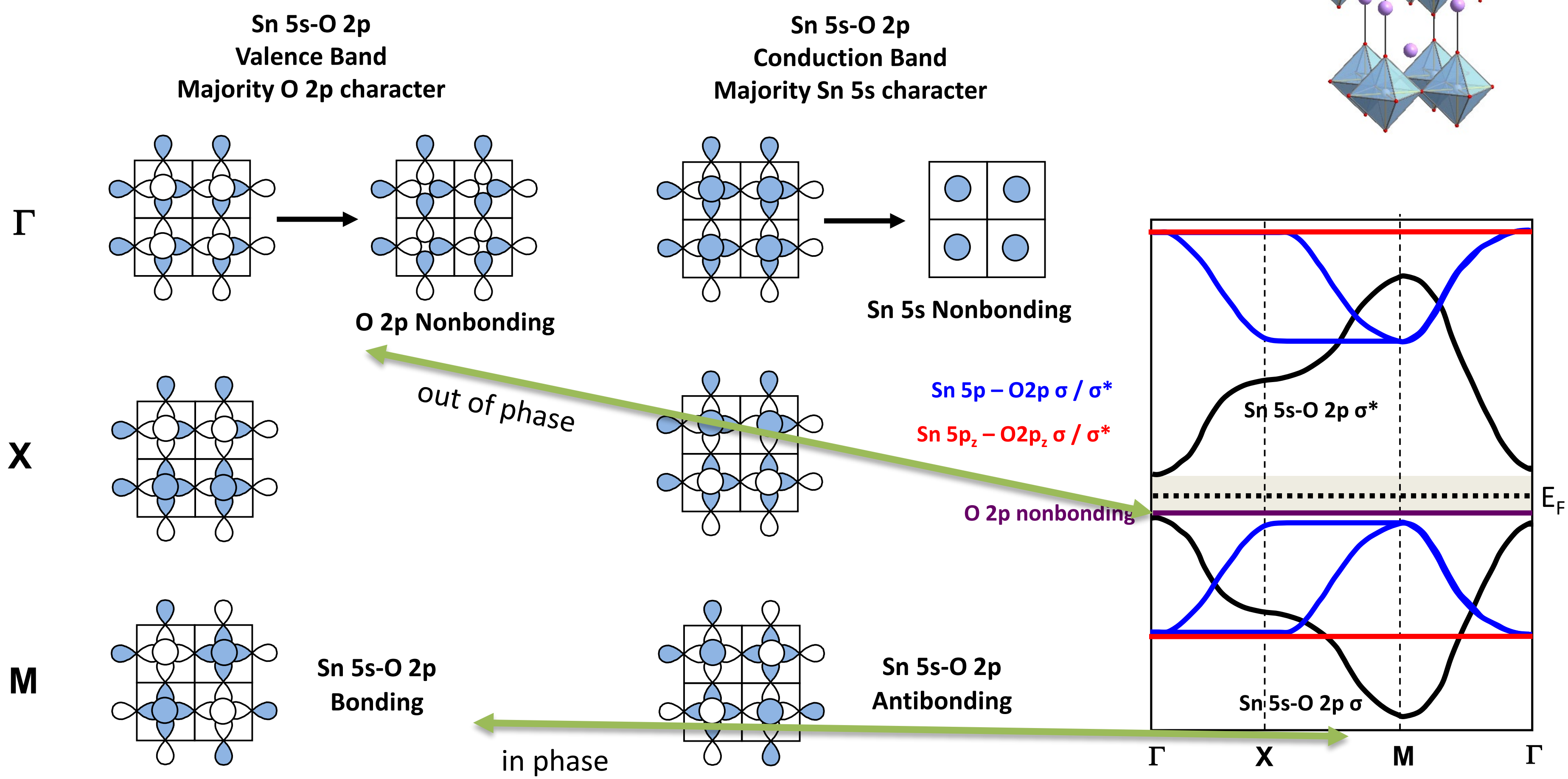


Orbitals and periodicity…

- Band structure
  - LCAO theory – square lattice

➢ Example 2D: Ba_2SnO_4, Ruddlesden-Popper phase, *I4/mmm*, consider building unit SnO_6

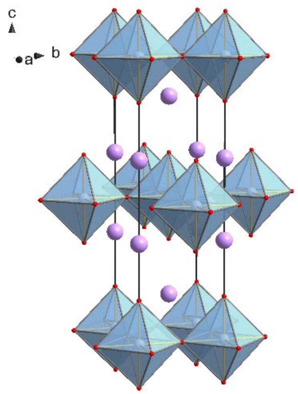


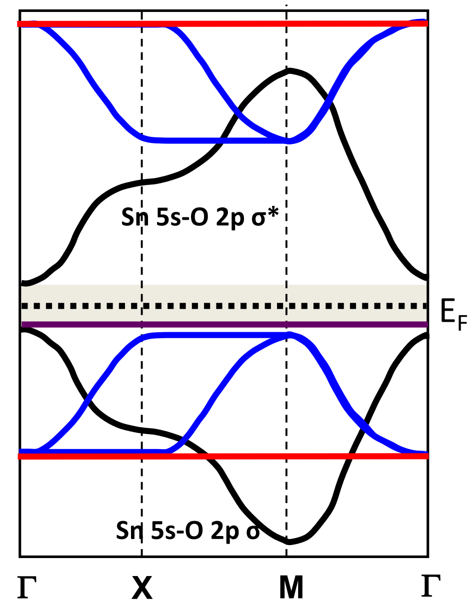


Orbitals and periodicity…

- **Band structure**
  - LCAO theory – square lattice

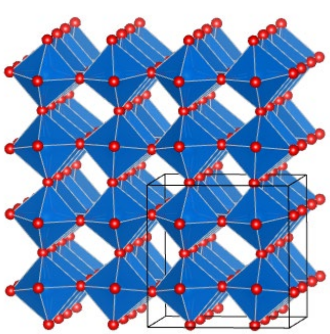
➢ Example 2D: Ba_2SnO_4, Ruddlesden-Popper phase, *I*4/*mmm*, consider building unit SnO_6

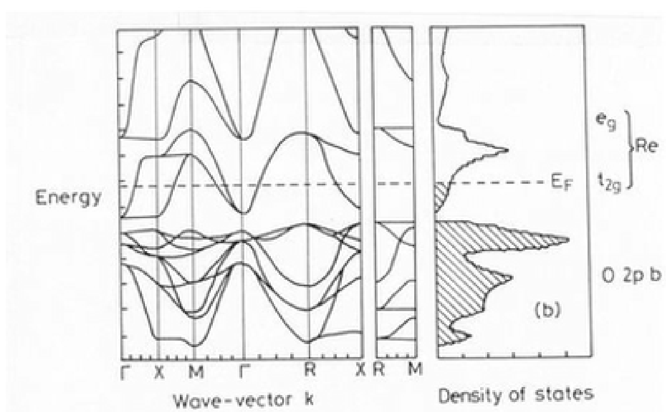




➢ Example 3D: ReO_4, *Im*-3

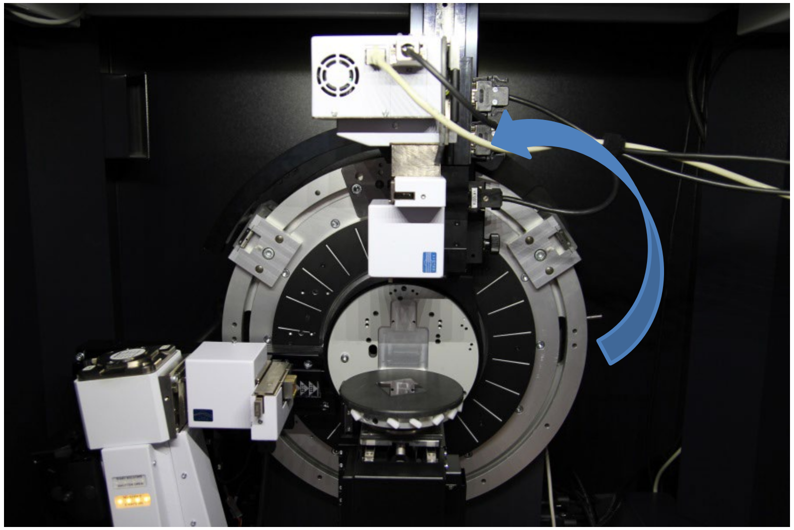
- All metal-based bands are disperse due to 3D structural nature
- Only flat bands generated by non-bonding O 2p states
- Fermi Level cuts π bands – metallic conductor

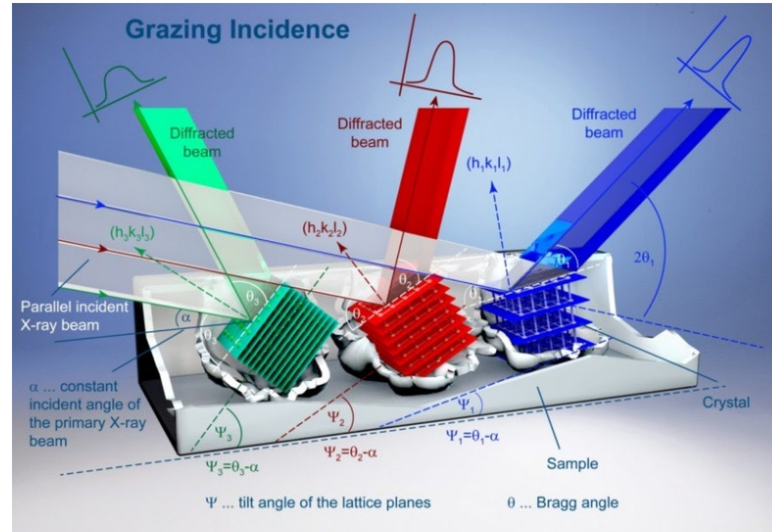




5 min break?

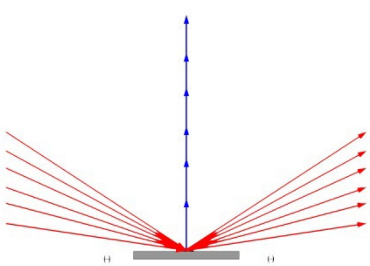
Grazing incidence diffraction – GID



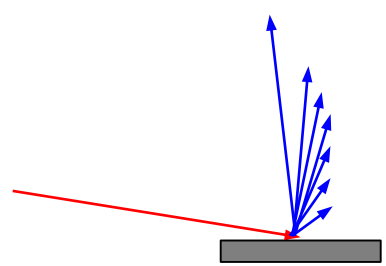


- Tube at fixed incident angle
- Bragg conditions collected by moving detector only (2θ scan)

Theta – 2Theta scan



GID – 2Theta scan



Surface Diffraction

Surface diffraction: GID, IP-GID

- **Information obtained**
- Provides same information as bulk XRD, but at lower resolution
- Visible diffraction vector can rotate in diffraction plane
- Surface sensitive
- Depth information on refinable parameters
- IP-GID allows accessing the in-plane diffraction pattern

- **Type of sample**
- Thin films (samples), layers. Poly or monocrystalline.
- Minimum thickness depends on crystallinity and scattering power (usually at least 5-6 nm on lab sources)

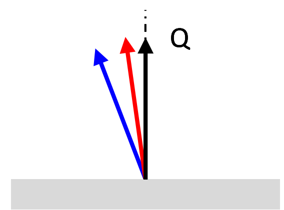
Surface diffraction: 2D-GIWAXS

- Same information as GID, but still lower resolution
- Texture at a snapshot
- Sample can be smaller since beam is smaller

Grazing incidence diffraction – GID

14nm RuO_2 on Si(001)

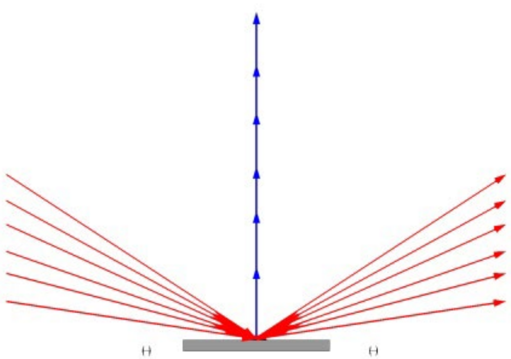
Offset θ/θ scan

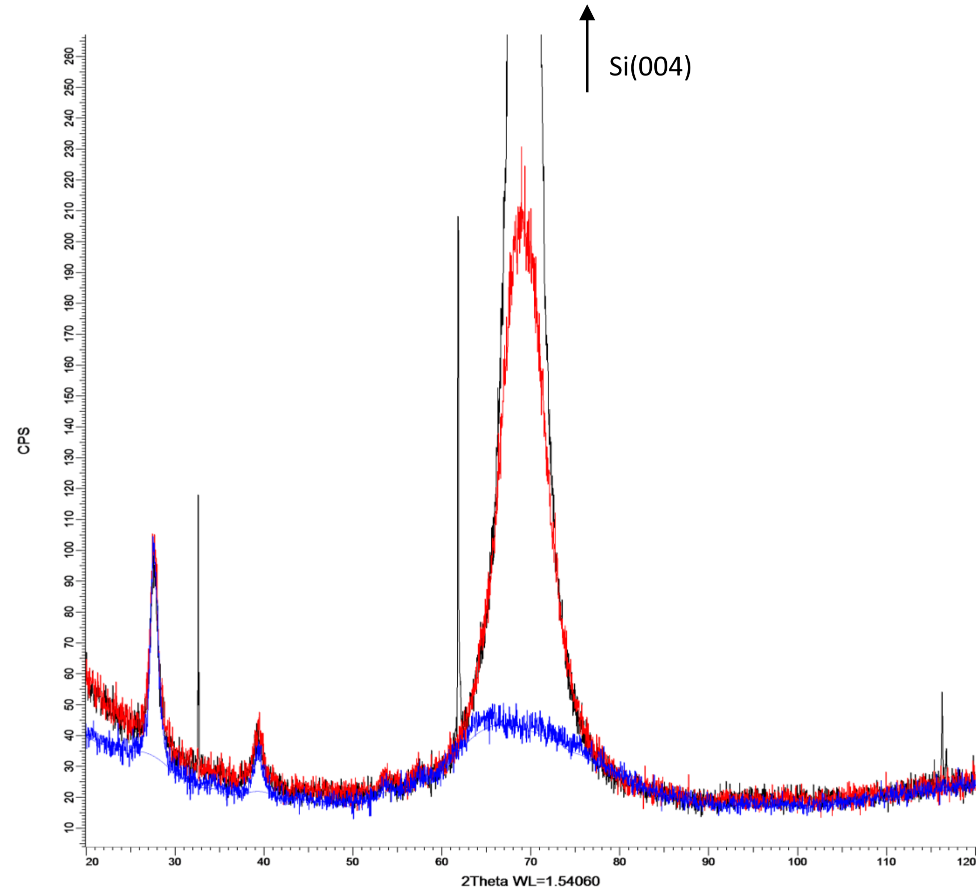


6°offset scattering

2°offset scattering

Symmetric scattering



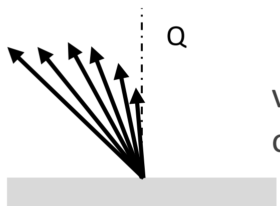


Possible to strongly reduce Si (004) but layer signal still weak

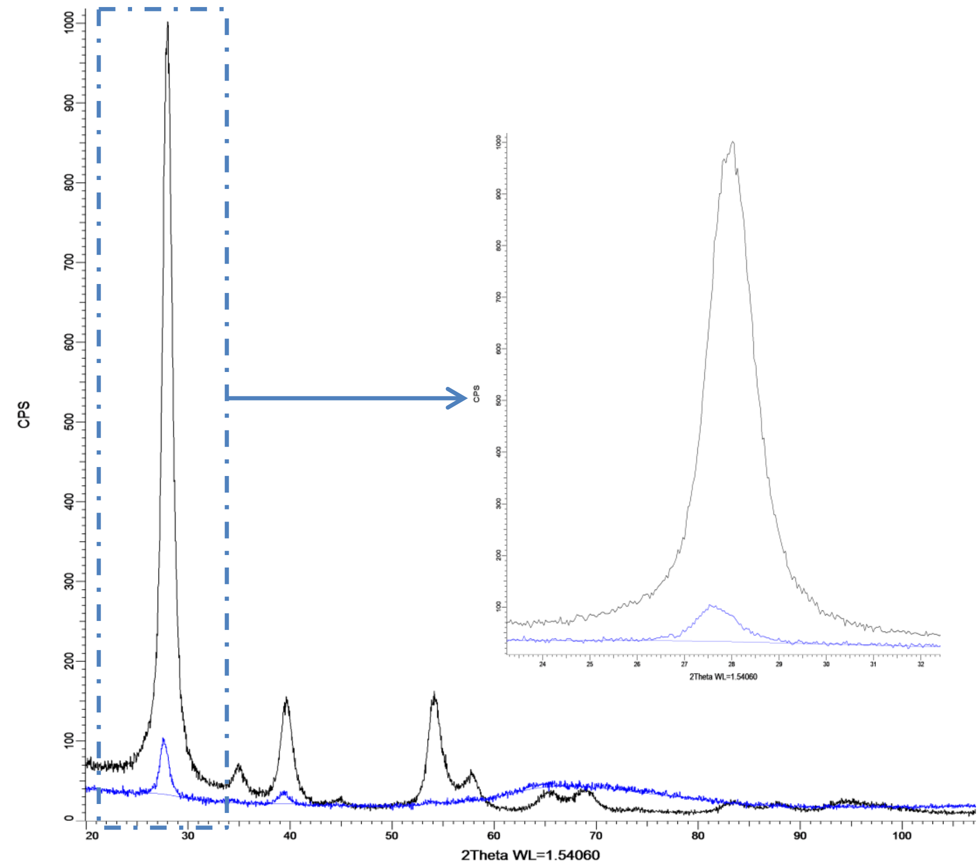
Grazing incidence diffraction – GID

14nm RuO_2 on Si(001)

Grazing incidence (2θ scan)



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

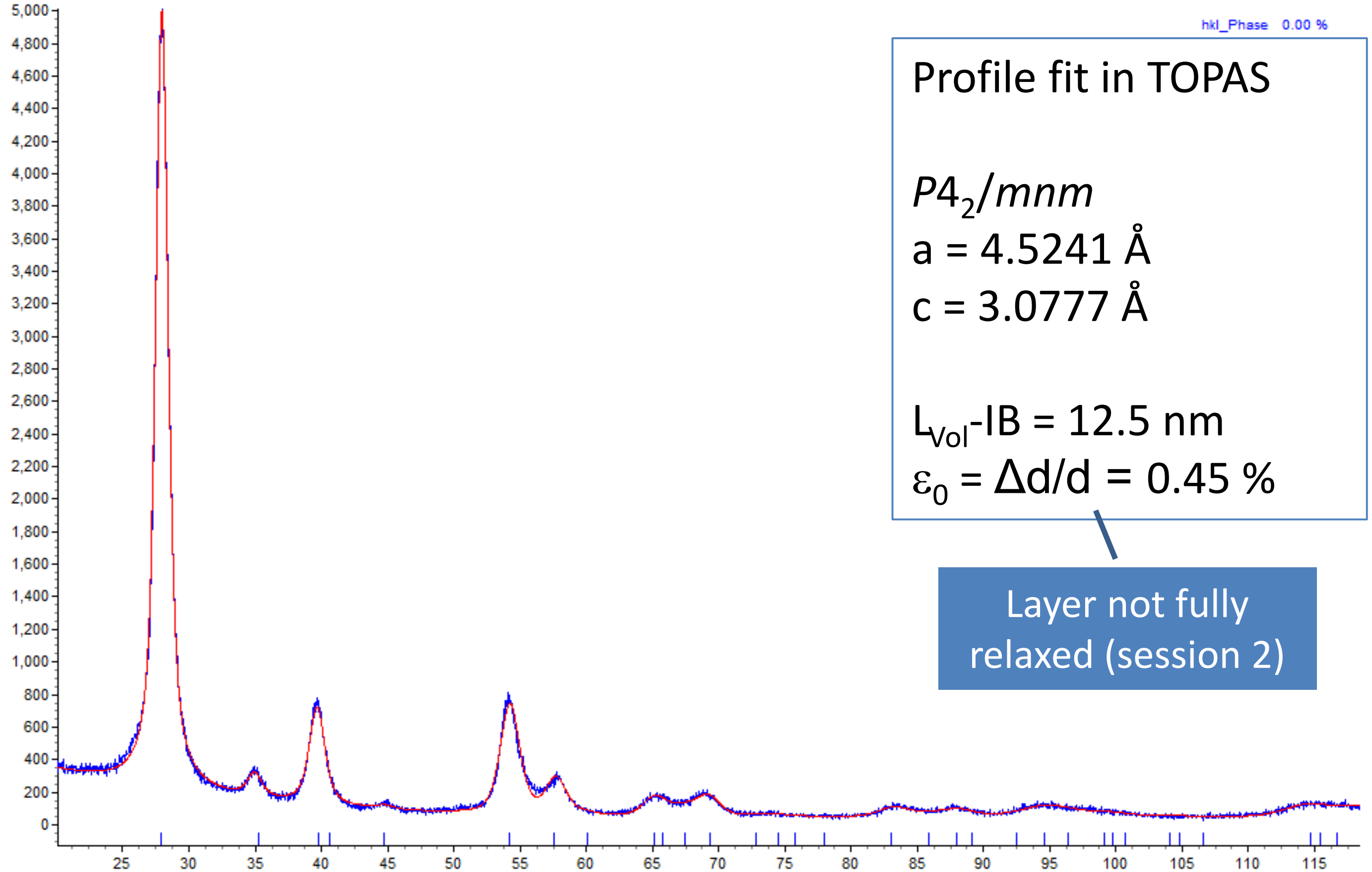


GIXRD *vs* 6° Offset θ/θ scan

Grazing incidence diffraction – GID

14nm RuO_2 on Si(001)

Grazing incidence (2θ scan)



Profile fit in TOPAS

$P4_2/mnm$

a = 4.5241 Å

c = 3.0777 Å

L_{Vol}-IB = 12.5 nm

$\varepsilon_0 = \Delta d/d = 0.45$ %

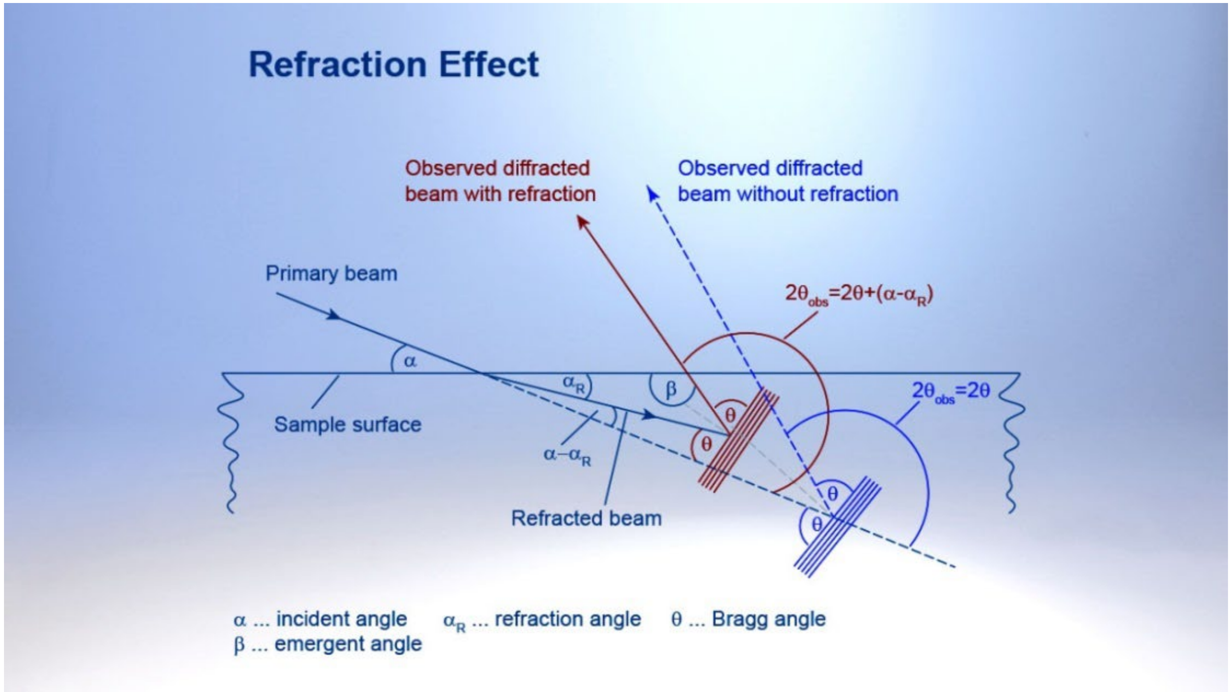
Layer not fully relaxed (session 2)

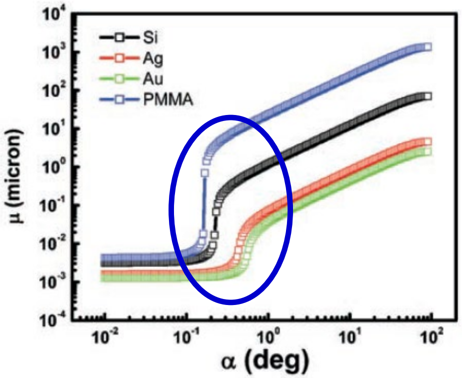
2θ san at fixed incident angle 0,45°c

Grazing incidence diffraction – GID

Refraction effect

Additional peak shift





- Incident beam refracted at air/layer interface
- Apparent peak position to be corrected from refraction

$$\Delta 2\Theta = \alpha - \alpha_R \cong \alpha - \sqrt{\alpha^2 - \alpha_C^2}$$

α_C...critical angle

Grazing incidence diffraction – GID

Penetration depth

calculate penetration depth (and optical properties) for X-rays

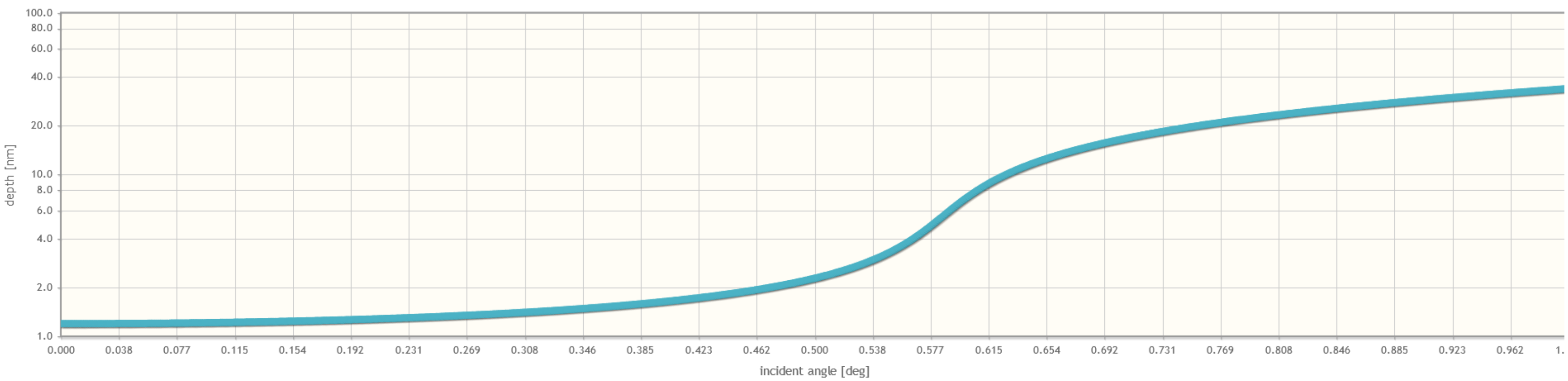
https://gixa.ati.tuwien.ac.at/tools/

Formula:	Pt1	(e.g.: Si1,Si1O2 or Hf1O2)
Density:	21.45	[g/cm^3]
Energy:	8050	[eV]
Angle:	0.0 - 1.0	[deg]

Execute Download

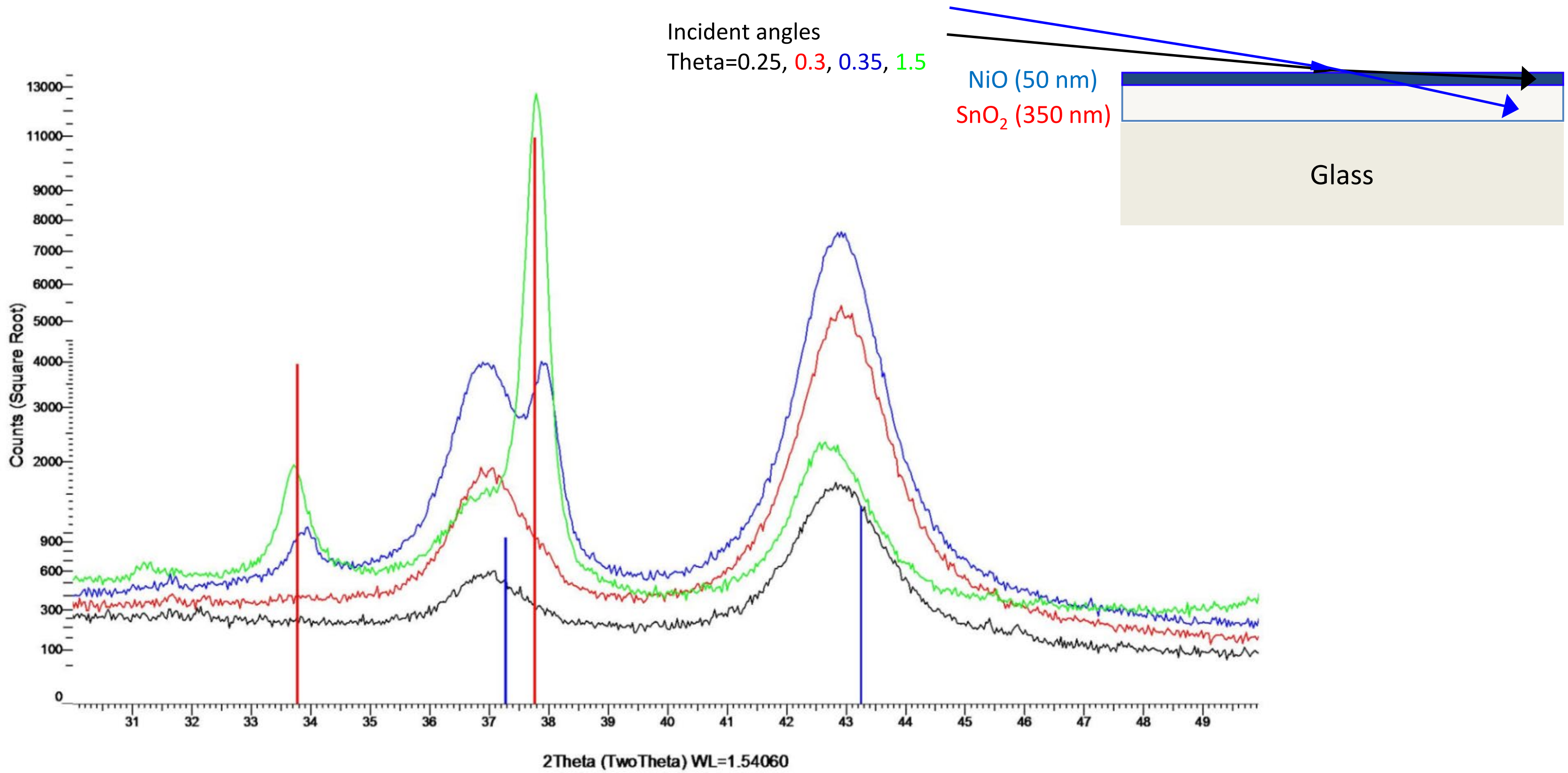
δ	5.188993459040156E-5
β	5.095781845479082E-6
ε	(0.9998962227974175, -1.0191034851384866E-5)
μ [1/cm]	4157.670528325295
Critical angle [deg]	0.5836858860295738

penetration depth for Pt1 (ρ=21.45) @ 8050.0eV



Grazing incidence diffraction

Phase ID depth profile on glass coating

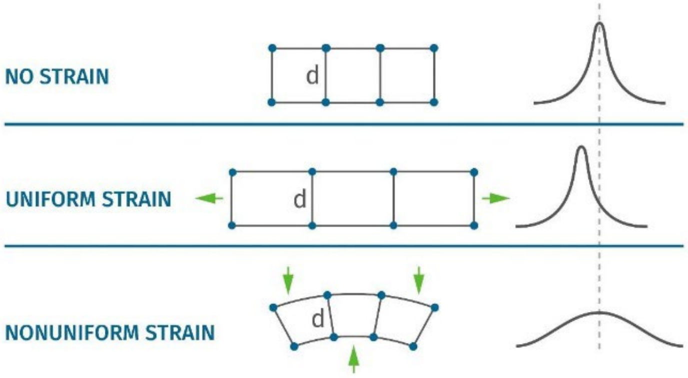


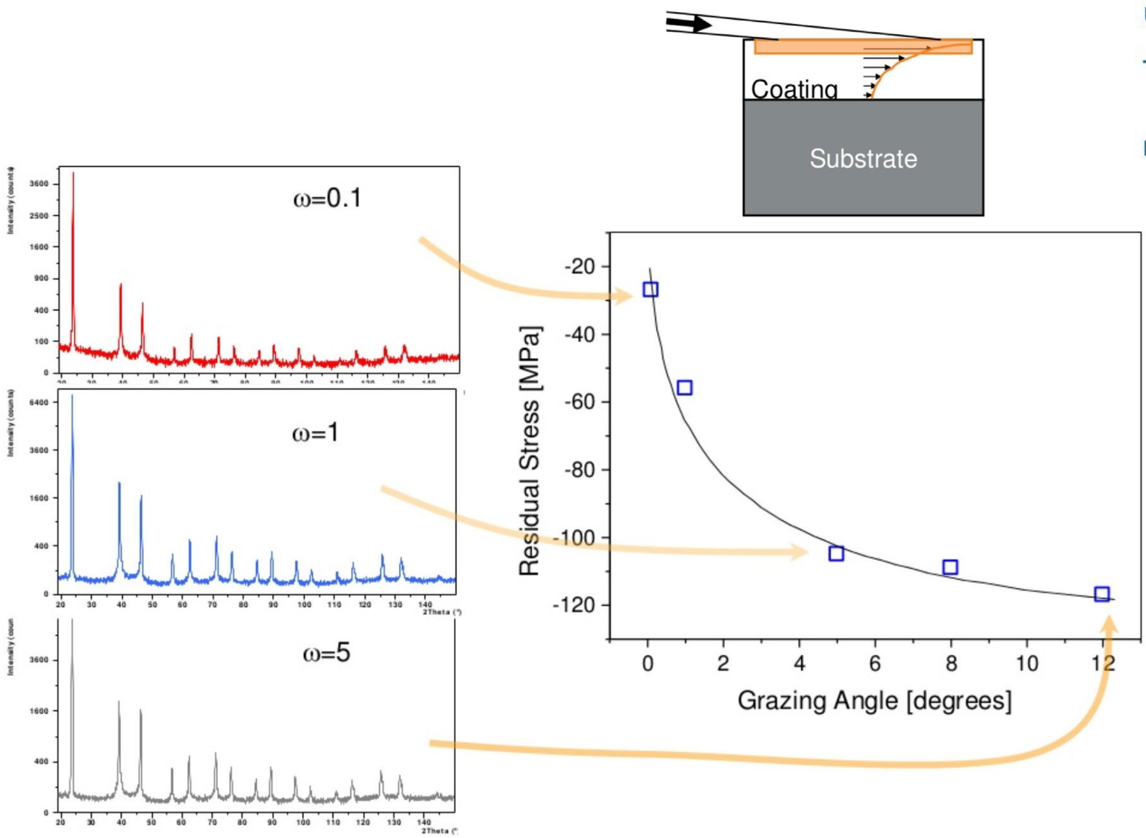
Coating on glass (St Gobain)

Grazing incidence diffraction

Stress gradient depth profile: CdTe layer of solar cell

- Measure strain (lattice parameter shift) $\varepsilon = \frac{d_n - d_0}{d_0}$
- Calcuate residual stres.



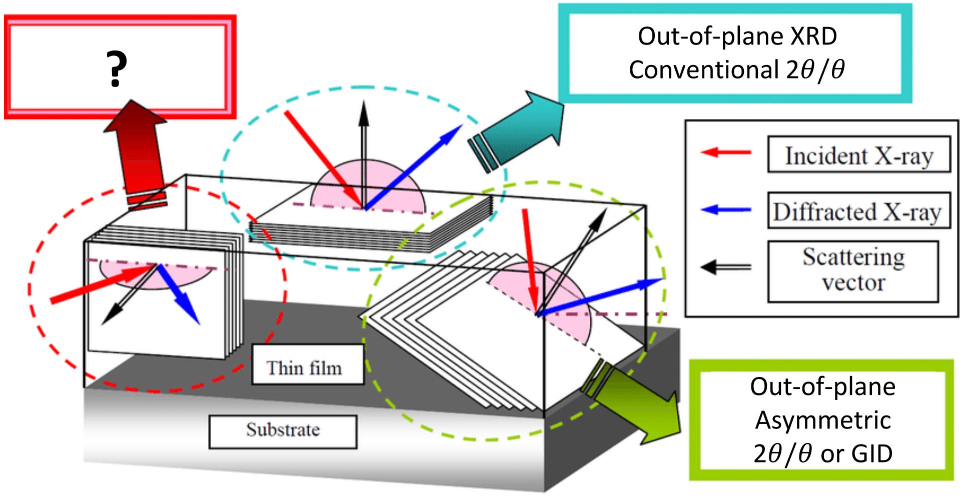


Q: How does stress arise in films?

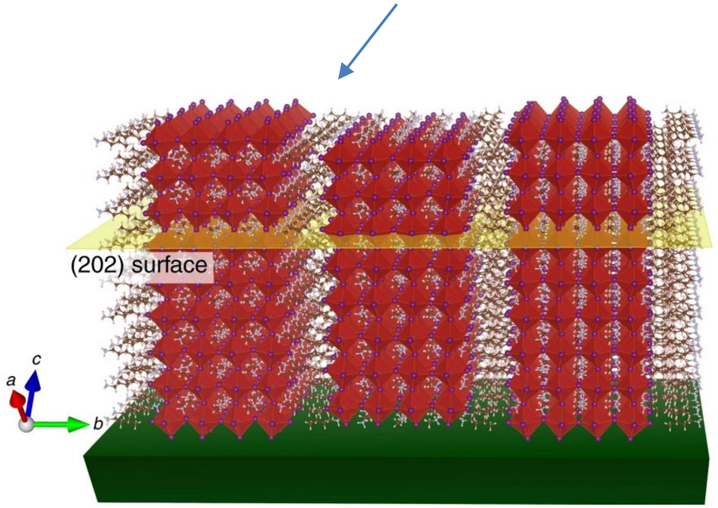
In-plane – GID

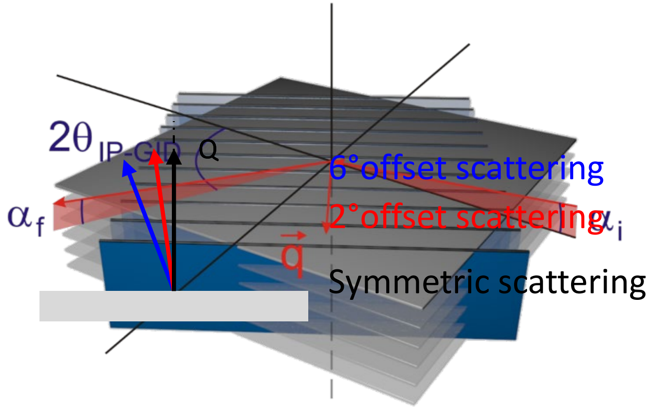
In-plane grazing incidence diffraction

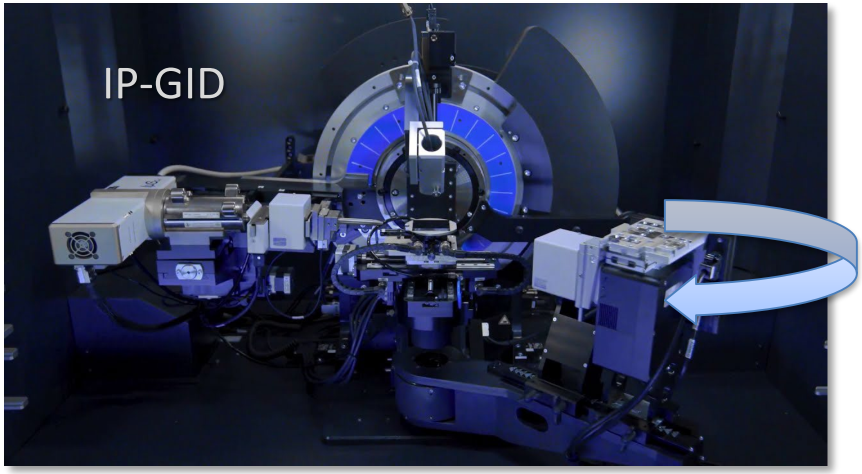
Scattering geometry



How do we measure layer spacing?





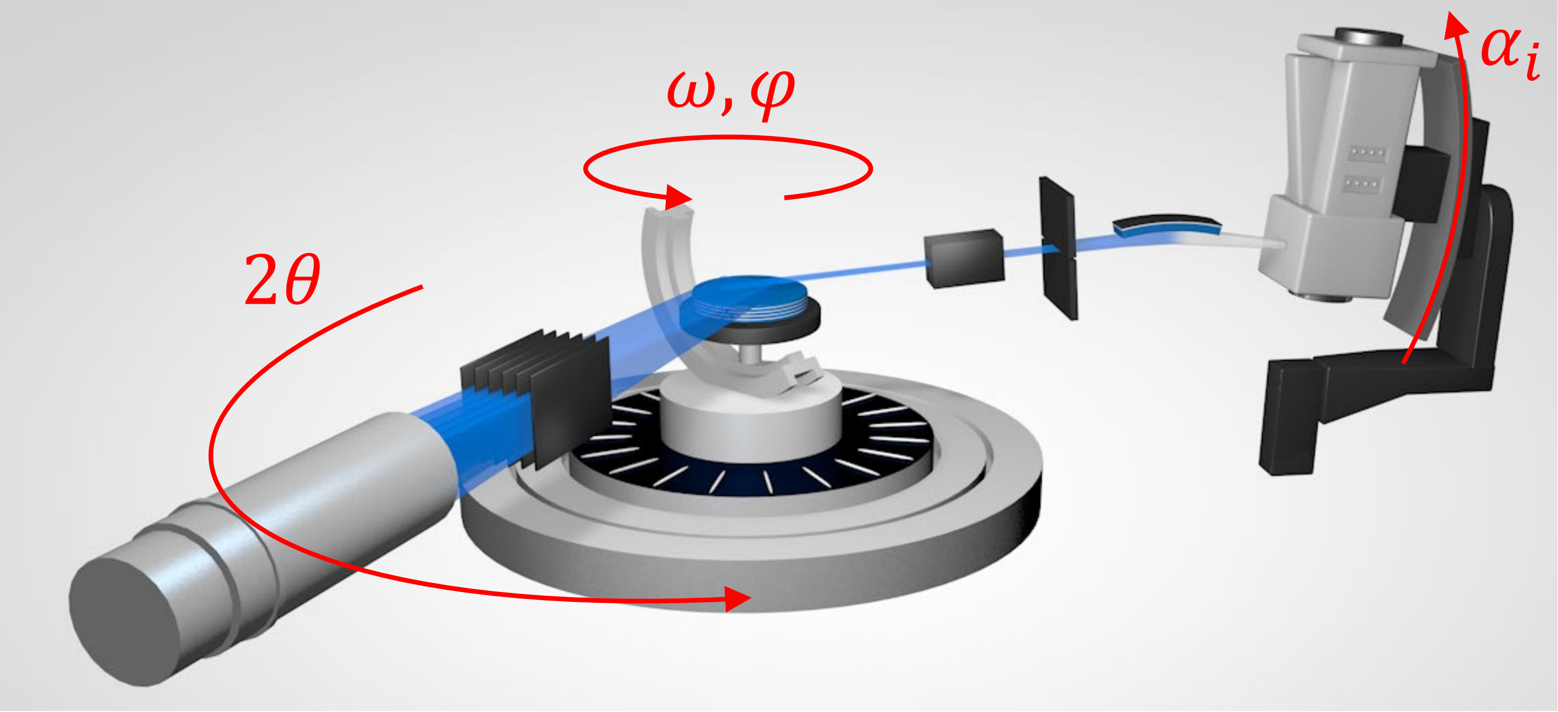


Nature Communications volume 9, Article number: 1336 (2018)

In-plane – GID

Optimized setup for IP surface diffraction

Scattering geometry



- Line focus is parallel to the sample surface: Good depths control.
- Angle of incidence is controlled by an separate drive.

In-plane – GID

In-plane grazing incidence diffraction

Applications

- Polycrystalline, oriented samples
- Strained polycrystalline films (also with no orientation)
- Epitaxially grown samples
- In general samples showing anisotropy in and out of plane

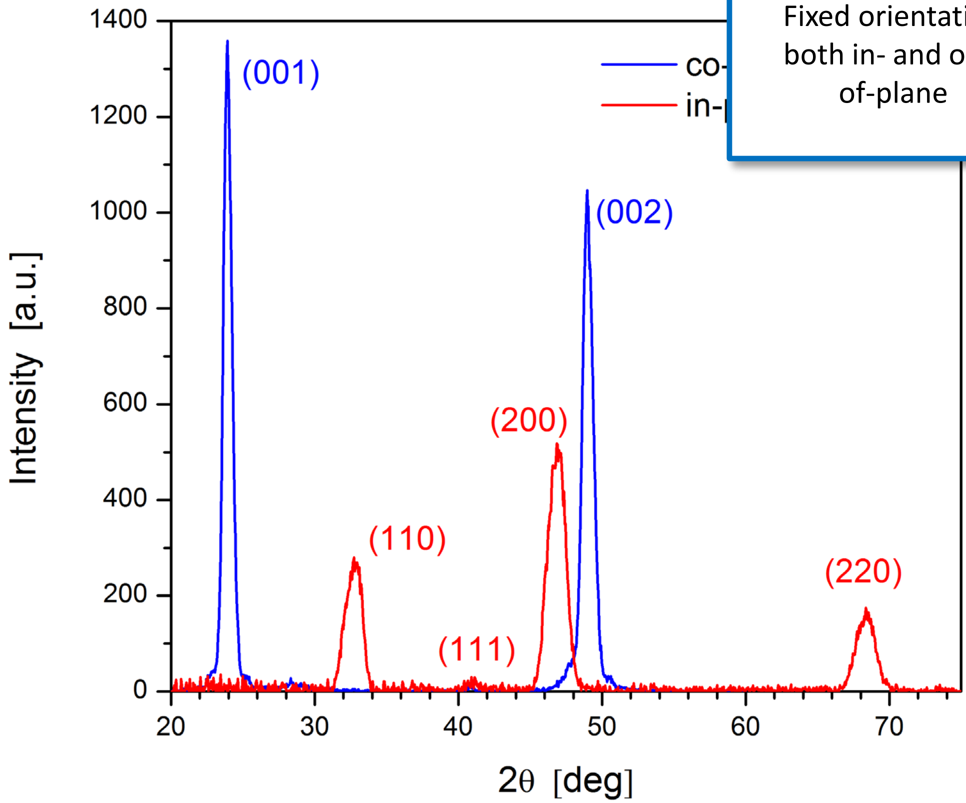
➢ Anything that can be measured with an out of plane scan, but on highly oriented samples

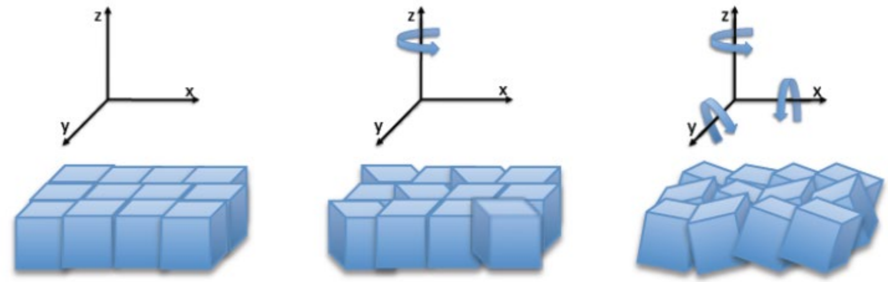
In-plane – GID

In-plane grazing incidence diffra

Examples:

Structure determination of poly





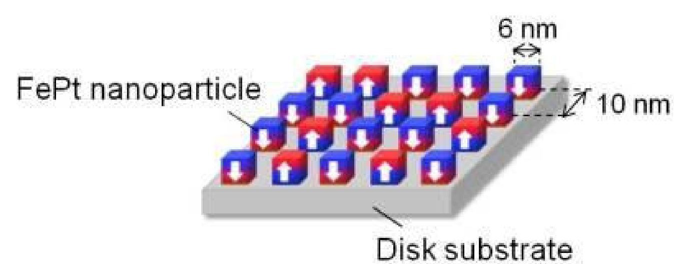
Polycrystalline, biaxially textured. Fixed orientation both in- and out-of-plane

Polycrystalline, uniaxial texture. Fixed orientation out-of-plane, random in-plane

Polycrystalline, randomly oriented.

film thickness.

- In-plane crystallite size is about 6.5nm
- In-plane fiber textured around (001)

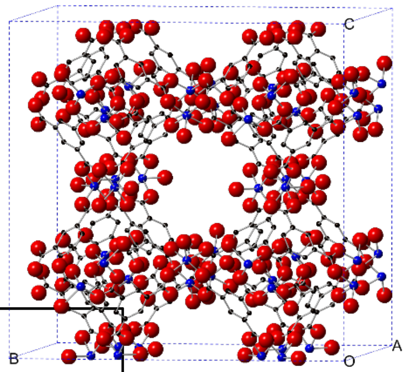


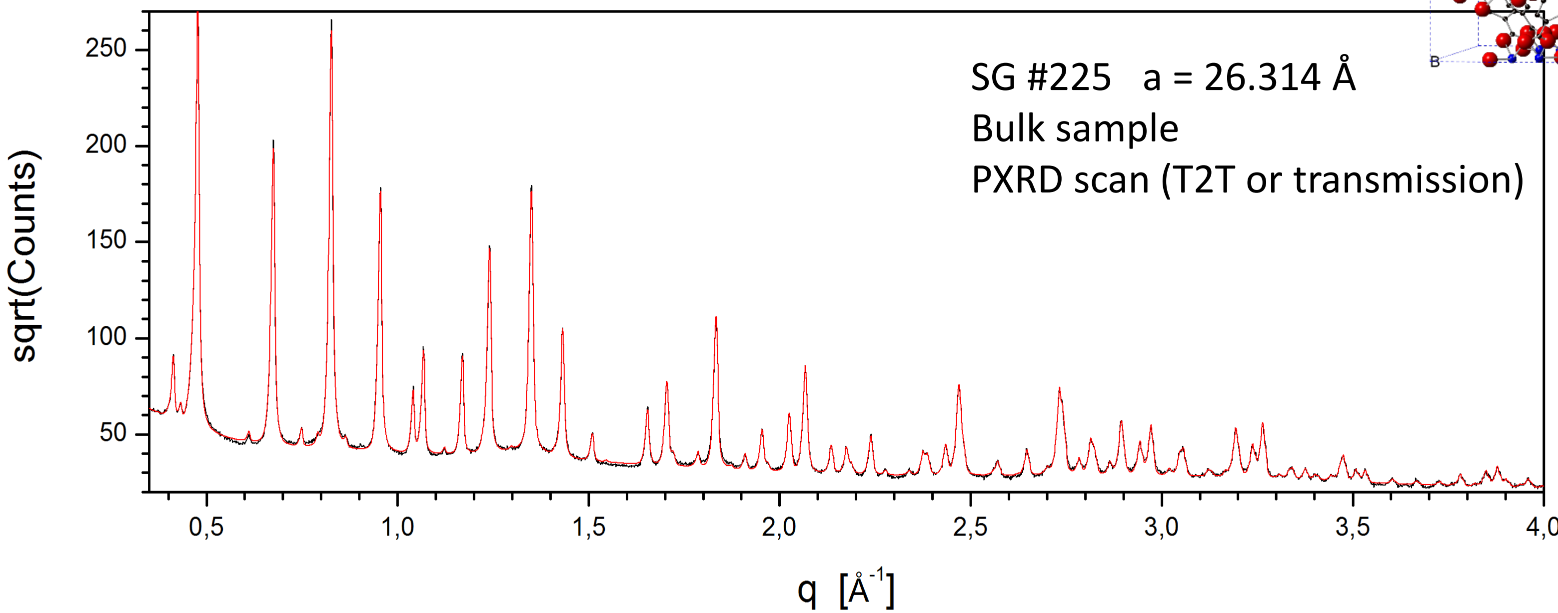
In-plane – GID

In-plane grazing incidence diffraction

Examples:

Structure determination of MOF film





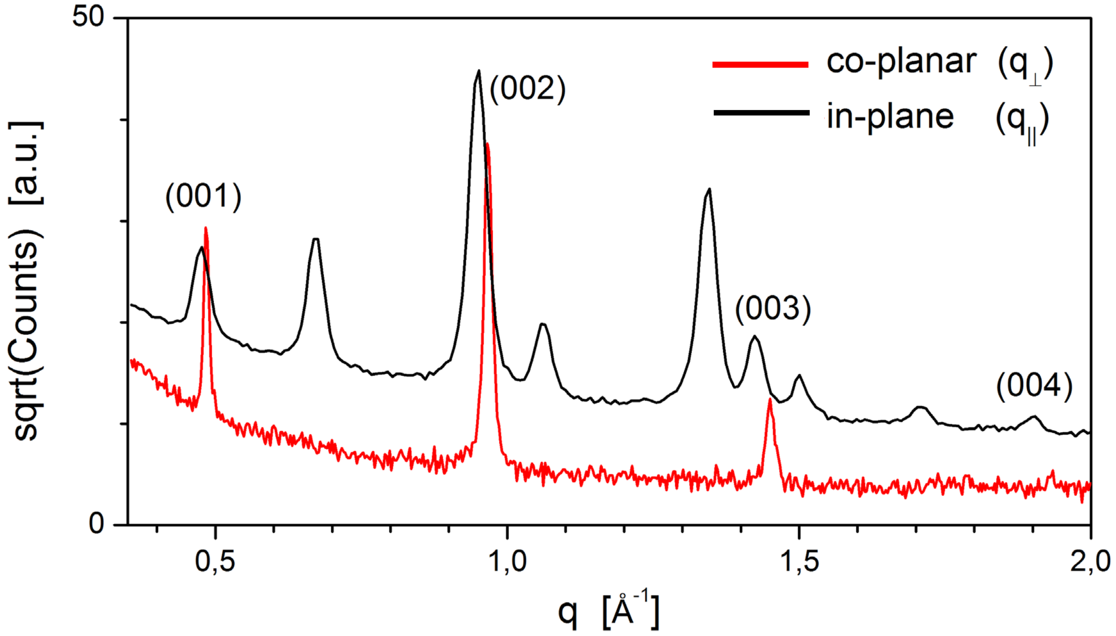
- Measurement of HKUST-1 powder provides structure information.
- Crystallite size is about 195nm.

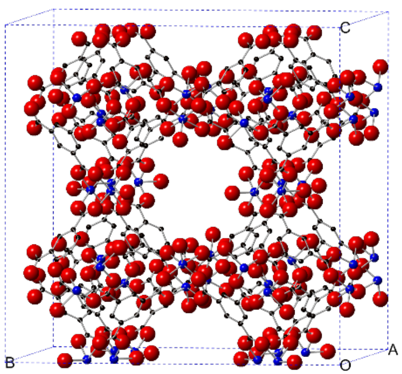
In-plane – GID

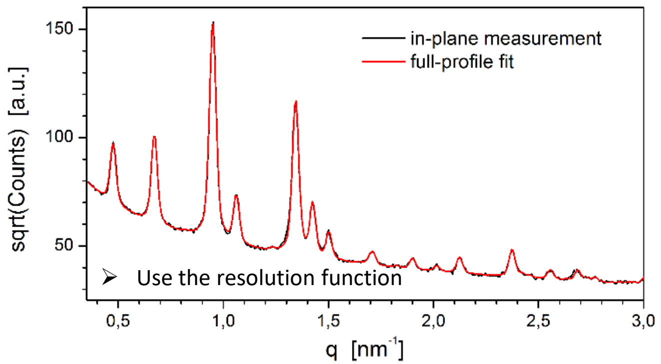
In-plane grazing incidence diffraction

Examples:

Structure determination of MOF film







- Measurement of HKUST-1 thin film: (001) surface normal and size of about 90nm.
- Fiber textured with 120nm crystallite size parallel to the surface

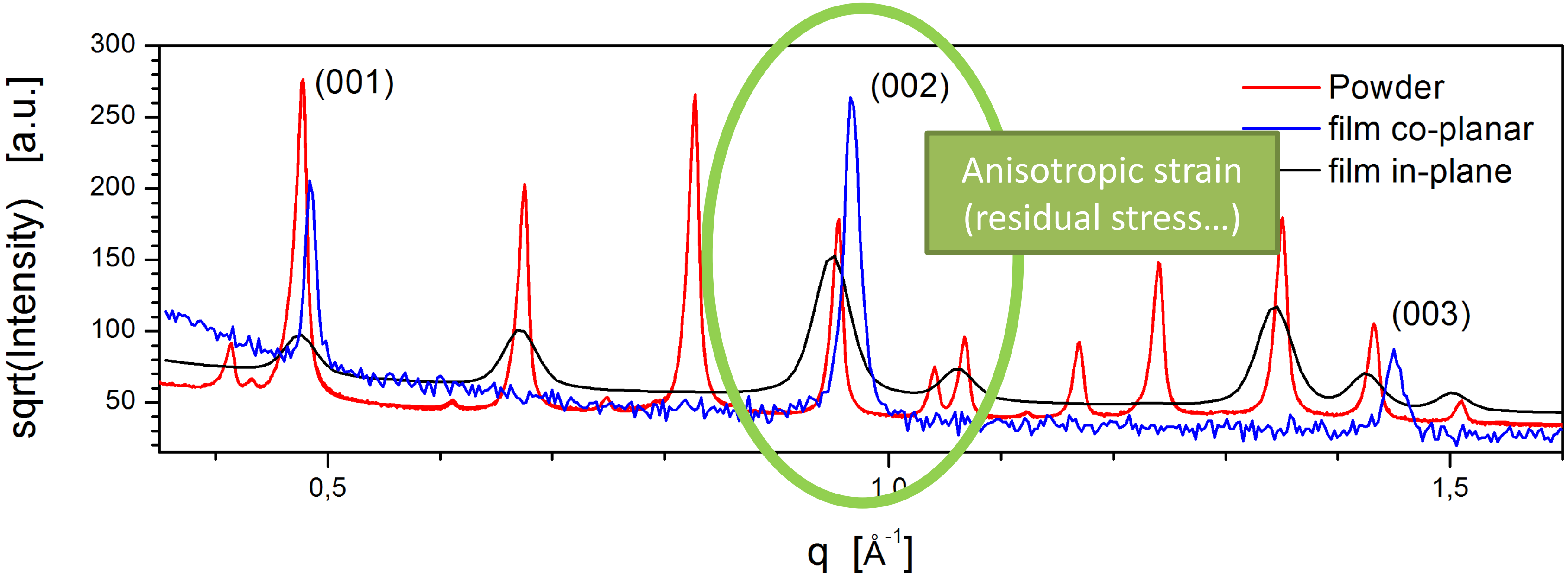
EPFL

In-plane – GID

In-plane grazing incidence diffraction

Examples:

Structure determination of MOF film



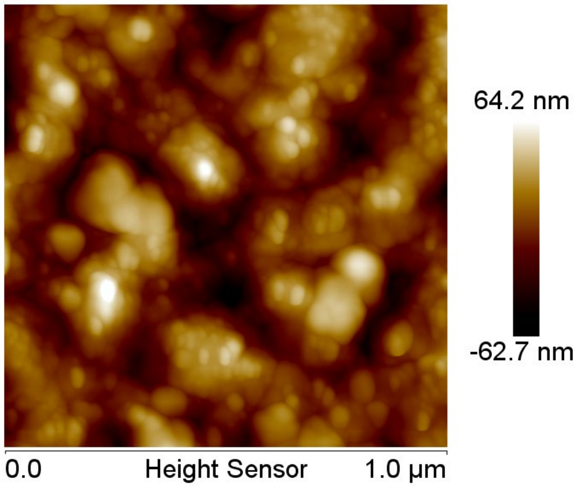
- Measurement of HKUST-1 thin film: (001) surface normal and size of about 90nm.
- Fiber textured with 120nm crystallite size parallel to the surface
- In-plane lattice parameter : 26.482Å (tensile strain)
- Co-planar lattice parameter : 26.0055Å (compressive strain) (powder: 26.314 Å)

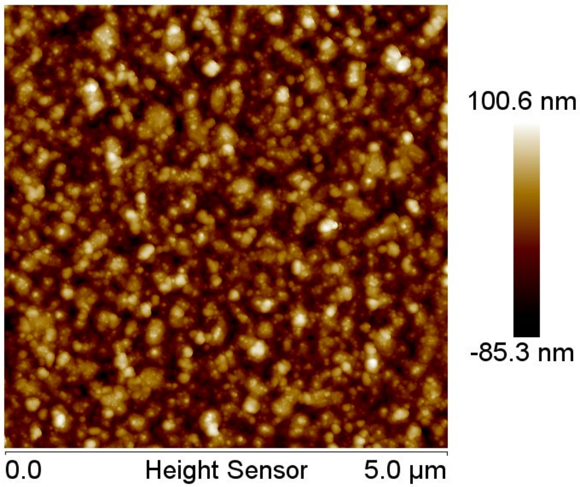
In-plane – GID

In-plane grazing incidence diffraction

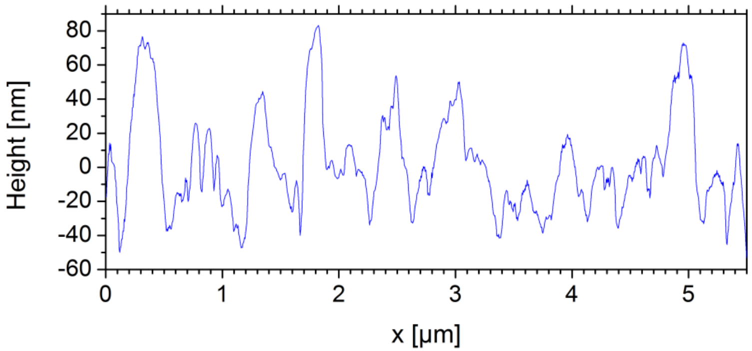
Examples:

Structure determination of MOF film





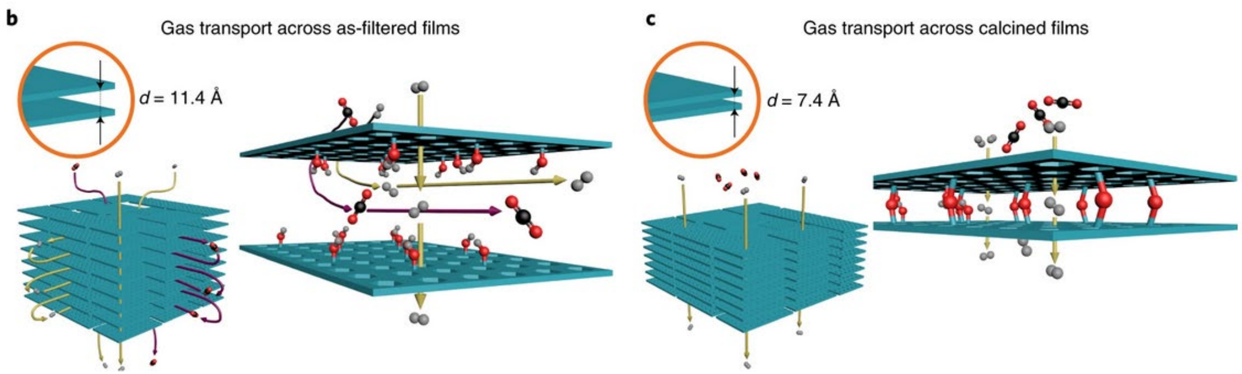
- The AFM pictures yield particles with size of 250-350nm.
- This is not the cystallite size.

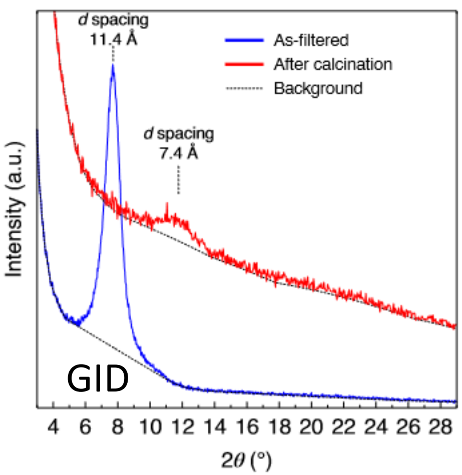


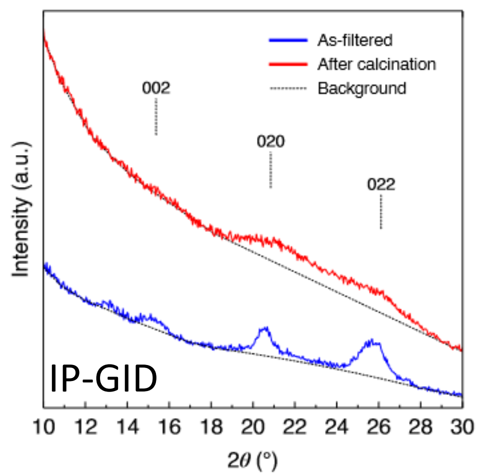
In-plane – GID

In-plane grazing incidence diffraction

Examples: Gas-sieving zeolitic membranes by the condensation of precursor nanosheets. In-plane coherence maintained?







- IP-GID proves coherence between sheets, membranes are crystalline.
- Layer spacing (out-of-plane) decreases after condensation, intra-layer structure unchanged (peak position IP).
- No turbostratic disorder due to fabrication (peak presence IP).

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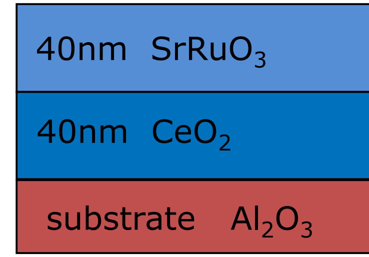
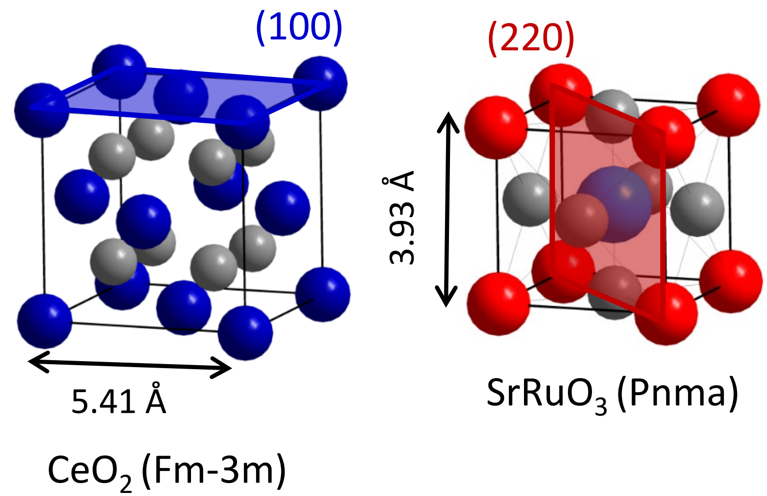
In-plane – GID

In-plane grazing incidence diffraction

Examples: epilayer

Probing in-plane symmetry directly





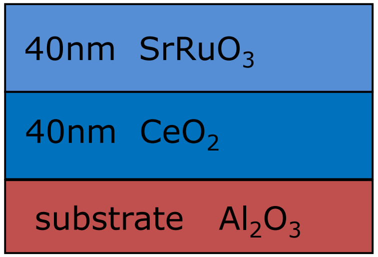
- Aim: determine the epitaxial relationship.
- Based on lattice mismatch one would expect the unit cells to exhibit a twisted cube on cube epitaxy.

In-plane – GID

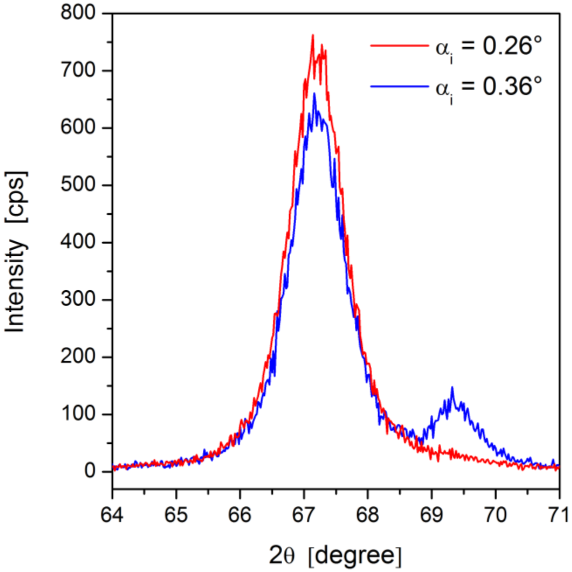
In-plane grazing incidence diffraction

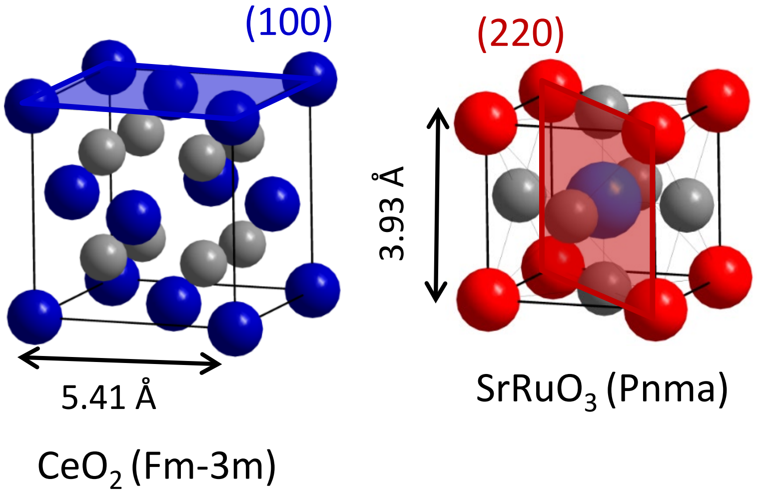
Examples: epilayer

Probing in-plane symmetry directly



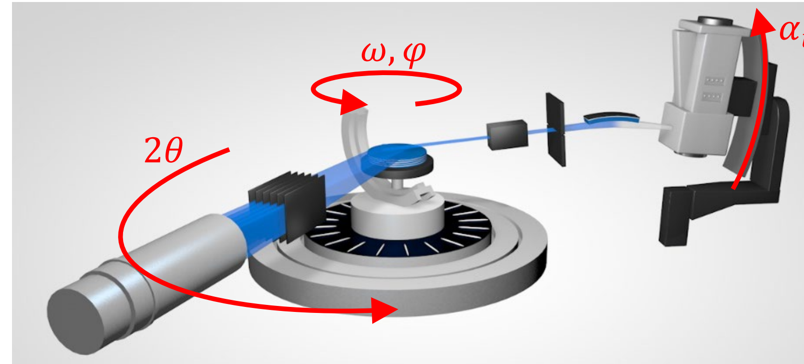
- θ/2θ-scan at SrRuO3 (220)





- SrRuO3 (220) || CeO2 (100) .
- Clear isolation of SrRuO3 (220) reflection by depth control.

EPFL In-plane – GID

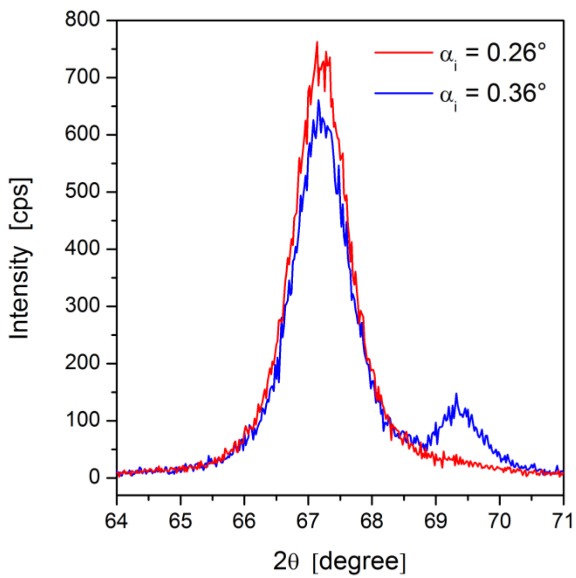


In-plane grazing incidence diffraction

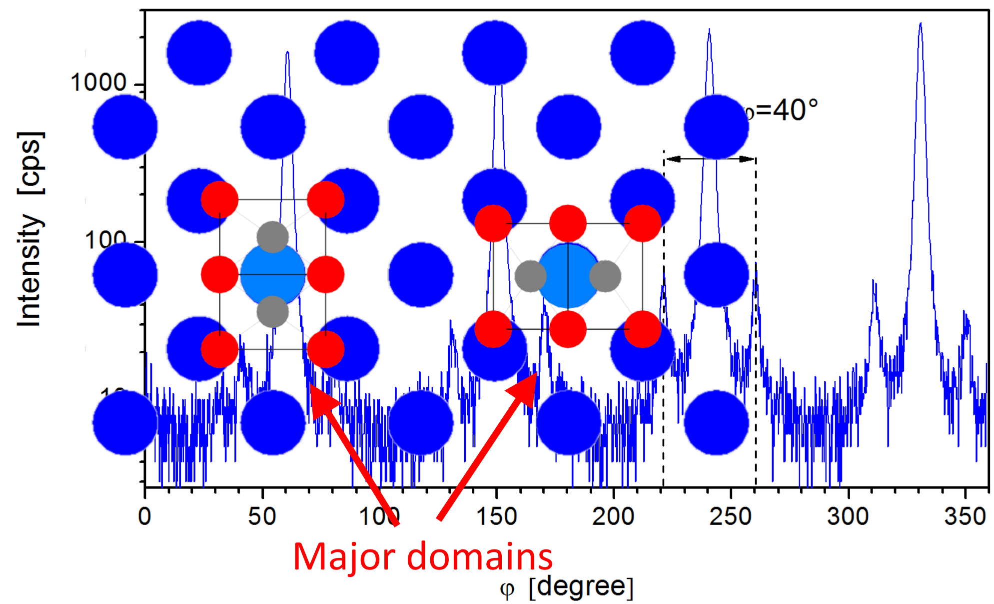
Examples: epilyer

Probing in-plane symmetry directly

- θ/2θ-scan at SrRuO3 (220)



- φ-scan at 2θ of SrRuO3 (220): **4 peaks** (should be 2 according to orth symmetry)

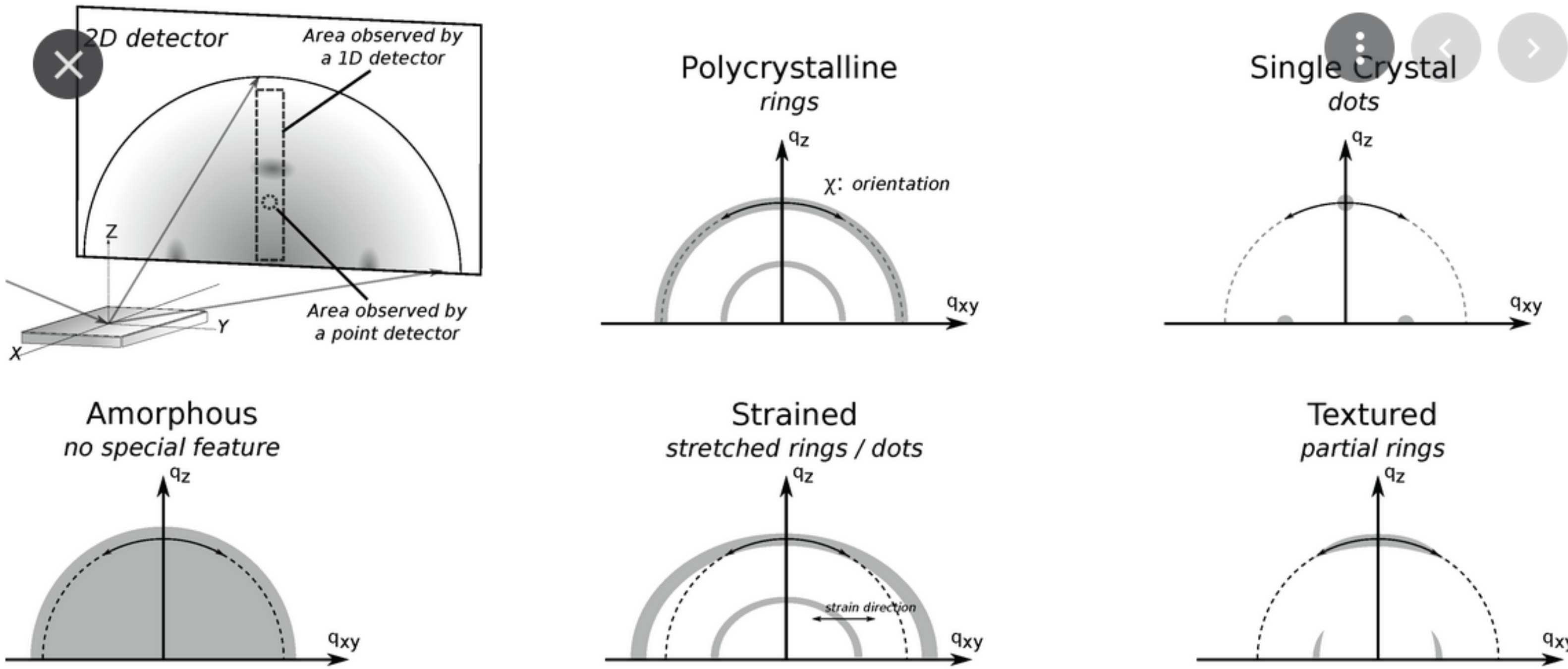


- SrRuO3 (220) || CeO2 (100) .
- Clear isolation of SrRuO3 (220) reflection by depth control.

- A simple rotation of the sample around the surface normal directly reveals the in-plane symmetry.
- Experimental: Requires surface normal || φ-axis.

Grazing incidence wide angle scattering

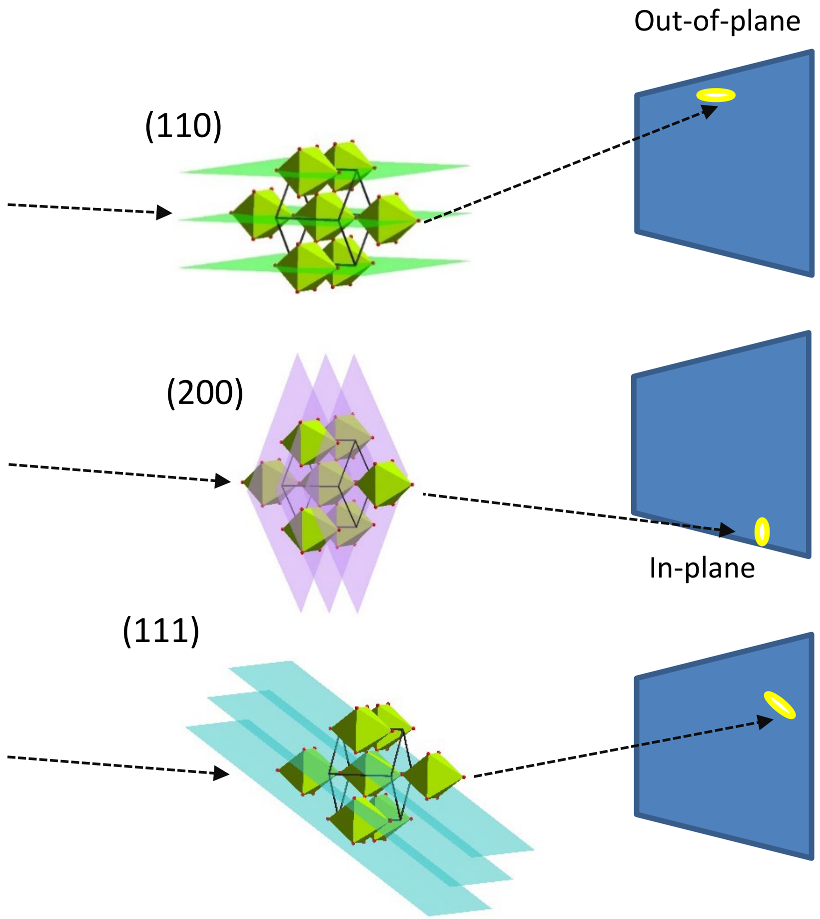
Formally identical to GID, but term GIWAXS misused for 2D application

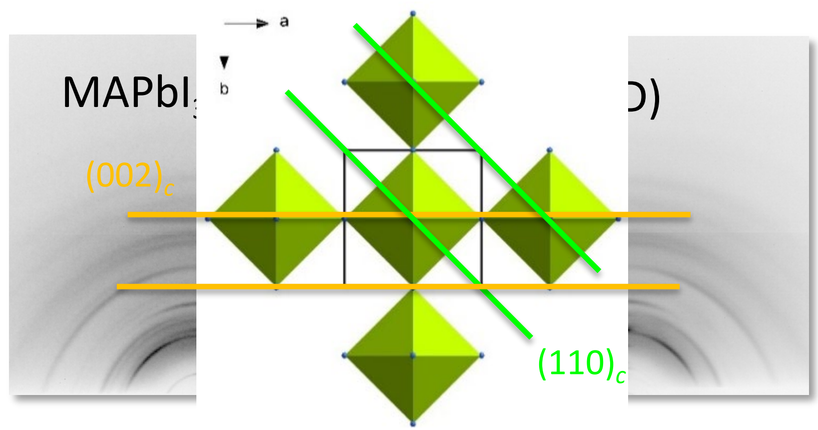


- As GID, but with additional information along the azimuth (gamma or in-plane direction) → 2 angle coordinates to reconstruct film architecture.

Grazing incidence wide angle scattering

Examples: crystallite (and structure) orientation





Q: What about (100): IP or OP?

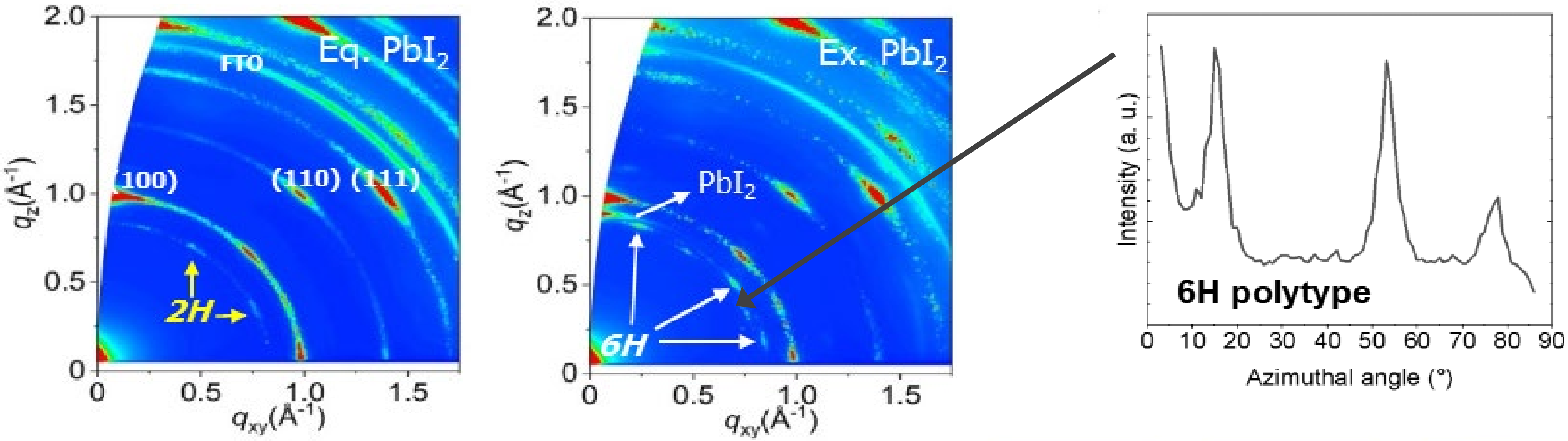
Q: What if in-plane disorder around [110] direction (edge-direction)

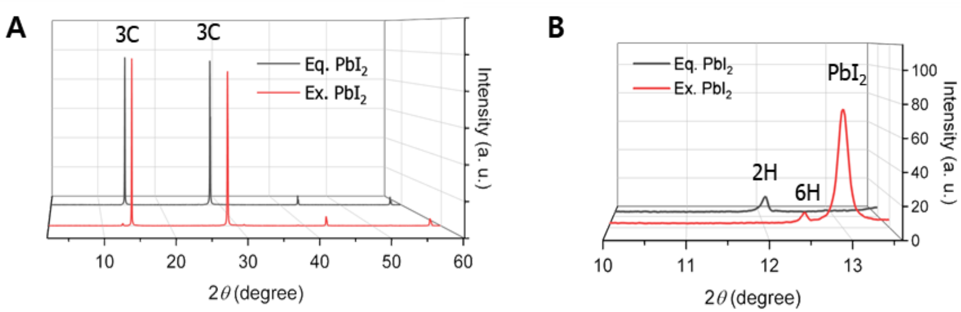
- Strong spots in out-of-plane direction (q_{xy} = 0), rings for rest.

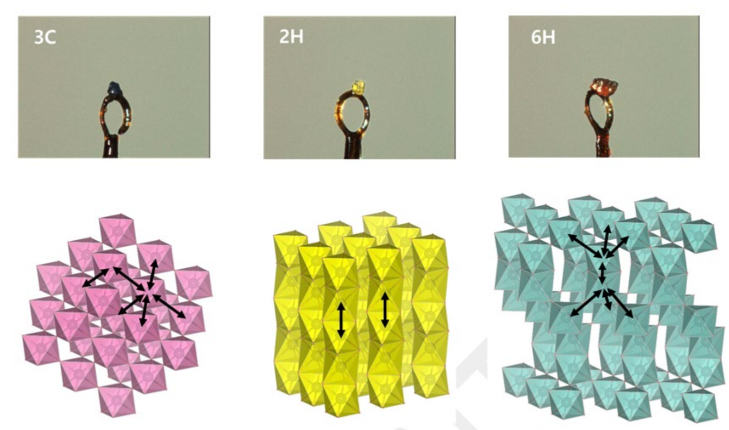
Grazing incidence wide angle scattering

Examples: $FAPI_3$ solar cells – texture with a snapshot

Azimuthal integration at constant 2Theta = 12.9°





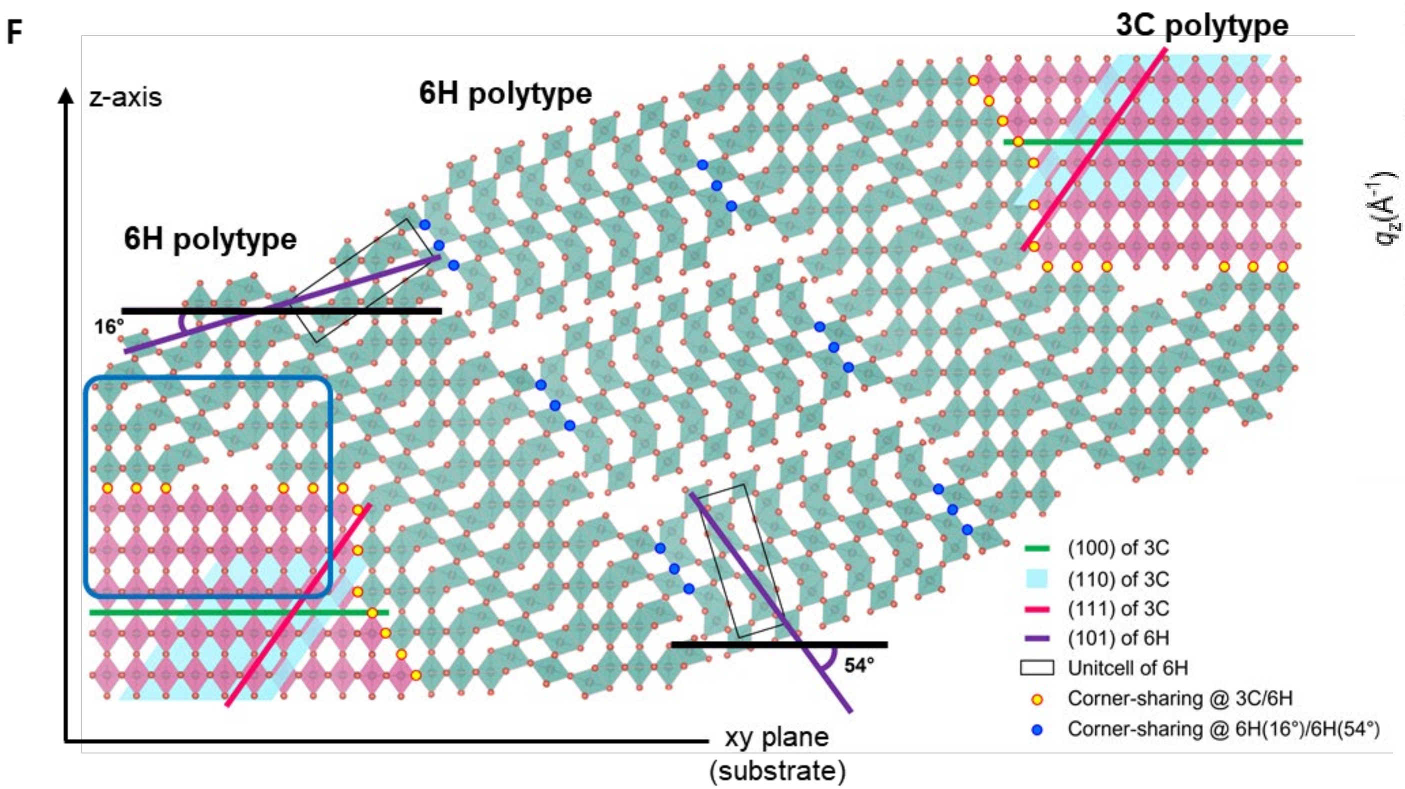


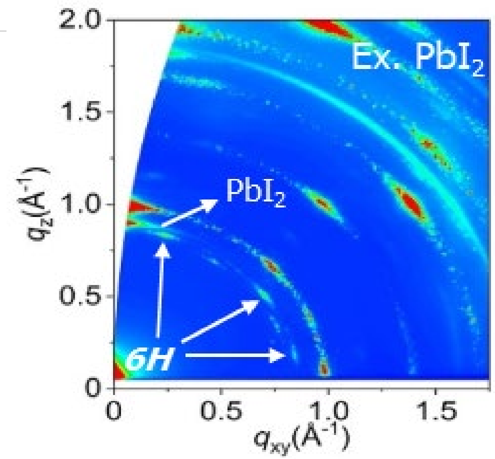
➢ Photoactive (3C) and non-active $FAPbI_3$ polymorphs

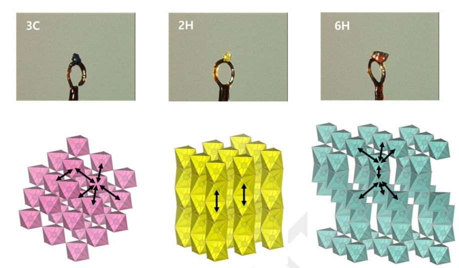
Grazing incidence wide angle scattering

Examples: $FAPI_3$ solar cells – texture with a snapshot

➢ Reconstruct complex film interfaces and connectivity between phases







Summary

- Surface diffraction (GID) is measured at fixed low incidence angle using a detector scan. It is a comparatively low resolution diffraction geometry.
- Depth control is achieved by varying the incident angle.
- The accessible diffraction-vector rotates within the scattering plane, allowing to access Bragg peaks invisible in conventional PXRD.
- Diffraction vectors lying in the sample place cannot by accessed by normal XRD nor GID. They can be measured with in plane GID.
- In-plane grazing incidence diffraction is useful on thin oriented samples in particular when anisotropy is expected.
- GIWAXS a GID experiment with a 2D detector. GIWAXS is particularly useful for qualitative texture analysis, and for kinetic studies on thin films.

Contents

- CH-633 – X-ray scattering: