NANYANG TECHNOLOGICAL UNIVERSITY SINGAPORE

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

X-ray Cluster 1 & 2 Training

FACTS X-ray Scientist

http://research.ntu.edu.sg/facts

Version 2020.001

Contents

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

- Background on X-rays
- X-ray diffraction analysis of polycrystalline materials
- Diffraction geometry: BBG vs GIXRD
- Hands-on training
- Other matters

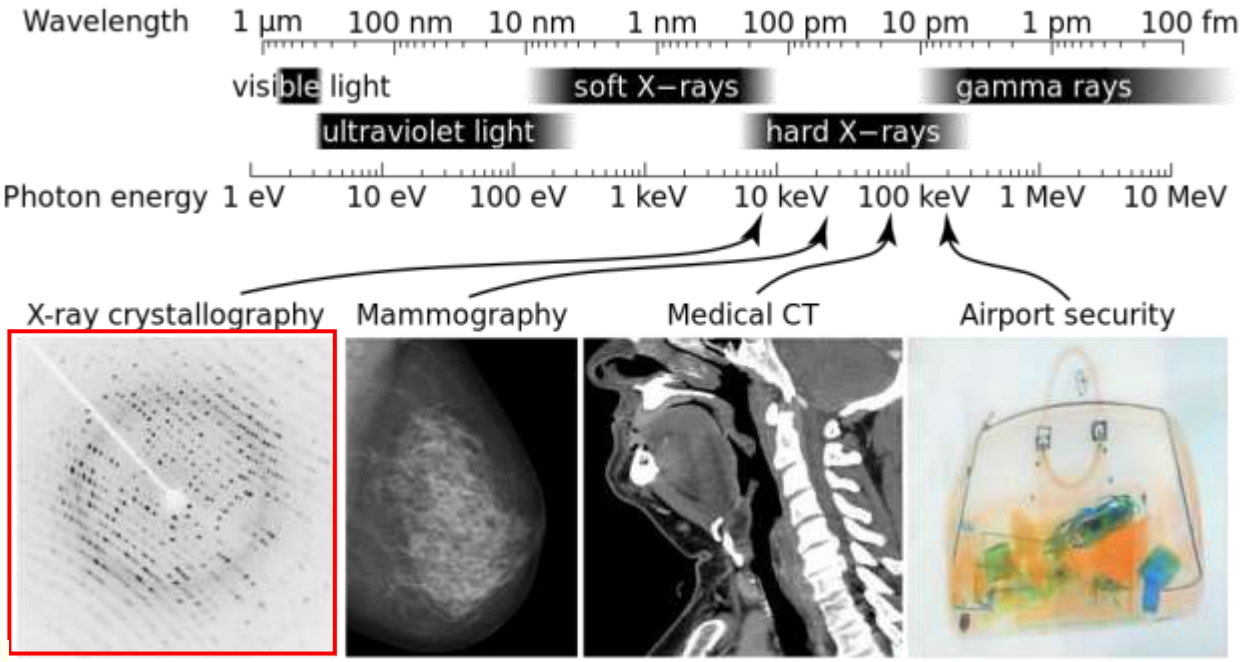
X-ray radiation

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

Electromagnetic radiation spectrum

X-rays are EM waves with:

- ✓ λ = 0.01 – 10 nm
- ✓ E = 0.125 – 125 keV



http://commons.wikimedia.org/wiki/File:X-ray_applications.svg

X-rays have wavelength in the same order as the interatomic distances in a crystalline material

NaCl
Space group 225, Fm-3m
a = 0.562 nm

X-ray safety

FACILITY FOR ANALYSIS F.A.C.T.S CHARACTERISATION TESTING SIMULATION

Dangers

- ionising radiation (λ<100nm), includes X-rays and gamma rays
- Biological effects (somatic & genetic), Carcinogen

Precautions

- Exposure limits (radiation worker @ 20 mSv/yr, Public 1 mSv/yr)
- Protection (distance, shielding, interlock, reduce time)

Monitoring

- Radiation survey meter, Area radiation monitors
- Personal dosimeters (TLD, electronic dosimeters)
- Background radiation (~0.1-0.3 μSv/hr)

X-ray safety in FACTS

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

X-ray instruments

- ✓ IEC 61010-1:2010 compliance for newer machines
- ✓ Safety interlocks, enclosure
- ✓ L3 license issued by NEA
- ✓ Room with card controlled access

Instrument manager

- ✓ L5 license issued by NEA
- ✓ Familiar with instrument set-up, proper operation and application
- ✓ Basic instrument trouble-shooting

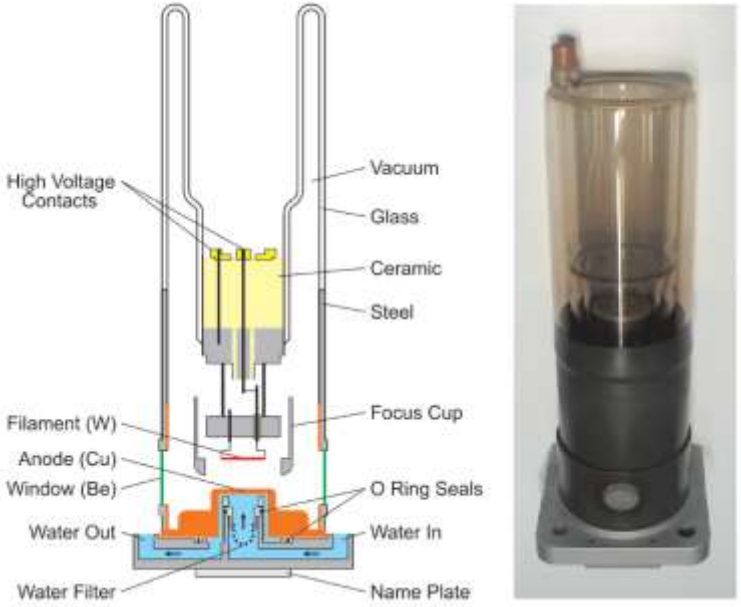
User

- ✓ 3 ionising radiation e-learning modules
- ✓ Personal X-ray dosimeter and dosage log

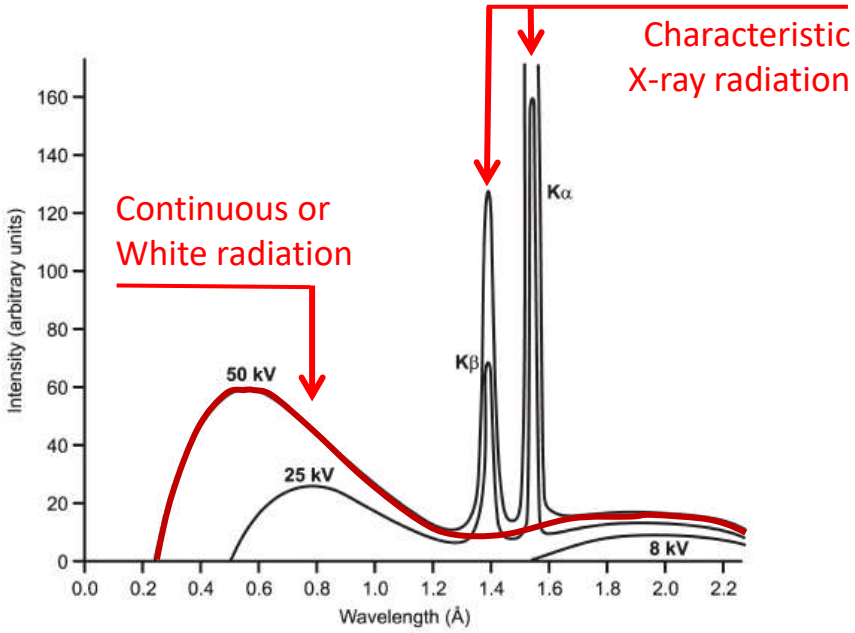
Generation of X-rays

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

Sealed Laboratory X-ray Tube Source

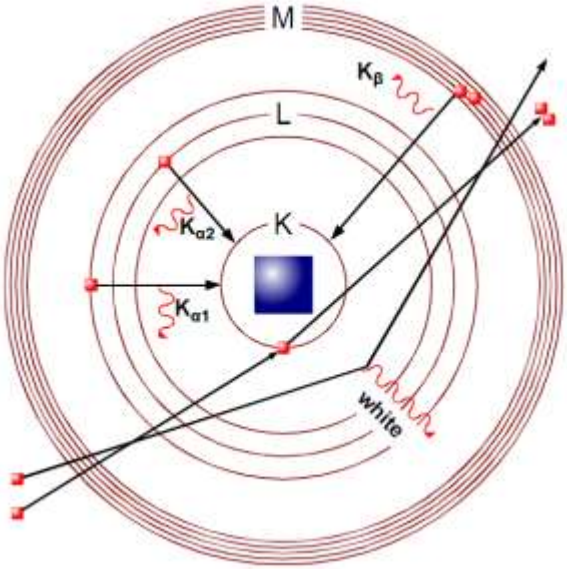


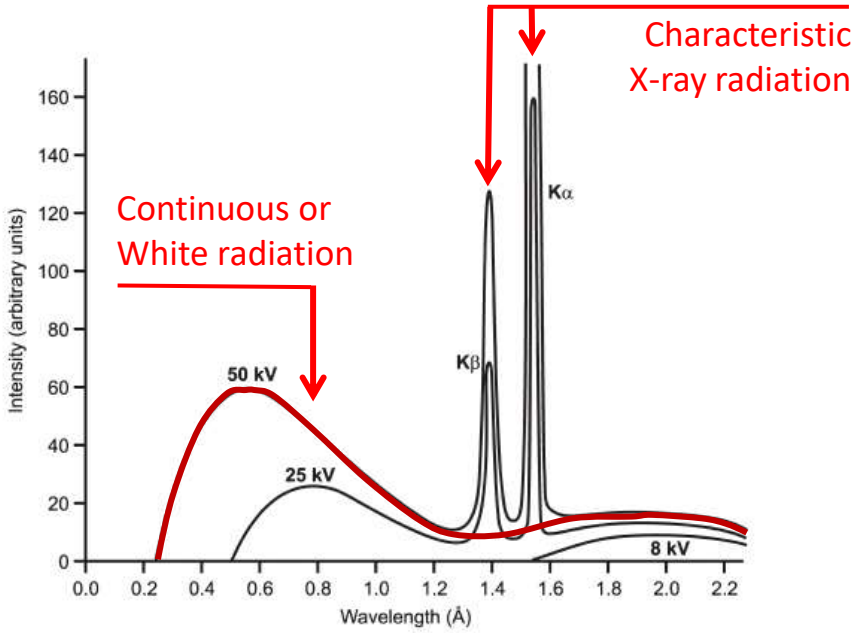
Source: "Ch.2 Experimental Setups" in Powder Diffraction Theory and Practice



Generation of X-rays

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION





Anode	Energy (keV for Kα)	Wavelength (nm)			
		Kα	Kα1	Kα2	Kβ
Ag	22.11	0.0560868	0.05594075	0.0563789	0.0497069
Mo	17.44	0.0710730	0.0709300	0.0713590	0.0632288
Cu	8.04	0.1541838	0.1540562	0.1544390	0.1392218
Co	6.93	0.1790260	0.1788965	0.179285	0.162079
Cr	5.41	0.2291	0.228970	0.2293606	0.208487

Kβ → removed using metal filters or monochromator

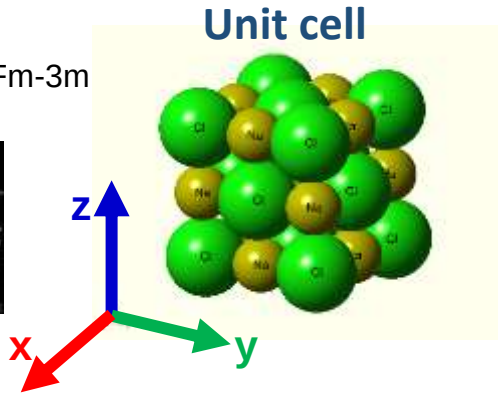
$K\alpha_2$ → removed as well for HRXRD

X-ray diffraction analysis

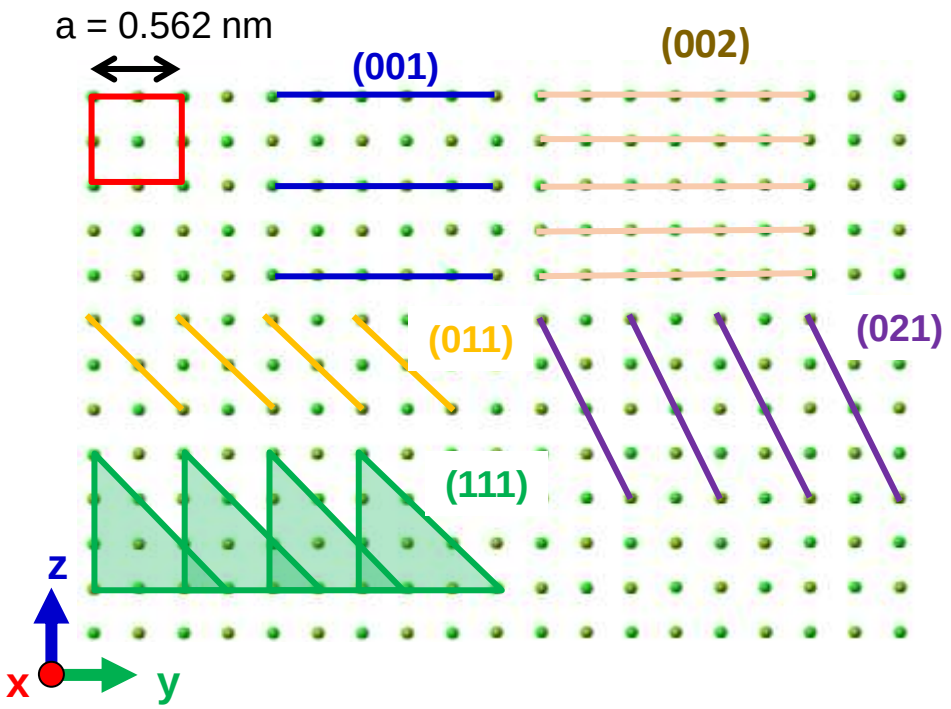
FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

Crystal
periodic arrangement of atoms in space

NaCl
Space group 225, Fm-3m
a = 0.562 nm



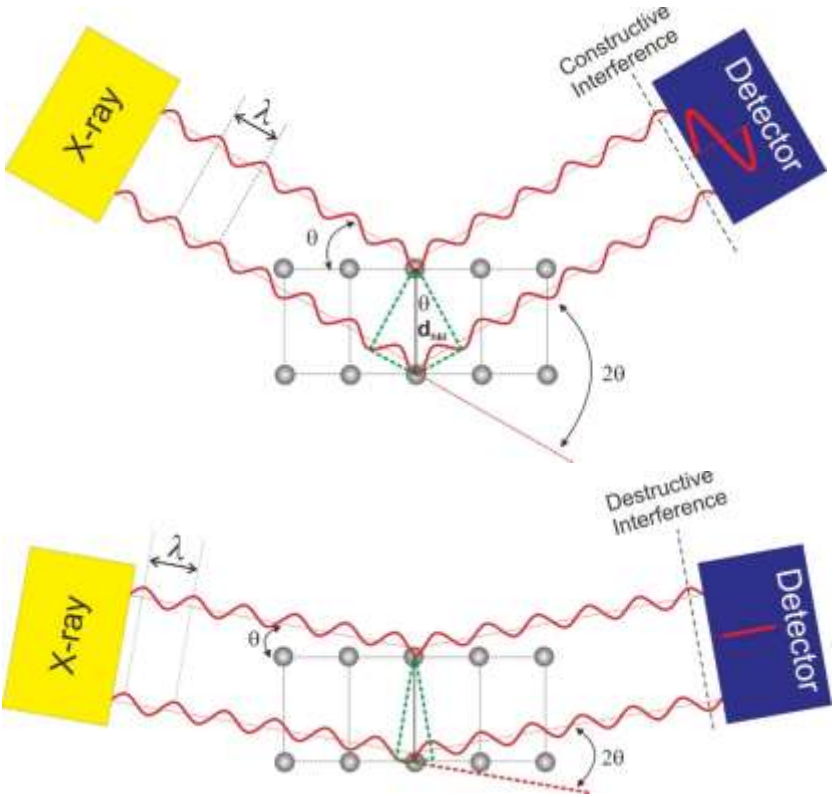
Crystallographic planes
hkl index, d-spacing,



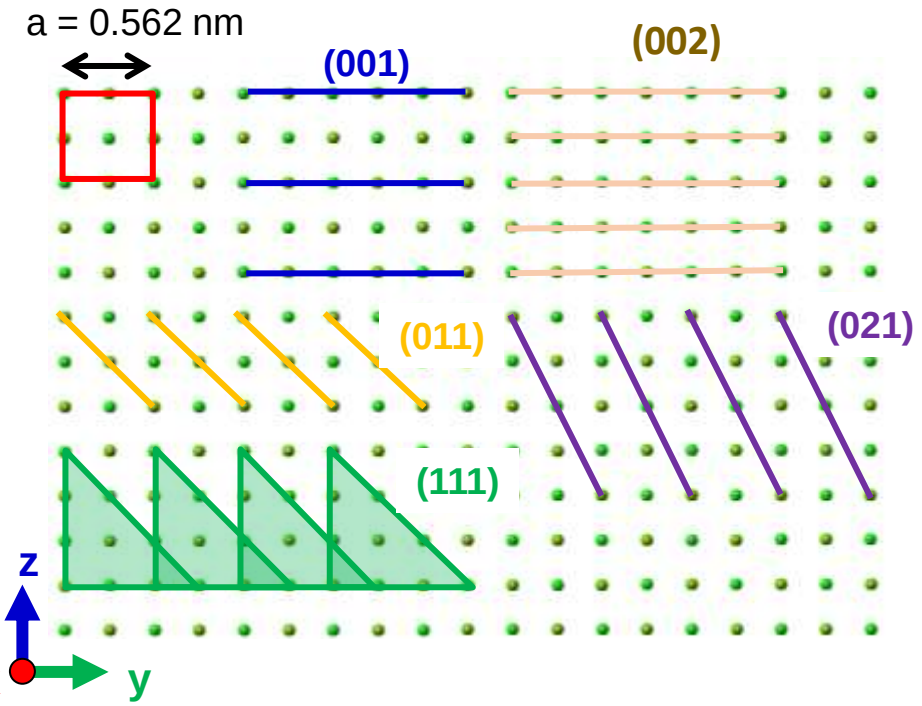
X-ray diffraction analysis

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

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



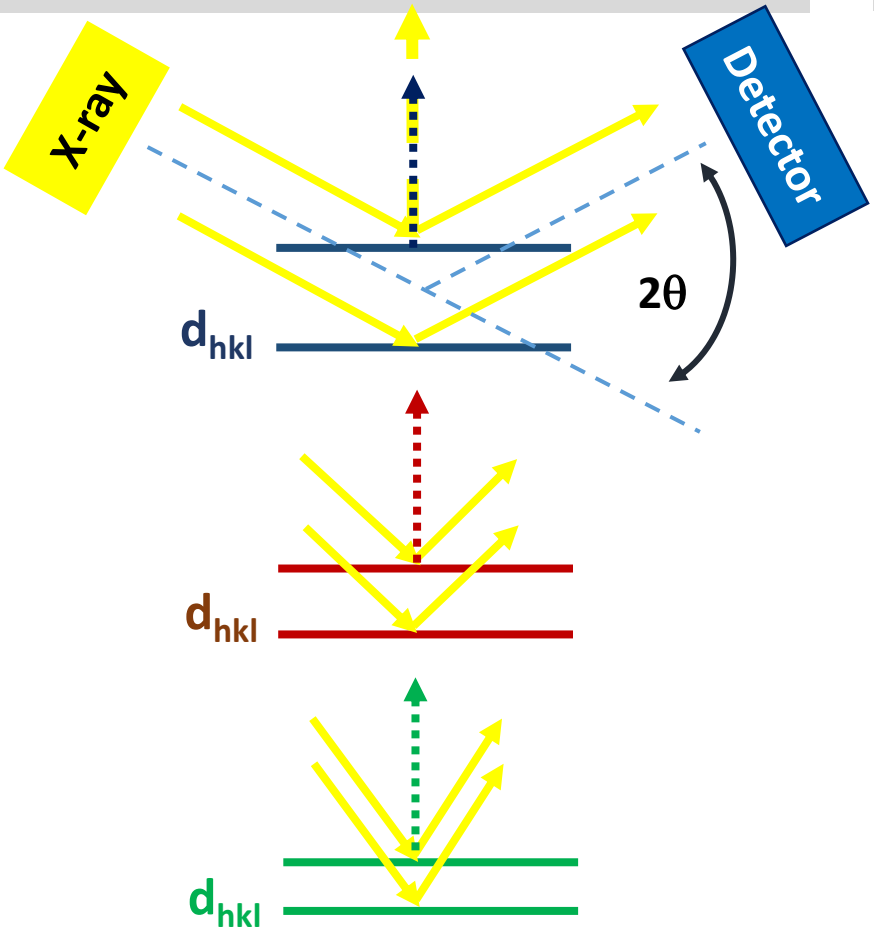
Crystallographic planes
hkl index, d-spacing (hkl),



X-ray diffraction analysis

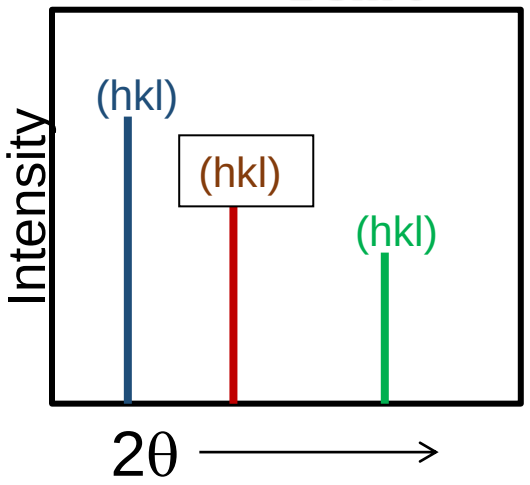
FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

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



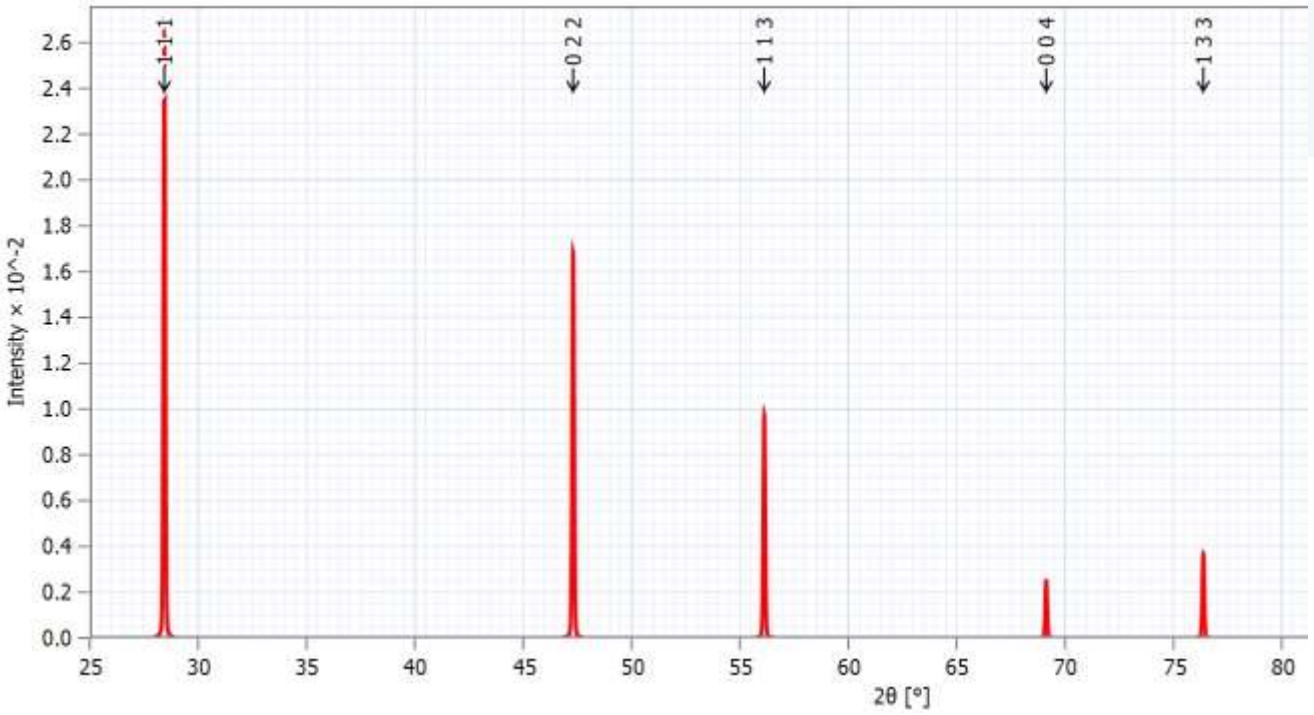
X-ray diffraction pattern
2θ-vs-Intensity plot, peaks (hkl)

$$d_{hkl} = \frac{n\lambda}{2\sin\theta}$$

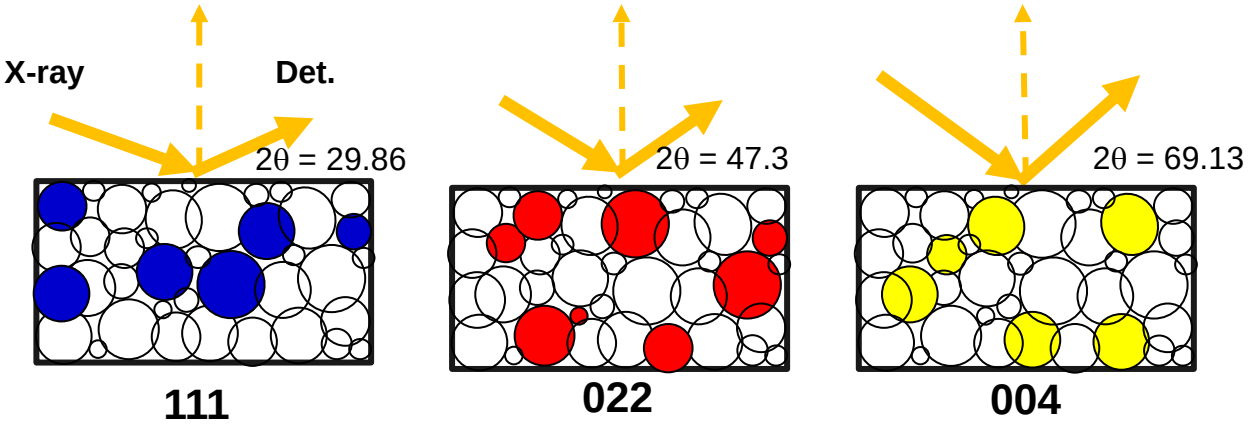


Peaks appear when hkl normal and diffraction vector are aligned parallel

XRD analysis: polycrystalline



Powder sample have randomly oriented crystals exposed to the incident X-rays. Some of them are perfectly aligned parallel with the diffraction vector.



X-ray diffraction analysis

$$I = |F|^2 p \left(\frac{1+\cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) A(\theta) e^{-2M}$$

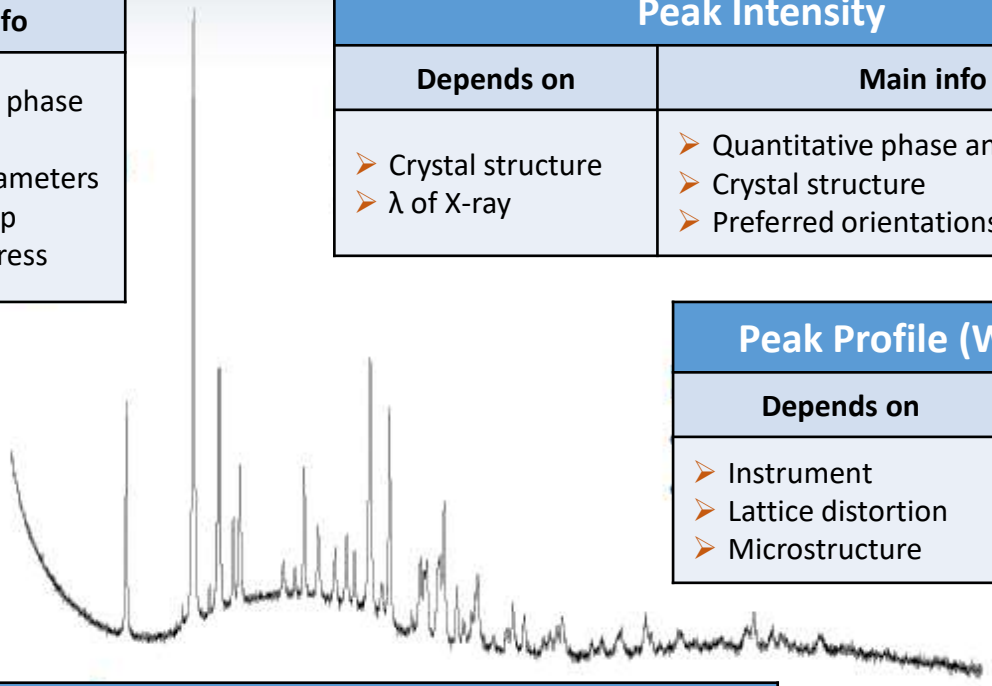
Multiplicity factor
Absorption factor
Structure factor
Polarization factor
Lorentz factor
Temperature factor

$$n\lambda = 2d\sin\theta$$

Peak Position	
Depends on	**Main info**
➢ Periodic arrangement of atoms/molecules ➢ λ of X-ray ➢ Sample preparation	➢ Qualitative phase analysis ➢ Lattice parameters ➢ Space group ➢ Residual stress

Peak Intensity	
Depends on	**Main info**
➢ Crystal structure ➢ λ of X-ray	➢ Quantitative phase analysis ➢ Crystal structure ➢ Preferred orientations/texture

Peak Profile (Width & Shape)	
Depends on	**Main info**
➢ Instrument ➢ Lattice distortion ➢ Microstructure	➢ Crystallite sizes ➢ Micro-strain



Background	
Depends on	**Main info**
➢ Sample environment i.e. air, holder ➢ Amorphous phase	➢ Amount of amorphous phase

Diffraction geometry

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

Bragg-Brentanno: θ/2θ scan

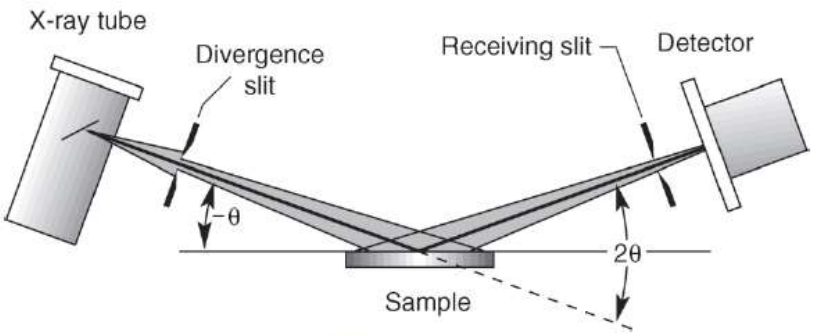


Figure 1. Bragg–Brentano diffraction geometry.

- ✓ Powder sample
- ✓ Bulk sample
- ✓ Thin film (with substrate)

GIXRD: 2θ scan at fixed θ or α

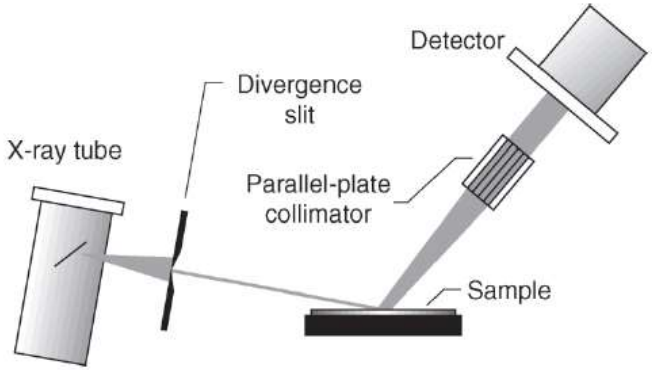
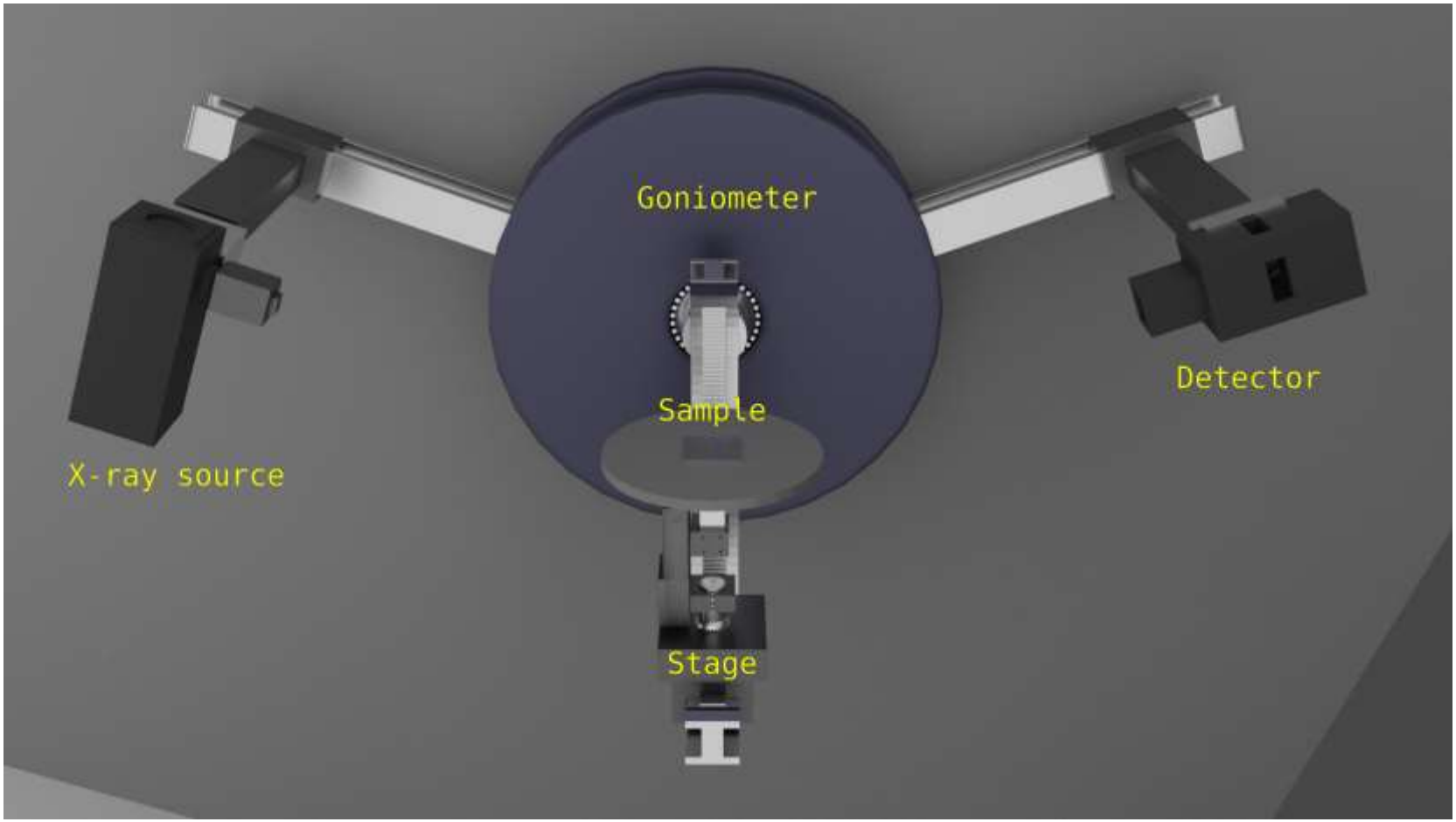


Figure 2. Thin-film diffraction geometry.

- ✓ Surface
- ✓ Thin film (without substrate)
- ✓ Depth profiling

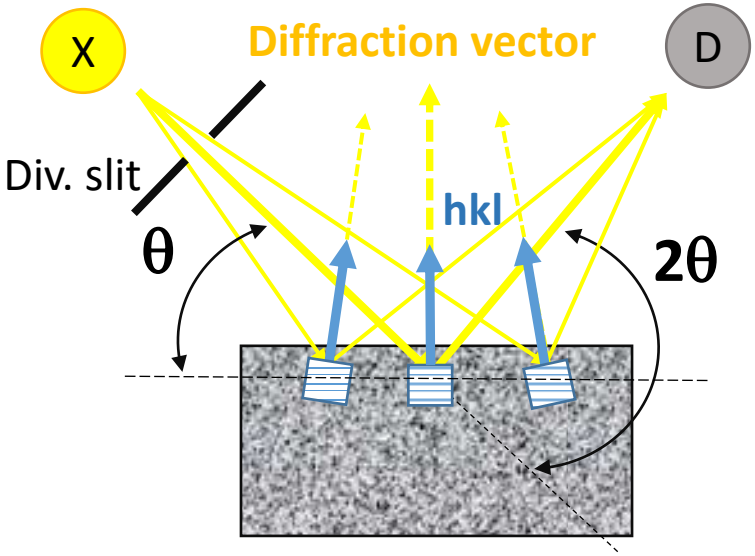
XRD scan modes

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION



https://youtu.be/HrWT2M63DbU?list=PLzN0KRQO_AyrEWBW54KFP-RRNdYF2MBoR

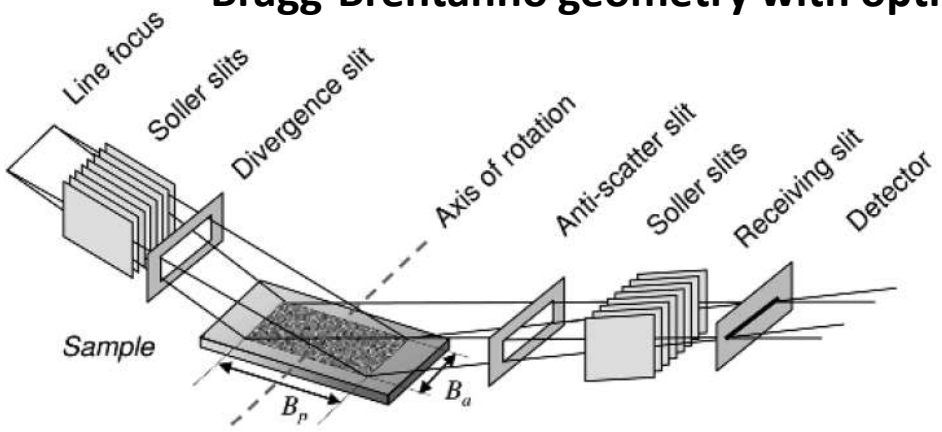
θ/2θ : Bragg-Brentanno geometry



Powder XRD:

- ✓ Bragg-Brentanno (parafocusing) geometry
- ✓ Divergent beam optics:
  - Including crystals with tilted hkl normal
- ✓ Angular resolution can be improved with narrow slits

Bragg-Brentanno geometry with optics

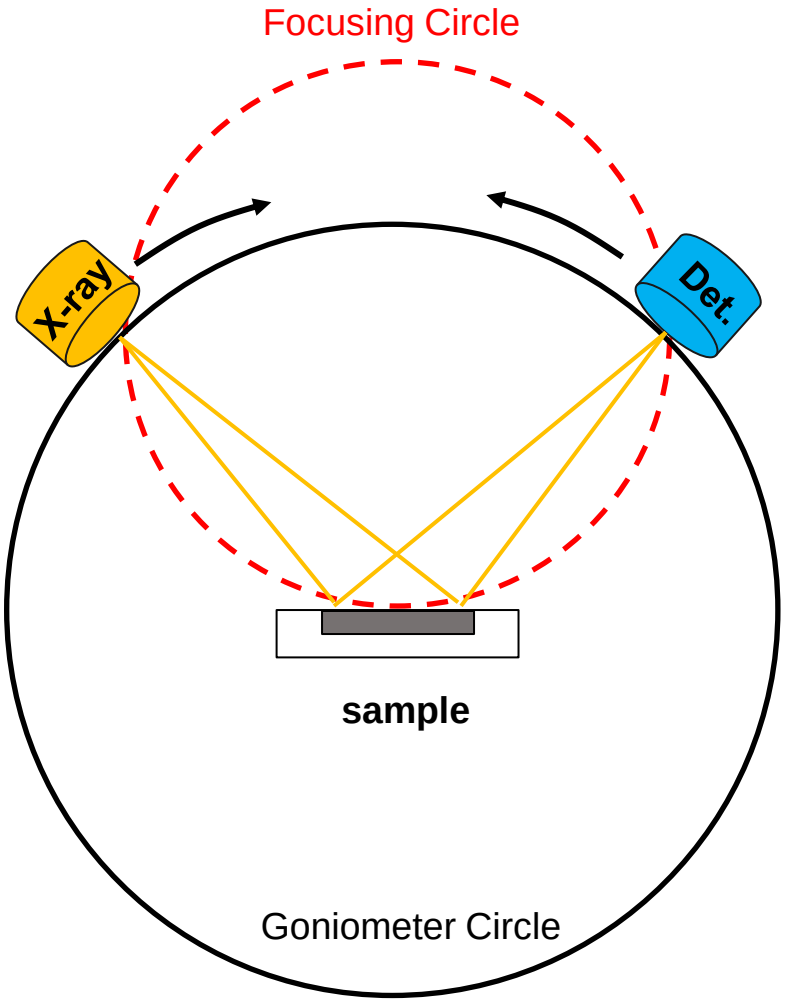


Focus length

$$B_p = R\frac{\sin\theta\sin\delta_{ds}}{\sin^2\theta - \sin^2(\delta_{ds}/2)}$$

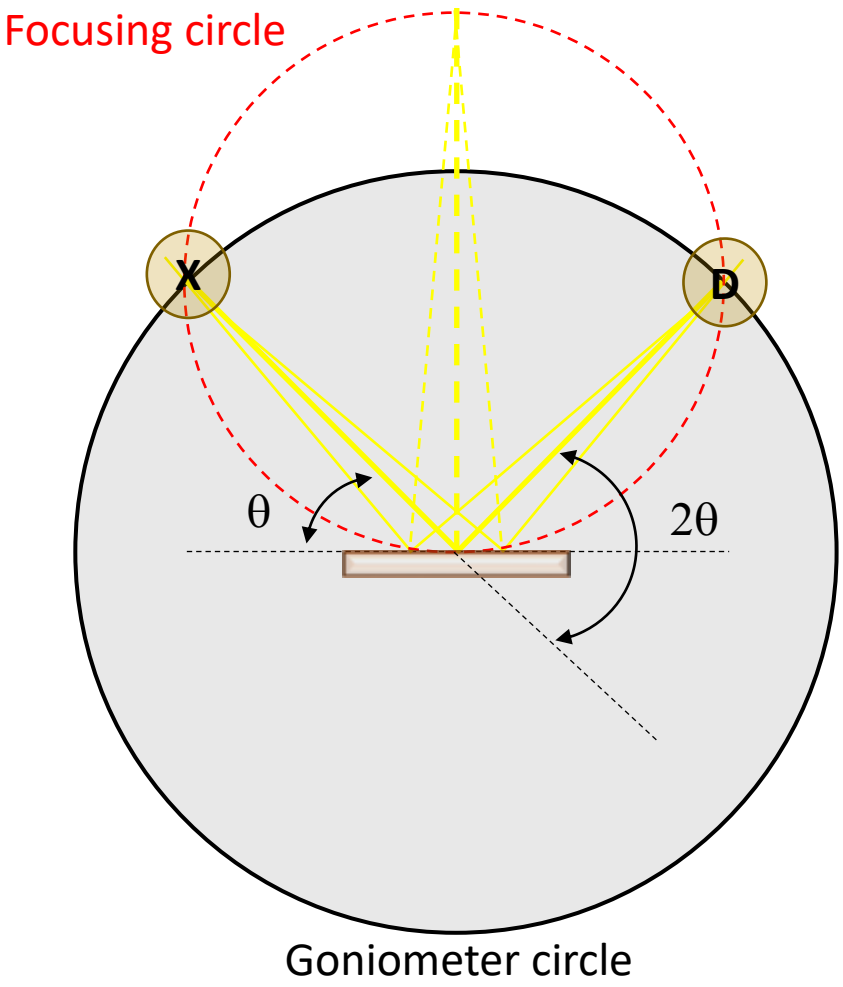
Bragg-Brentano Geometry

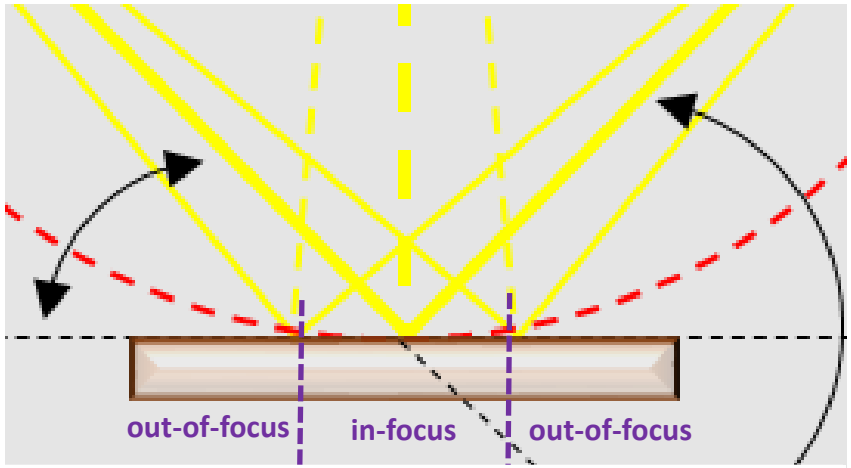
FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

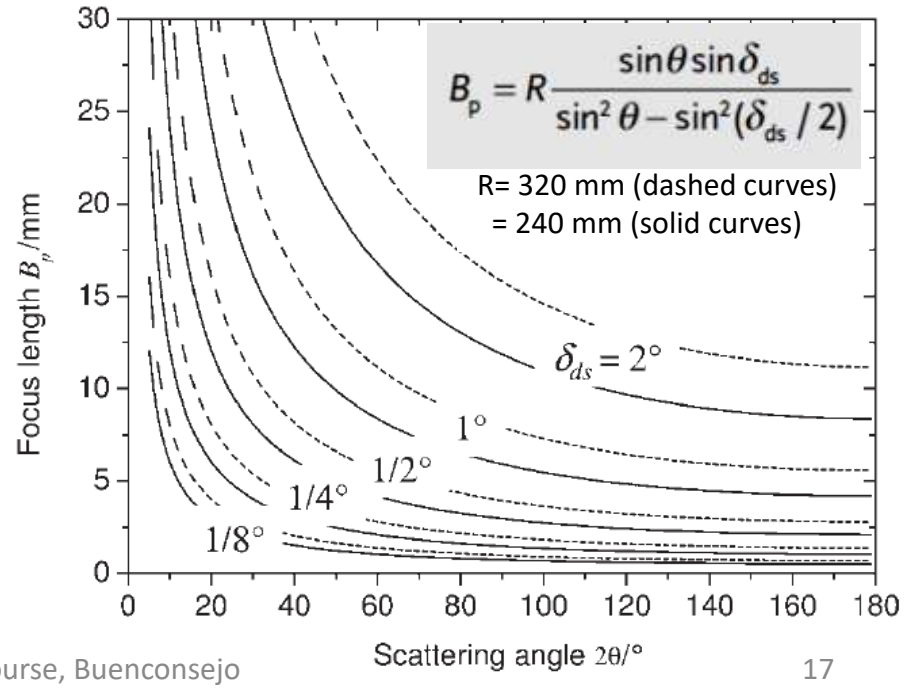


- Geometry has to be very precise
- Sample should be on the focusing circle
- Randomly oriented crystals/grains (1 – 10 microns) to prevent preferred orientation
- Goniometer provides the precision and accuracy required to keep the diffraction experiment in the correct geometry
- X-ray optics (Incident/diffracted) conditions the beam for optimum data collection.

θ/2θ: Bragg-Brentanno geometry

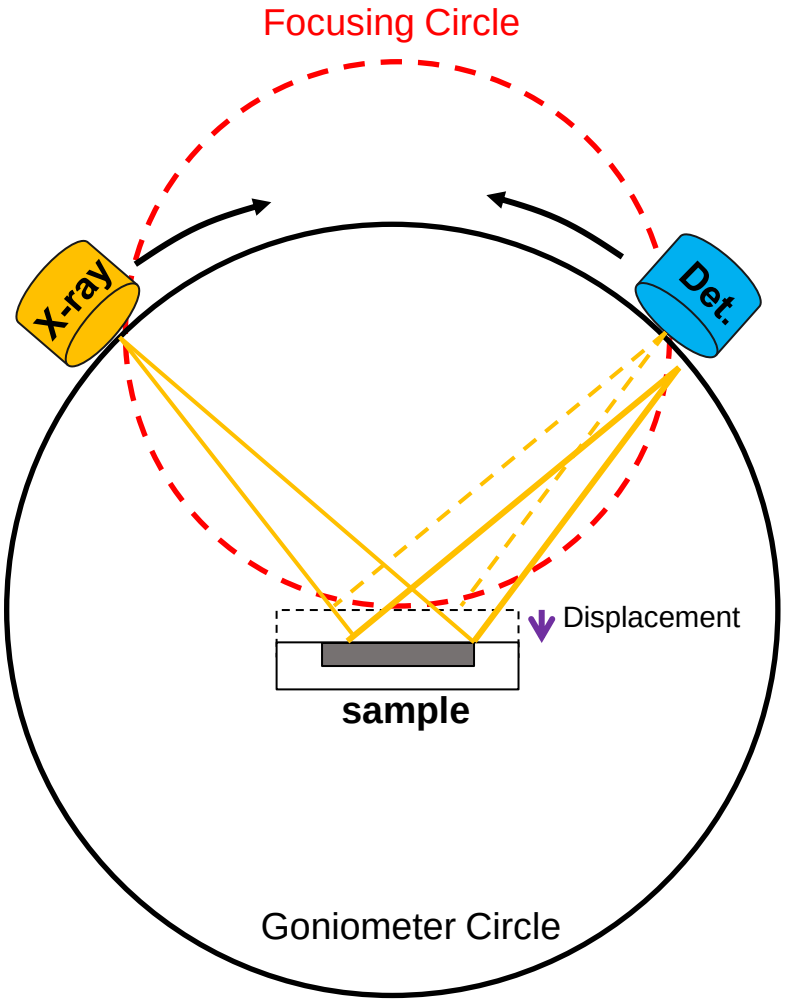






Common errors in Powder XRD experiment: Sample displacement error

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION



$$\Delta 2\theta = -\frac{2s\cos\theta}{R}$$

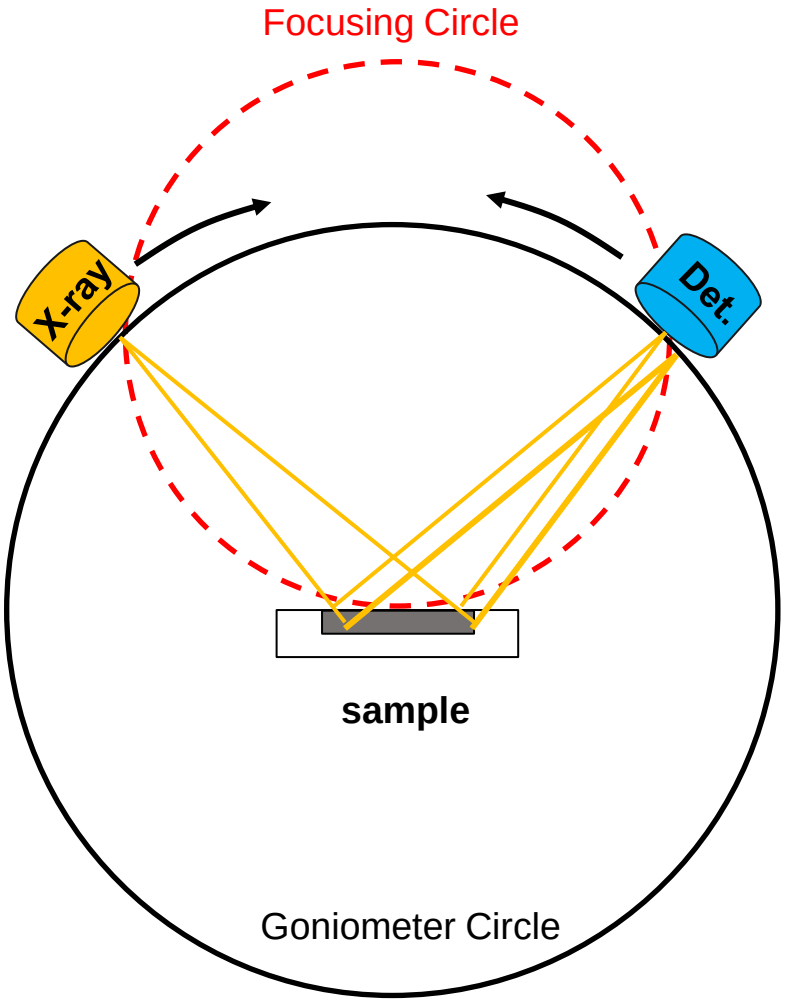
s = displacement
R = Goniometer radius

↓ Peaks shift to lower angle

↑ Peaks shift to higher angle

Common errors in Powder XRD experiment: Transparency error

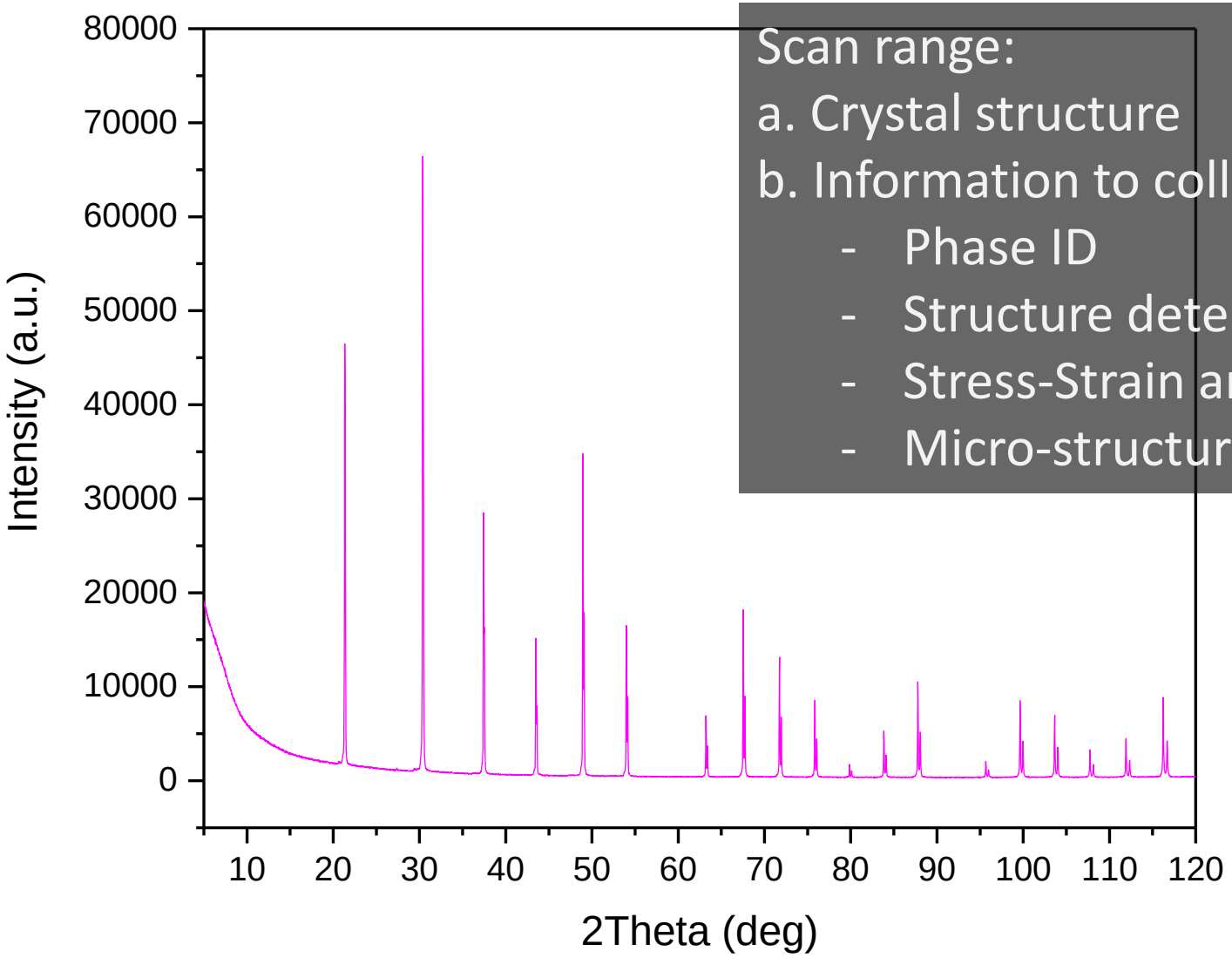
FACILITY FOR ANALYSIS F.A.C.T.S CHARACTERISATION TESTING SIMULATION



- Incident X-rays penetrate too much into the sample
- Peak asymmetry towards low angle
- Typical for organic samples.
- Can be avoided by using parallel beam and grazing incident set-up.

Scan parameters

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION



Scan range:

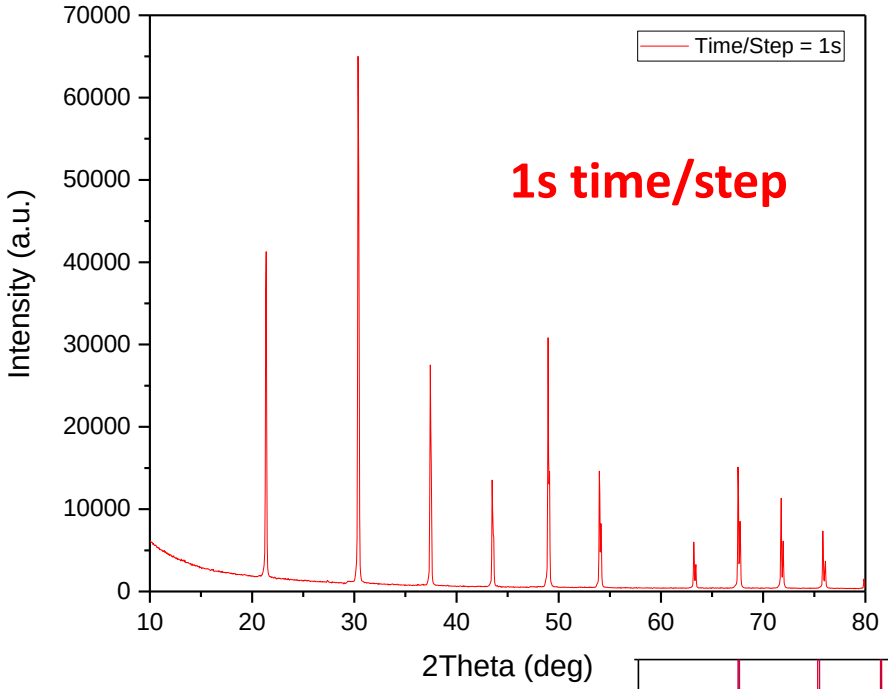
a. Crystal structure

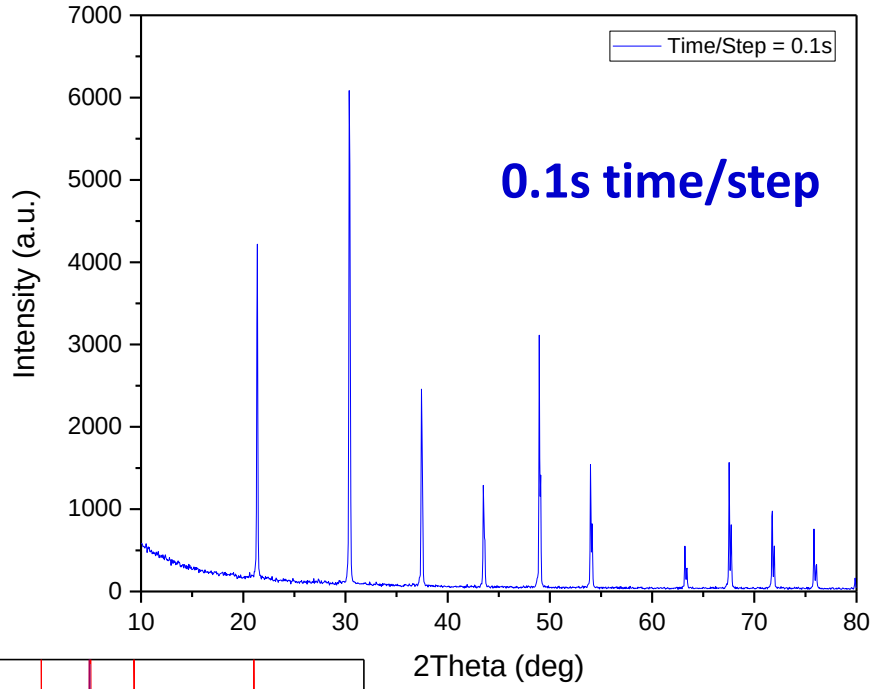
b. Information to collect

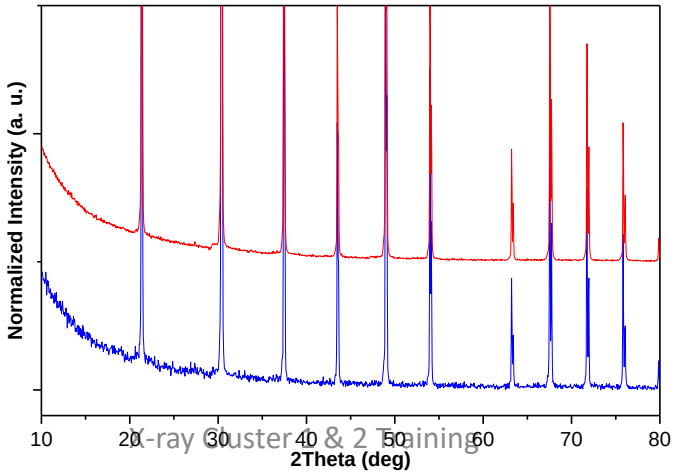
- Phase ID
- Structure determination
- Stress-Strain analysis
- Micro-structure

Scan parameters: Scan time

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION



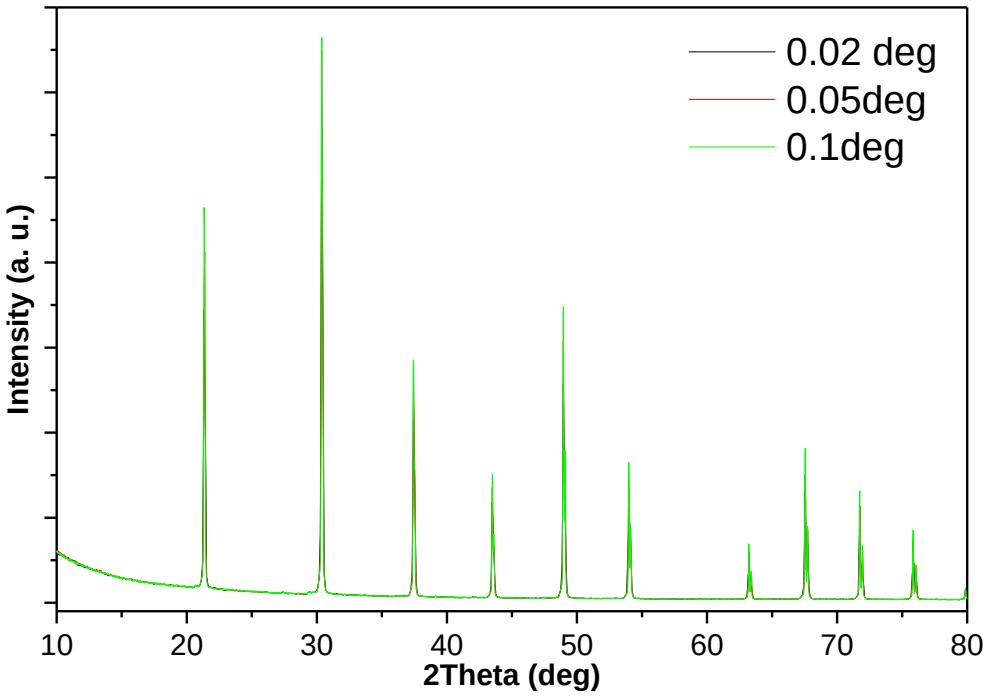


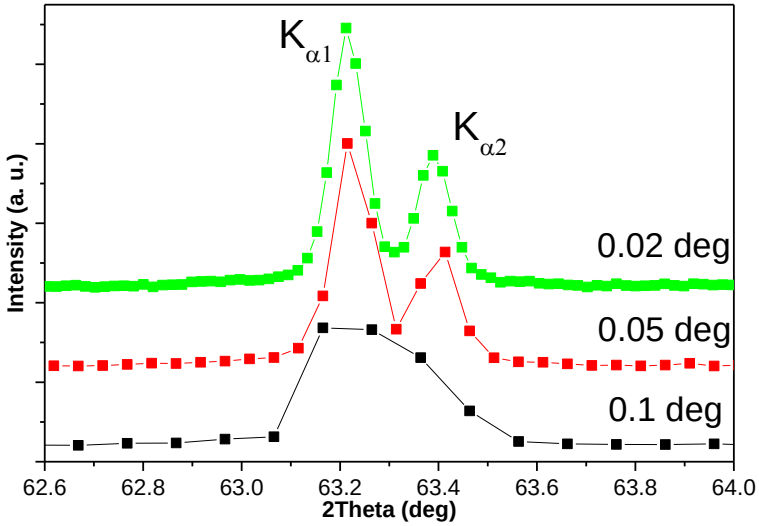


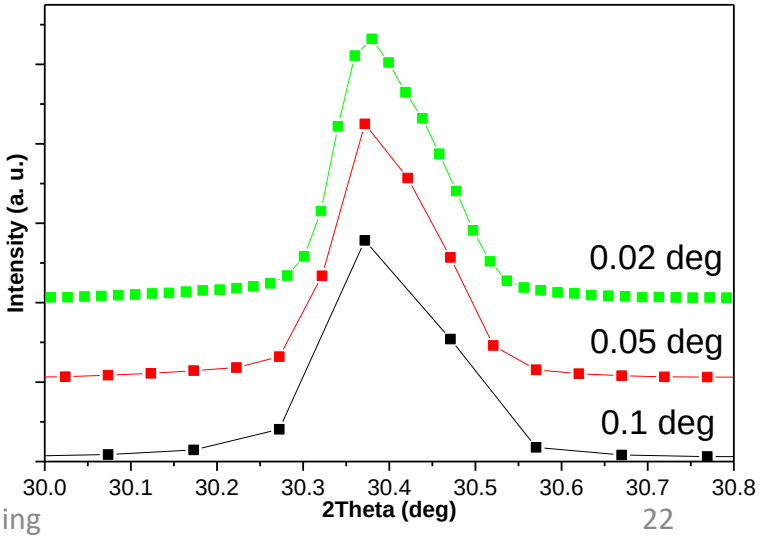
1s time/step

0.1s time/step

Scan Parameters: Step size

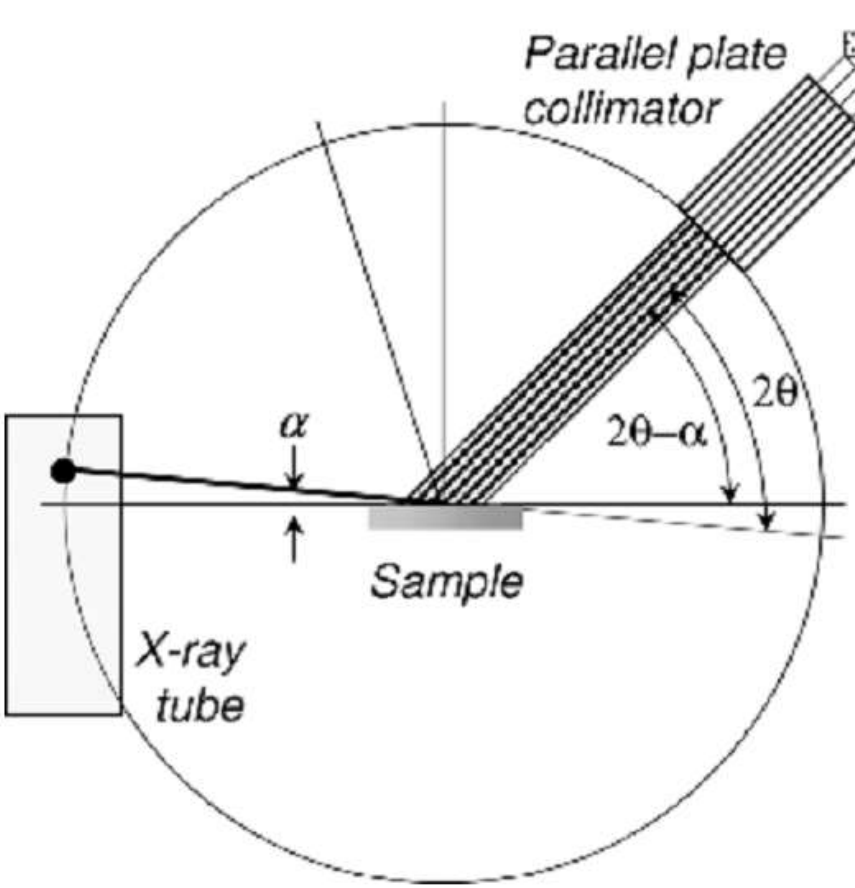


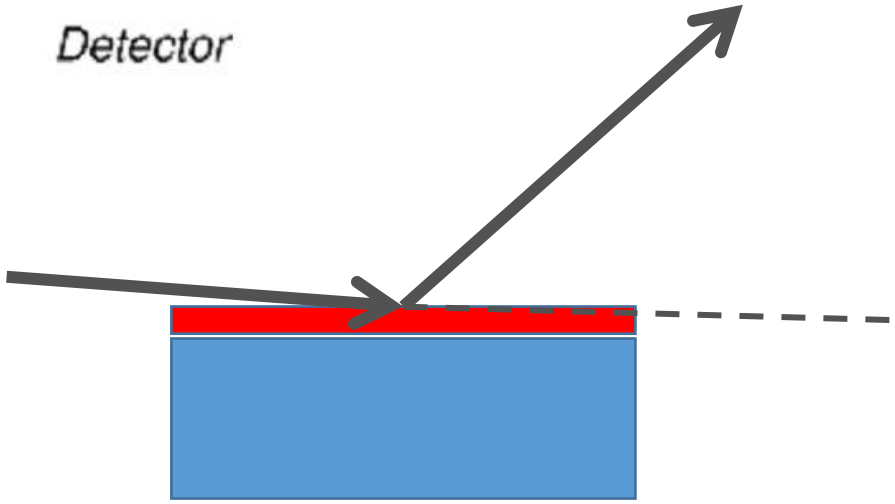




Grazing Incident XRD (GIXRD)

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

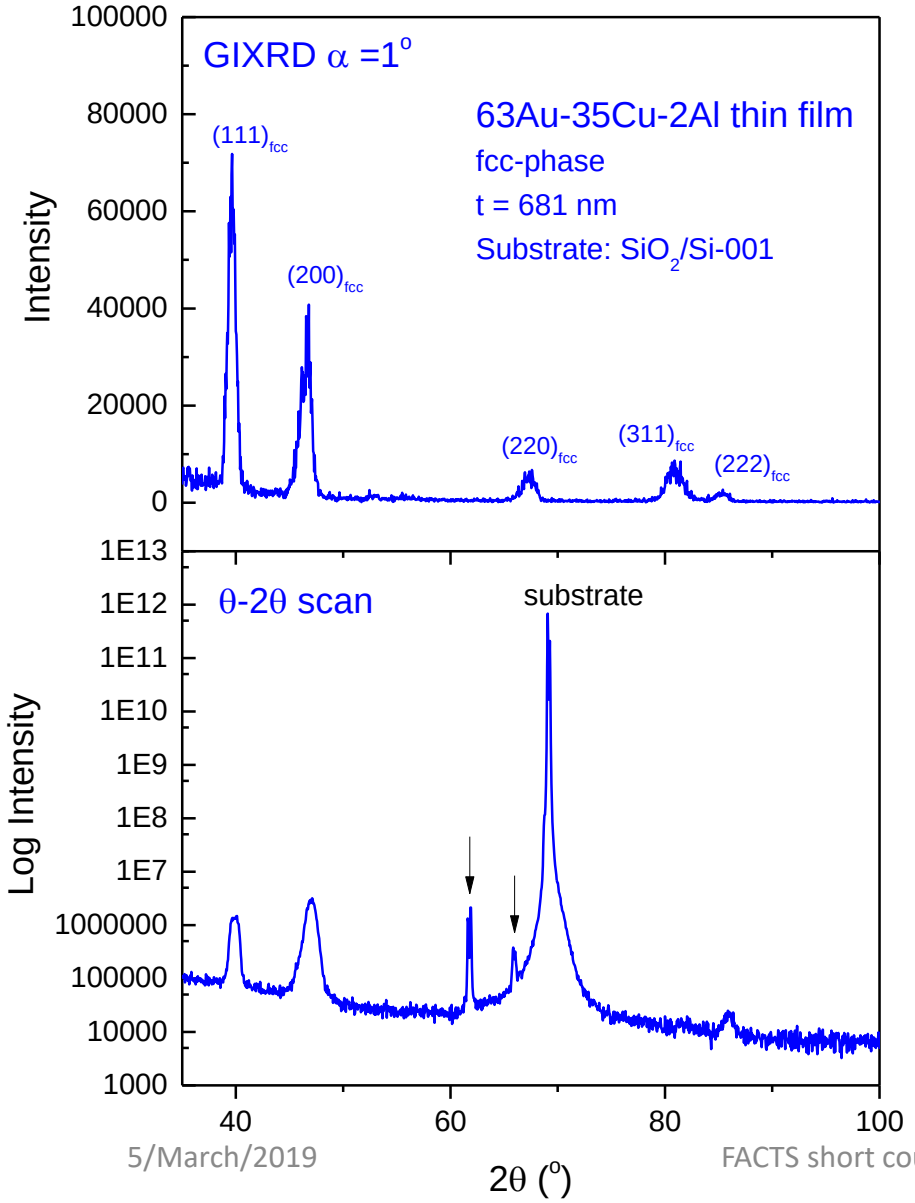




Why Grazing Incidence?
Low α shallow penetration
To avoid the substrate!

Source: "Ch. 4 Grazing Incidence Configuration" in Thin Film Analysis by X-ray Scattering. M. Birkholz

Examples: GIXRD versus BBG scan



GIXRD:

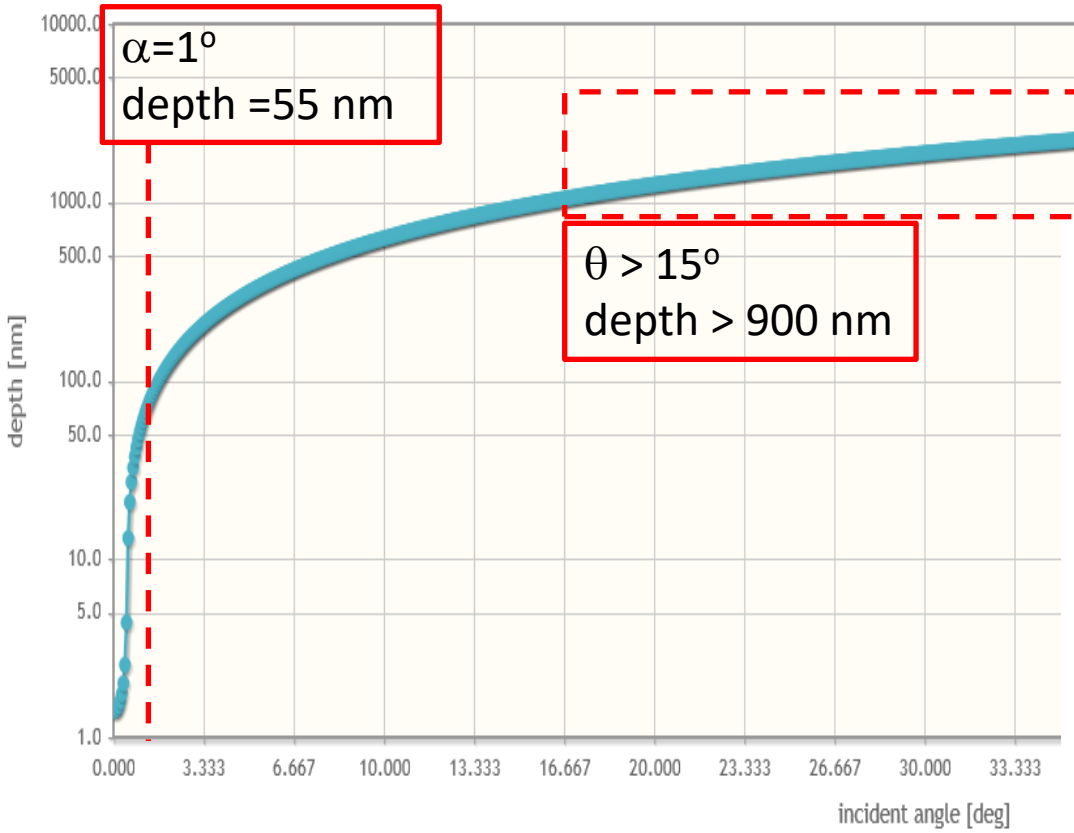
- ✓ Probes the thin film region only
- ✓ Relative Intensity is lower

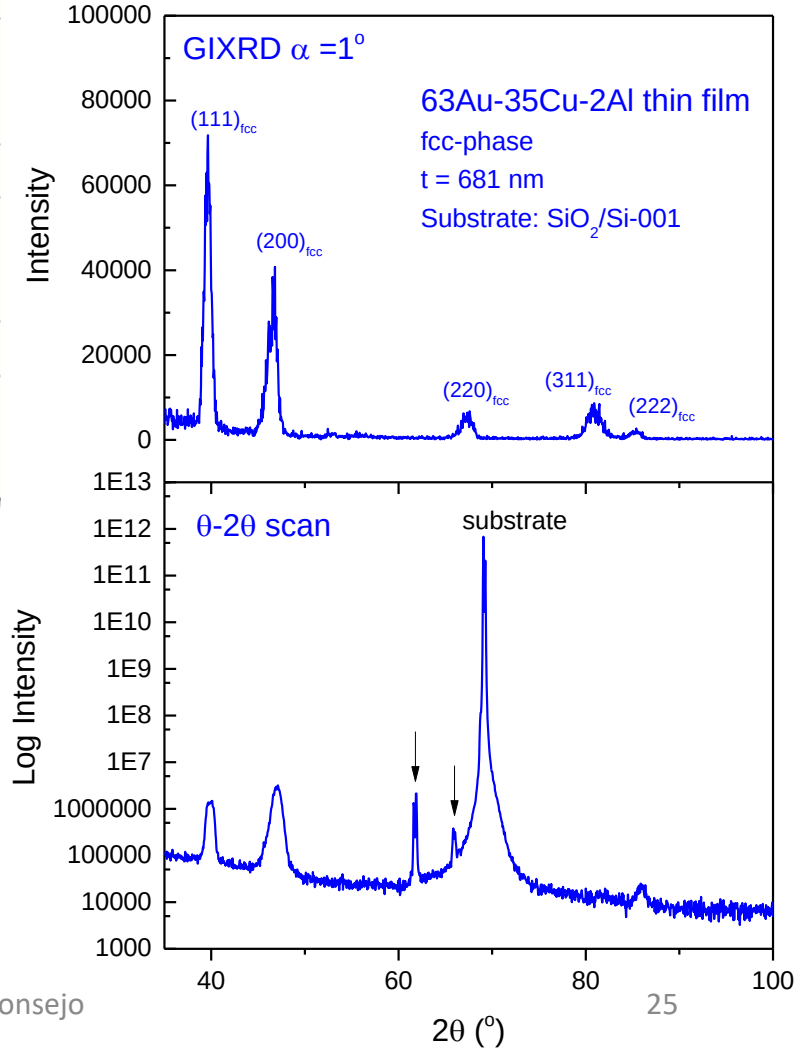
Bragg-Brentanno (θ/2θ scan):

- ✓ Additional contribution from the substrate
- ✓ Very high intensity

How much difference in the absorption and penetration depth?

penetration depth for Au63Cu35Al2 (ρ=15.36) @ 8040.0eV





---Note-----

i) Porosity, columnar grains, voids, defects in the material could reduce the effective density of the film and therefore the penetration depth could be deeper.

ii) Thin film density could be measured using XRR.

Hands-on training

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

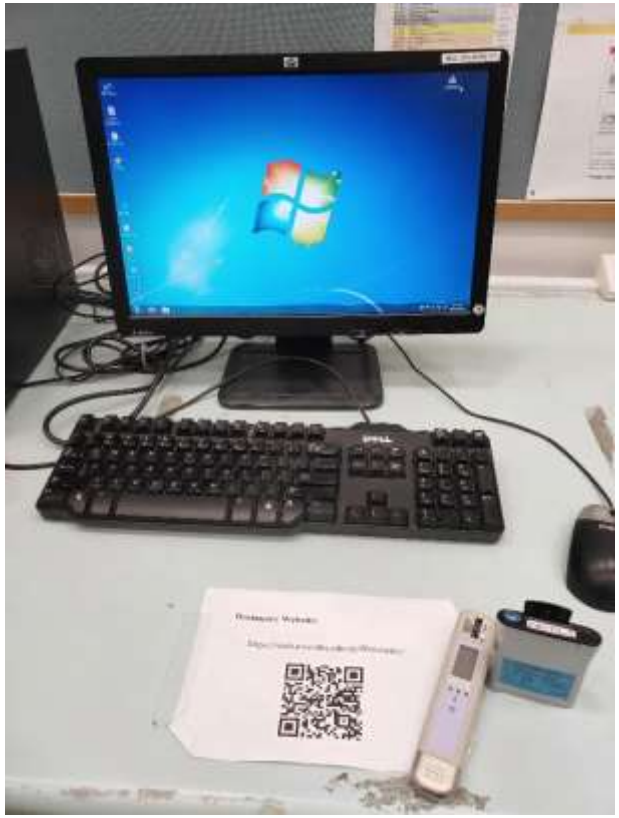
1. X-ray safety measures in FACTS
   - ✓ Dosimeter usage and e-logging
   - ✓ XRD room access
2. Sample preparation
   - ✓ Shimadzu (Cluster 1)
   - ✓ Bruker & Panalytical (Cluster 2)
3. Standard operating procedure
   - ✓ Shimadzu (Cluster 1)
   - ✓ Bruker & Panalytical (Cluster 2)
4. Post data collection analysis
   - ✓ Match software for Phase ID, Quantitative analysis

X-ray safety in FACTS

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

Access only for XRD users

Personal Dosimeter



Resources

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
ULATION

https://www.ntu.edu.sg/facts/home/research-focus/x-ray-cluster/x-ray-usage-training

NANYANG TECHNOLOGICAL UNIVERSITY SINGAPORE

> Facility for Analysis, Characterisation, Testing and Simulation (FACTS) > Scientific facilities > X-ray cluster > X-ray cluster: Usage & Training

Phase ID, Quantification, Structure determination/refinement

X-ray cluster 1: Shimadzu powder and thin film XRD
X-ray cluster 2: Bruker D8 Advance and Panalytical XRD

Requirements before training:

- Submit all the requirements (details)
- Attend the mandatory briefing (register here)

For enquiries please email: Weiling Liu or Pio Buenconsejo

Training resources:

- Presentation slides:
  1. X-Ray cluster 1 and 2 training 2020 FACTS.pdf
- X-ray cluster 1 training videos:
  1. Shimadzu XRD Sample Preparation
  2. Shimadzu XRD SOP
- X-ray cluster 2 training videos:
  1. XRD Sample Preparation
  2. Panalytical XRD Sample Loading
  3. Panalytical XRD SOP
  4. Bruker D8 Advance XRD Sample Loading
  5. Bruker D8 Advance XRD SOP
- XRD data analysis videos:
  1. XRD Phase ID and Quantification using MATCH

X-ray cluster

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

- Cluster 1:
  - Shimadzu Powder XRD & Thin Film XRD
- Cluster 2:
  - Bruker D8 Advance & Panalytical Xpert Pro
- Cluster 3: Training is by appointment only
  - Bruker Apex II Single Crystal XRD
  - Bruker D8 Discover HRXRD (multipurpose)
  - Rigaku Smartlab High-flux (9kW X-ray source) XRD
  - Xenocs Nanoinxder SAXS/WAXS, GISAXS/GIWAXS
  - Anton Paar SAXSess SAXS/WAXS

Sample Loading

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

Shimadzu Powder XRD

- Bulk sample holder is shorter in length by about 5mm. Need to consider this as offset when loading the sample.

Sample Loading

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

Shimadzu Thin Film XRD

Set stage height to
8.3 – 0.966 = 7.334 mm

Turn on the pump to fix the sample on the stage

X-ray cluster

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

- Cluster 1:
  - Shimadzu Powder XRD & Thin Film XRD
- Cluster 2:
  - Bruker D8 Advance & Panalytical Xpert Pro
- Cluster 3: Training is by appointment only
  - Bruker Apex II Single Crystal XRD
  - Bruker D8 Discover HRXRD (multipurpose)
  - Rigaku Smartlab High-flux (9kW X-ray source) XRD
  - Xenocs Nanoinxder SAXS/WAXS, GISAXS/GIWAXS
  - Anton Paar SAXSess SAXS/WAXS

Data analysis

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

- MATCH for Phase ID, quantification
- PDF 4+, ICSD database: for checking structure and Cif files
- TOPAS, EVA

Important things to remember after training

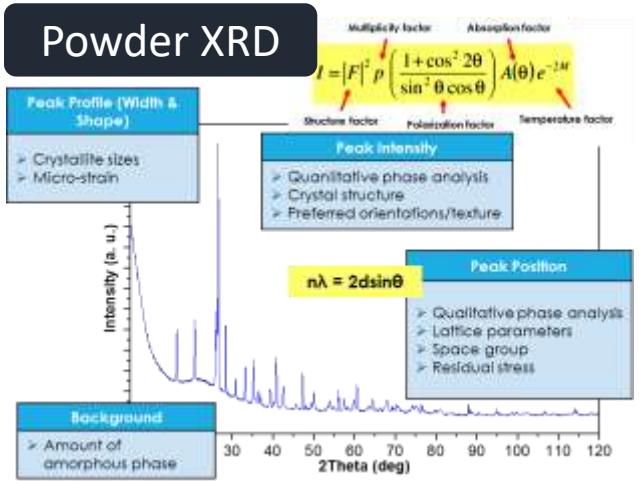
FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

1. Only official NTU staff with NTU staff card; students and exchange students with NTU matriculation card are allowed to use FACTS facilities.
2. After training, XRD users must use **> 3 hours** within the **first 30 days** of training, or their access will be automatically deactivated. To regain access, user must wait for at least the following month for retraining. There will be charges for retraining.
3. If there is no usage of instrument within **365 days** from the last usage, access will be automatically removed by the FOM server. Retraining with charges is applicable in this case.
4. For booking of instruments, users are encouraged to cancel the booking early if they do not need the slots. Charges will still apply if users cancel booking within **24 hours** or fail to turn up for usage thereafter.
5. If a user uses an instrument booked under the name by a different user, this constitutes as unauthorized usage. Penalties including access removal to ALL FACTS equipment will apply. Users are advised to request FACTS staff to change the booking to the correct user, instead of simply allowing access to someone who needs the access.
6. Users will bear the cost of any equipment damage and instrument access will be revoked for any misuse.

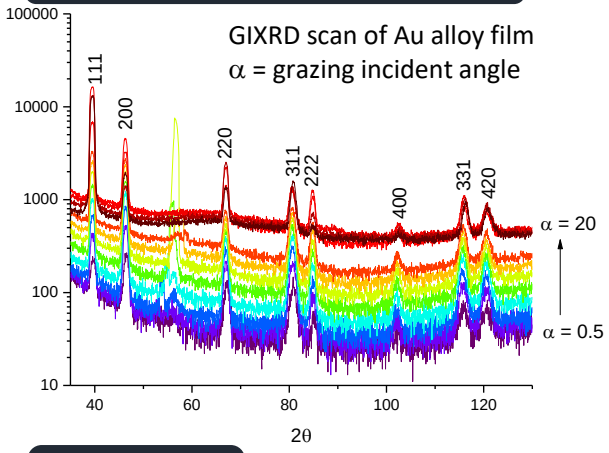
X-ray Scattering Analysis @FACTS

FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

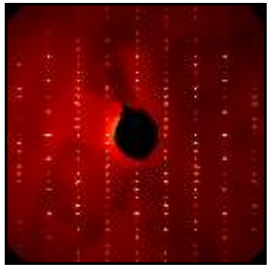
Powder XRD



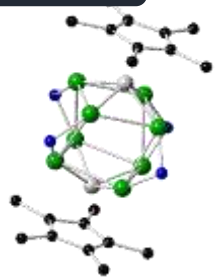
Grazing Incident XRD



Single Crystal XRD



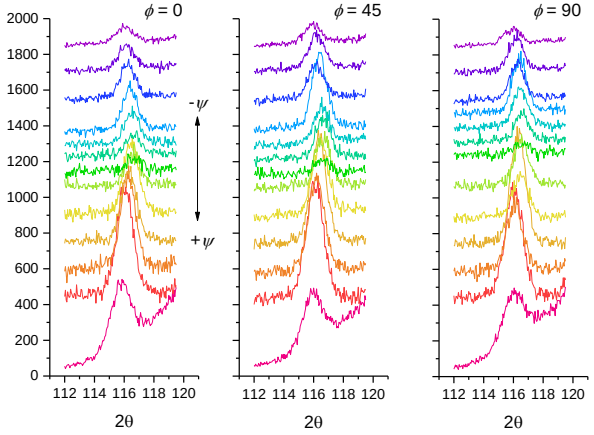
Precession image of a diffraction pattern



Solved crystal structure:
C (black), Al (blue), Ti (grey) and F (green)

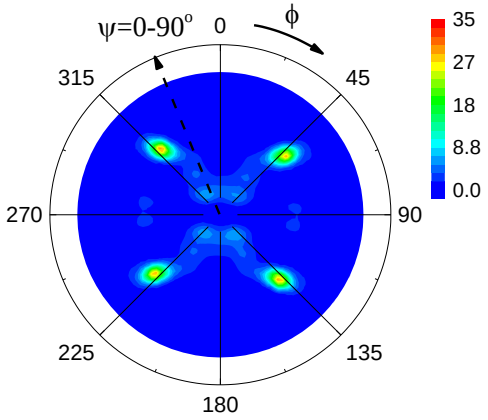
Residual Stress

Triaxial residual stress analysis of Au alloy film



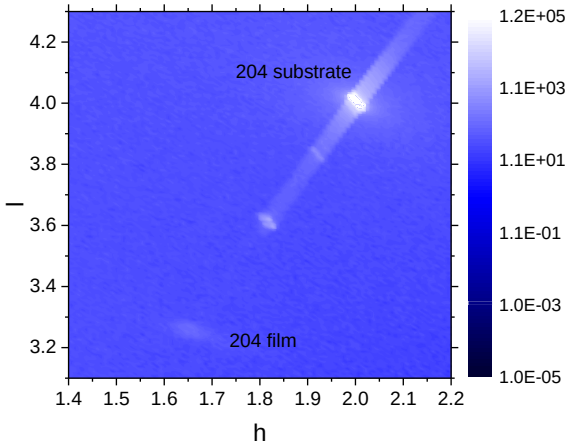
Texture

(111) PF of a Cu foil



High-Resolution XRD

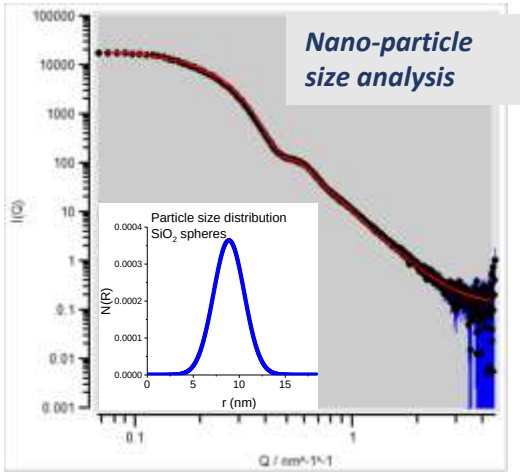
Reciprocal space map of an epitaxial thin film



X-ray Scattering Analysis @FACTS

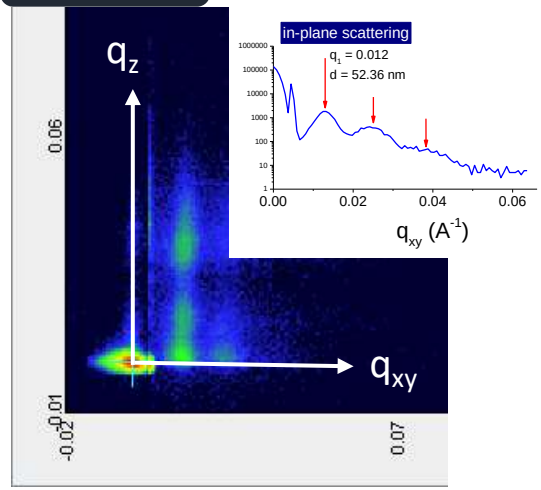
FACILITY FOR ANALYSIS
F.A.C.T.S
CHARACTERISATION
TESTING SIMULATION

SAXS

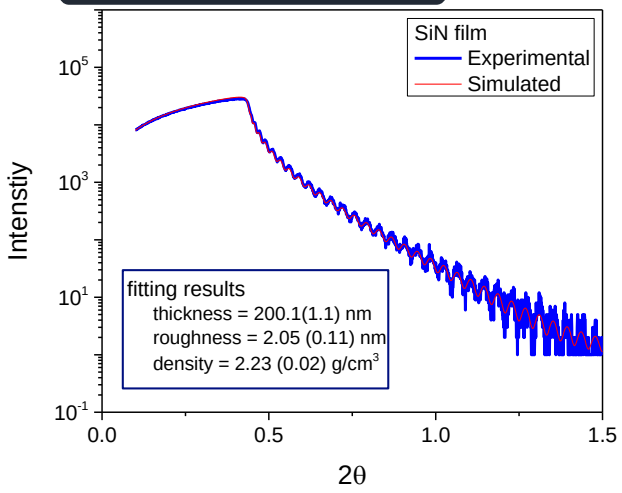


GISAXS

Nanostructured material



X-Ray Reflectivity



We also have:

- In-situ heating/cooling stage
- High-power X-ray source (Rigaku Smartlab)
- XRF for composition analysis
- Wide range of software for XRD data analysis

We can always discuss on:

- Ad-hoc in-situ experiments with supervision
- Design of experiment
- Data treatment and analysis