Materials Research Laboratory

X-ray analysis:
Mauro Sardela Jr.
Advanced Materials Characterization Workshop
AMC2019
University of Illinois at Urbana-Champaign

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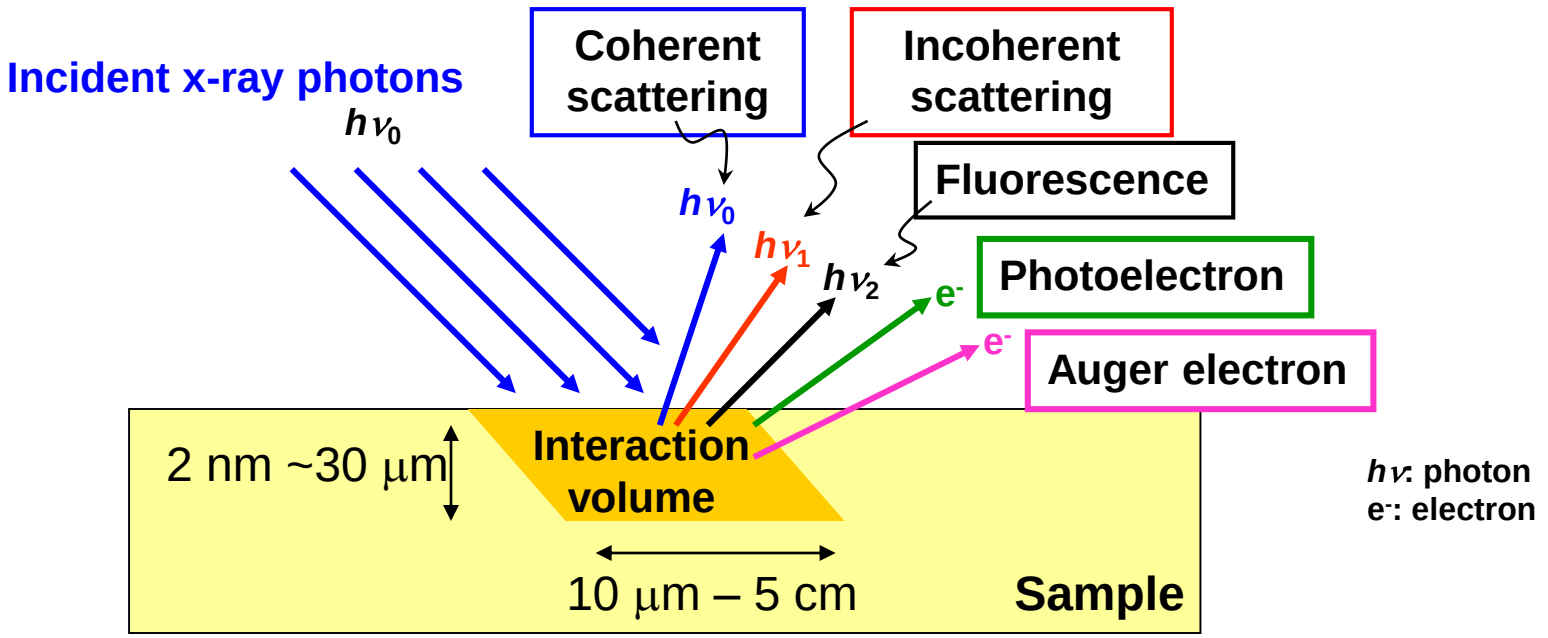
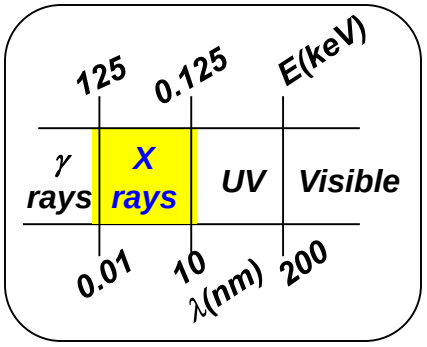
X-ray interactions with matter





X-ray radiation mostly used in lab instruments:
***Cu* radiation**

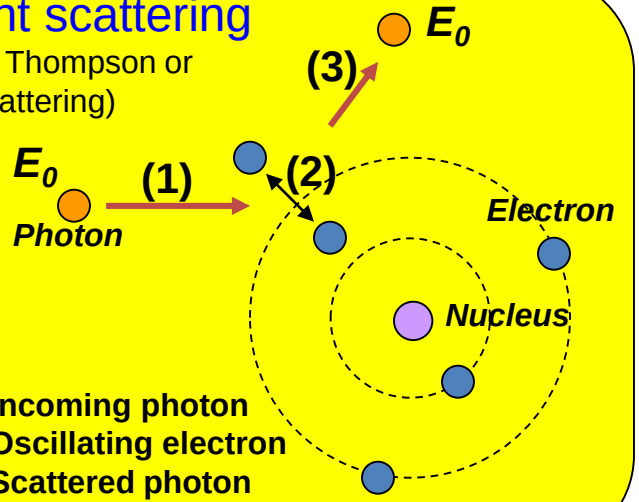
- ***Cu*** **Kα: λ= 0.15418 nm**
(8.05 keV, conventional resolution)

- ***Cu*** **Kα1: (λ= 0.15056 nm (high resolution)**

X-ray interactions with matter

Coherent scattering

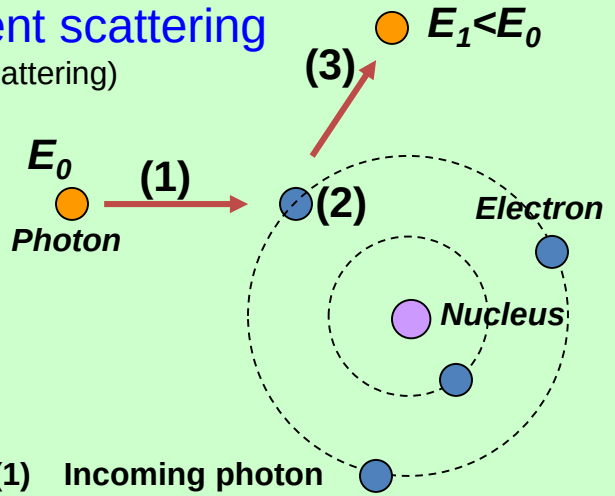
(Diffraction, Thompson or Rayleigh scattering)



(1) Incoming photon
(2) Oscillating electron
(3) Scattered photon
No loss of energy.

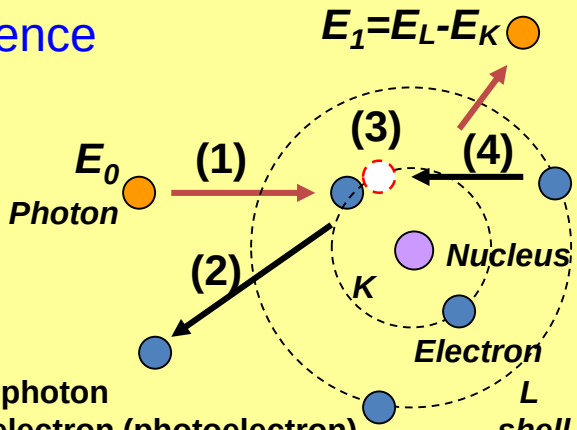
Incoherent scattering

(Compton scattering)



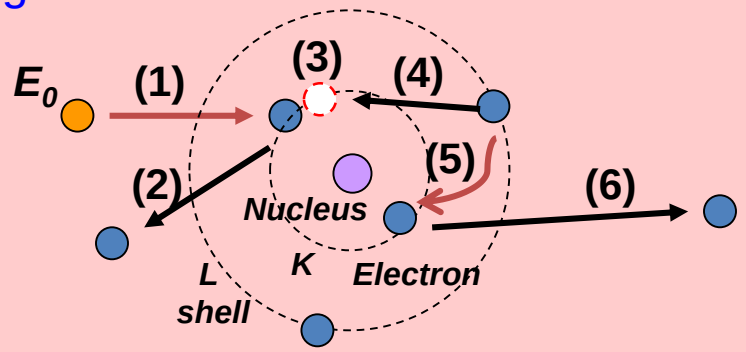
(1) Incoming photon
(2) Energy is partially transferred to electron
(3) Scattered photon (energy loss).

Fluorescence



(1) Incoming photon
(2) Expelled electron (photoelectron)
(3) Hole is created in the shell
(4) Outer shell electron moves to the inner shell hole
(5) Energy excess emitted as characteristic photon.

Auger electron



(1-4) Hole created (3) after photoelectron emission (2) is occupied by outer electron (4).
(5) Excitation energy is transferred to electron
(6) Electron ejected from atom (Auger electron)

Fundaments of diffraction

"Real" space

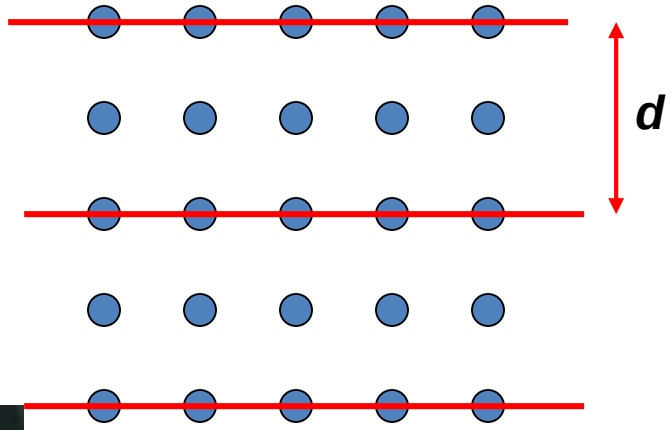
$\mathcal{F}$

Reciprocal space

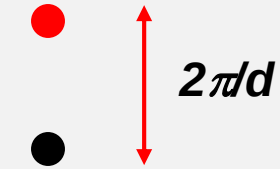
Set of planes

Point

(h k l)



h k l



origin

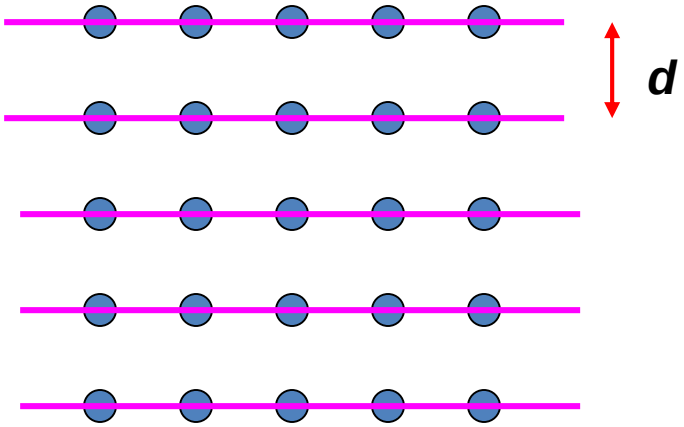
M. von Laue 1879-1960
X-rays from crystals, 1912.

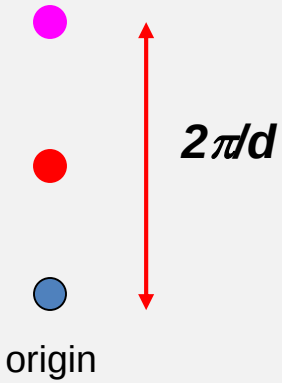
Fundaments of diffraction

"Real" space

$\mathcal{F}$

Reciprocal space



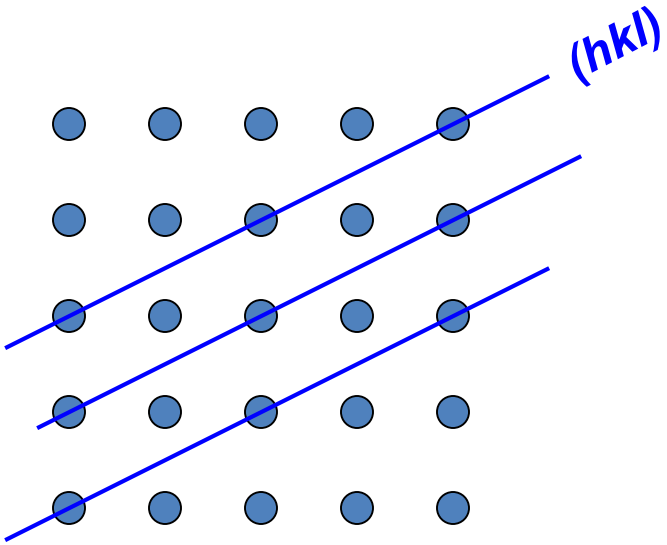


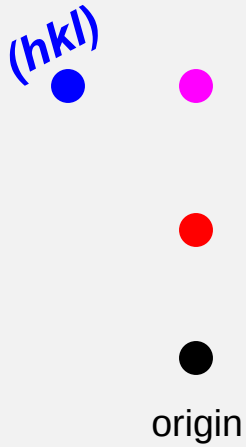
Fundaments of diffraction

"Real" space

$\mathcal{F}$

Reciprocal space

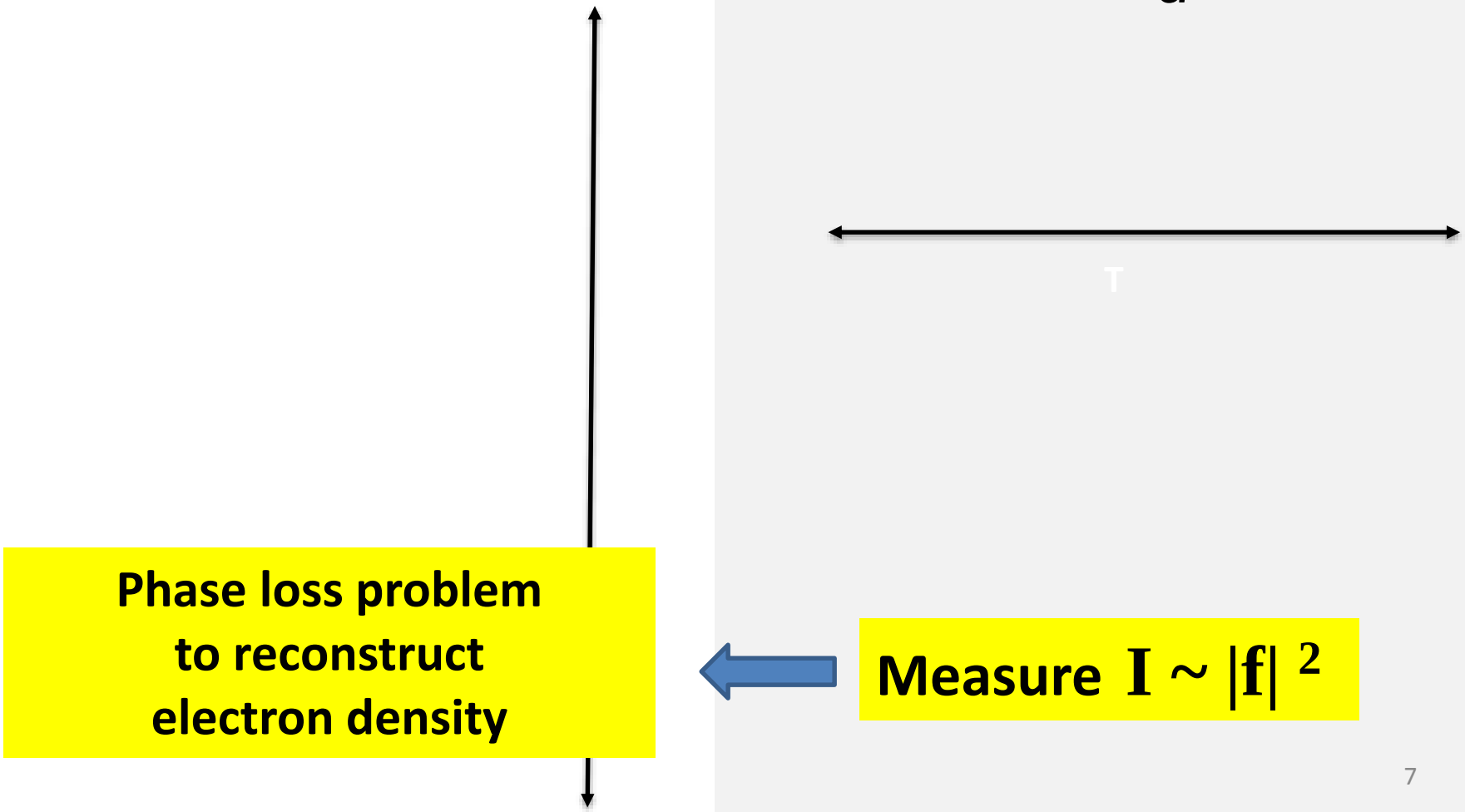




Fundaments of diffraction

"Real" space $\xrightarrow{\mathcal{F}}$ Reciprocal space

d $\qquad$ $\frac{1}{d}$



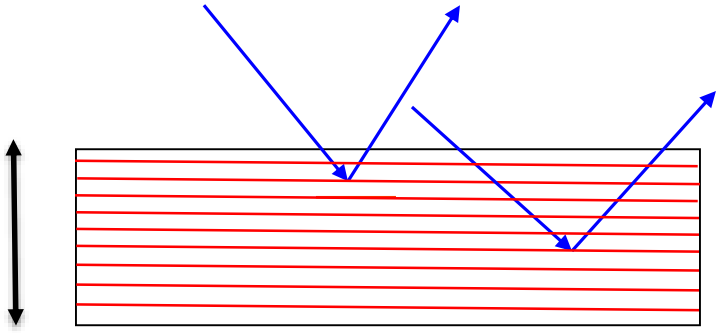
Phase loss problem to reconstruct electron density

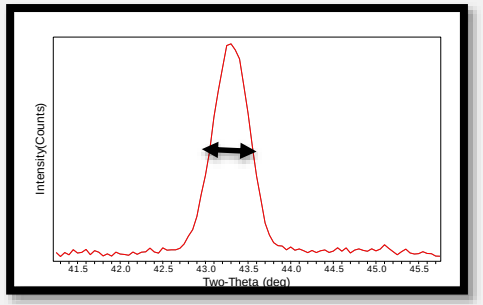
Measure $I \sim |f|^2$

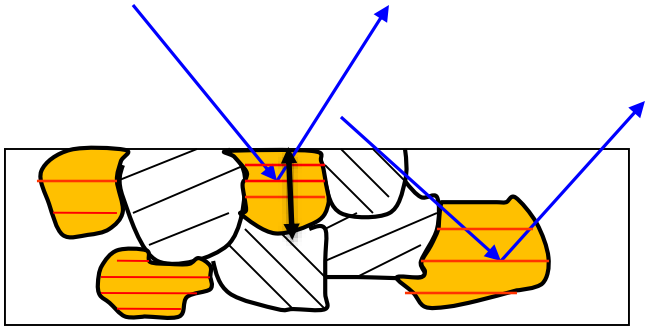
Fundaments of diffraction

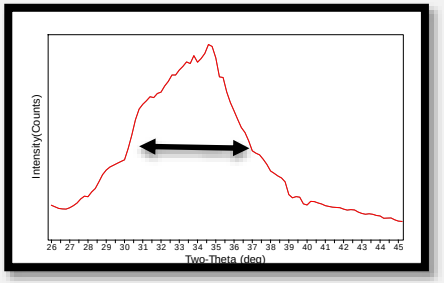
"Real" space $\xrightarrow{\mathcal{F}}$ Reciprocal space

d $\qquad$ $\frac{1}{d}$





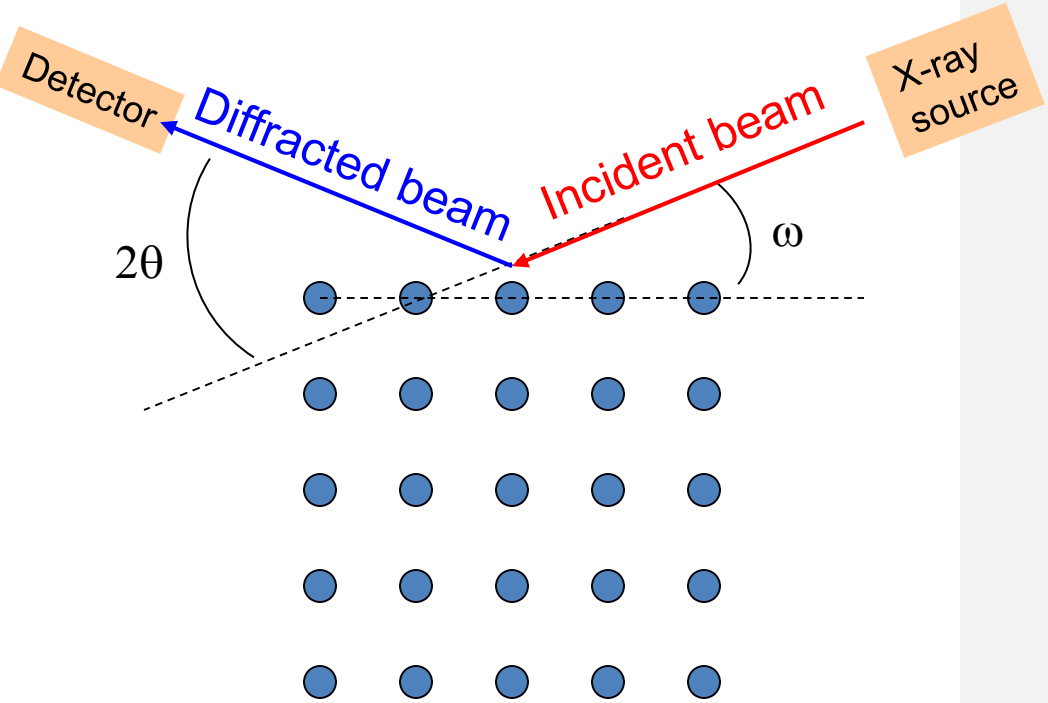




Bragg's law and Ewald's sphere

"Real" space $\xrightarrow{\mathcal{F}}$ Reciprocal space

Bragg's law

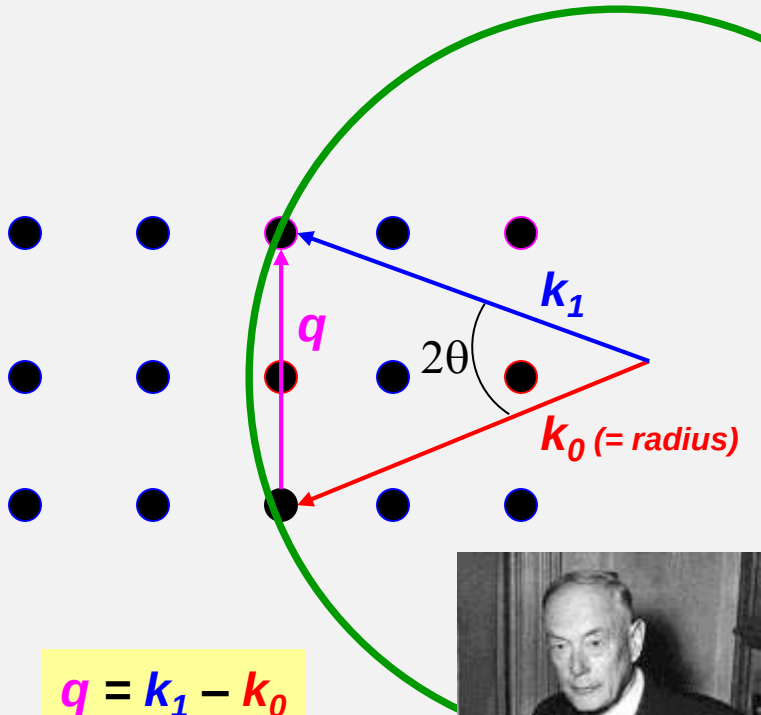


1862–1942 1890-1971

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

Elastic (Thompson's) scattering

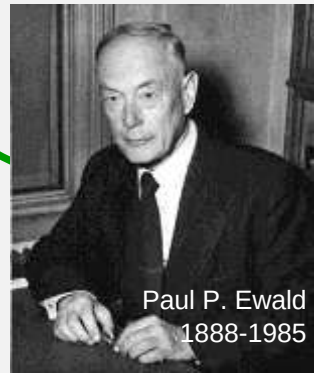
Ewald's sphere



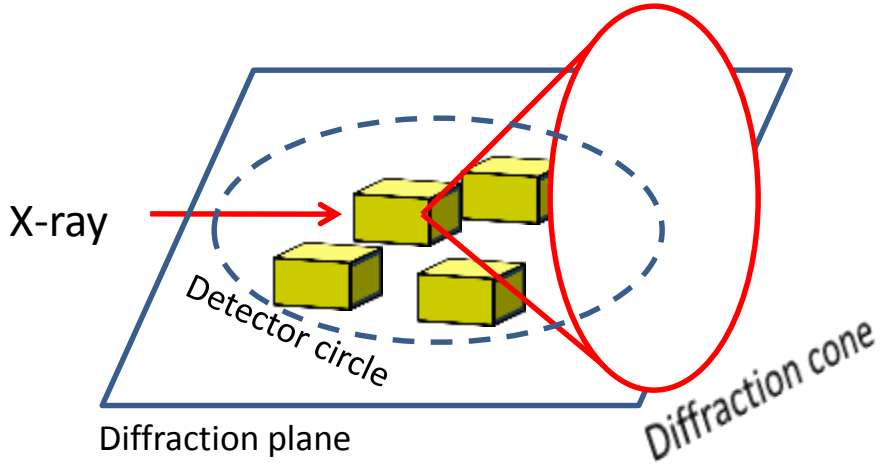
$q = k_1 - k_0$

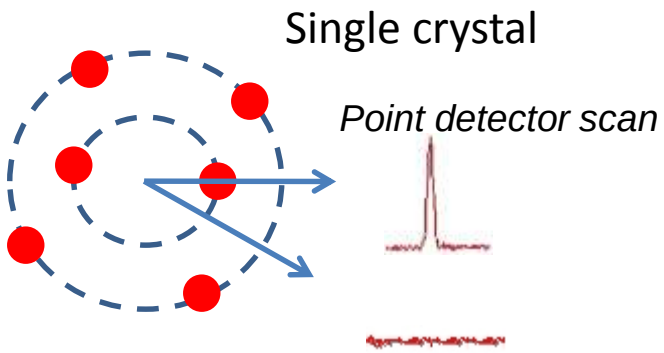
q: scattering vector

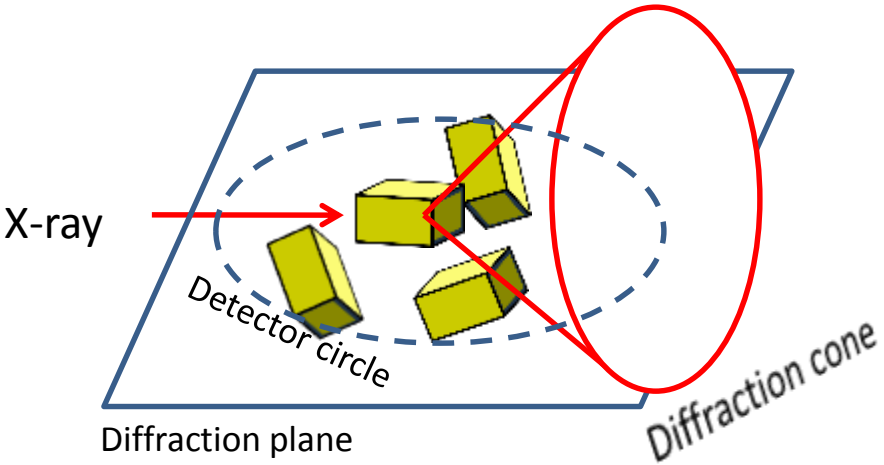
$q = (4\,\pi/\lambda)\,\sin\theta$

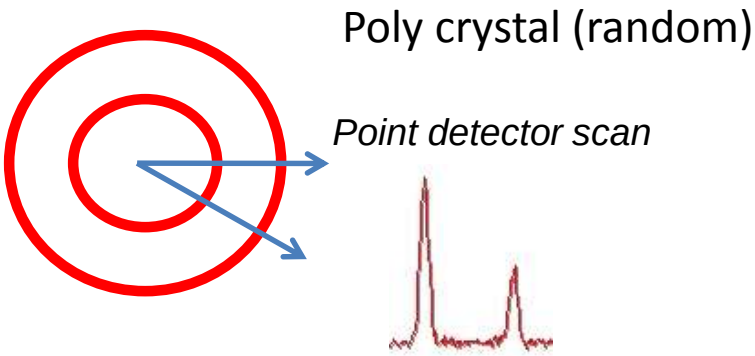


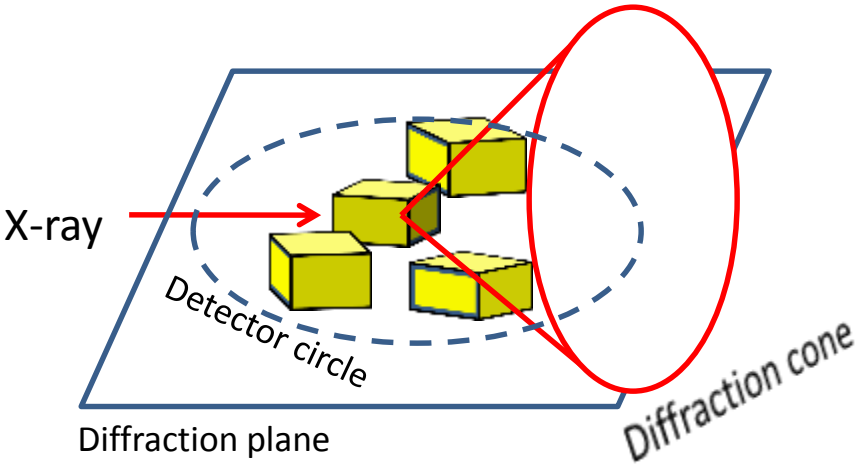
Paul P. Ewald
1888-1985

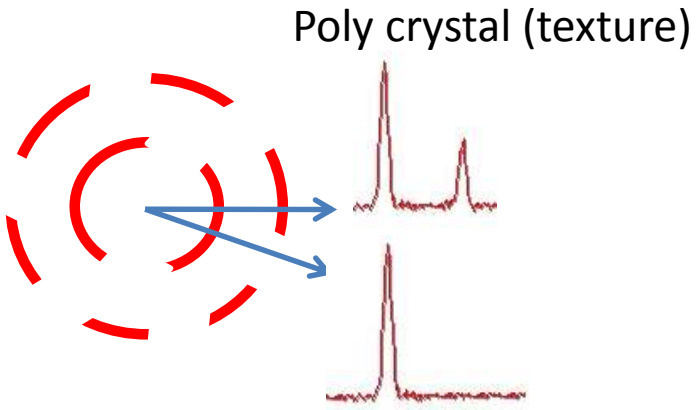

X-ray
Detector circle
Diffraction plane
Diffraction cone


Single crystal
Point detector scan

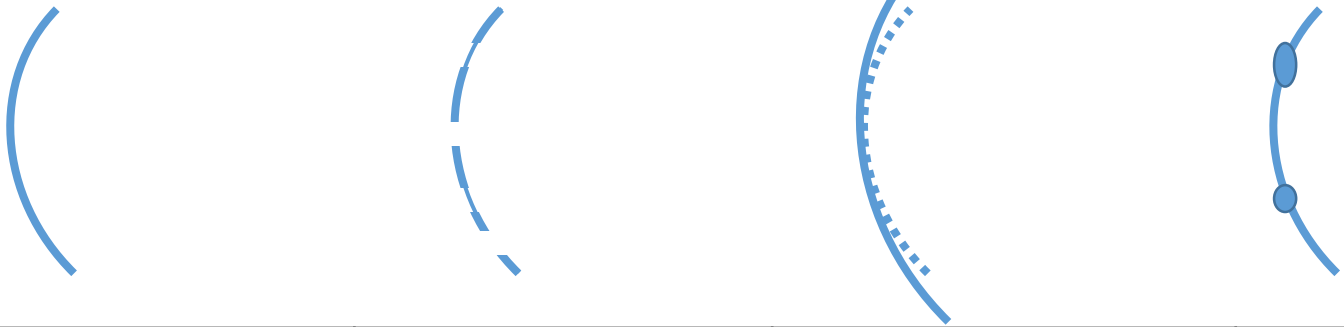

X-ray
Detector circle
Diffraction plane
Diffraction cone


Poly crystal (random)
Point detector scan

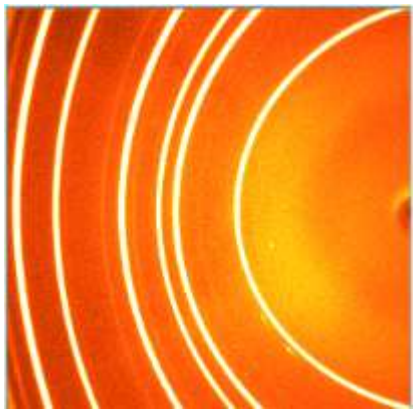

X-ray
Detector circle
Diffraction plane
Diffraction cone

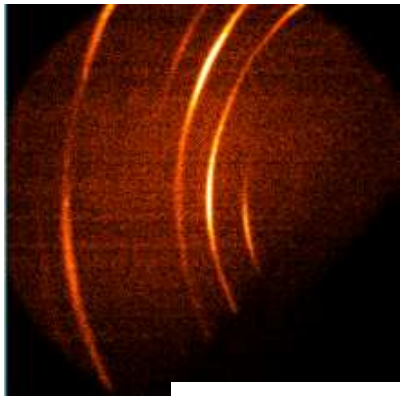

Poly crystal (texture)

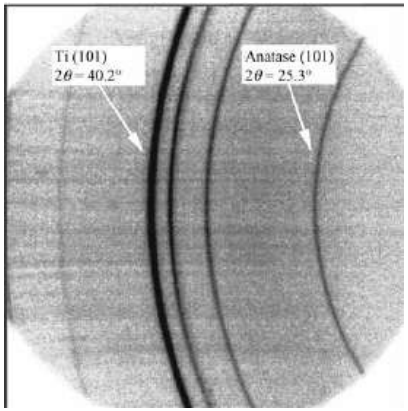
Two-dimensional XRD:

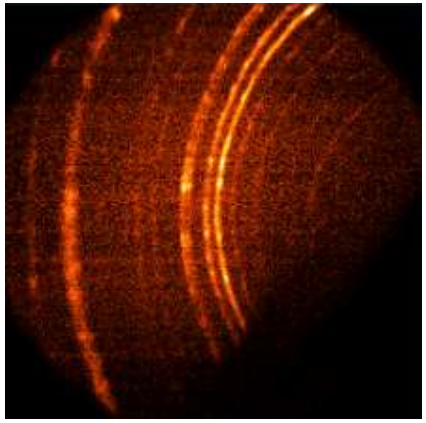


Continuous intensity distribution along diffraction ring, no distortion	Intensity varies along the ring	Distortion / shift of the diffraction ring	Spotty features in the diffraction ring
No texture. Homogenous grain size distribution.	Texture	Residual stress	Non homogenous distribution of grain sizes; spots due to large grains

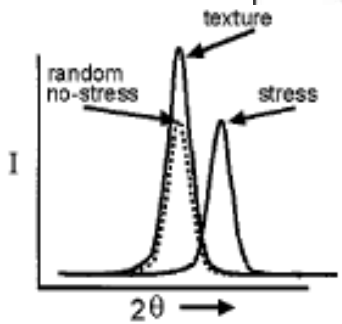


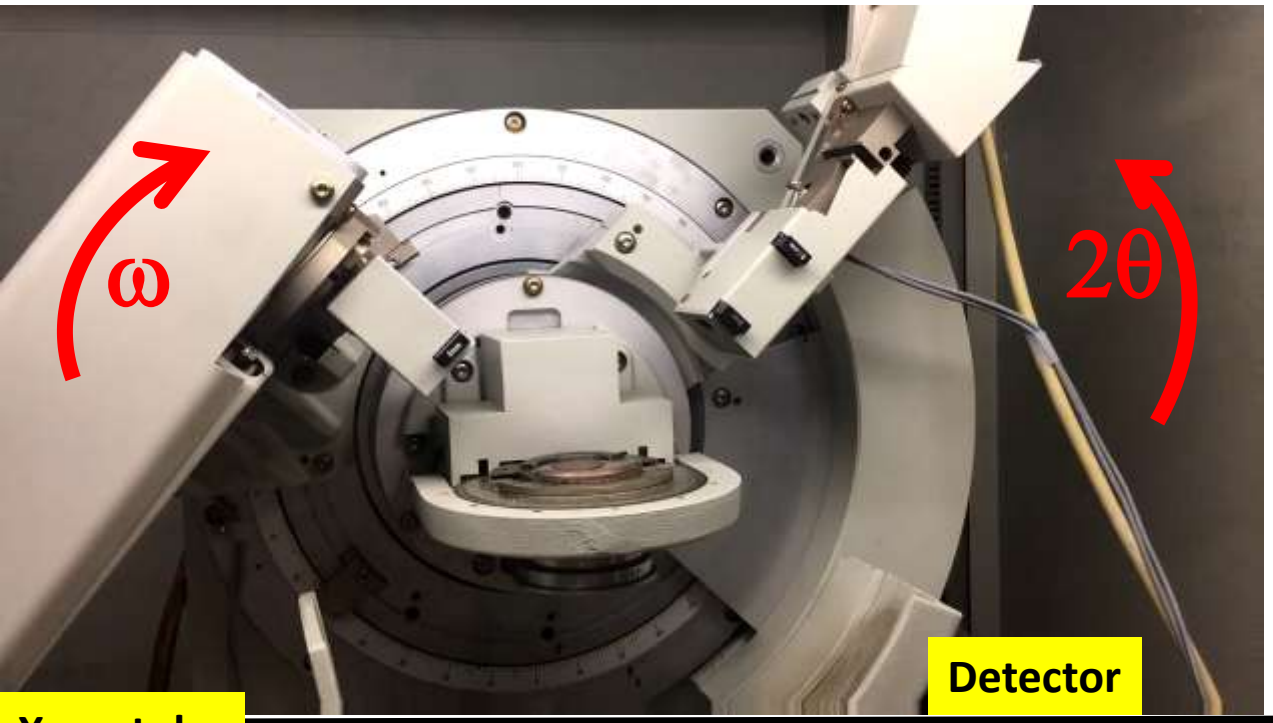




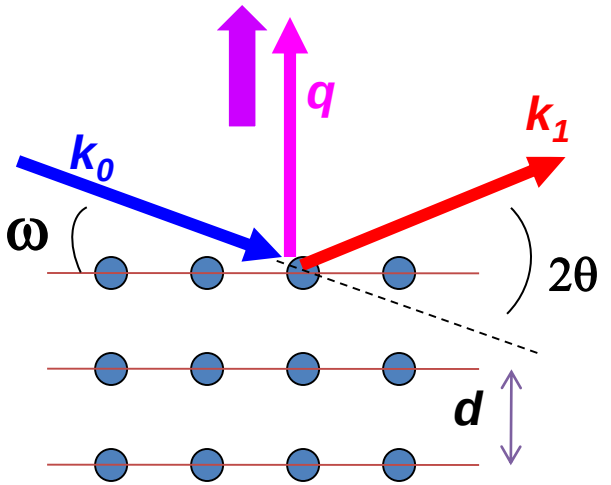


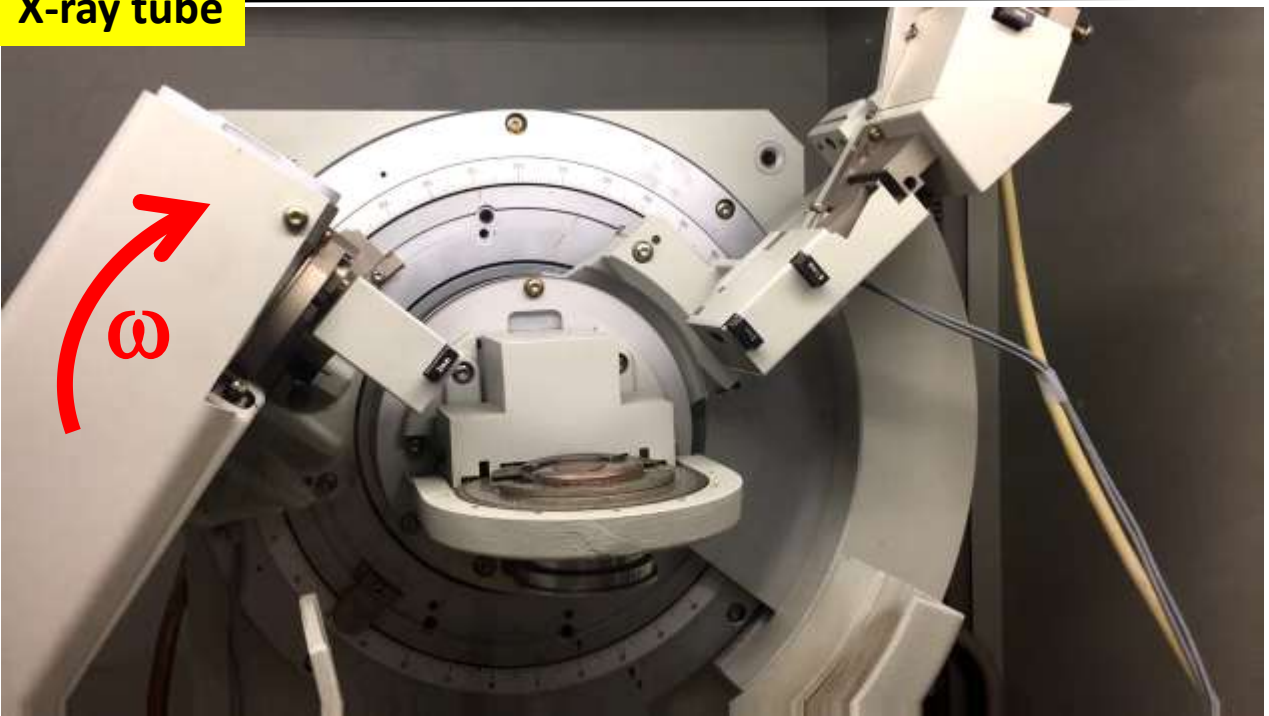
Data from: He et al, Adv in X-ray Analysis 37, vol 46 (2003)





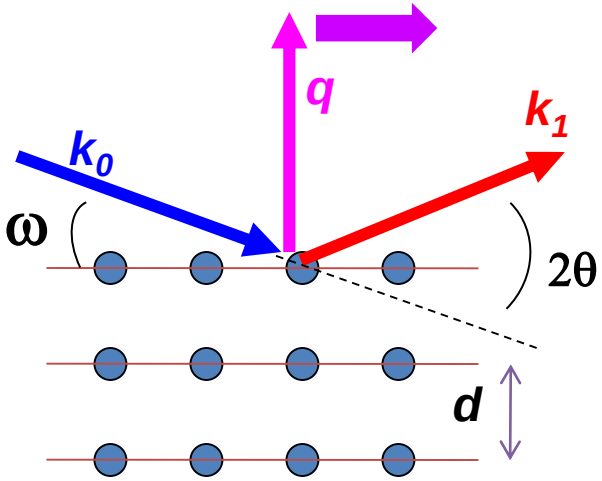
2theta/omega scan

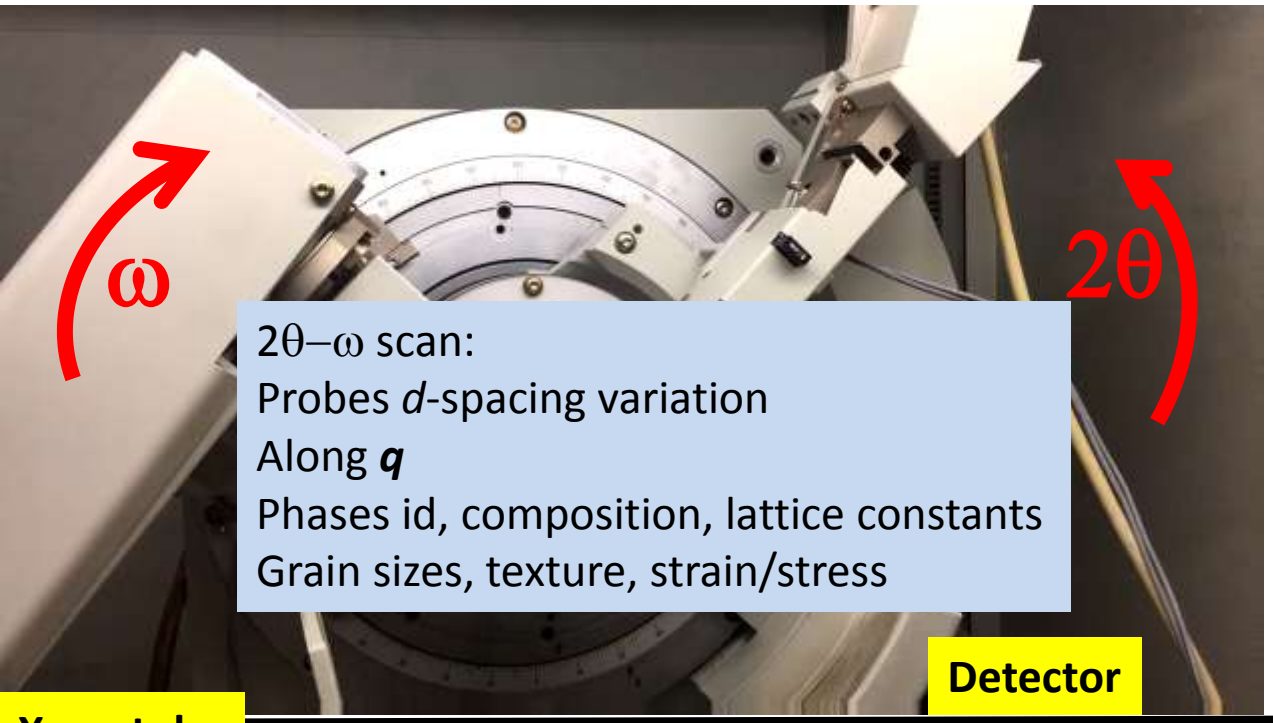




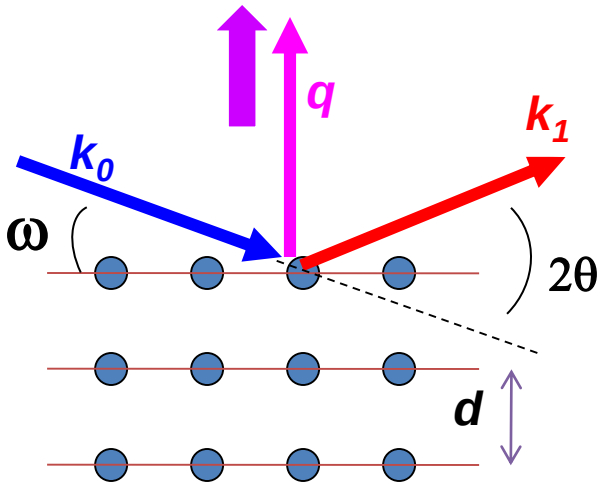
omega scan

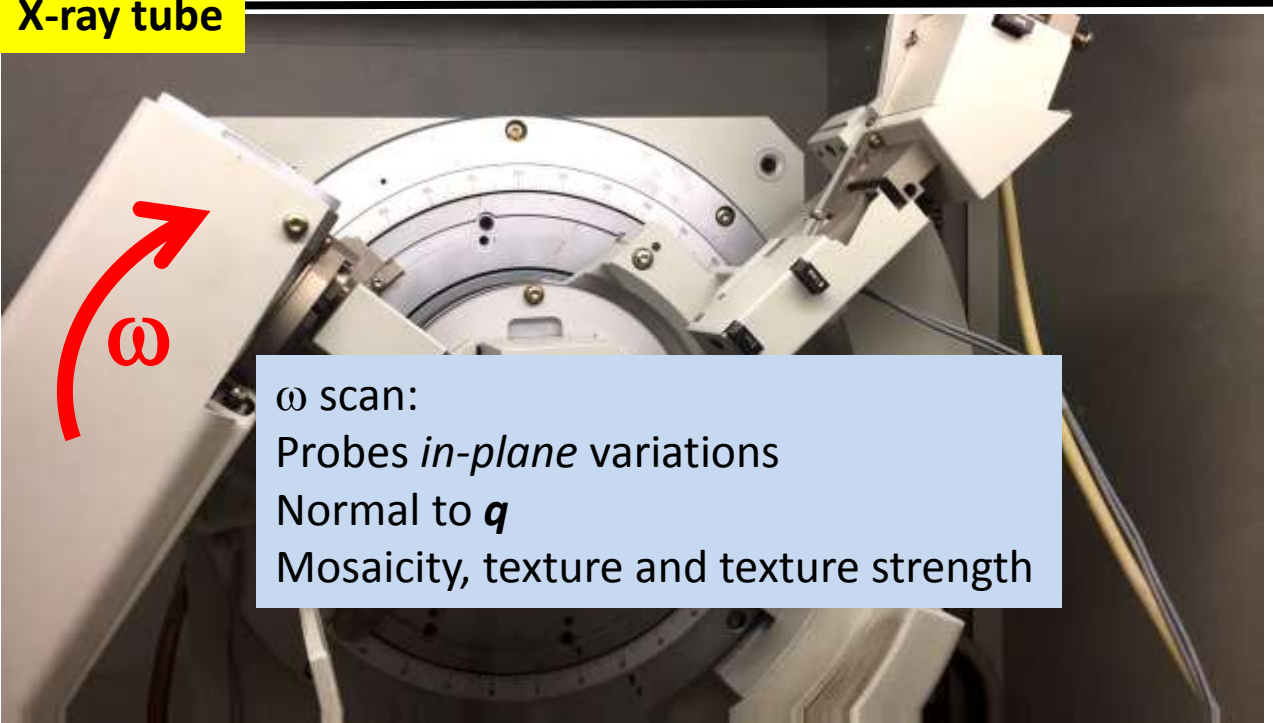
(rocking curve)





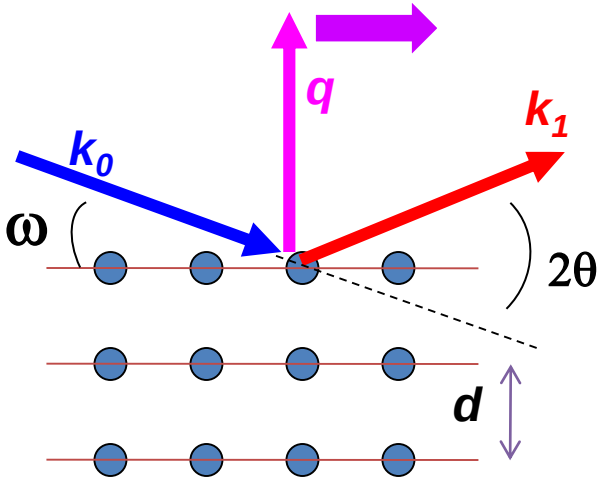
2theta/omega scan

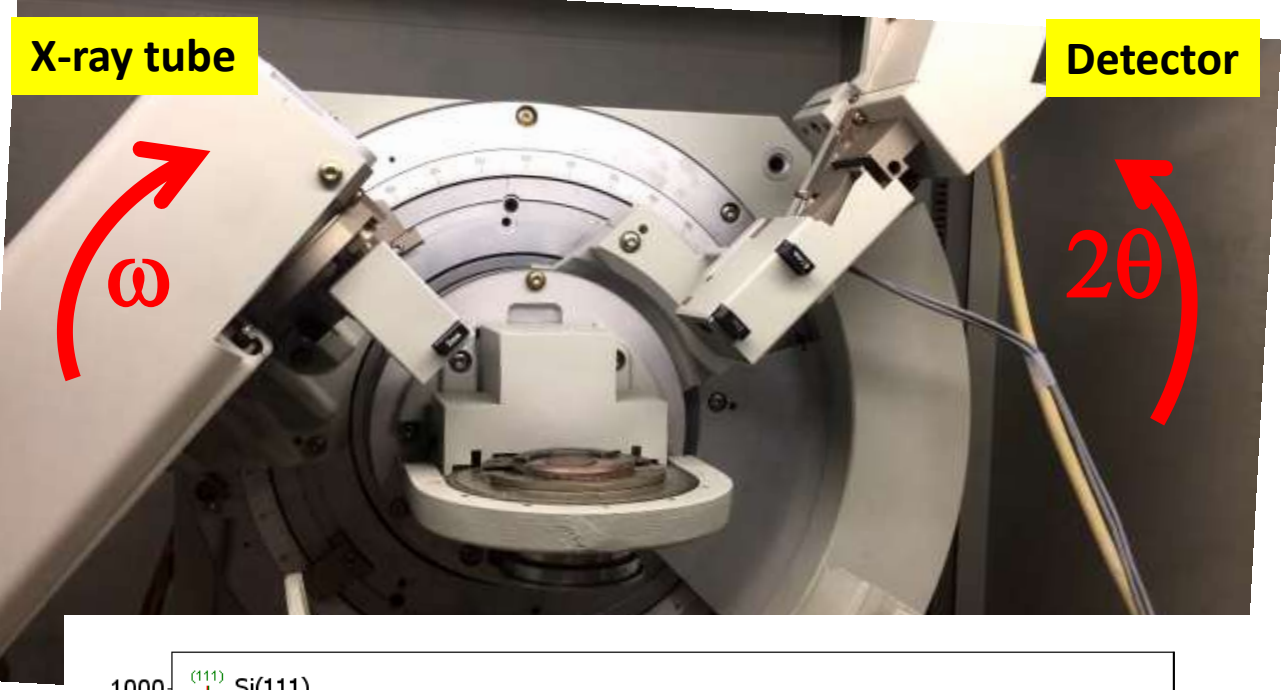




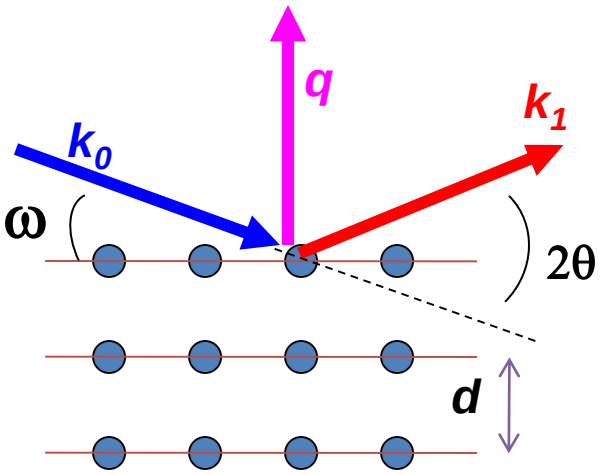
omega scan

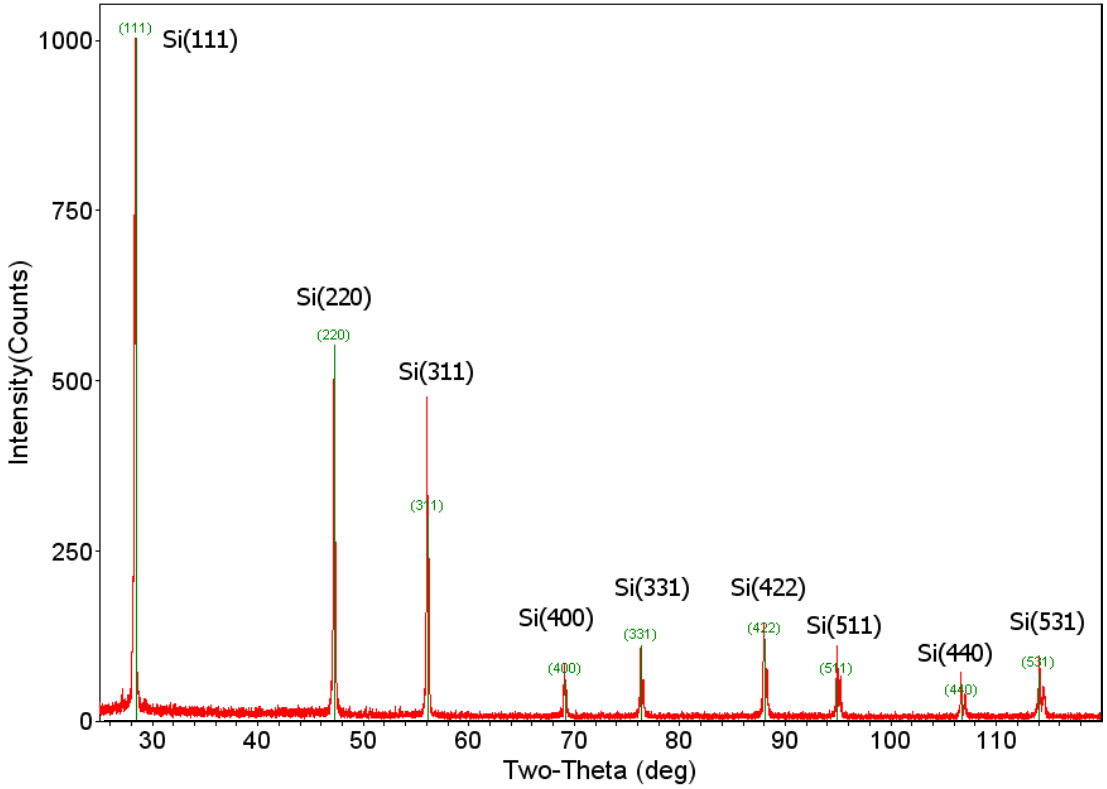
(rocking curve)

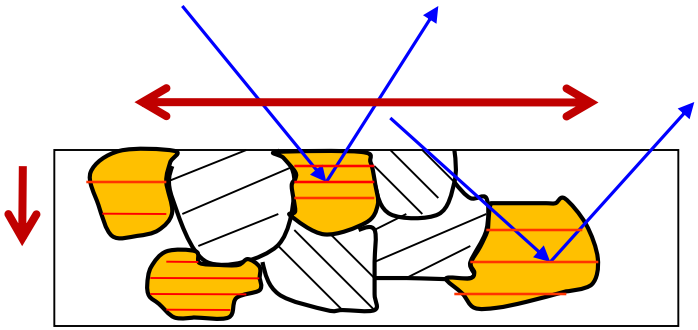




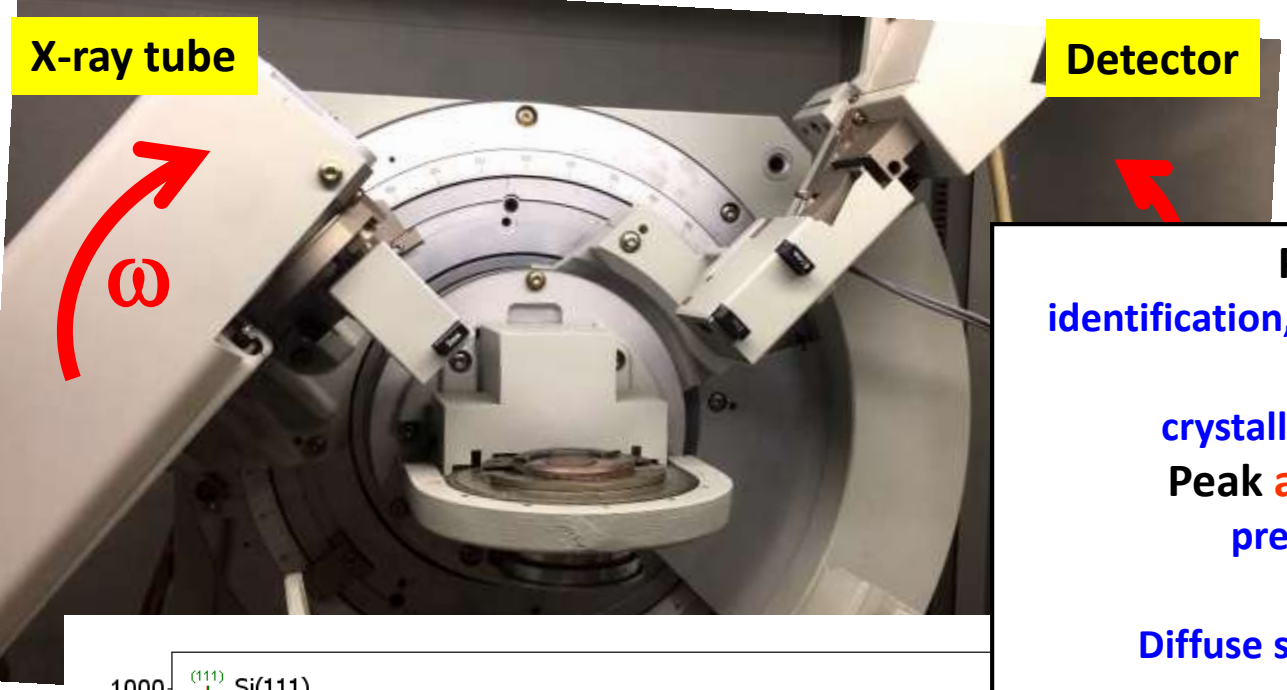
2theta/omega scan



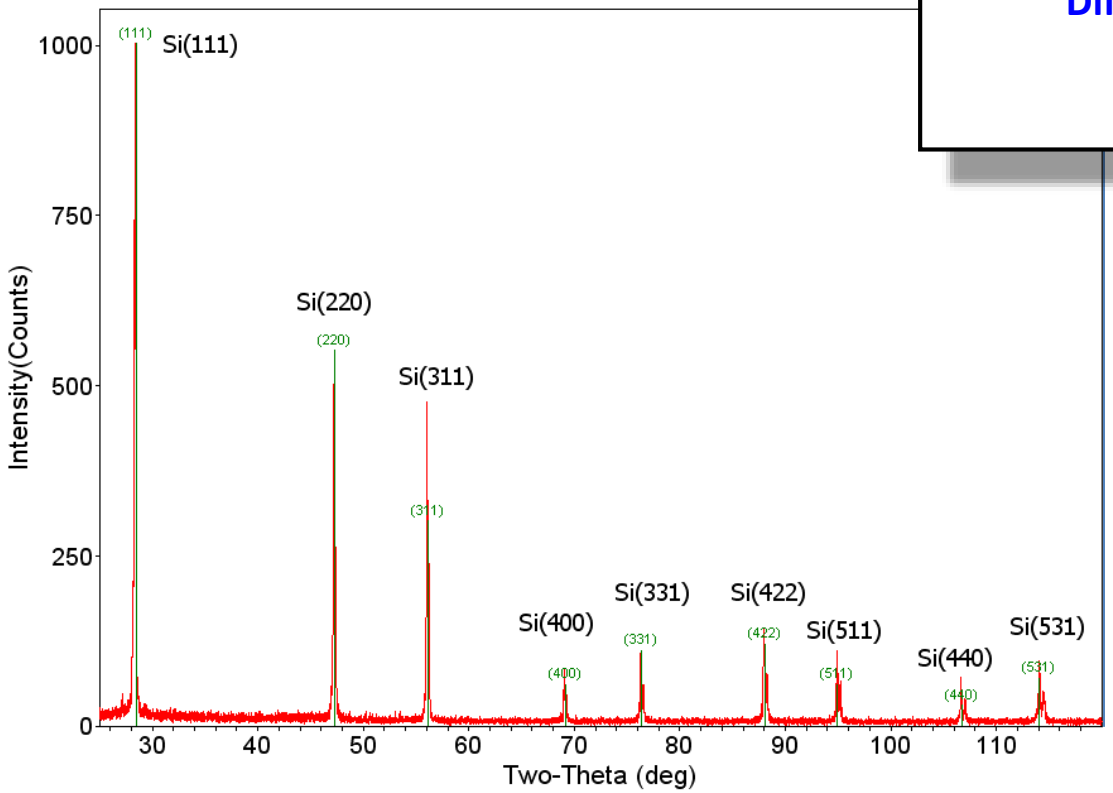


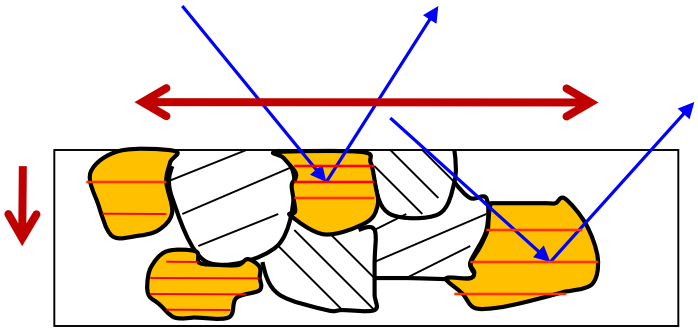


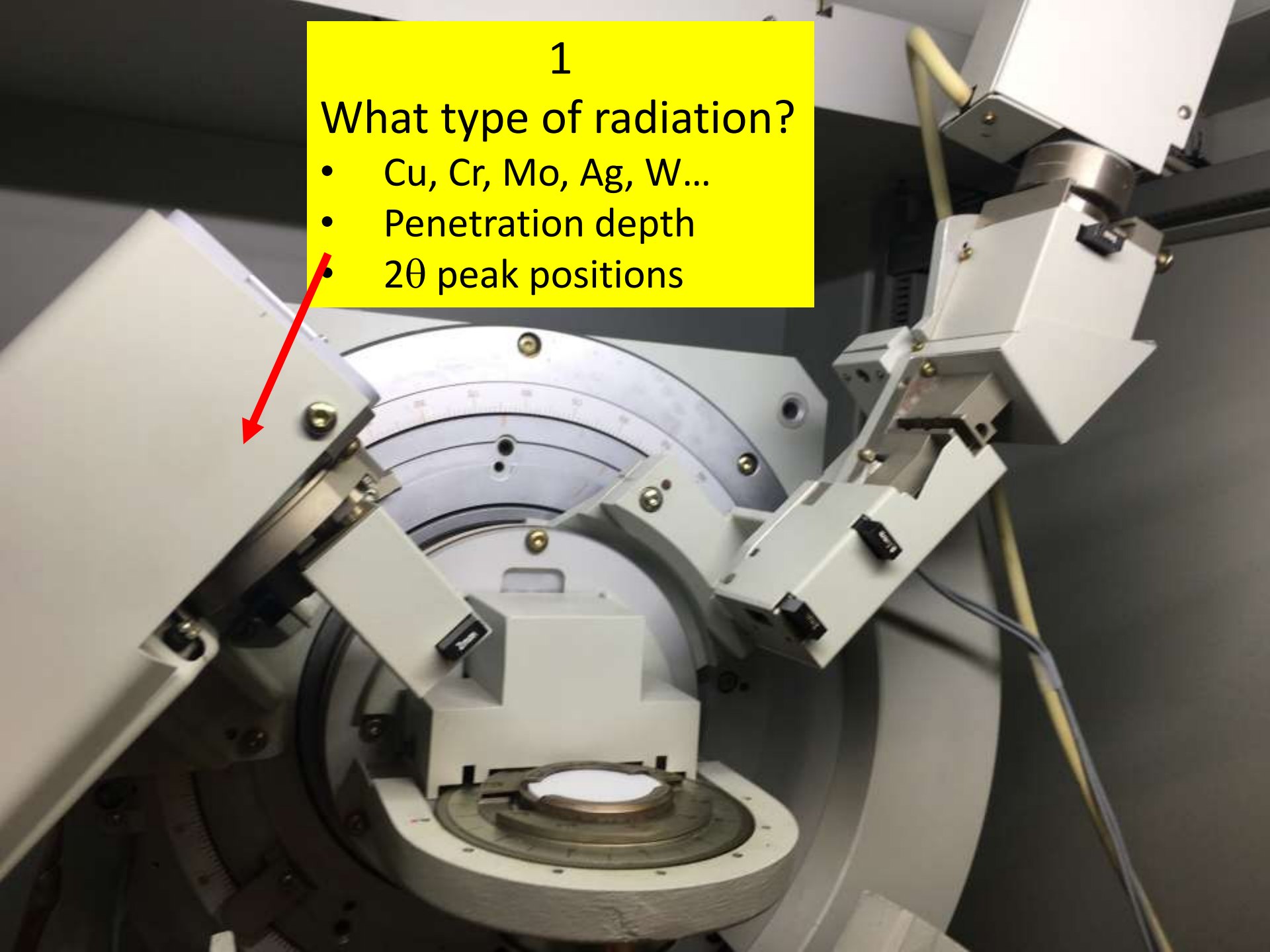
2theta/omega scan

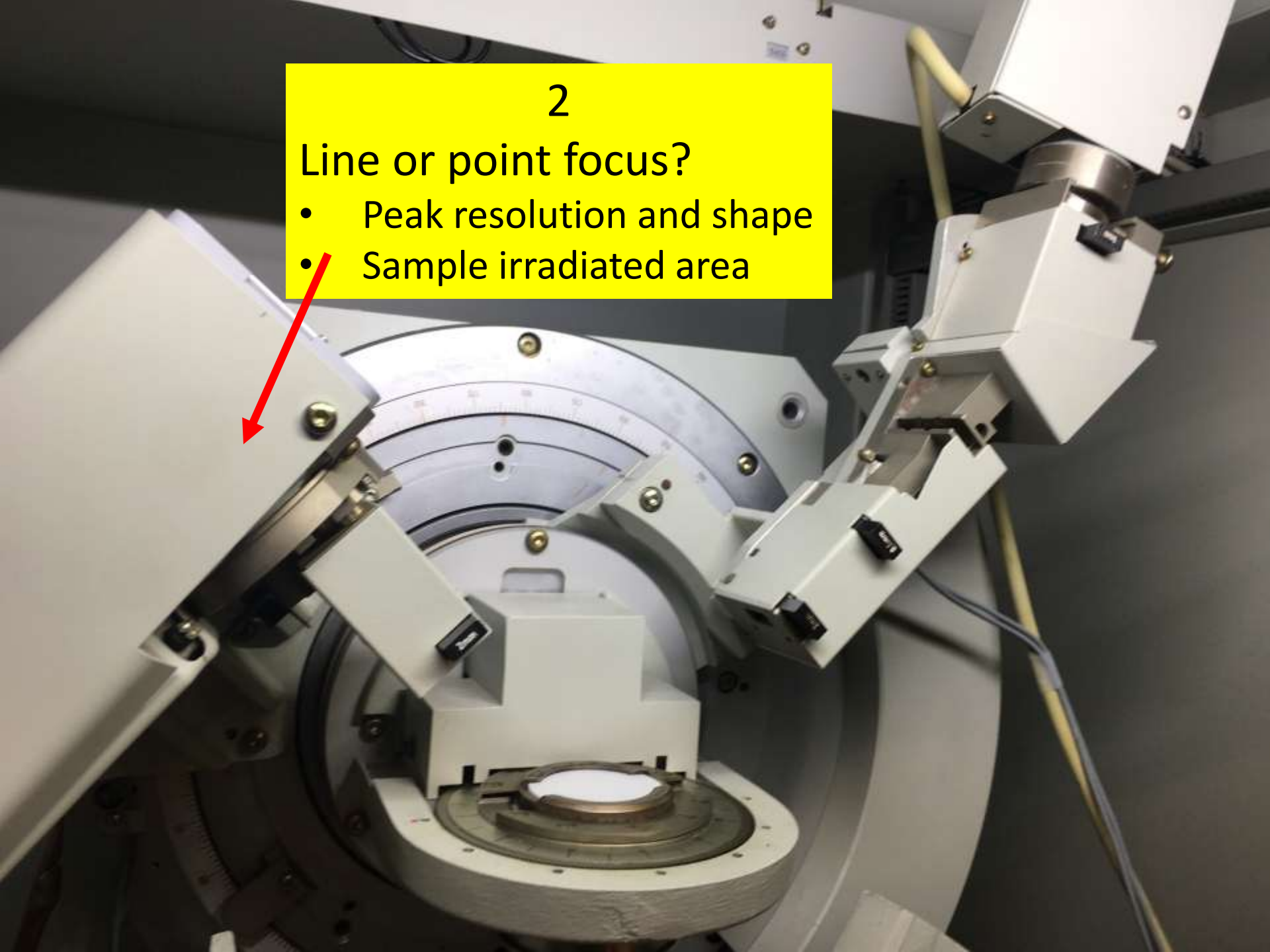


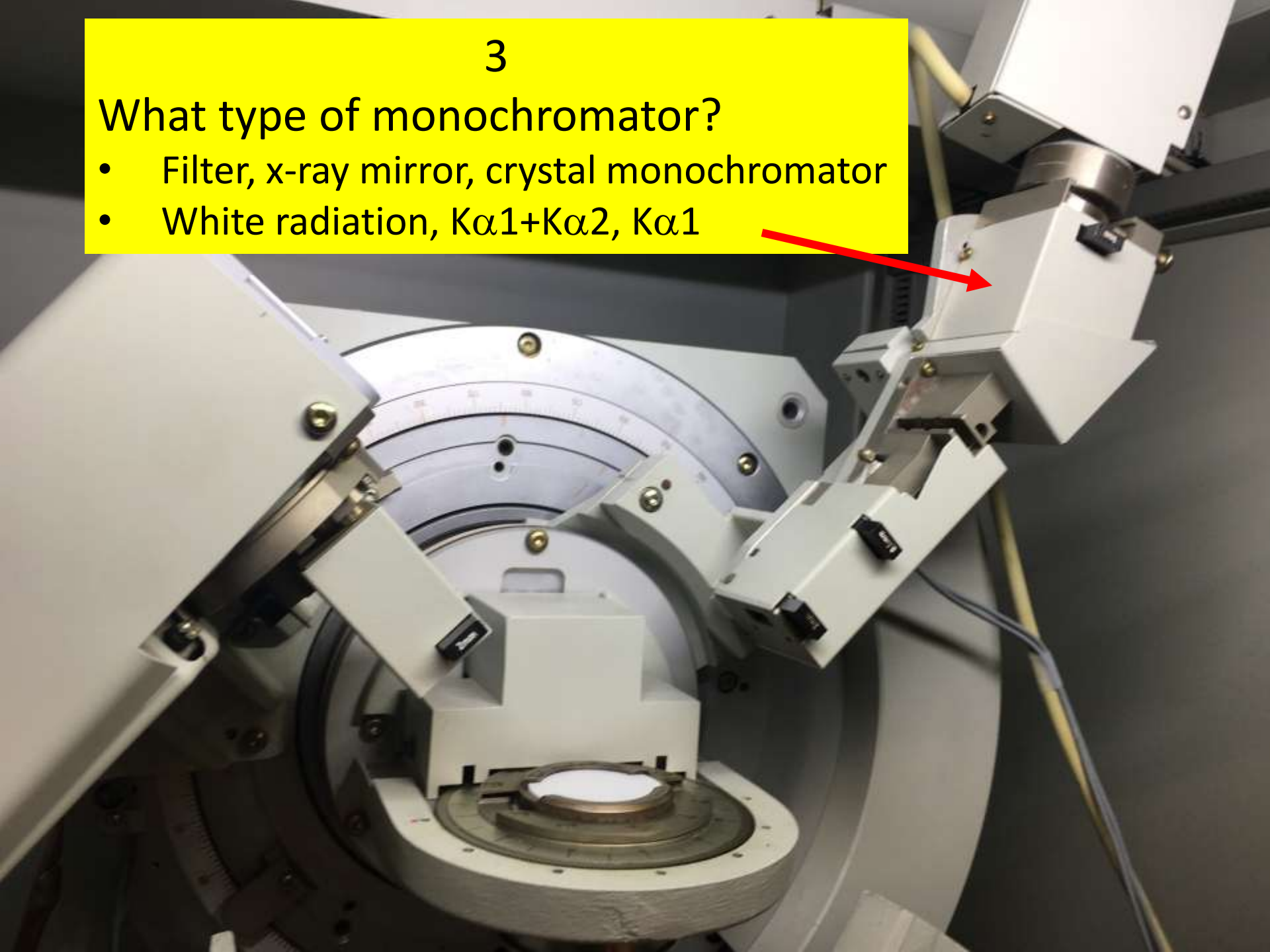
Peak position:
identification, structure, lattice parameter
Peak width:
crystallite size, strain, defects
Peak area or height ratio:
preferred orientation
Peak tails:
Diffuse scattering, point defects
Background:
amorphous contents

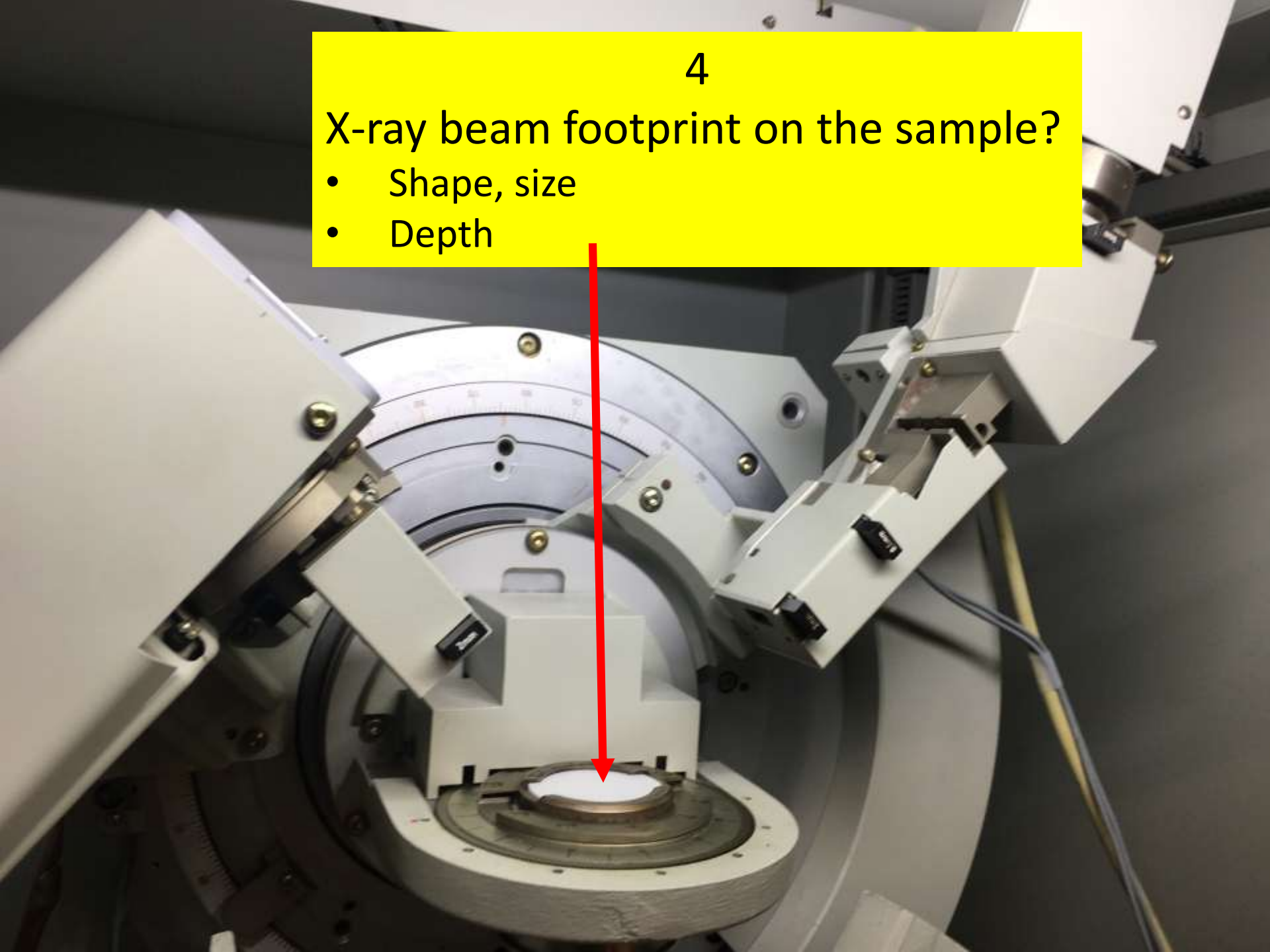


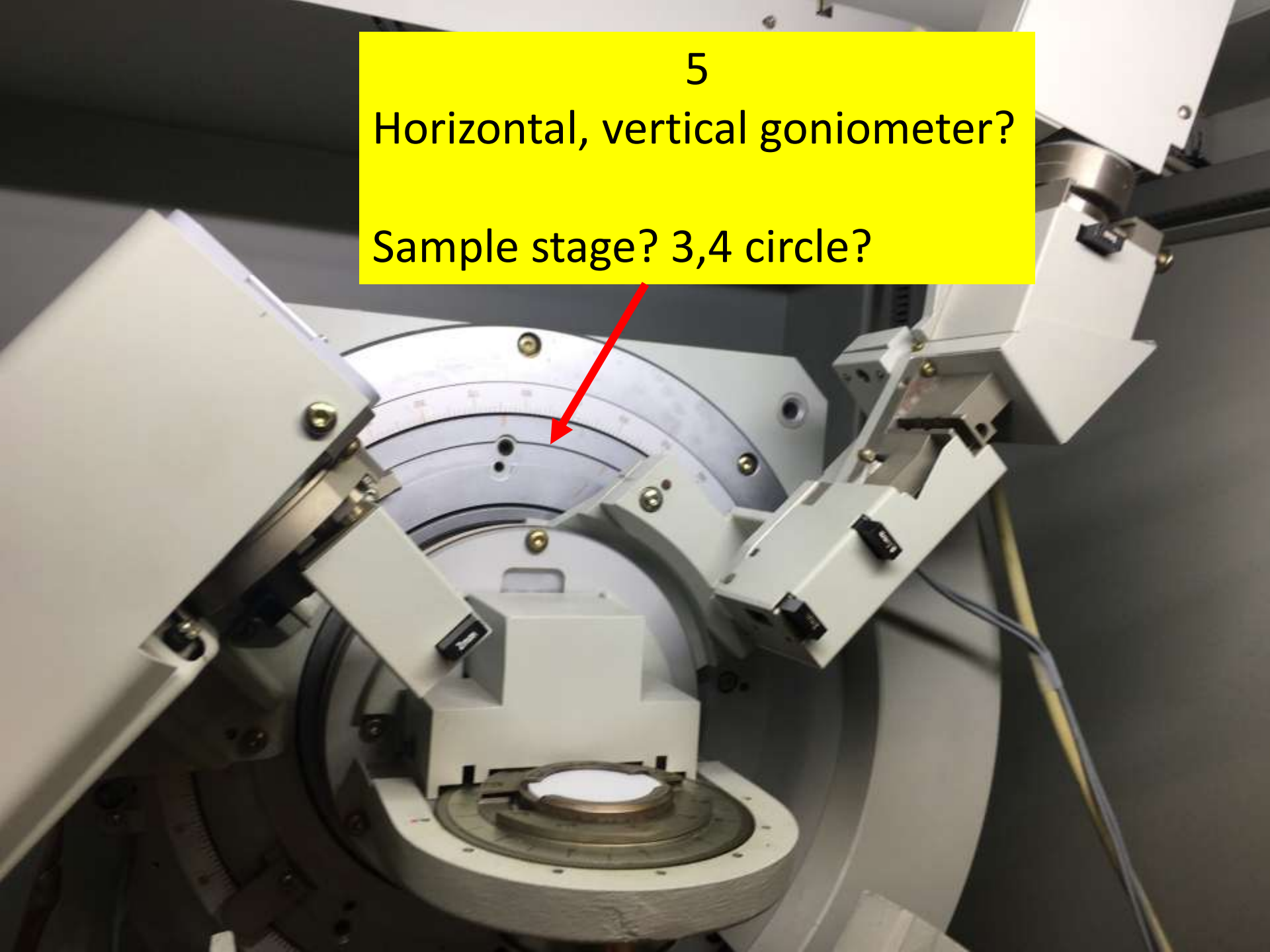


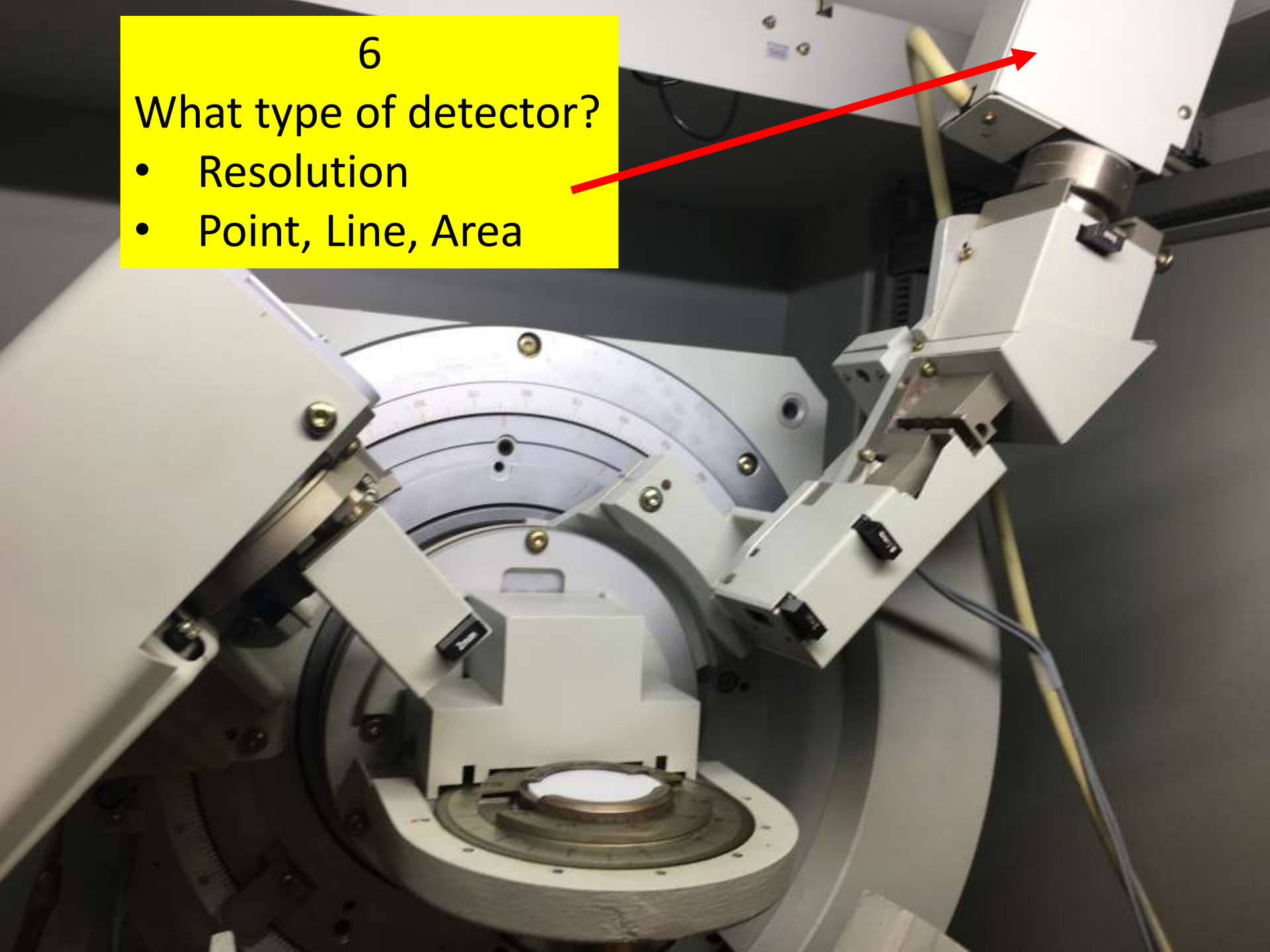

1
What type of radiation?
• Cu, Cr, Mo, Ag, W…
• Penetration depth
• 2θ peak positions

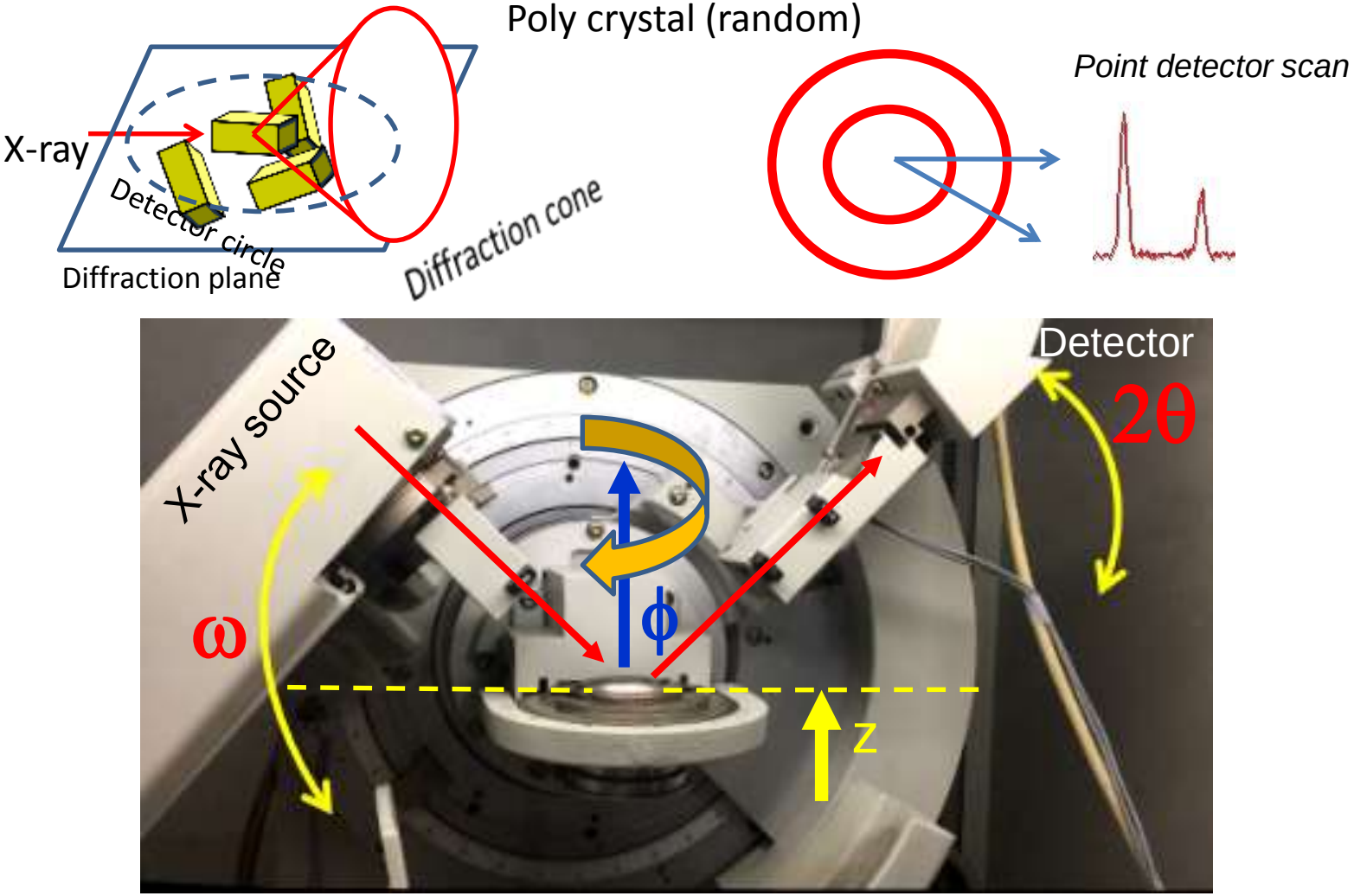

2
Line or point focus?
• Peak resolution and shape
• Sample irradiated area


3
What type of monochromator?
• Filter, x-ray mirror, crystal monochromator
• White radiation, Kα1+Kα2, Kα1

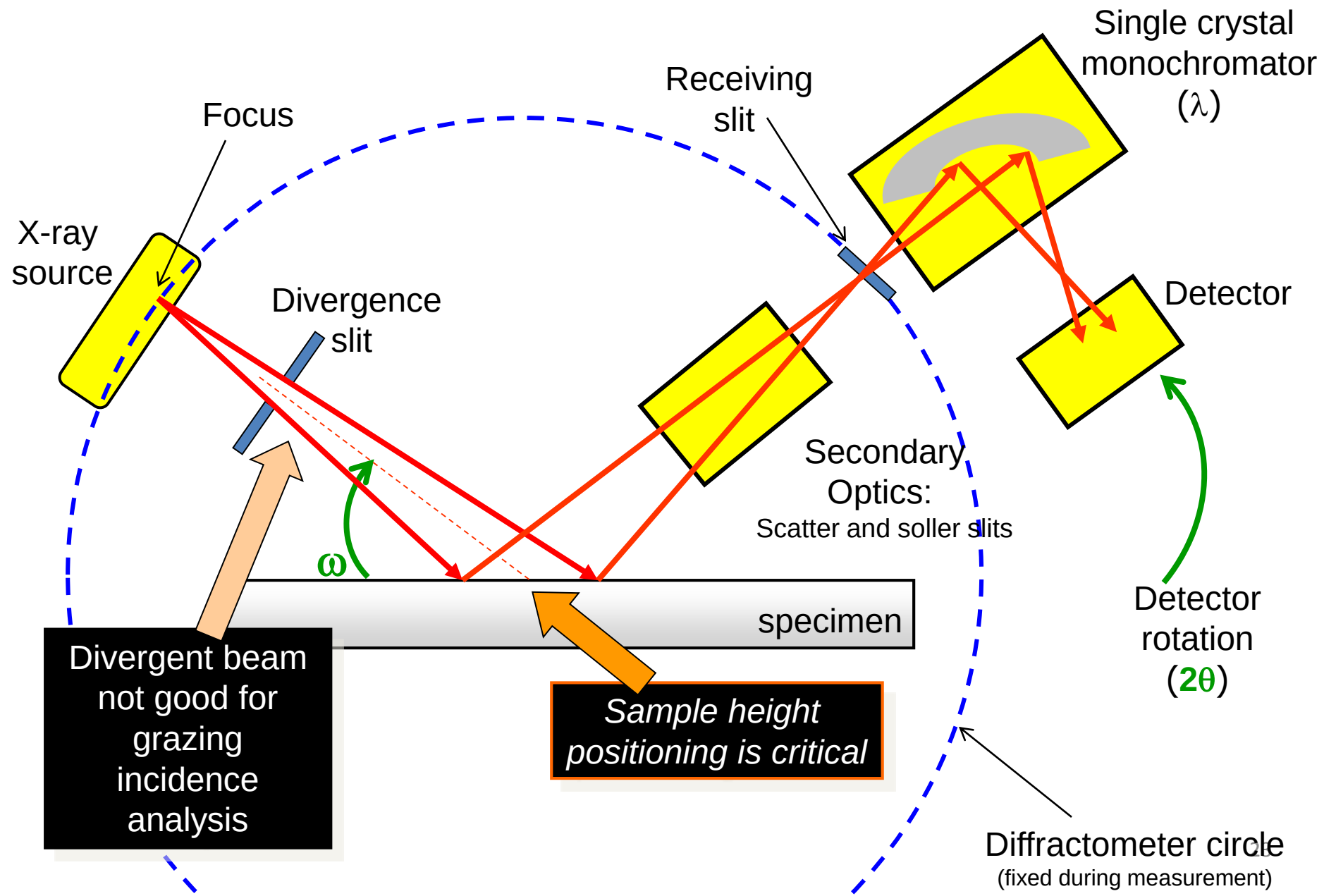

4
X-ray beam footprint on the sample?
• Shape, size
• Depth


5
Horizontal, vertical goniometer?
Sample stage? 3,4 circle?

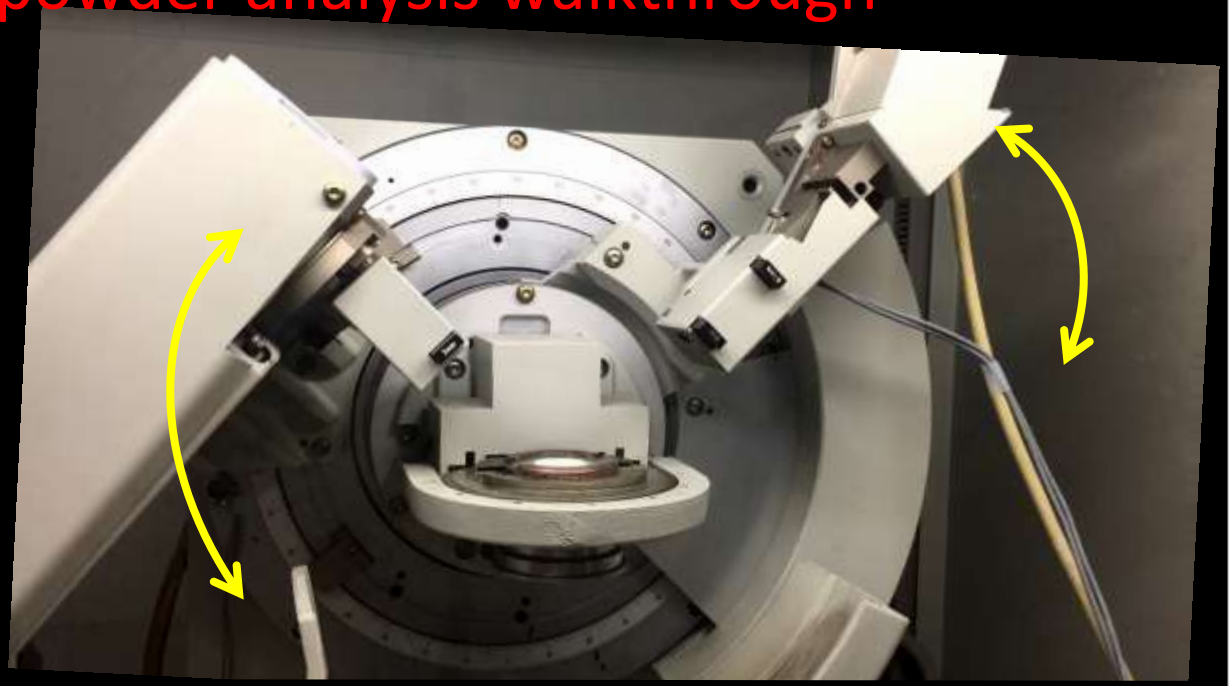

6
What type of detector?
• Resolution
• Point, Line, Area


Poly crystal (random)
Point detector scan
X-ray
Detector circle
Diffraction plane
Diffraction cone
X-ray source
Detector
2θ
ω
ϕ
z
Poly crystal (texture)
X-ray
Detector circle
Diffraction plane
Diffraction cone

Bragg-Brentano focusing configuration



XRD powder analysis walkthrough



Crystalline phases

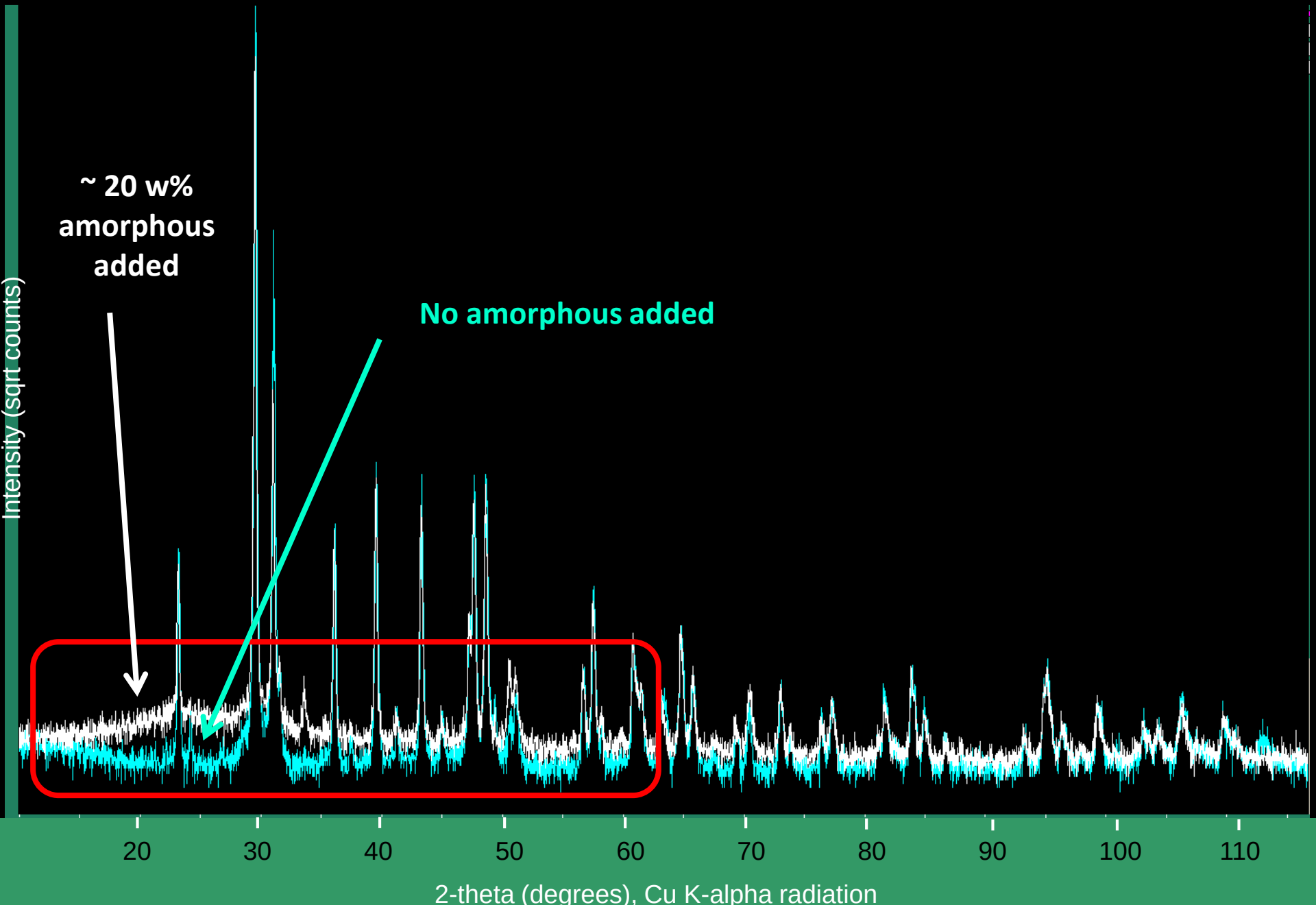
Amorphous (zero background holder)

Intensity (sqrt counts)

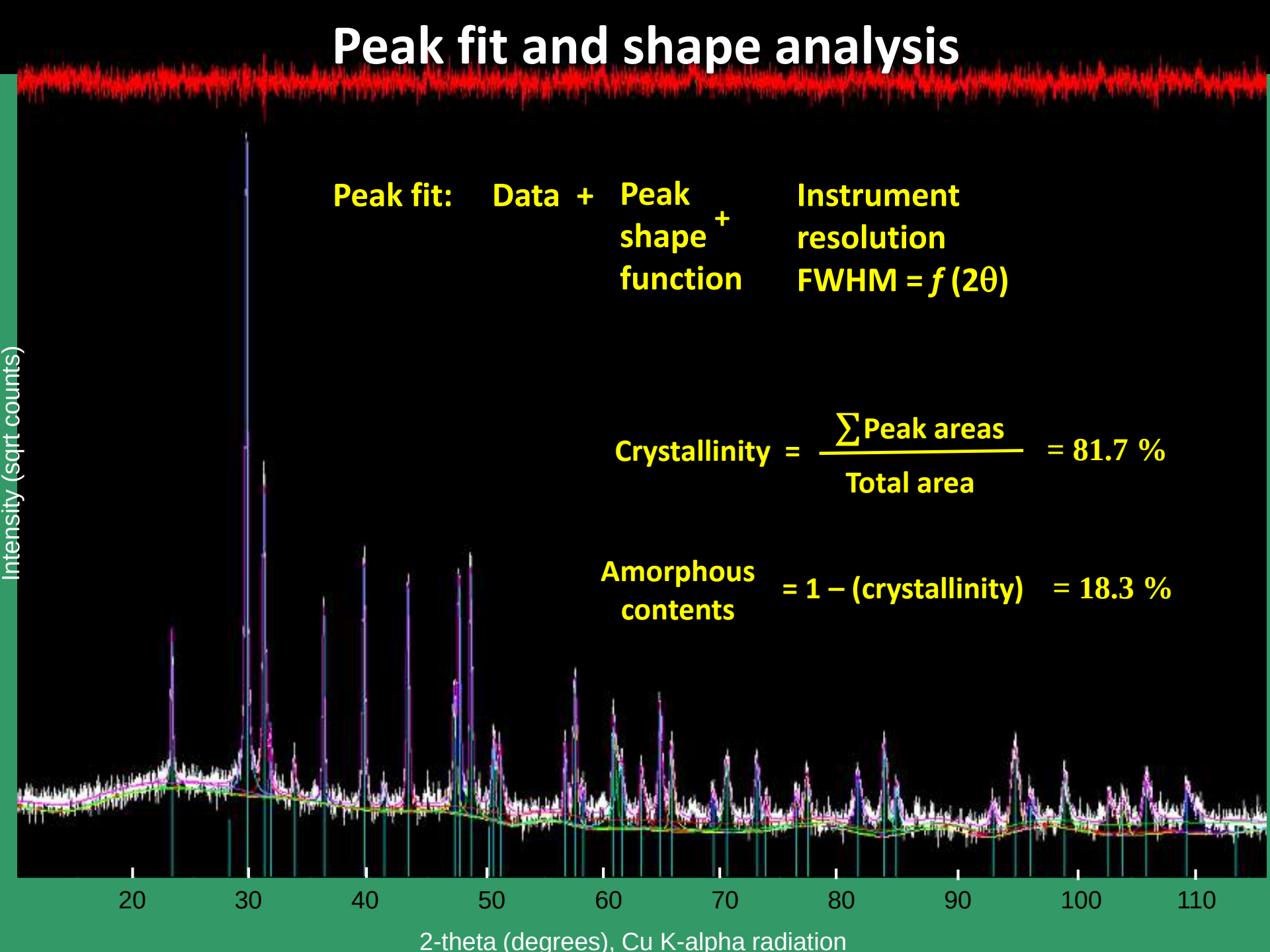
20 30 40 50 60 70 80 90 100 110

2-theta (degrees), Cu K-alpha radiation

XRD powder pattern

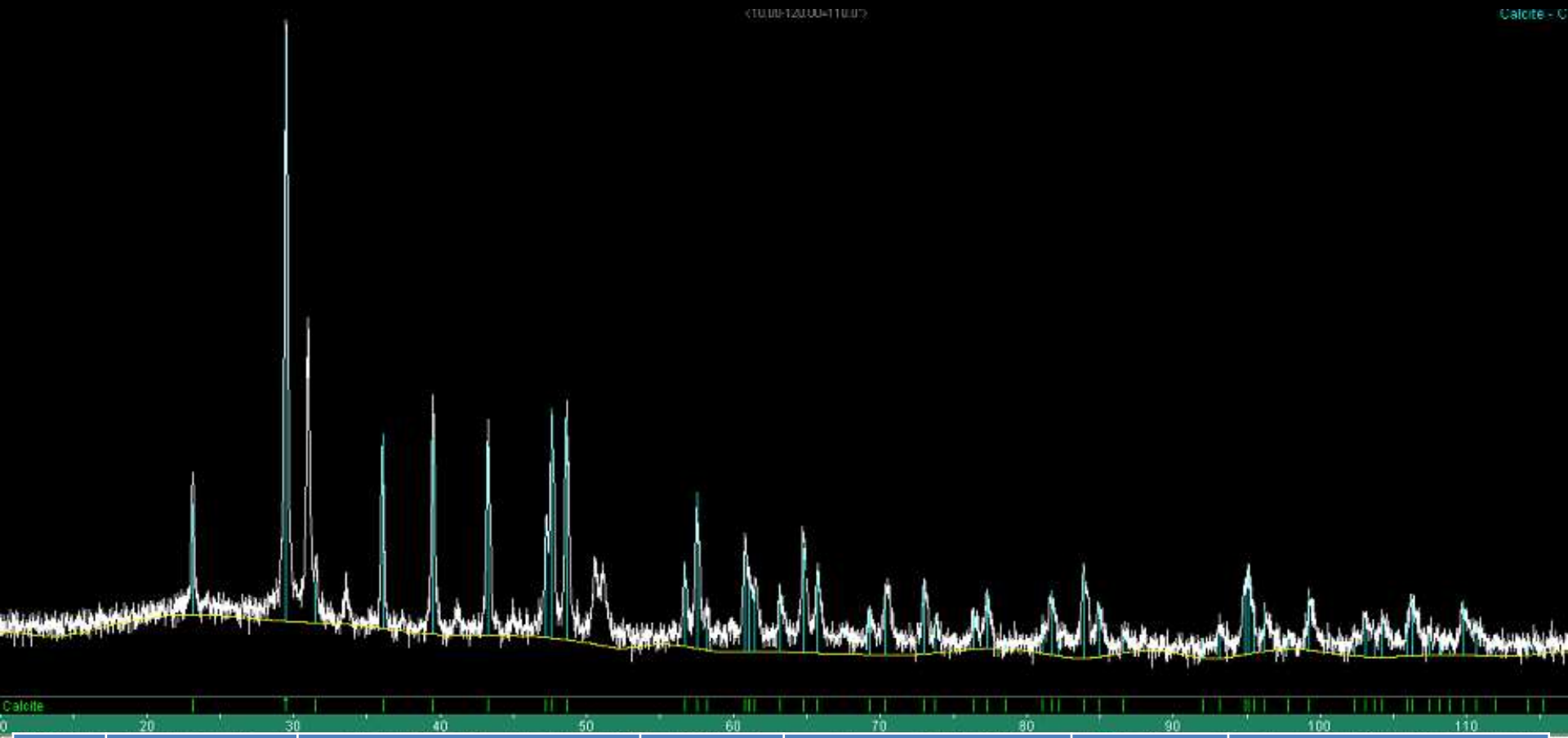


Peak fit and shape analysis



Search / match

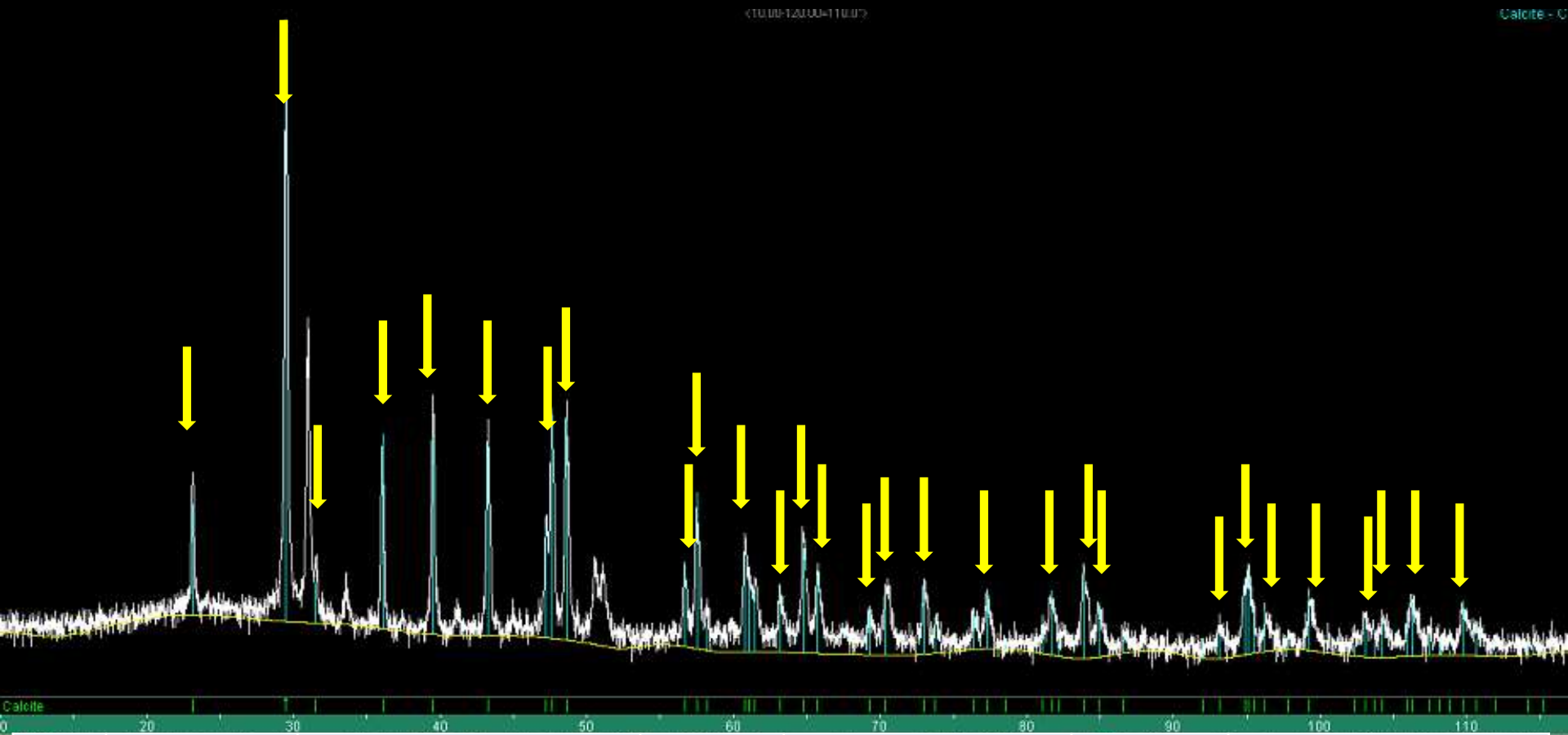
Peak position + intensity ratio → Search against… → ICDD PDF4 database ICSD, etc. → Match! Fingerprinting identification of phases



	Hits	Formula	FOM	PDF	RIR	Space group
	Calcite	$CaCO_3$	1.1	04-012-0489	3.45	R-3c(167)
	Dolomite	$Ca_{1.07}Mg_{0.93}(CO_3)_2$	15.0	04-011-9830	2.51	R-3(148)

Search / match

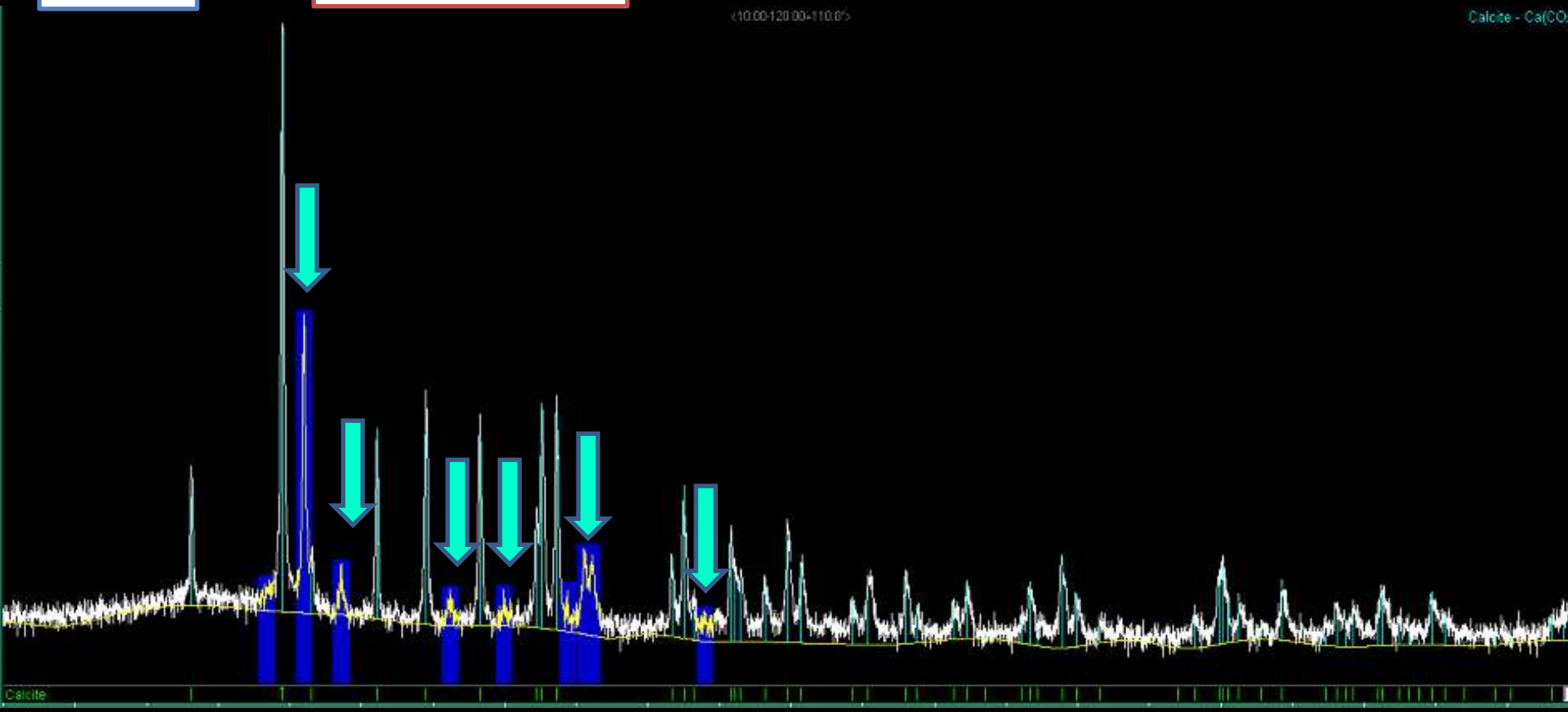
Peak position + intensity ratio → Search against… → ICDD PDF4 database ICSD, etc. → Match! Fingerprinting identification of phases



	Hits	Formula	FOM	PDF	RIR	Space group
√	Calcite	$CaCO_3$	1.1	04-012-0489	3.45	R-3c(167)
	Dolomite	$Ca_{1.07}Mg_{0.93}(CO_3)_2$	15.0	04-011-9830	2.51	R-3(148)

Search / match

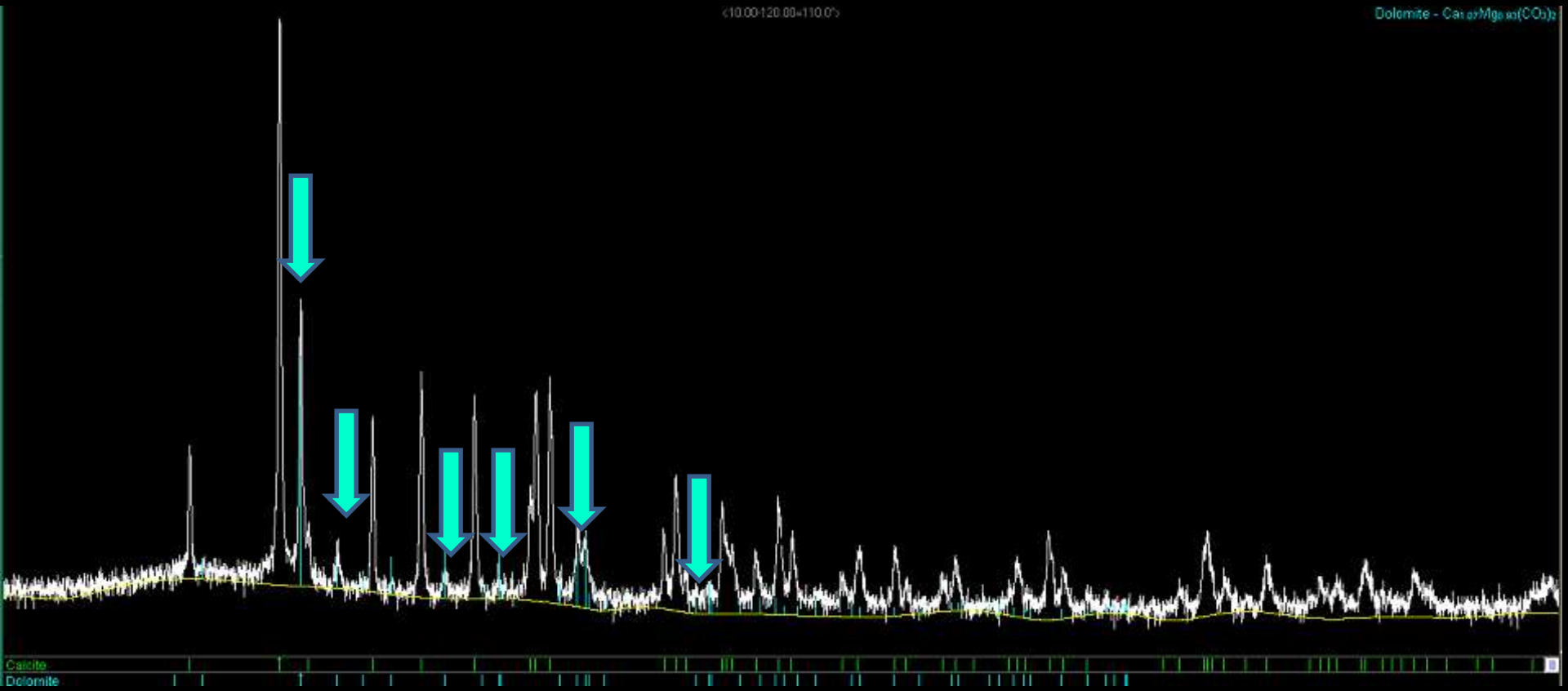
Second round → Focus on unmatched peaks



	Hits	Formula	FOM	PDF	RIR	Space group
√	Calcite	$CaCO_3$	1.1	04-012-0489	3.45	R-3c(167)
	Dolomite	$Ca_{1.07}Mg_{0.93}(CO_3)_2$	15.0	04-011-9830	2.51	R-3(148)

Search / match

Second round → Focus on unmatched peaks → Search / Match → Identify additional phases (~ > 1 w%)

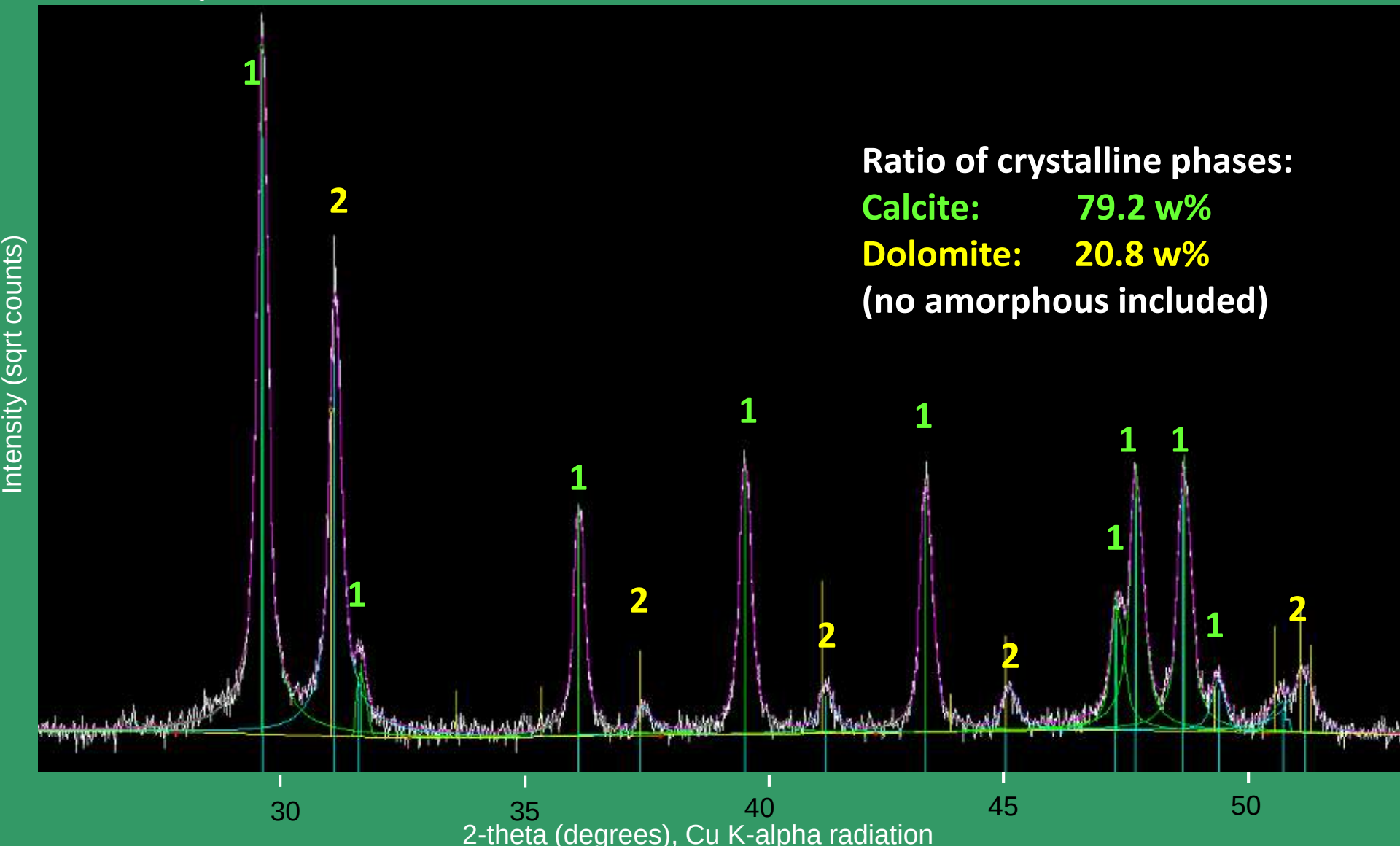


	Hits	Formula	FOM	PDF	RIR	Space group
√	Calcite	$CaCO_3$	1.1	04-012-0489	3.45	R-3c(167)
√	Dolomite	$Ca_{1.07}Mg_{0.93}(CO_3)_2$	15.0	04-011-9830	2.51	R-3(148)

Quant: RIR reference intensity ratio

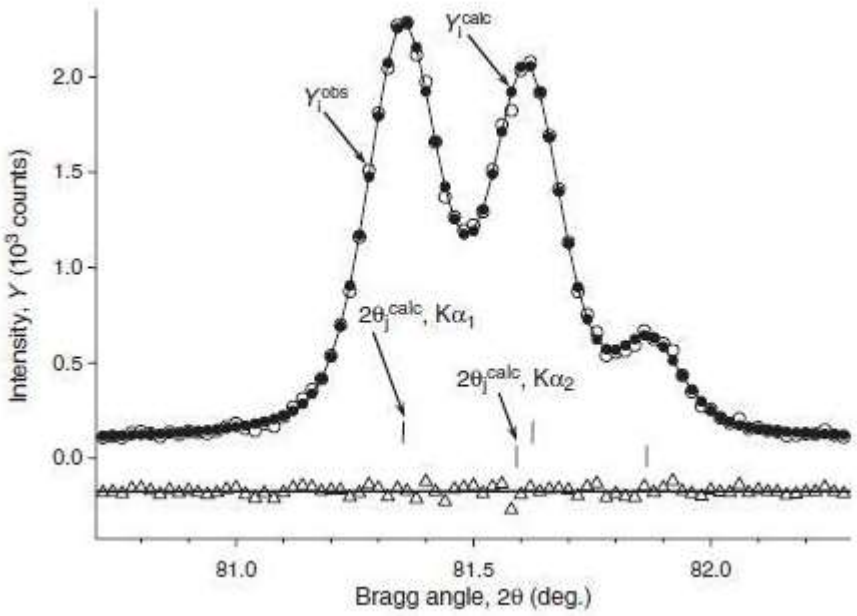
$$\left(\text{Ratio of crystalline phases}\right) \sim \left(\text{Ratio of peak areas corrected by RIR of each phase}\right)$$

$$RIR \sim I / I_{corundum}$$



Ratio of crystalline phases:
Calcite: 79.2 w%
Dolomite: 20.8 w%
(no amorphous included)

Rietveld refinement



Non-linear least square minimization

For each data point *i*:

$$Y_1^{calc} = kY_1^{obs}$$
$$Y_2^{calc} = kY_2^{obs}$$
$$\dots$$
$$Y_n^{calc} = kY_n^{obs}$$

H. Rietveld (1932-2016)

Minimize this function:

$$\Phi = \sum_{i=1}^{n} w_i (Y_i^{obs} - Y_i^{calc})^2$$

Sum over *n* data points

$$\Phi = \sum_{i=1}^{n} w_i \left(Y_i^{obs} - \left[b_i + \sum_{l=1}^{p} K_l \sum_{j=1}^{m} I_{l,j} y_{l,j}(x_{l,j})\right]\right)^2$$

n data points

p phases

m Bragg reflections for each data *i*

w_i, b_i, K_l, $Y_{l,j}$ weight, background, scale factor and peak shape function

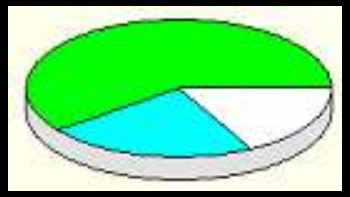
Data + preliminary structure:

<u>Refinement of parameters</u>:

Background
Sample displacement, transparency and zero-shift correction
Peak shape function
Unit cell dimensions
Preferred orientation
Scale factors
Atom positions in the structure
Atomic displacement parameters

Minimize and converge figures of merit/quality: *R*

Rietveld refinement



Calcite: 80.7 w%
Dolomite: 22.2 w%
Amorphous: 17.1 w%

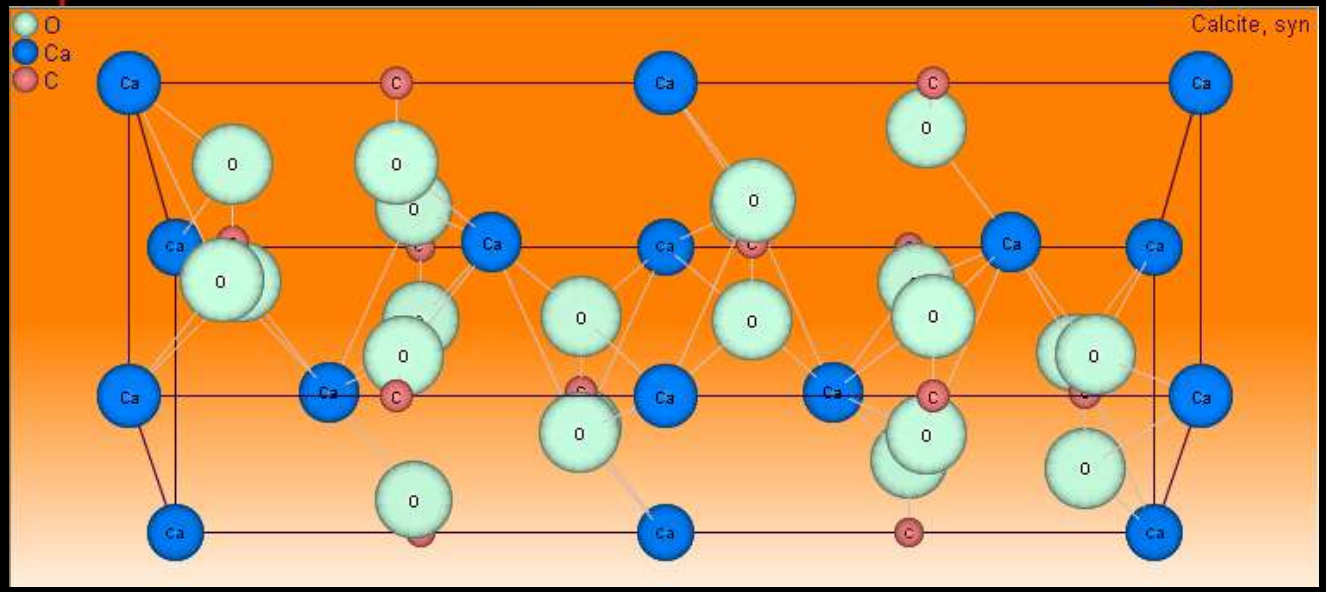
Crystallite size:
Calcite: 56.8 nm
Dolomite: 35.6 nm

Intensity (sqrt counts)

20 30 40 50 60 70 80 90 100 110

2-theta (degrees), Cu K-alpha radiation

Rietveld refinement



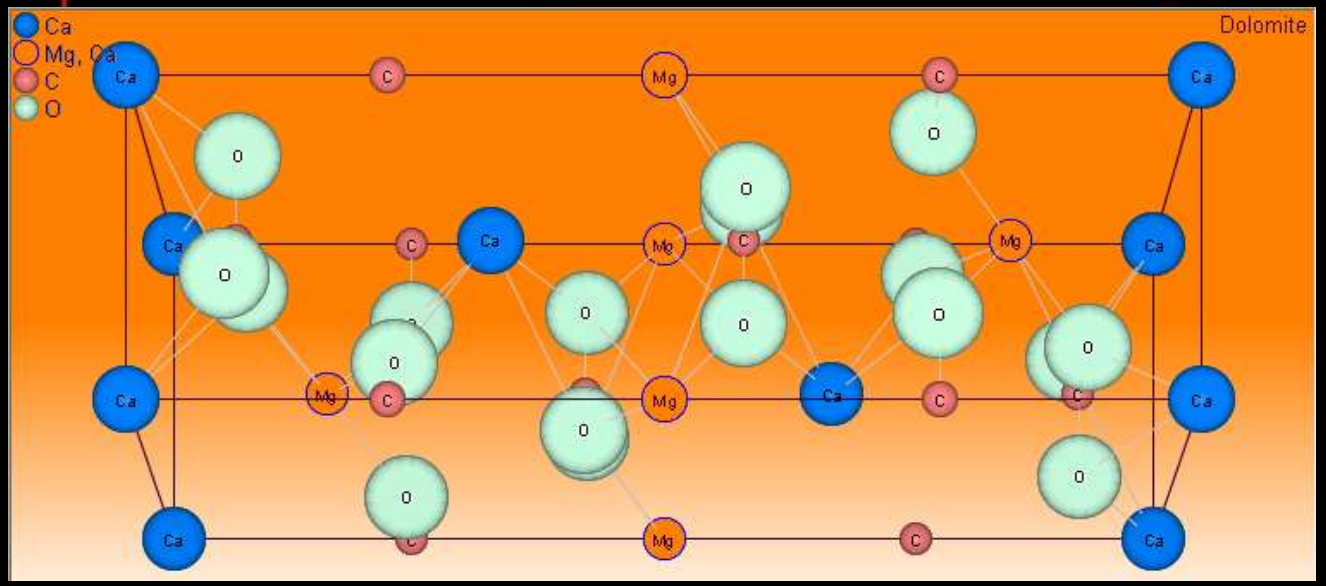
Calcite, $CaCO_3$, hexagonal, $R\bar{3}c$ (167)
0.499 nm/ 0.499 nm / 1.705 nm <90.0/90.0/120.0>

Intensity (sqrt counts)

20 30 40 50 60 70 80 90 100 110

2-theta (degrees), Cu K-alpha radiation

Rietveld refinement



Dolomite, $Ca_{1.07}Mg_{0.93}(CO_3)_2$, hexagonal, R3 ($\bar{1}$48)
0.481 nm/ 0.4819 nm / 1.602 nm <90.0/90.0/120.0>

Intensity (sqrt counts)

20 30 40 50 60 70 80 90 100 110

2-theta (degrees), Cu K-alpha radiation

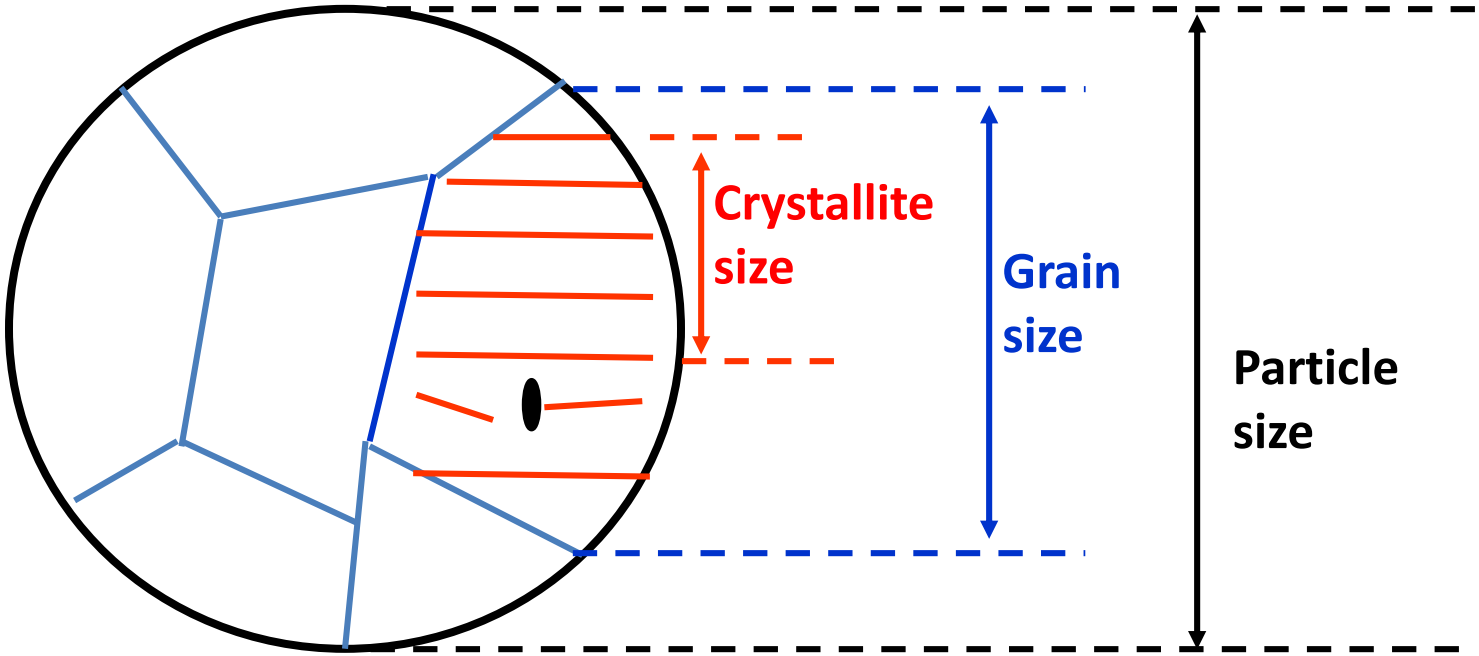
~ XRD, TEM

~ SEM

~ SEM (number average)
SAXS (volume average),
DLS (volume^2 average), …

Crystallite size ≤ **Grain size** ≤ **Particle size**

Domain of coherent diffraction



Crystallite size analysis

Scherrer's equation:

$$\text{Size} = \frac{k * \lambda}{\cos(\theta) * (\text{FWHM})}$$

k : shape factor (0.8-1.2)

λ: x-ray wavelength

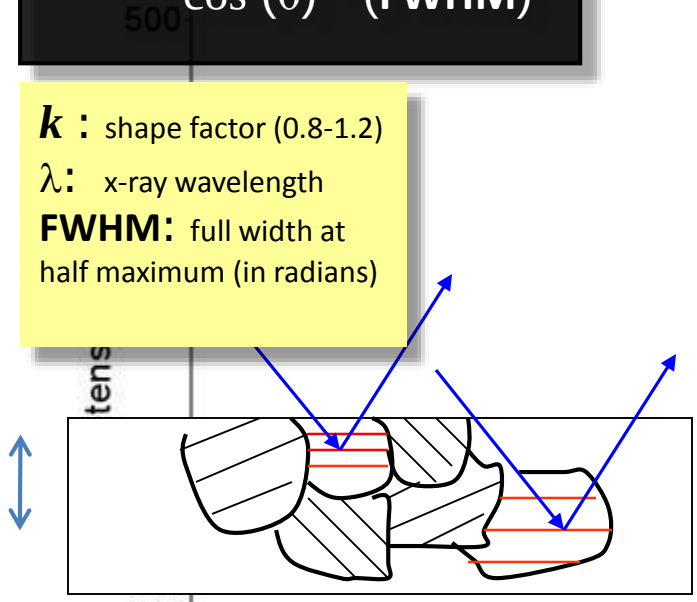
FWHM: full width at half maximum (in radians)

Simplistic approximation!

Not accounting for peak broadening from strain and defects

Directional measurement!

Measured along the specific direction normal to the (hkl) lattice plane given by the 2θ peak position

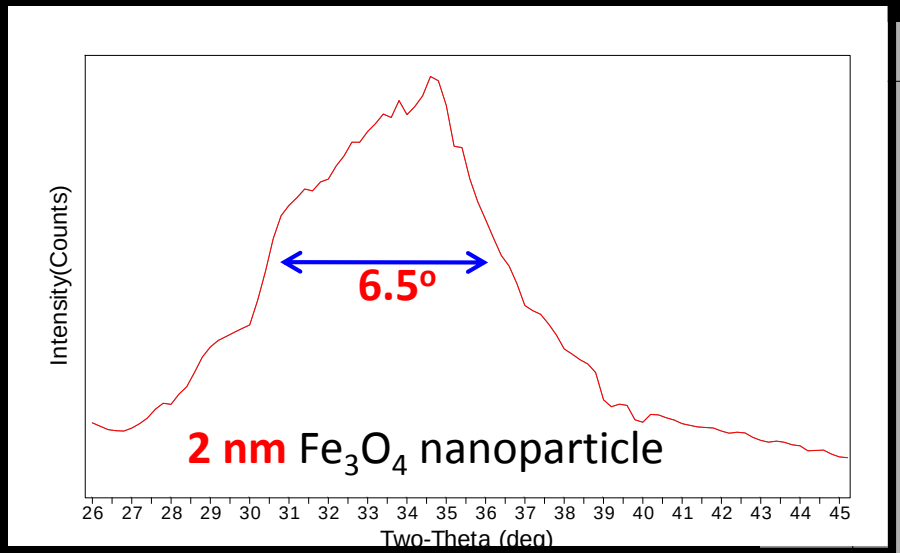


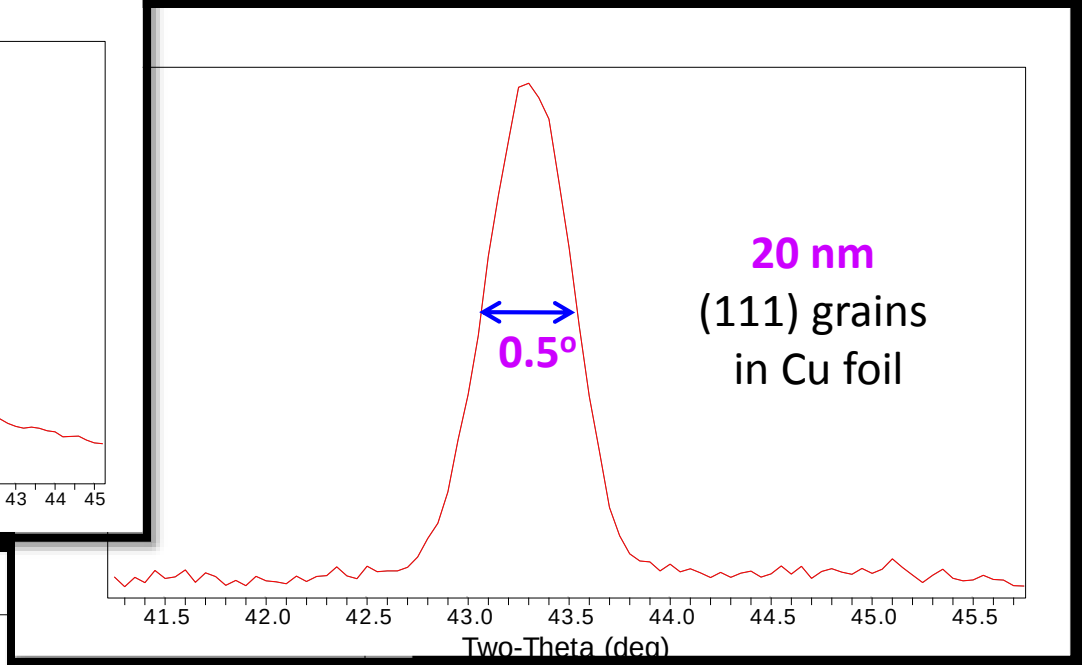
Peak width

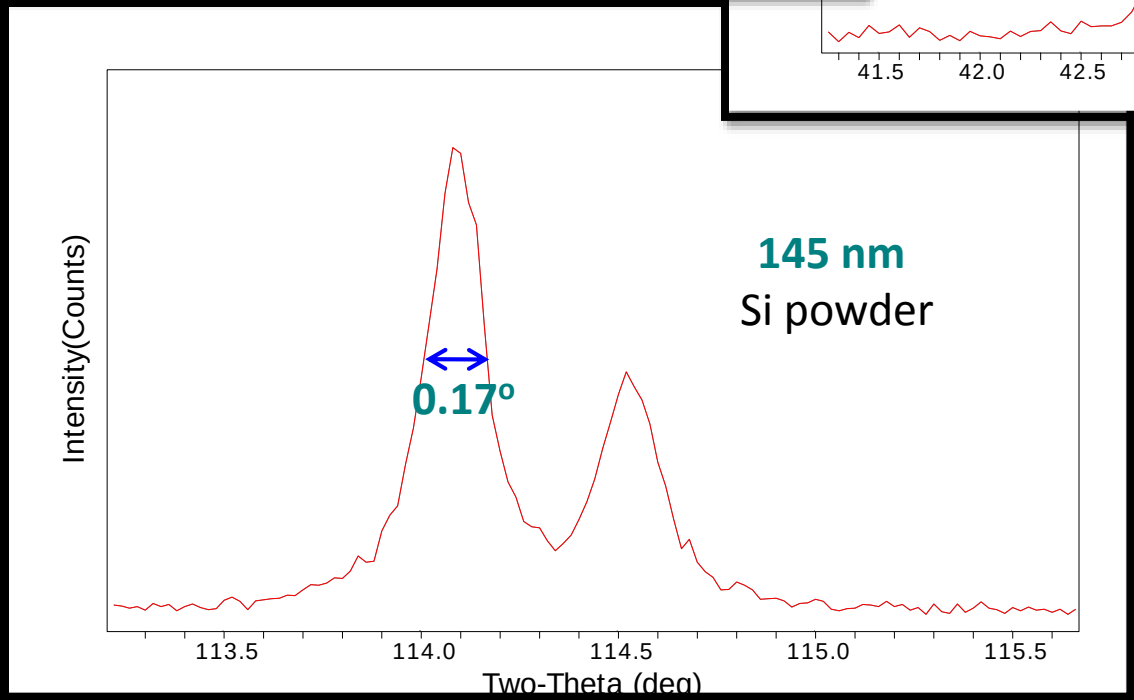
(FWHM or integral breadth)

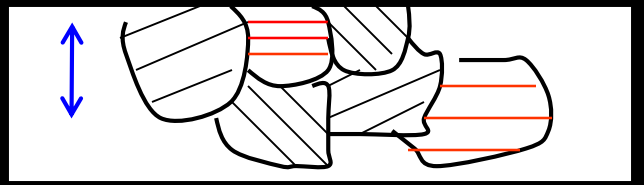
Peak position 2θ

Crystallite size analysis



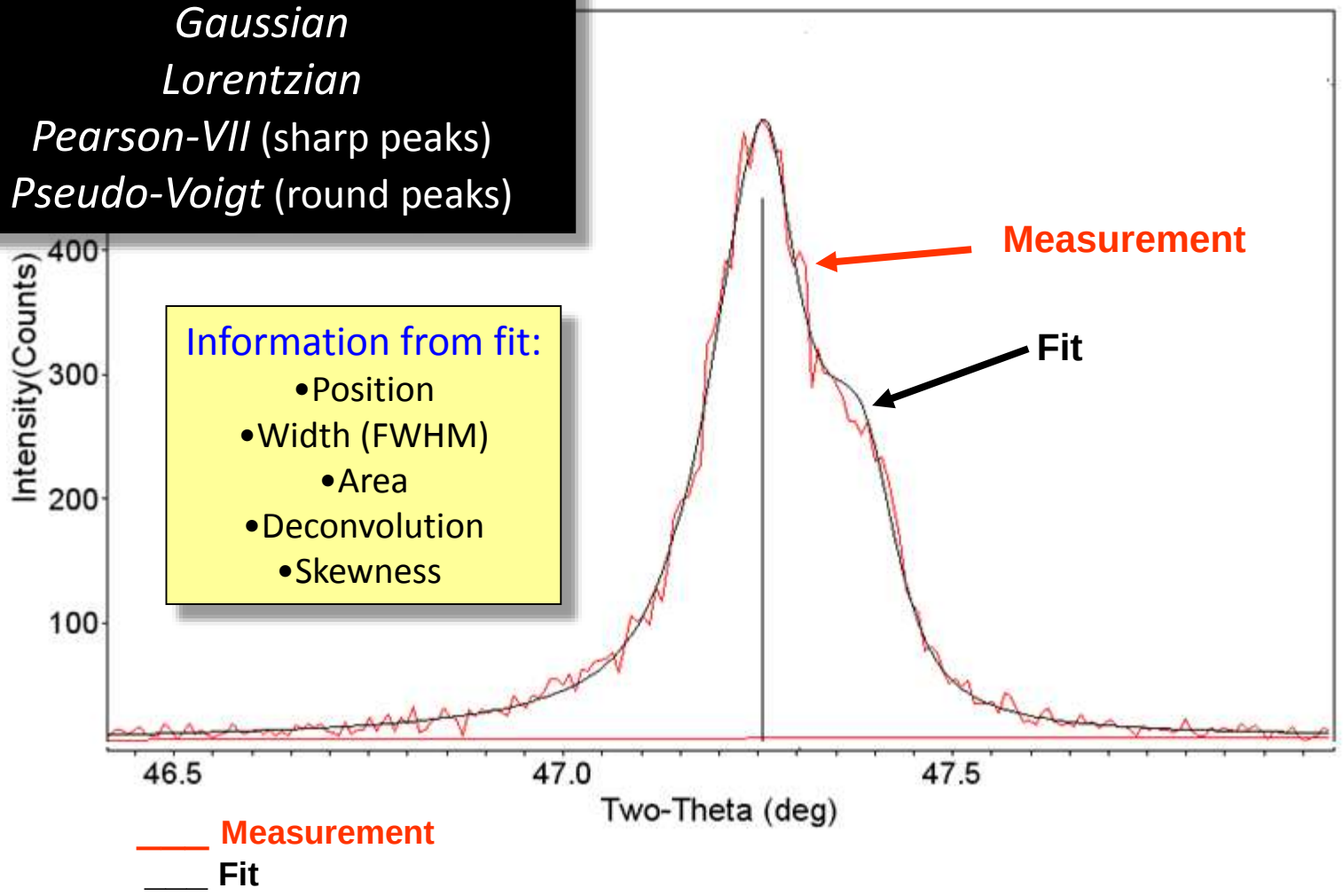






Peak shape analysis

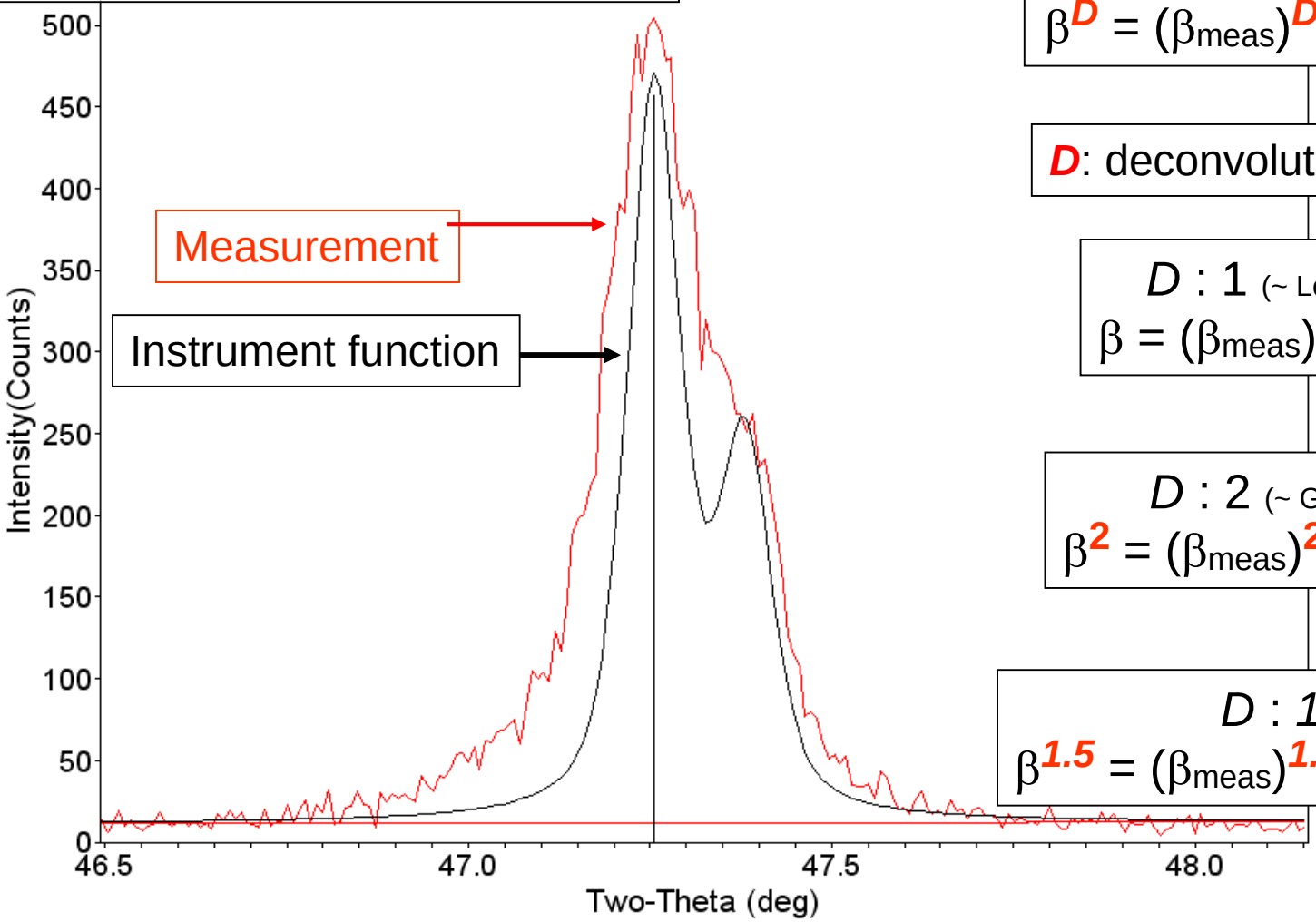
Peak fit functions:
Gaussian
Lorentzian
Pearson-VII (sharp peaks)
Pseudo-Voigt (round peaks)



Information from fit:
- Position
- Width (FWHM)
- Area
- Deconvolution
- Skewness

Correction for instrument resolution

Use FWHM curve as a function of 2θ from standard sample (NIST LaB_6): specific for each diffractometer



FWHM: β

$\beta^{D} = (\beta_{meas})^{D} - (\beta_{instr})^{D}$

D: deconvolution parameter

D : 1 (~ Lorentzian)

$\beta = (\beta_{meas}) - (\beta_{instr})$

D : 2 (~ Gaussian)

$\beta^{2} = (\beta_{meas})^{2} - (\beta_{instr})^{2}$

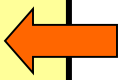
D : *1.5*

$\beta^{1.5} = (\beta_{meas})^{1.5} - (\beta_{instr})^{1.5}$

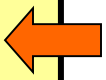
Potential artifacts in size determination

For this calculation assume:
- Instrument resolution ~ 0.15°
- Cu radiation

$2\theta = 40^o$ Measured peak width	**Size**, nm *D = 1* (Lorentzian) $\beta = \beta_{meas} - \beta_{instr}$	**Size**, nm *D = 1.5* $\beta^{1.5} = (\beta_{meas})^{1.5} - (\beta_{instr})^{1.5}$	**Size**, nm *D = 2* (Gaussian) $\beta^2 = (\beta_{meas})^2 - (\beta_{instr})^2$
0.30°	**56.4**	**38.0**	**32.6**
0.50°	**24.2**	**19.2**	**17.7**
0.75°	**14.1**	**12.0**	**11.5**
1.00°	**10.1**	**8.8**	**8.6**
1.50°	**6.3**	**5.8**	**5.7**
2.00°	**4.6**	**4.3**	**4.2**

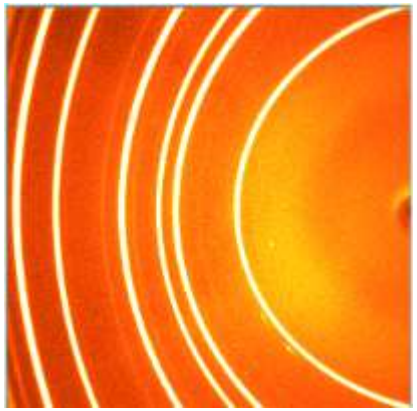


~ 48% difference for narrow peaks (large sizes)

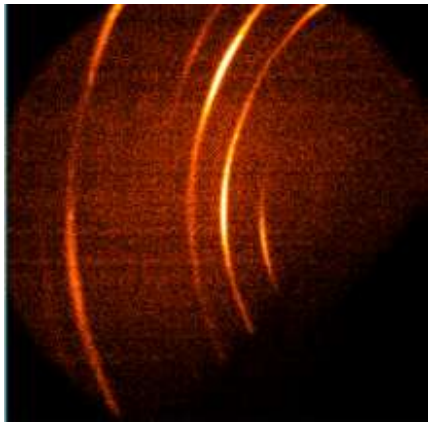


Smaller difference (~ 10%) for broad peaks (small sizes)

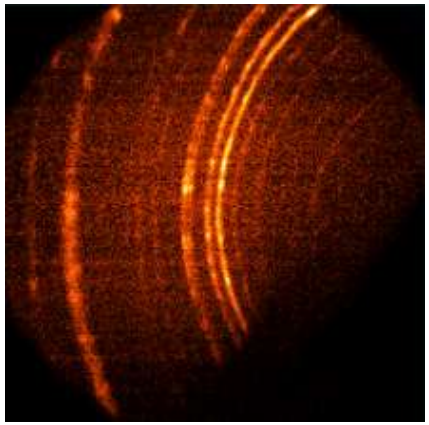
He et al, Adv in X-ray Analysis 37, vol 46 (2003)



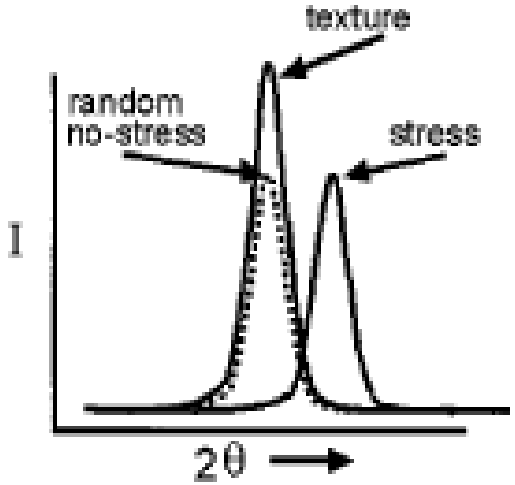
Small grains,
No texture



Non uniform
rings
(texture)

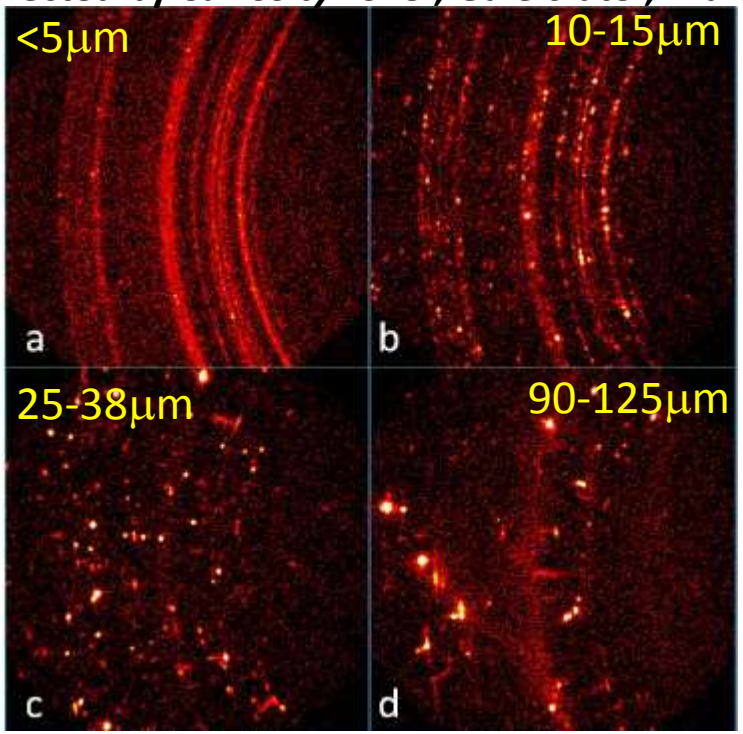


Spotty
rings
(large
grain
size)



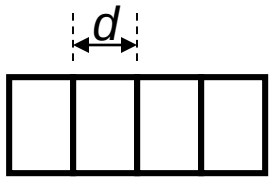
Pyroxene: increasing grain sizes

Collected by *Curiosity* rover, Gale crater, Mars

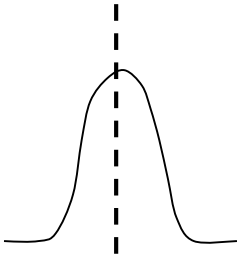


Bramble et al, 45th Lunar and Planetary Science Conference (2014)

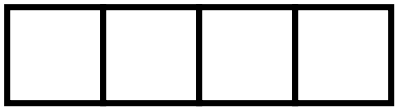
Strain effects in diffraction lines



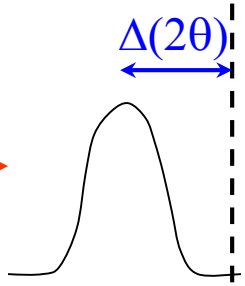
No strain



Macrostrain
uniform tensile or compressive stress (lattice expansion or contraction)

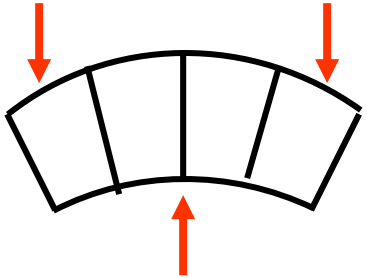


Uniform strain

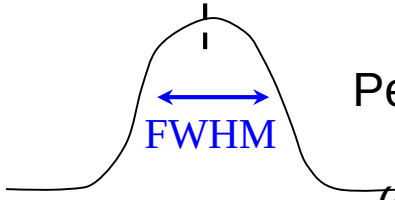


Peak position shift (lattice constant change)

Microstrain
nonuniform strain (both tensile and compressive stresses) (lattice distortion). Dislocations, vacancies, defects, thermal effects.



Nonuniform strain



Peak width change (symmetric broadening)

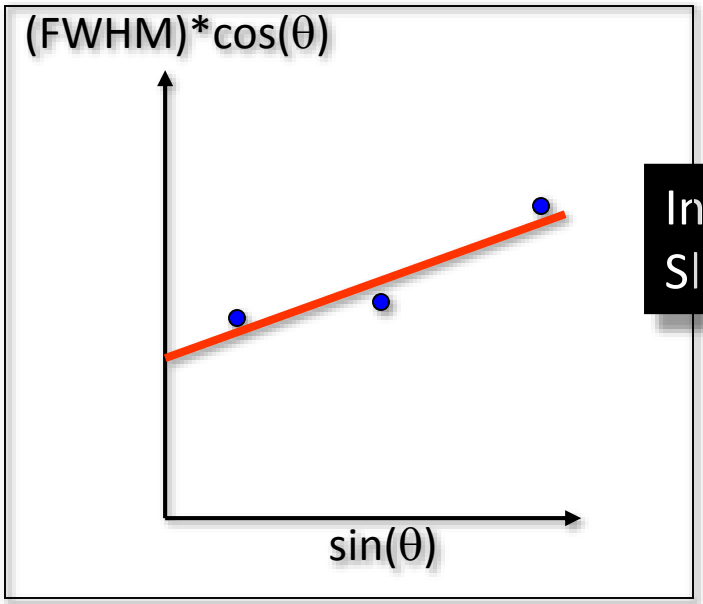
Size and strain in peak shape analysis

$FWHM_{strain} = 4 * (strain) * \tan\theta$

Williamson-Hall Method

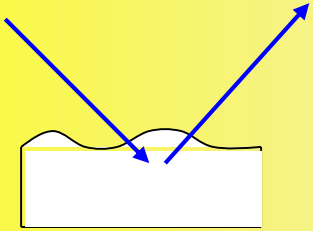
Acta Metall. ***1*** *(1953) 22.*

$(FWHM)*\cos(\theta) = k\lambda/(size) + (strain)*\sin(\theta)$

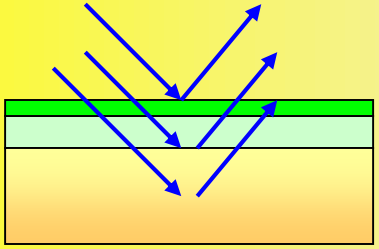


Intercept ~ 1/(size)
Slope ~ micro strain

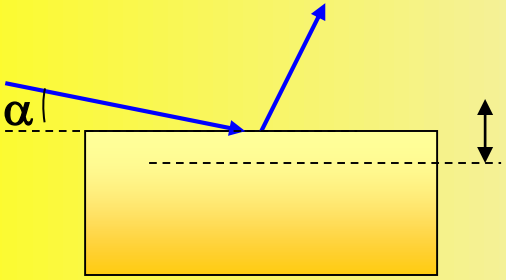
X-ray parallel beam methods



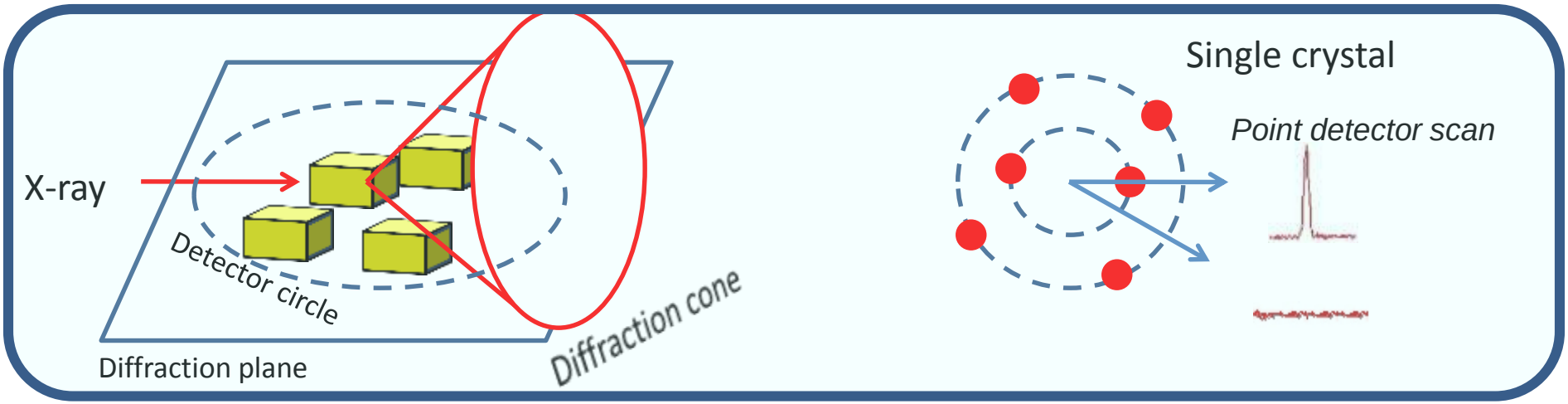
Rough, irregular surfaces

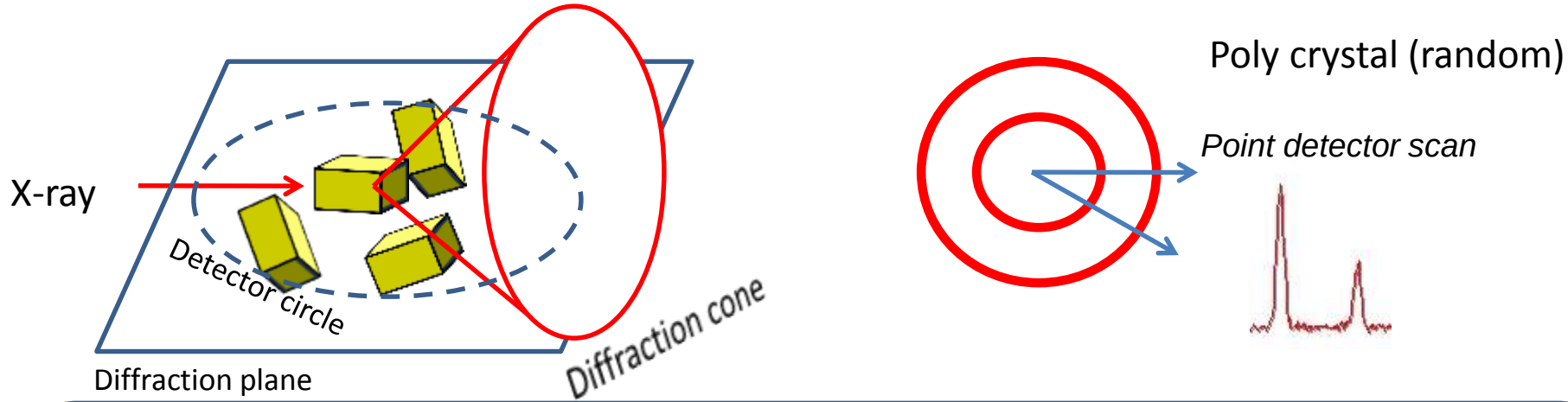


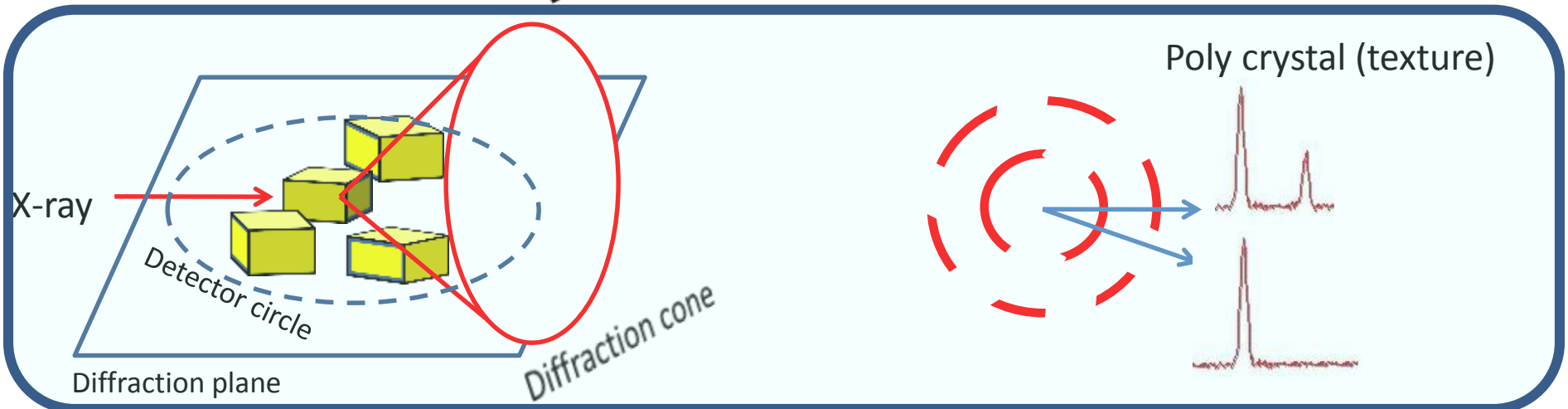
Film / Substrate systems



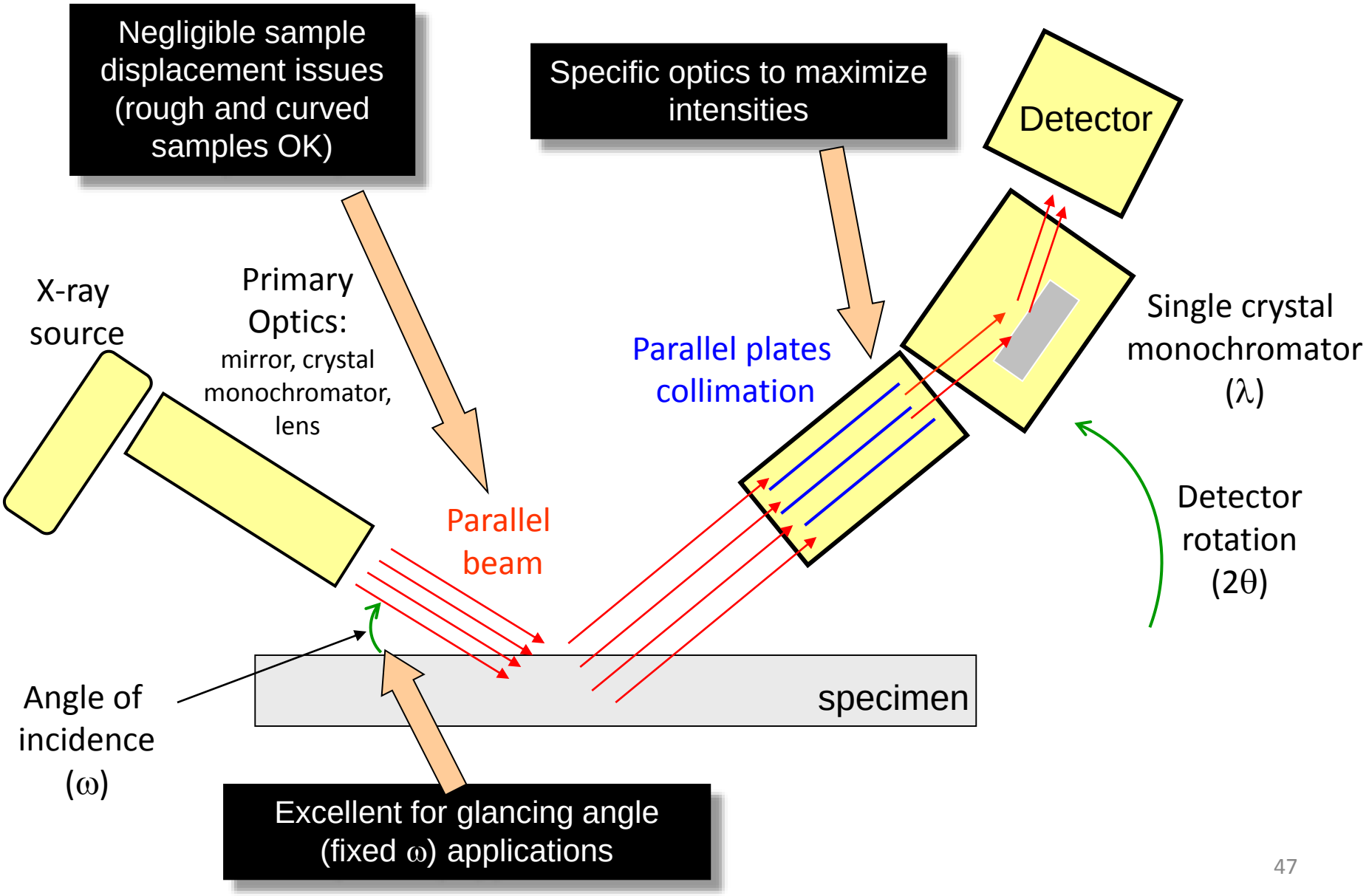
Glancing / grazing angle applications.
Phase, stress gradients (depth profiles)


X-ray
Detector circle
Diffraction plane
Diffraction cone
Single crystal
Point detector scan


X-ray
Detector circle
Diffraction plane
Diffraction cone
Poly crystal (random)
Point detector scan


X-ray
Detector circle
Diffraction plane
Diffraction cone
Poly crystal (texture)

Parallel beam configuration



Thin film analysis walkthrough:

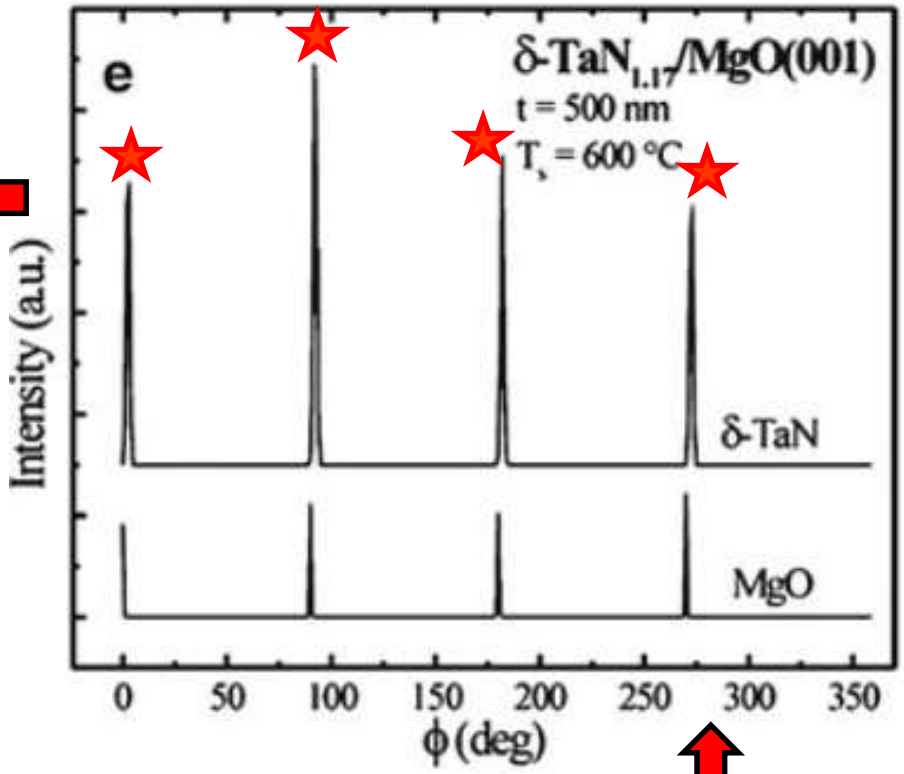
TaN film

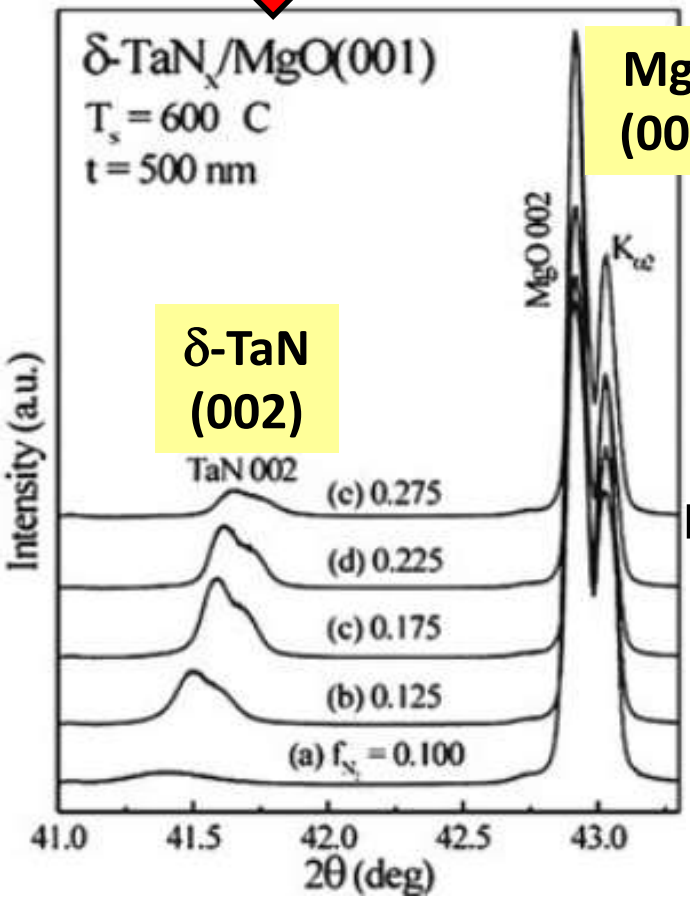
MgO (001) substrate

Cube on cube epitaxy:

$(001)_{TaN}//(001)_{MgO}$

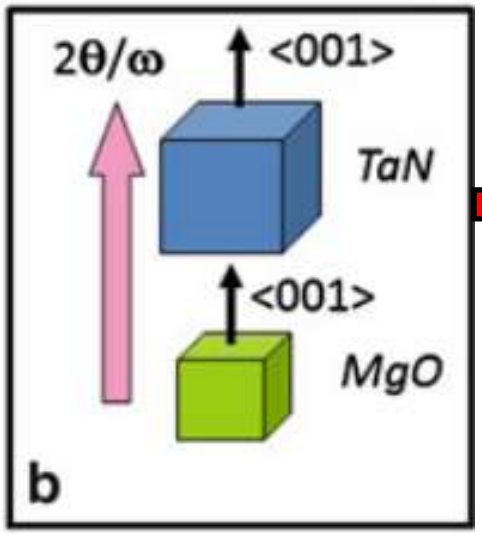
$(100)_{TaN}//(100)_{MgO}$

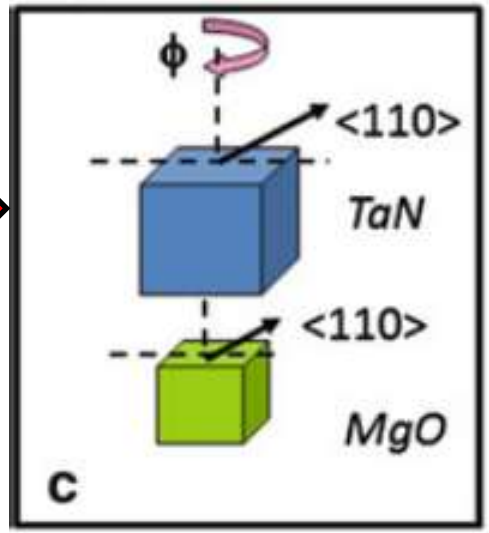




MgO (002)

δ-TaN (002)



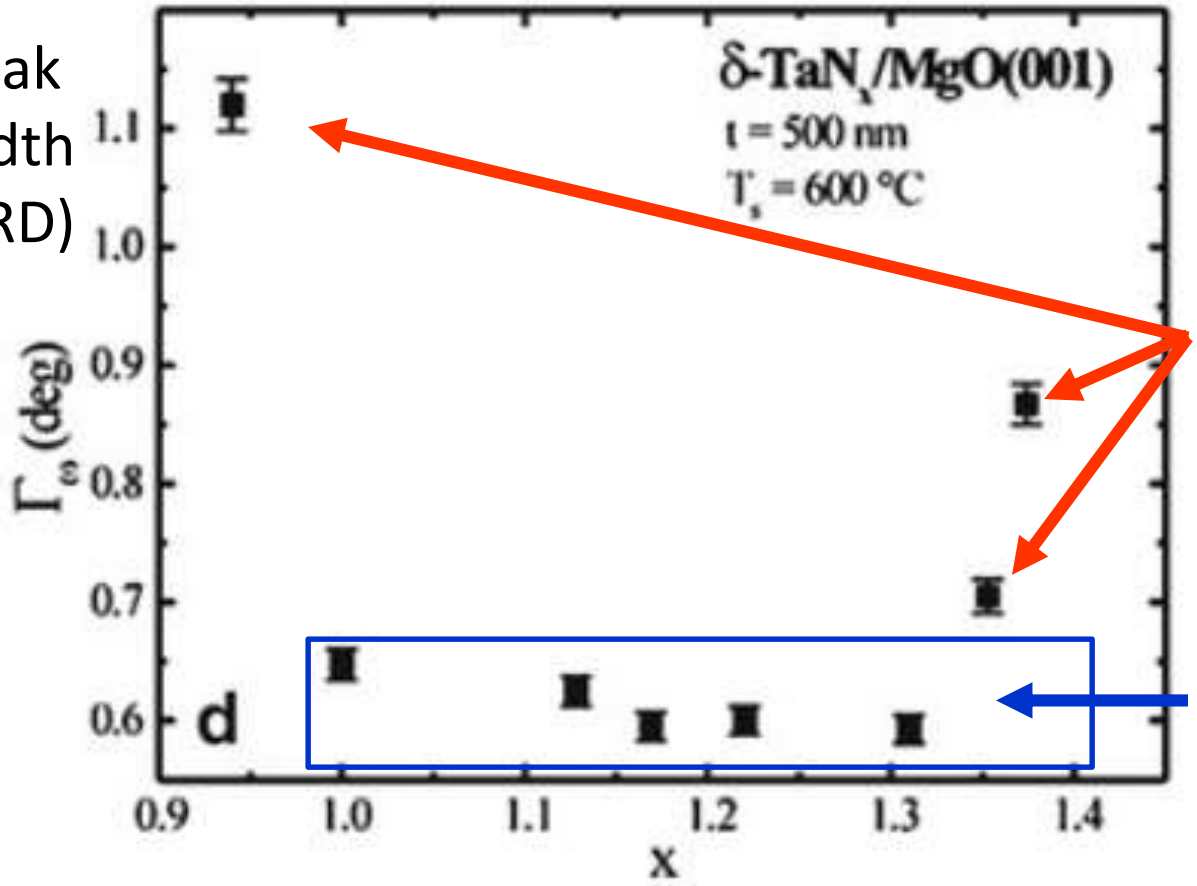


After Shin et al, TSF (2002)

Thin film analysis walkthrough:

TaN film
***MgO* (001) substrate**

Peak shape analysis: TaN(002) rocking curve omega scans

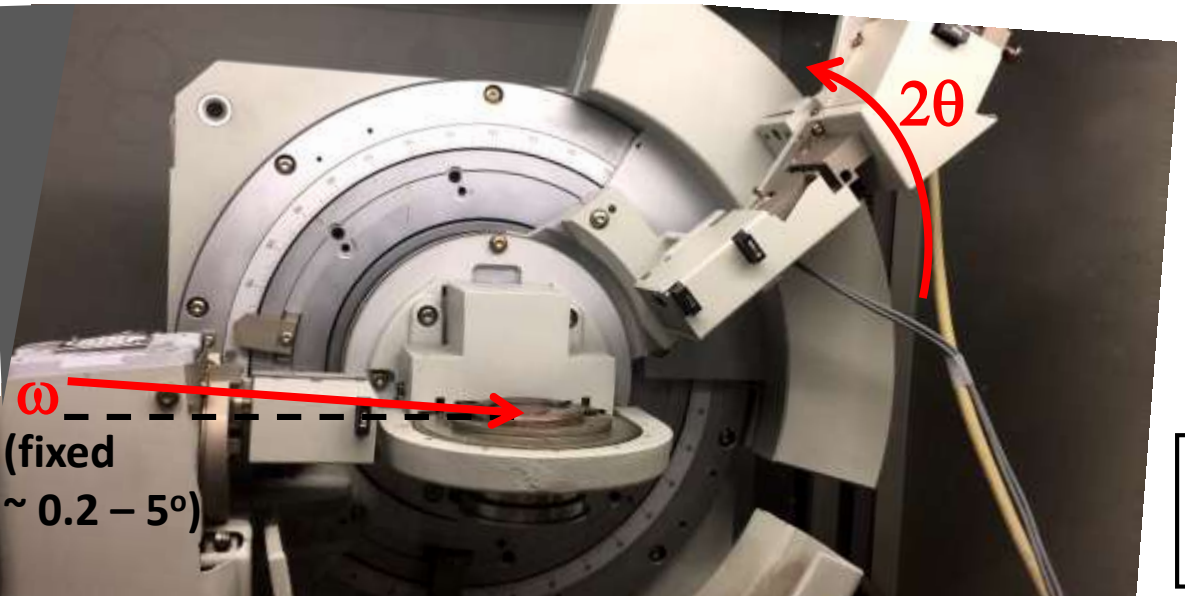


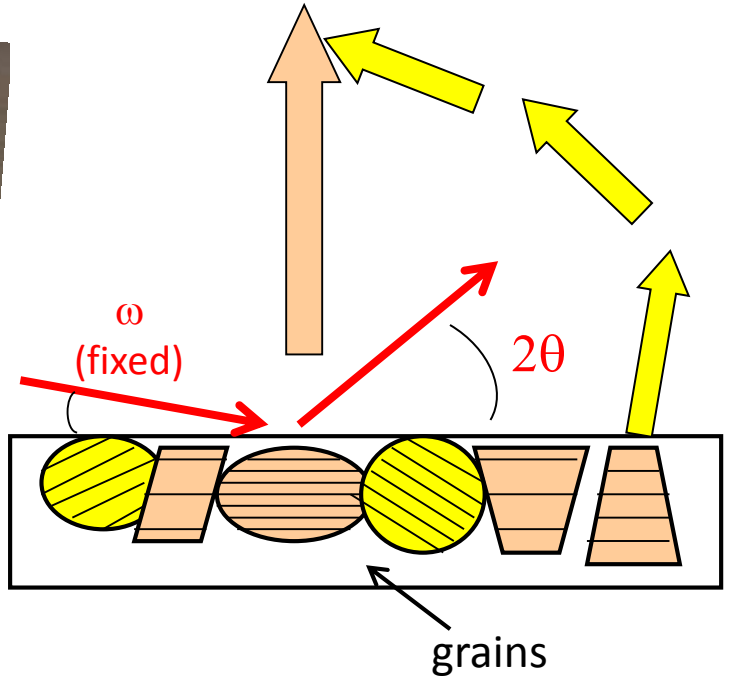
Lower texture

Higher texture

After Shin et al, TSF (2002)

Glancing incidence x-ray diffraction (GI-XRD)

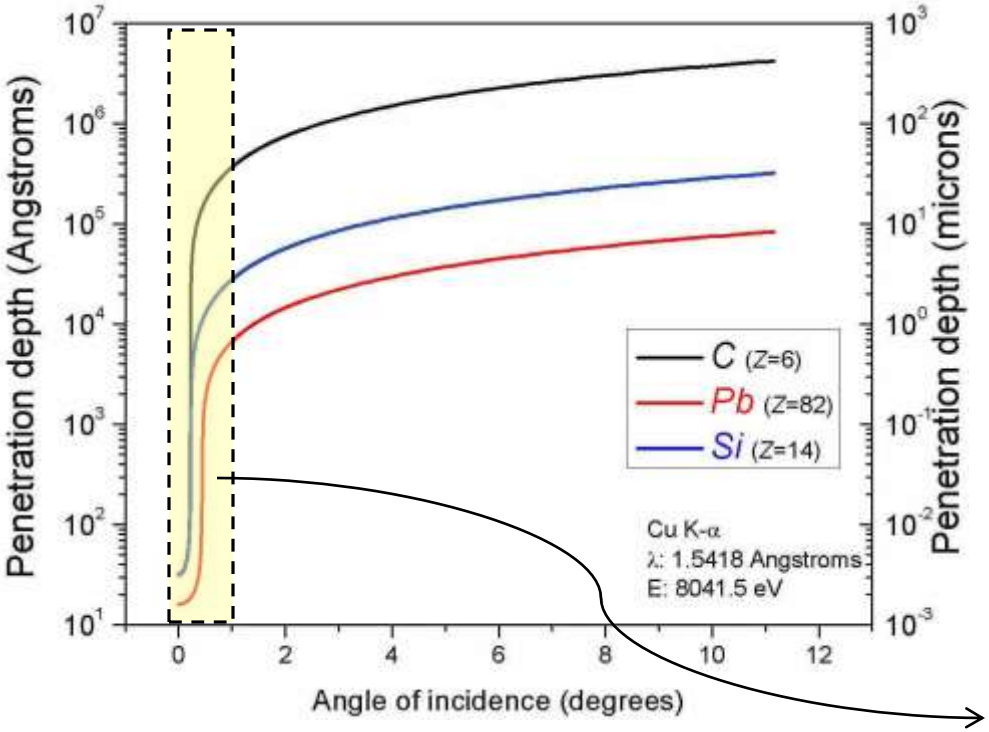


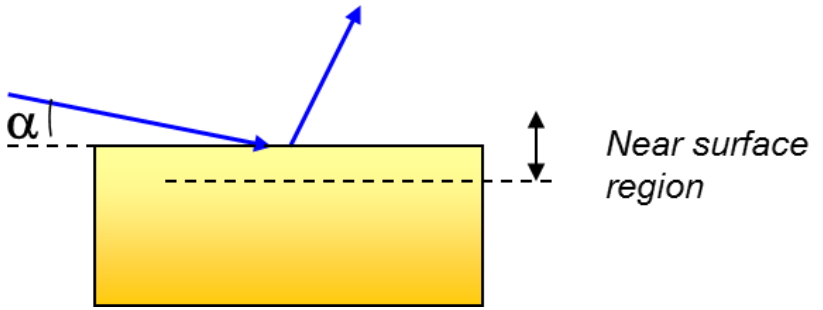


: **conventional** Bragg-Brentano configuration
2θ–ω scans probe only grains aligned parallel to the surface

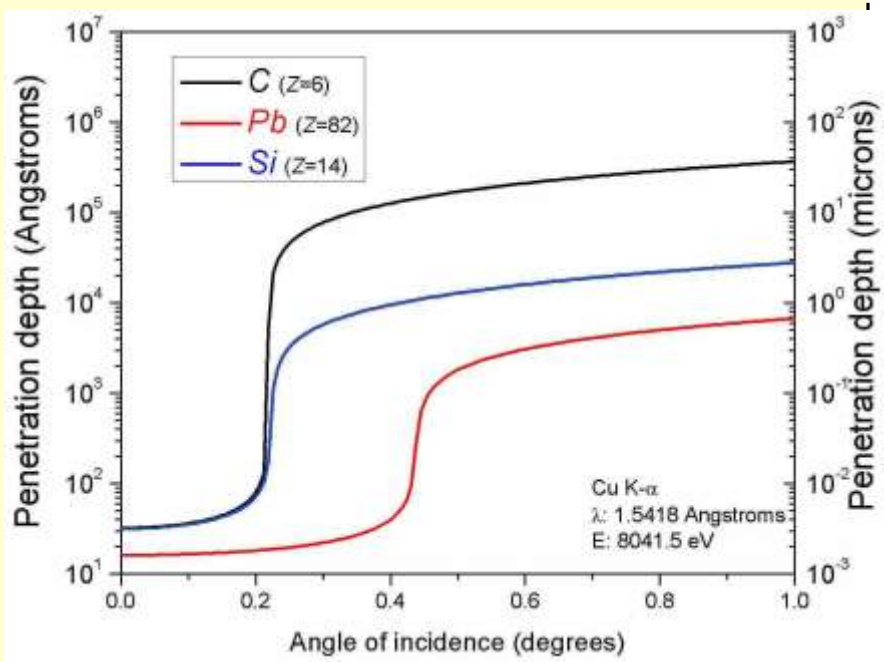
\+ : parallel-beam **glancing incidence** configuration
2θ scans probe grains in **all** directions

X-ray penetration depth vs. angle of incidence





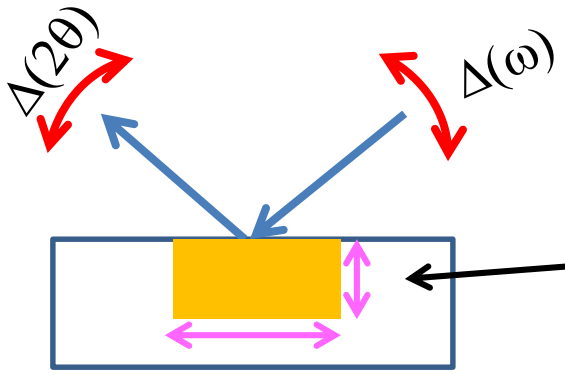
Low angle region



-Type of radiation
- Angle of incidence
- Material (*Z*, *A*, *r*, *m*)

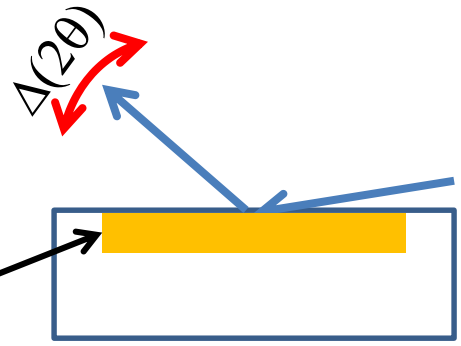
Regular 2θ–ω scan vs. glancing incidence 2θ scan

Regular 2θ–ω scan



Probe depth:
Variable (deep)
Constant (shallow)

Glancing incidence 2θ scan



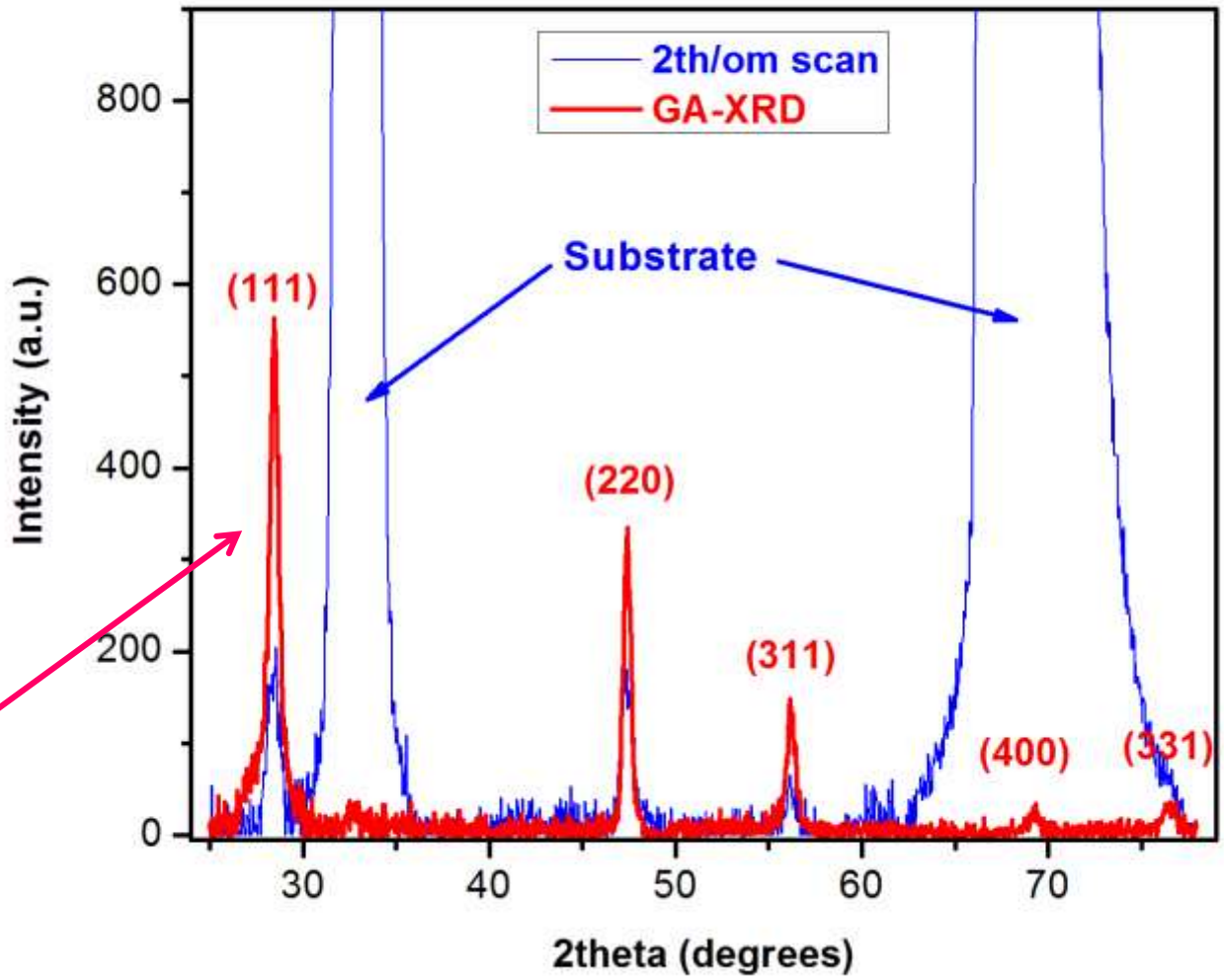
ω (fixed, small)

	Regular 2θ–ω scan	Glancing incidence 2θ scan
Grain orientations	Directions ⊥ to surface	Various directions
Depth resolution	Constant, many mm	• From few nm to mm Depth profiling possible by varying angle of incidence • Sensitive to surface • Ideal for ultra-thin layers
Best configuration	Bragg Brentano Parallel beam	Parallel beam (less sensitive to sample displacement)

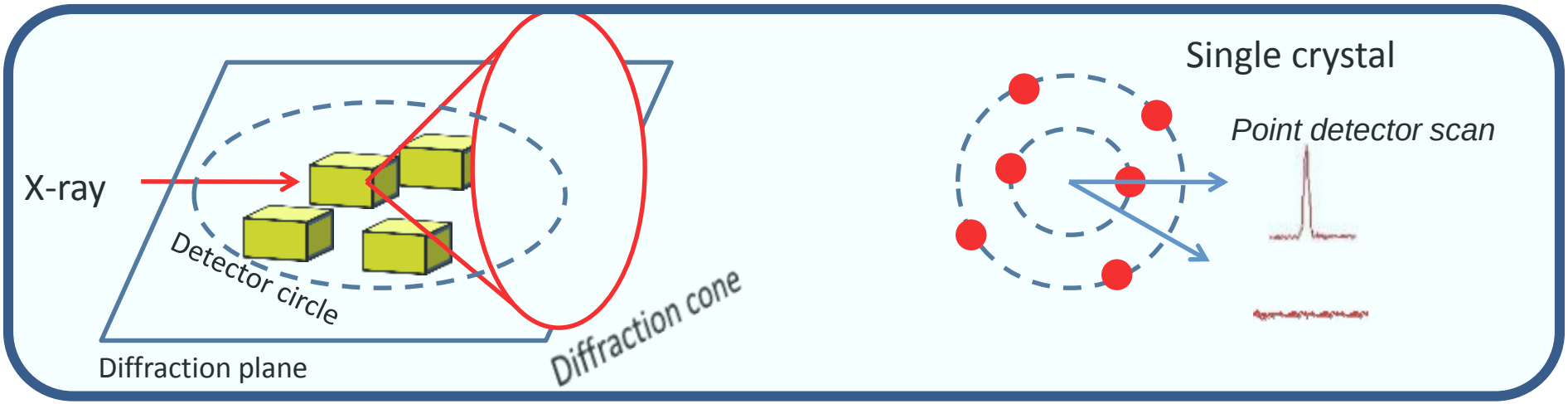
Glancing incidence x-ray analysis

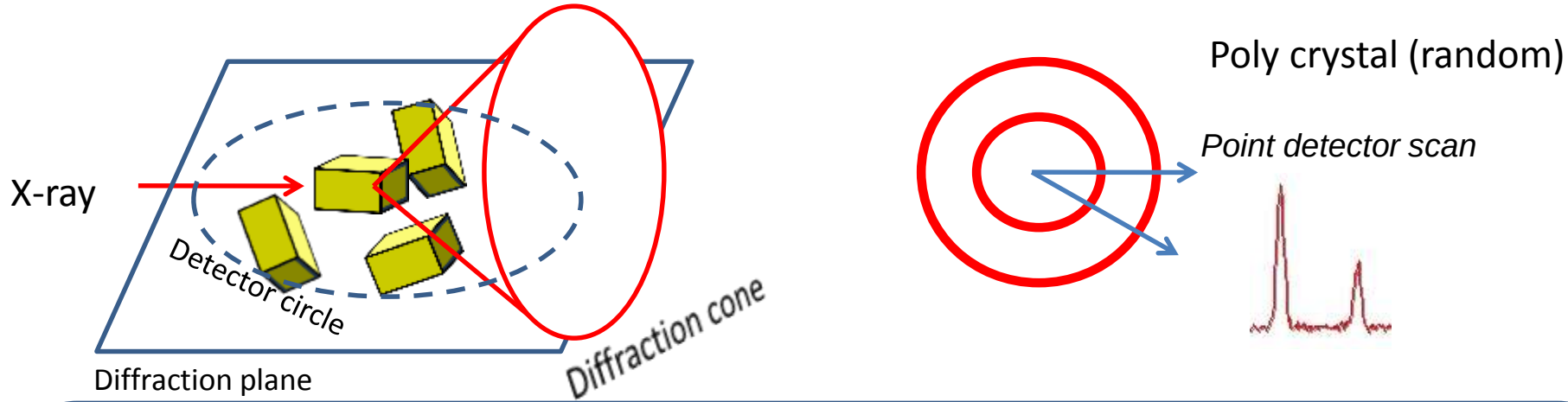
Example: Poly-Si ga

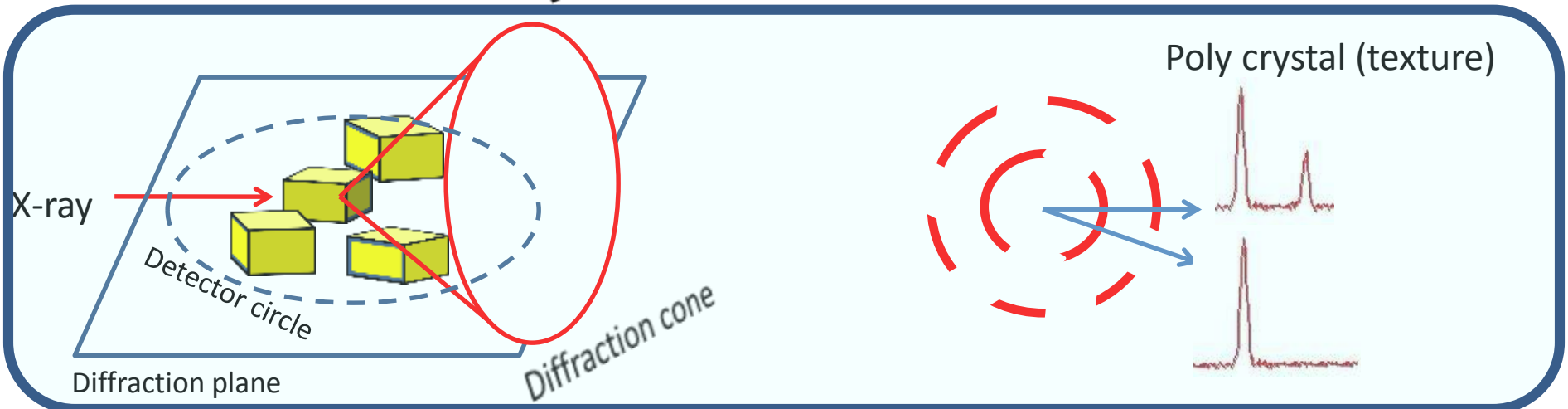
Poly-Si (~ 100 nm)
Si(001) substrate



Glancing incidence


X-ray
Detector circle
Diffraction plane
Diffraction cone
Single crystal
Point detector scan

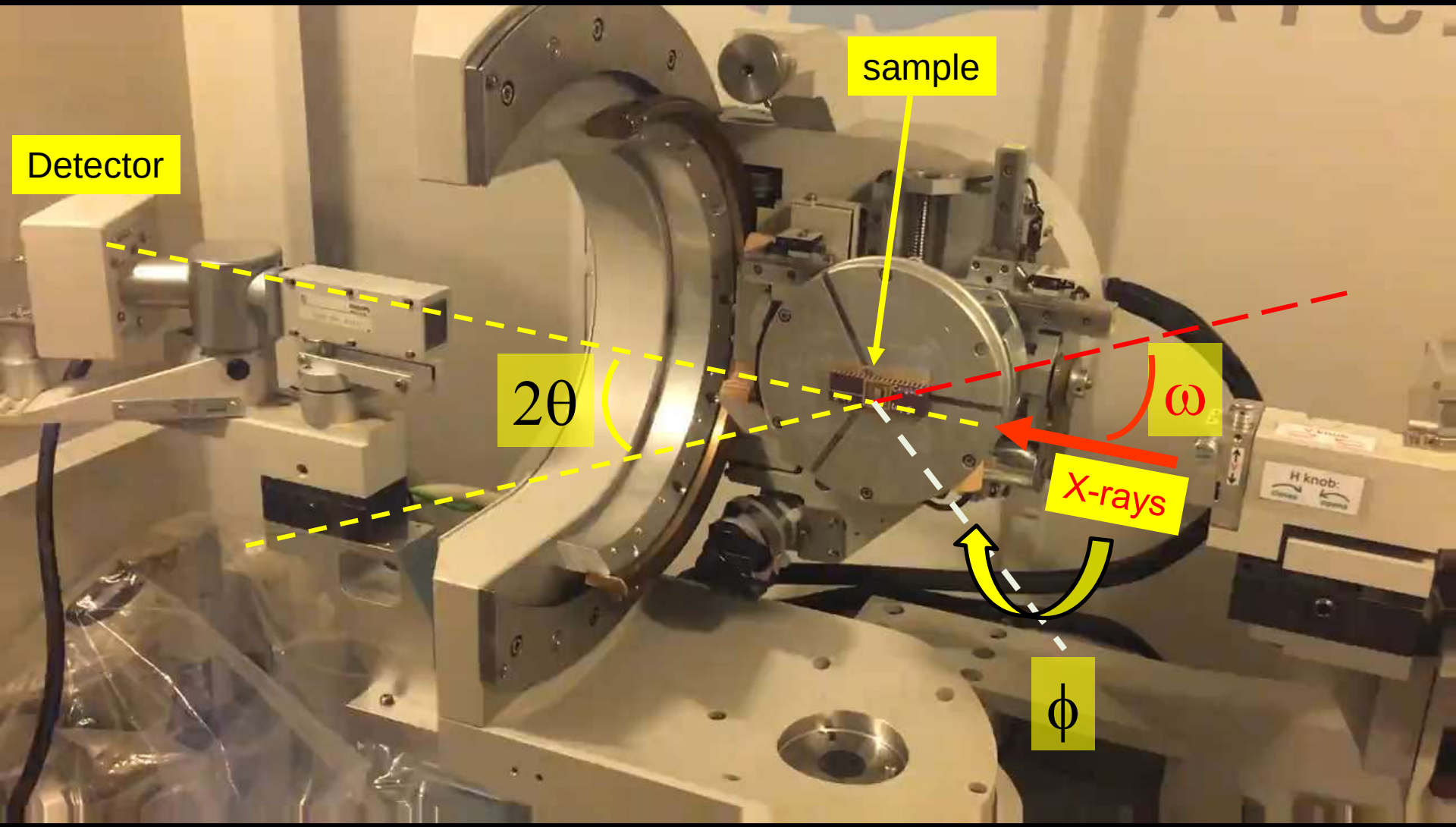

X-ray
Detector circle
Diffraction plane
Diffraction cone
Poly crystal (random)
Point detector scan


X-ray
Detector circle
Diffraction plane
Diffraction cone
Poly crystal (texture)

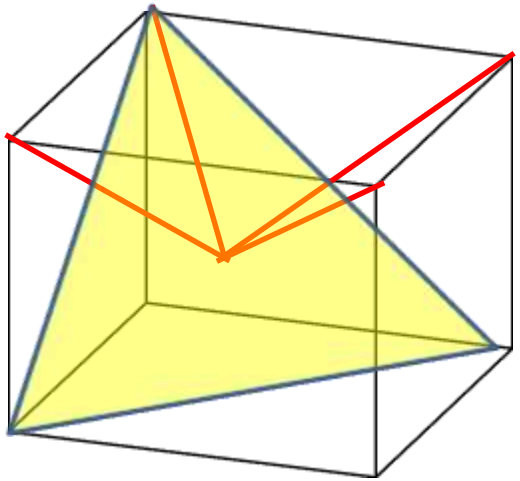
Determination of preferred orientation

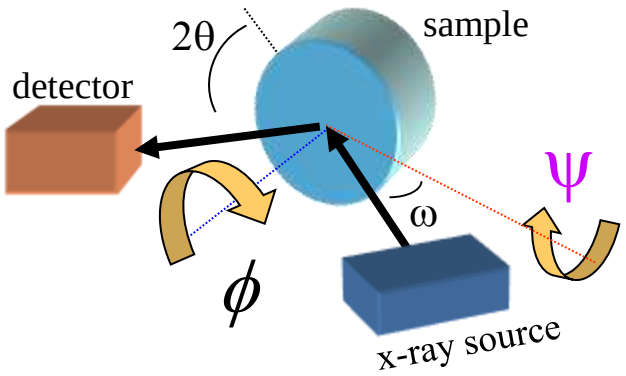
Method	Measurement	Principle	Results
Lotgering factor (L_{hkl})	2θ-ω scans	Compare I_{peak} or A_{peak} with expected values from random samples (PDF)	L_{hkl} as measure of texture strength
March-Dollase (MD)	2θ-ω scans	Use I_{peak} or A_{peak} with MD formalism	% of grains that are more oriented along a specific direction
Rocking curve	ω scans	Measure FWHM from ω scan for a particular *(hkl)*	FWHM decreases with stronger texture
Pole figure	ϕ scans at various tilts ψ	Pole plots of intensities from a particular *(hkl)*	Texture distribution for a single *(hkl)*
Orientation Distribution Function (ODF)	Pole figures from various *(hkl)* 's	Calculate ODF from various pole figures with background and defocussing correction	% of grain orientation distribution in all directions (Euller angles).

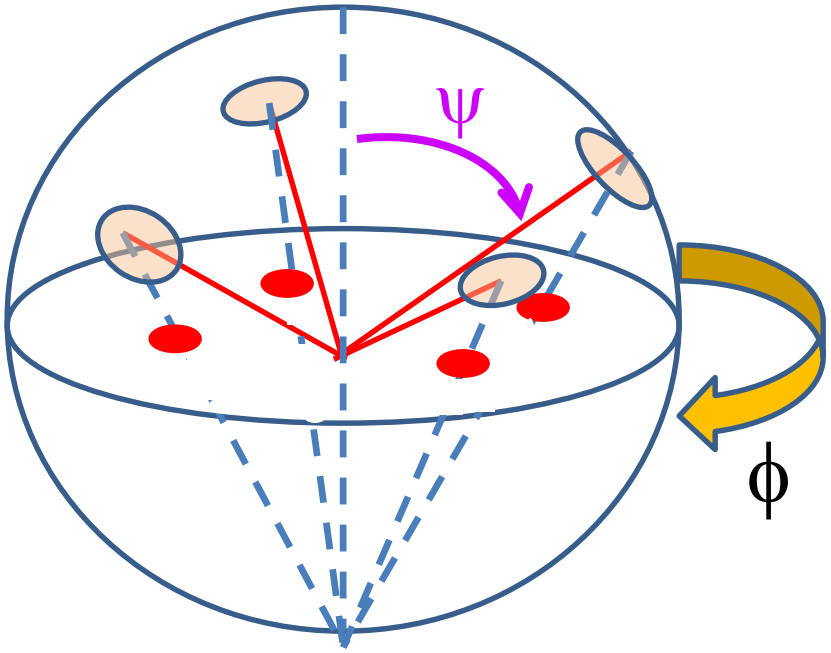
Pole figure measurement

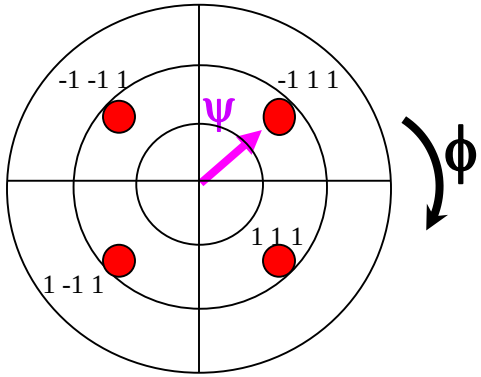


Pole figures







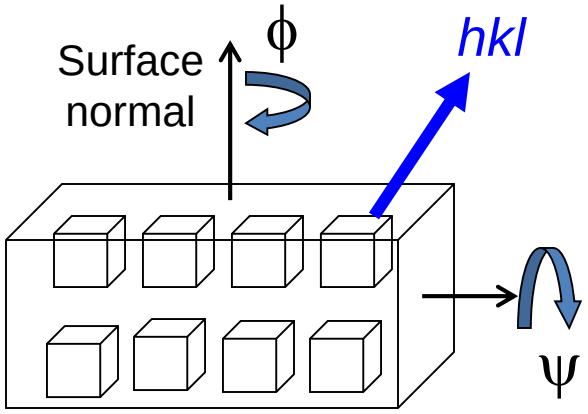


Azimuth
ϕ= 45°, 135°, 225°, 315°

Tilt ψ= 54.7°

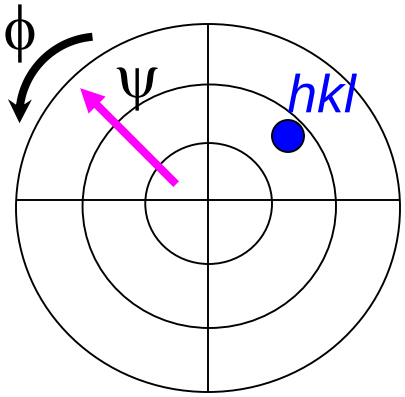
ψ: [100],[111]

Basics of pole figure analysis



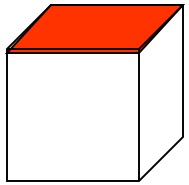
Example: (100) cubic crystal

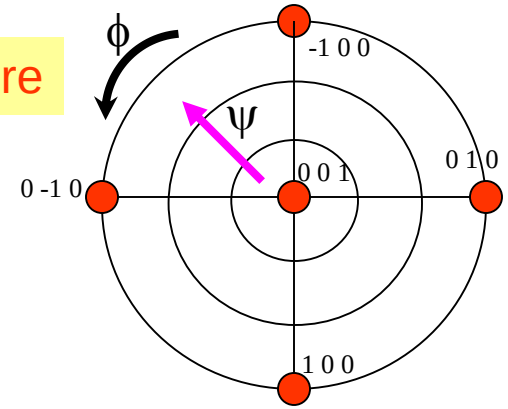
Pole figure plot



ψ(radial / tilt)
ϕ (azimuthal rotation)

(100) Pole figure



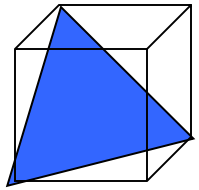


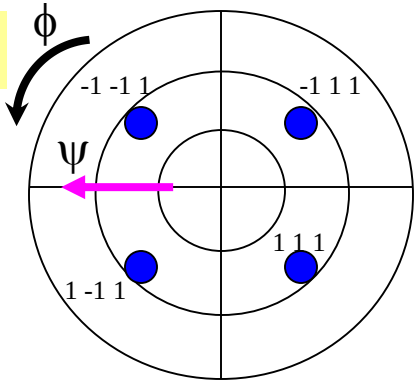
Azimuth
ϕ= 0, 90°,
180°, 270°

Tilt
ψ= 0, 90°

ψ: [100],[100]

(111) Pole figure



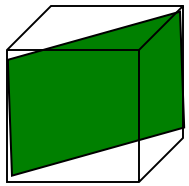


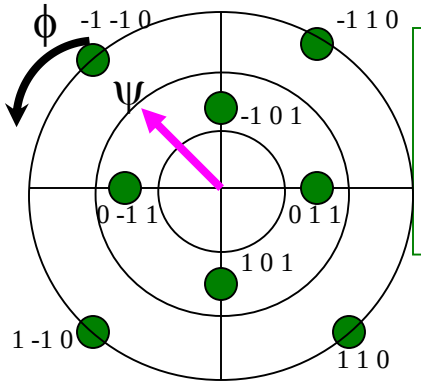
Azimuth
ϕ= 45°, 135°,
225°, 315°

Tilt ψ= 54.7°

ψ: [100],[111]

(110) Pole figure





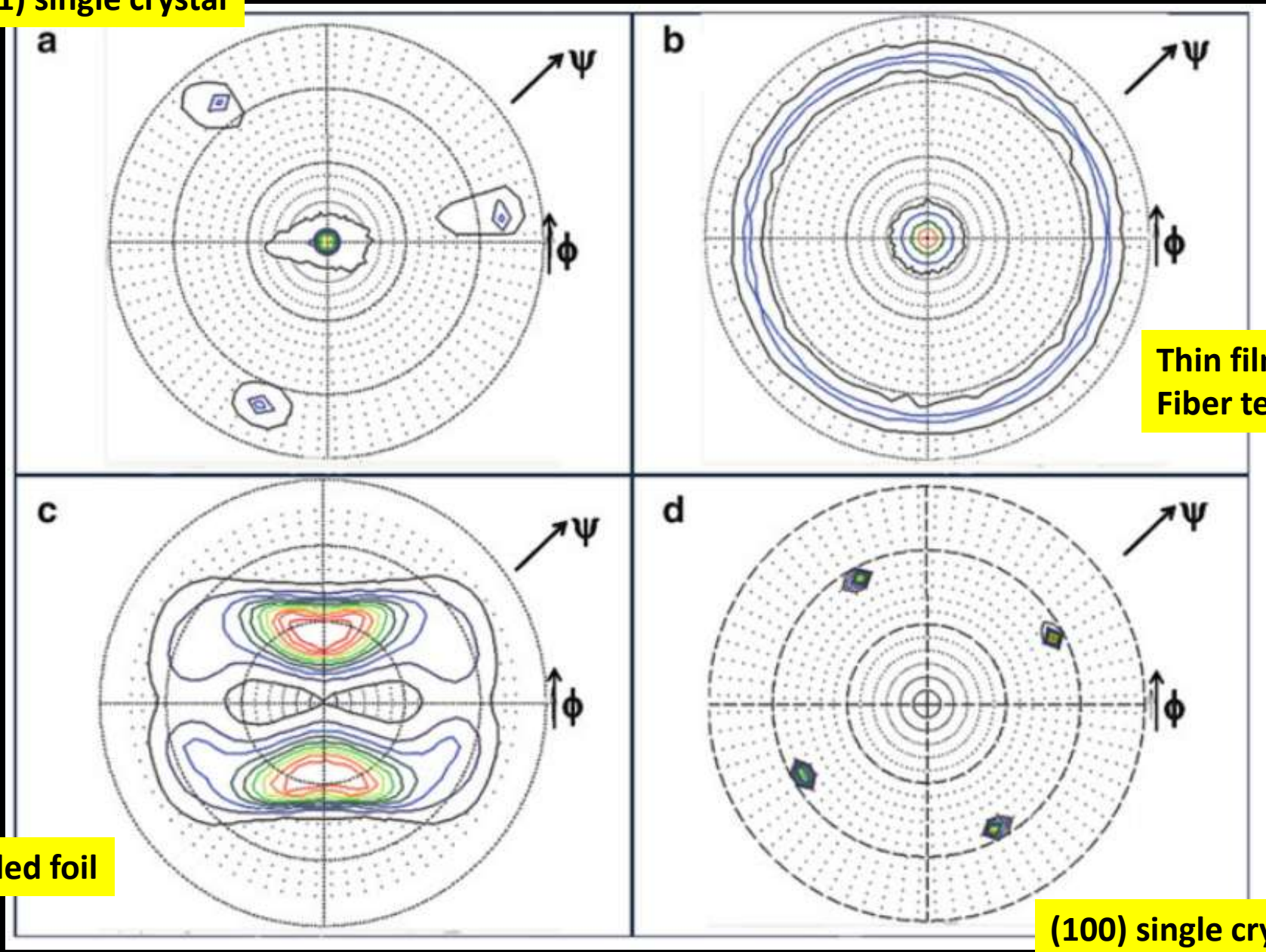
Azimuth
ϕ= 0, 90°, 180°,
270°,45°, 135°,
225°, 315°

Tilt ψ= 45°,90°

ψ: [100],[110]

Cu (111) pole figure

(111) single crystal



Thin film
Fiber texture

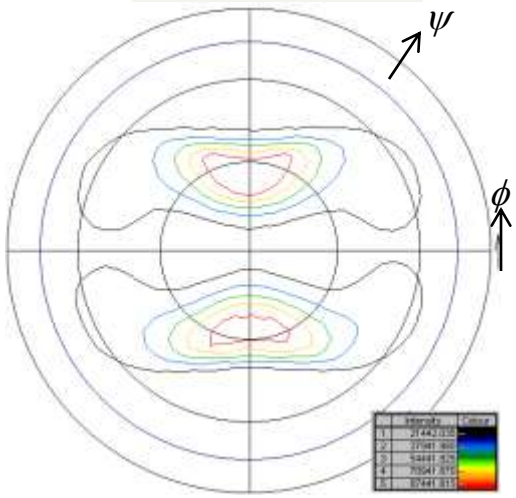
Rolled foil

(100) single crystal

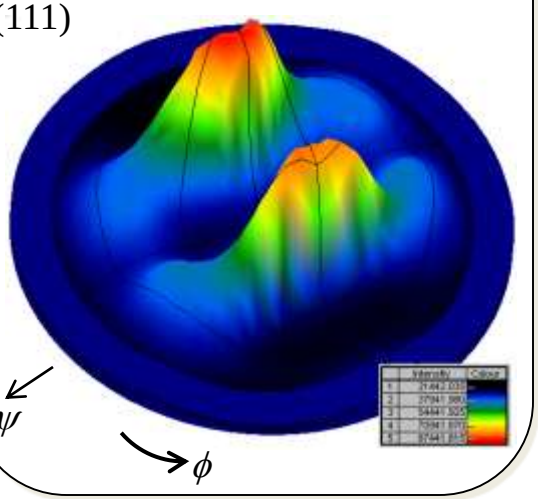
X-ray pole figure analysis of textured materials

Texture results from a rolled *Cu* foil

Pole figures

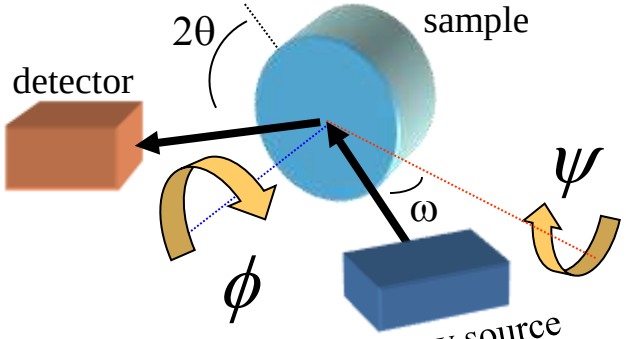


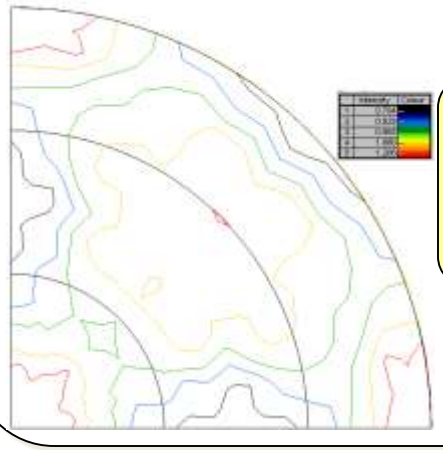
(111)



Data: Sardela, UIUC

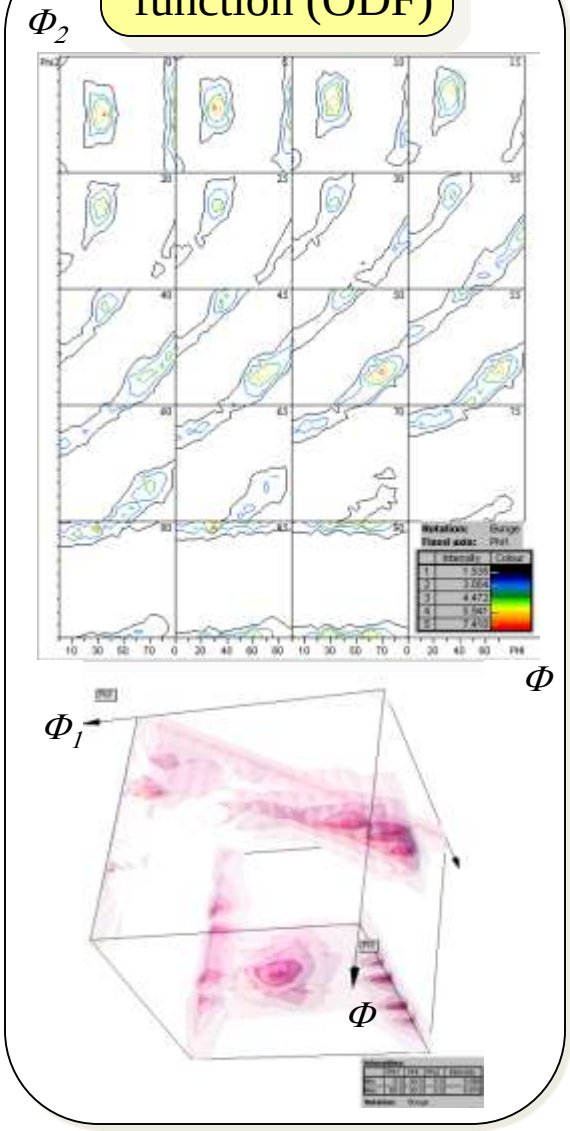
- Texture orientation and quantification.
- Volume fraction of textured grains, twinning and random distributions.
- Texture strength and sharpness.
- Crystallographic orientation.
- Crystallographic relationship between layers and substrate.





Inverse pole figures

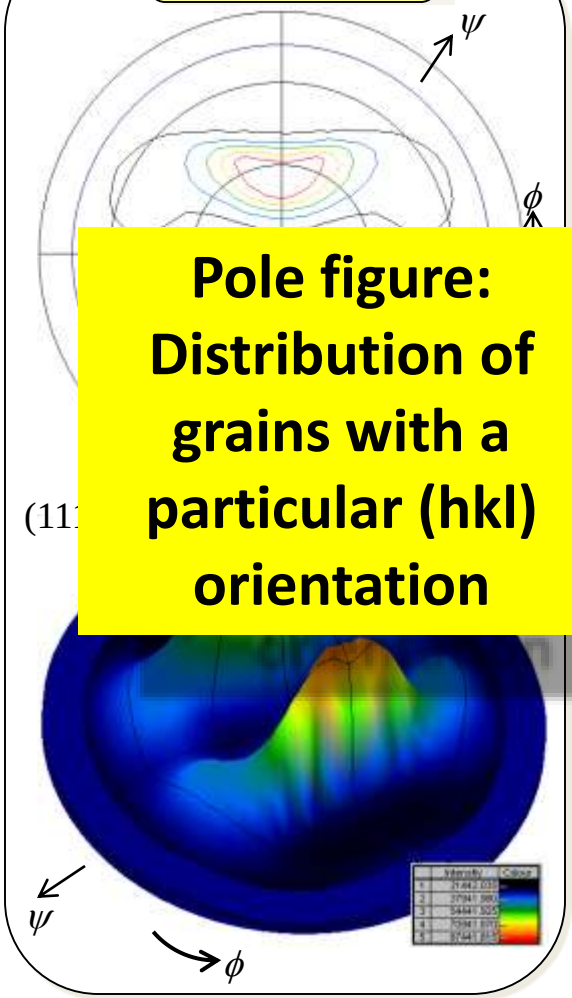
Orientation distribution function (ODF)



X-ray pole figure analysis of textured materials

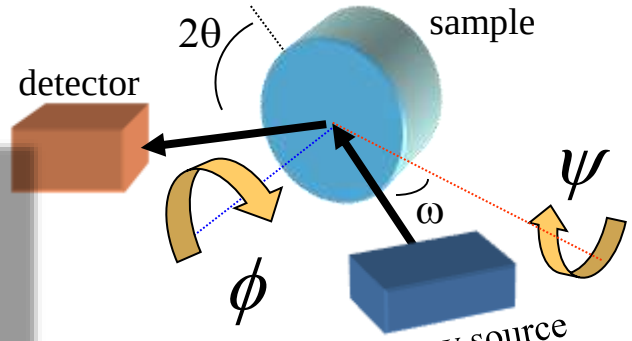
Texture results from a rolled *Cu* foil

Pole figures

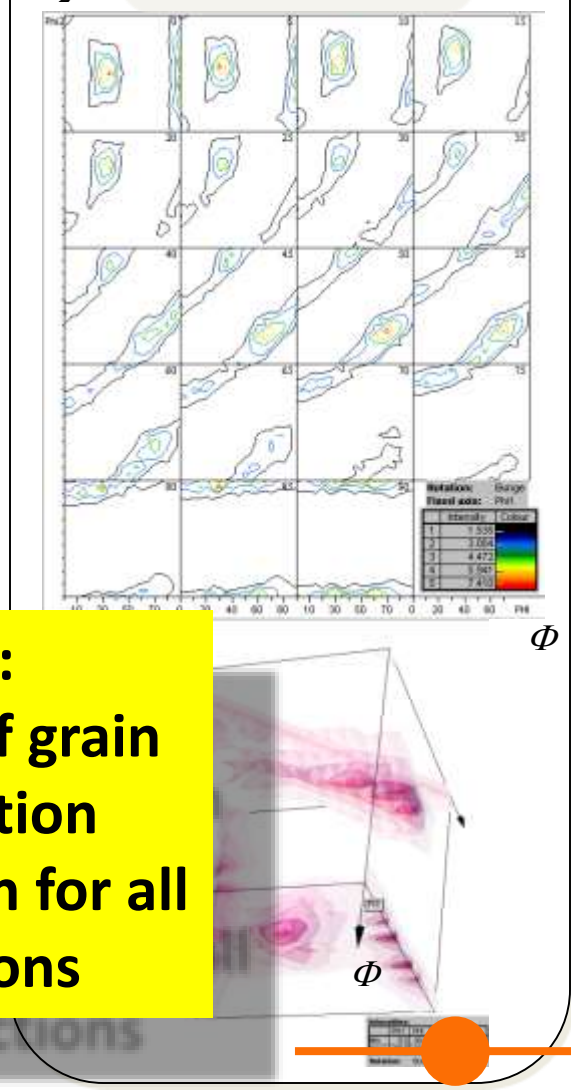


Pole figure: Distribution of grains with a particular (hkl) orientation

- Texture orientation and quantification.
- Volume fraction of textured grains, twinning and random distributions.
- Texture strength and sharpness.
- Crystallographic orientation.
- Crystallographic relationship between layers and substrate.



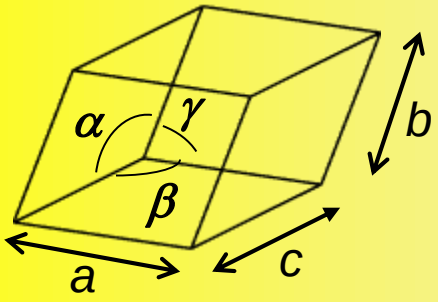
Orientation distribution function (ODF)



ODF: fraction of grain orientation distribution for all directions

Data: Sardela, UIUC

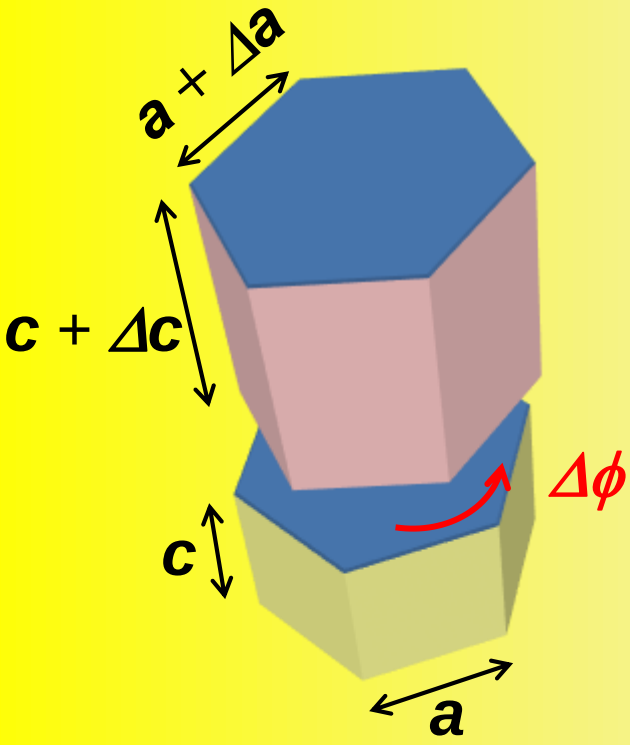
High resolution XRD methods



Single crystals:

Accurate measurements of ***a, b, c, α, β, γ***

Detailed peak shapes: defects, mosaicity.

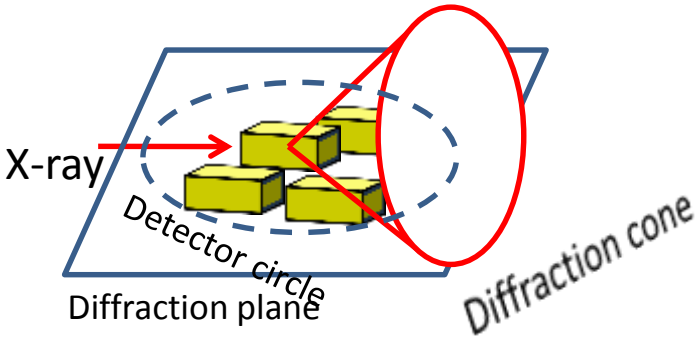


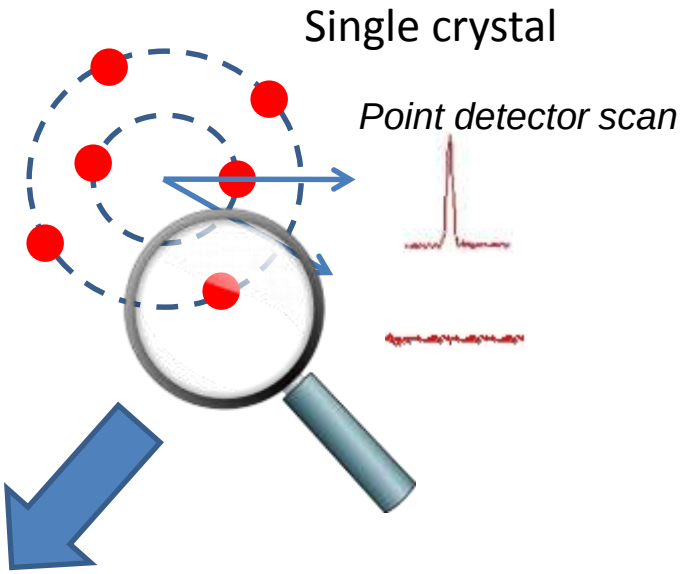
Film / substrate epitaxial systems:

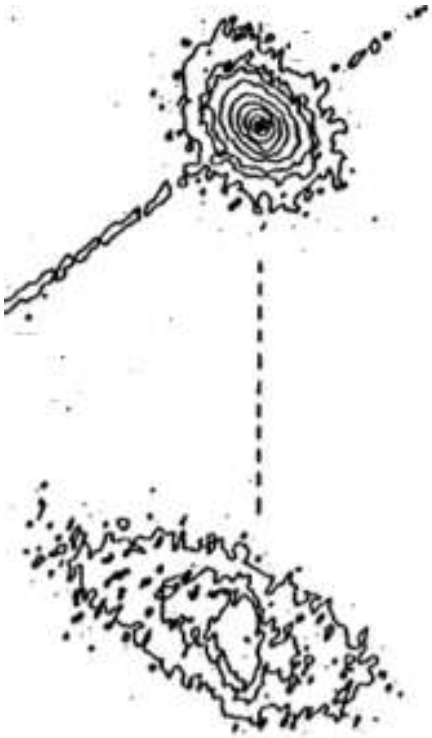
Measure small variations Δa, Δc,… (~ 10^{-5}).

Measure layer tilts $\Delta\phi$, ...

Detailed peak shapes: defects, strain, mosaicity.



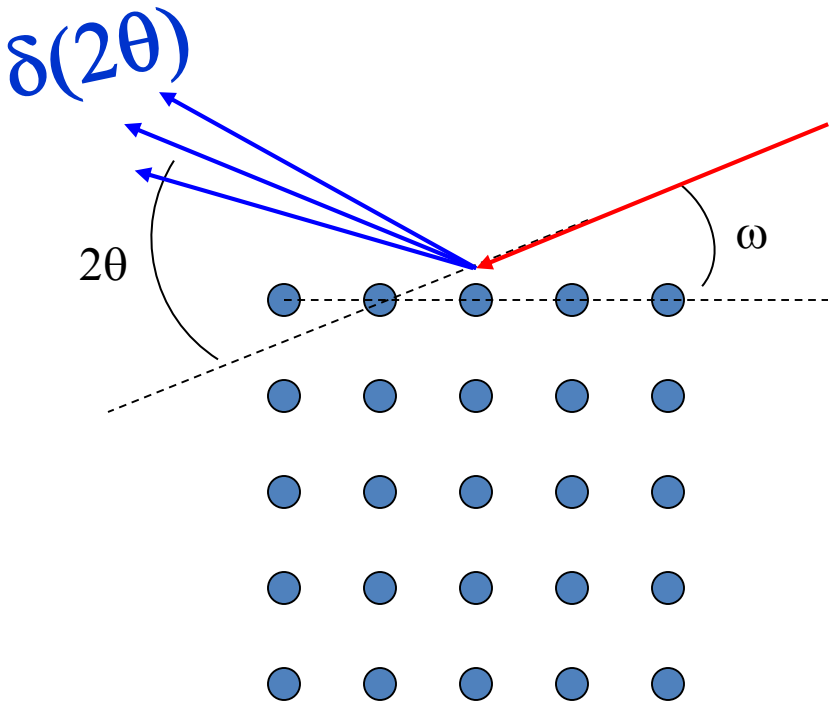




Multiple rlp's
Relative position
Orientation
Shape

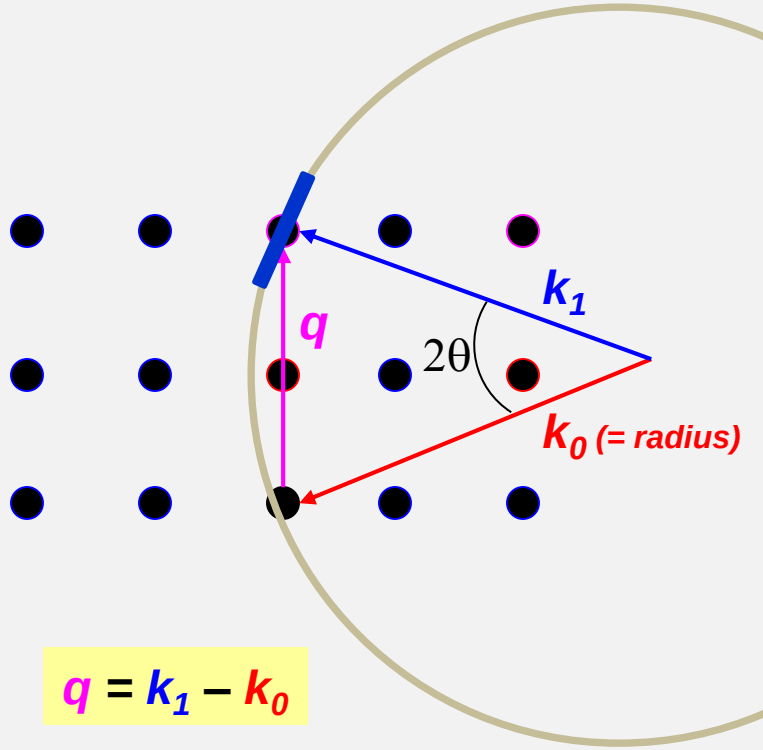
Instrument resolution in reciprocal space

"Real" space



Reciprocal space

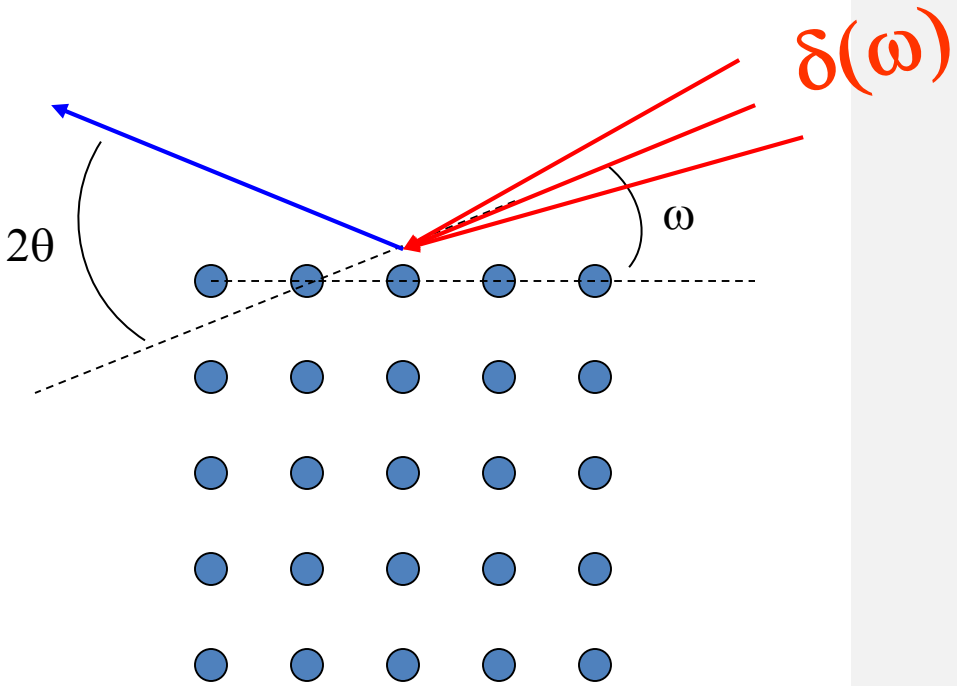
Ewald's sphere



$q = k_1 - k_0$

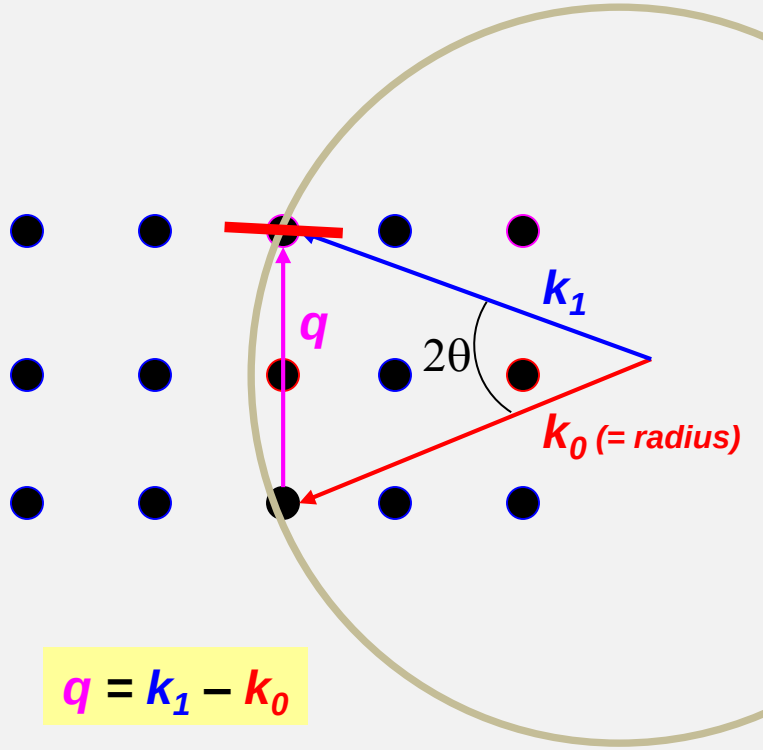
Instrument resolution in reciprocal space

"Real" space



Reciprocal space

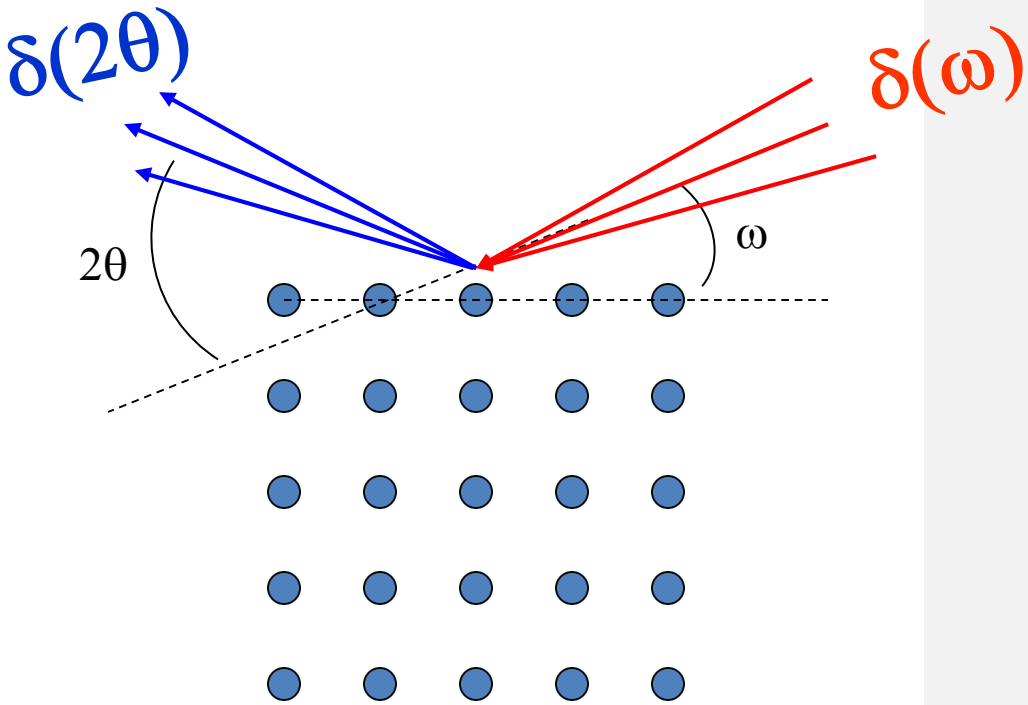
Ewald's sphere



$q = k_1 - k_0$

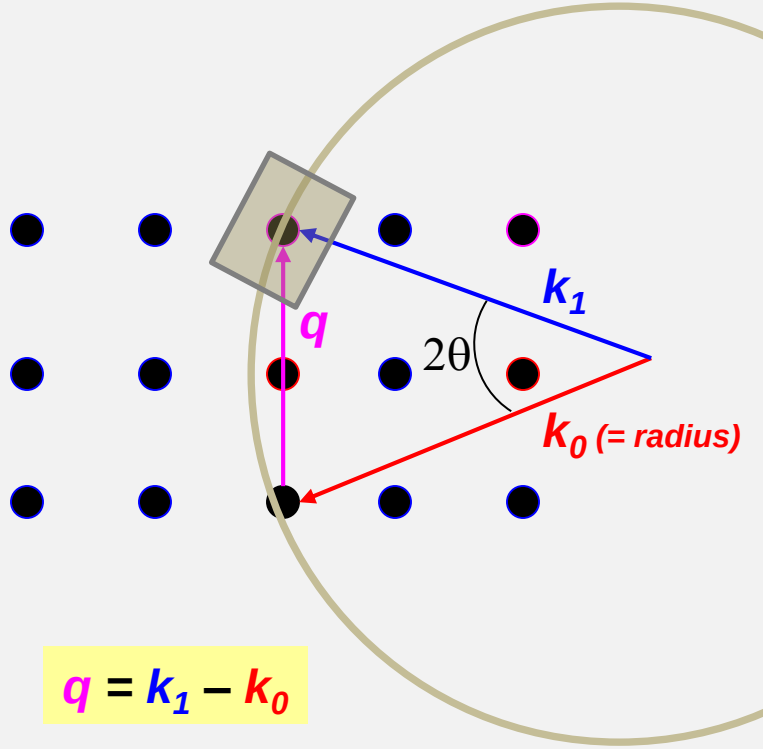
Instrument resolution in reciprocal space

"Real" space



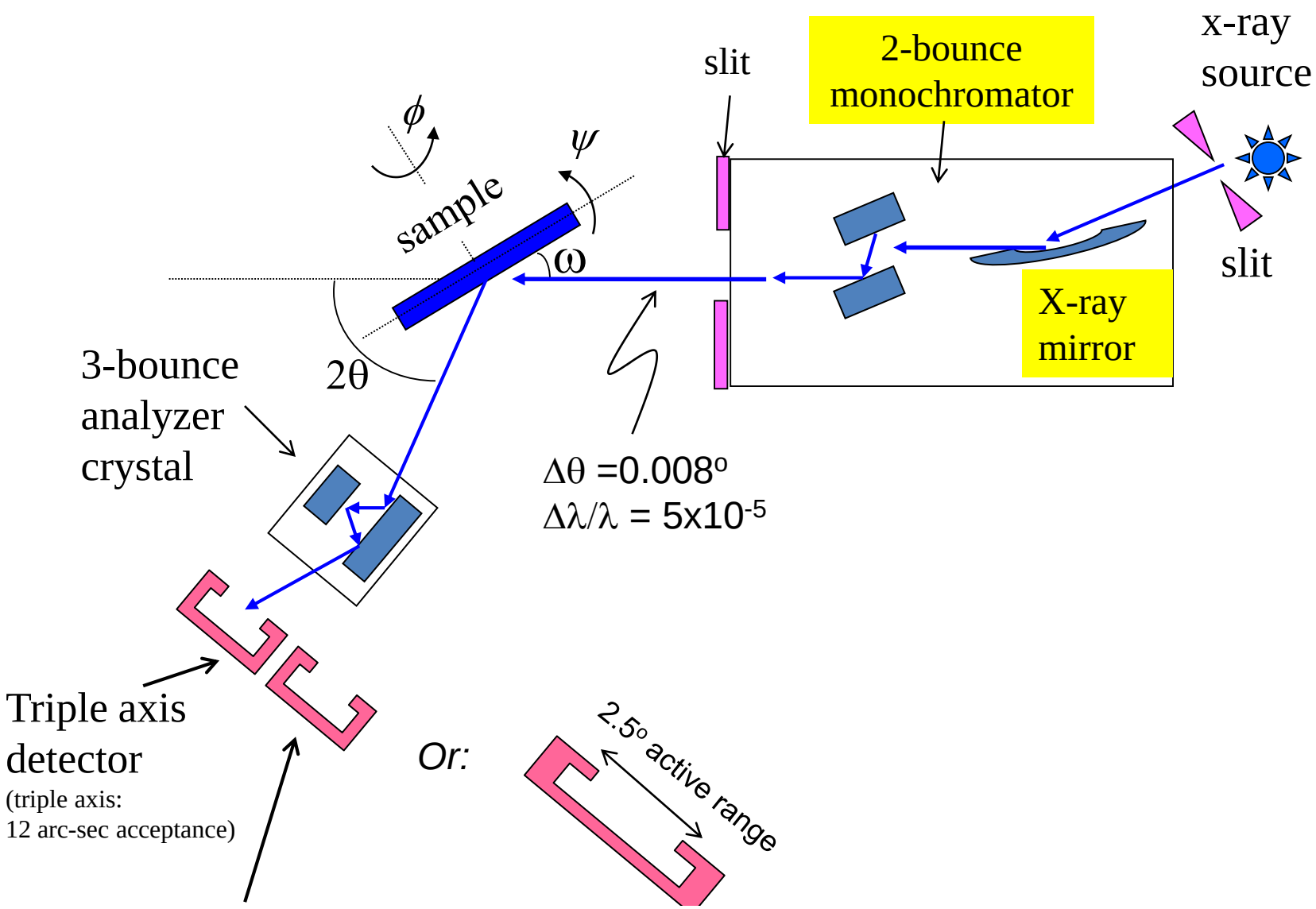
Reciprocal space

Ewald's sphere



$q = k_1 - k_0$

Instrumentation: high resolution configuration

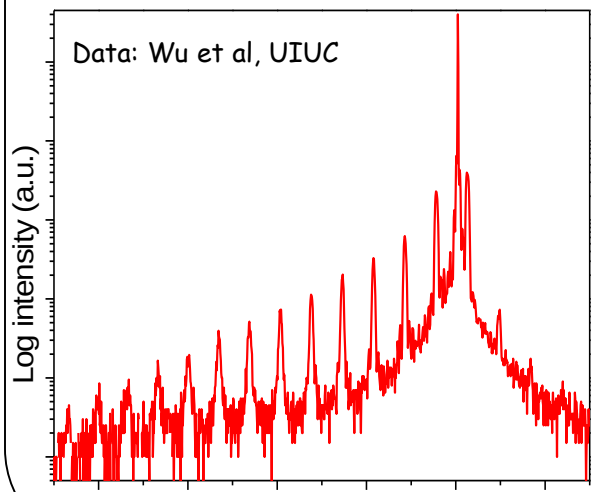


High resolution x-ray analysis

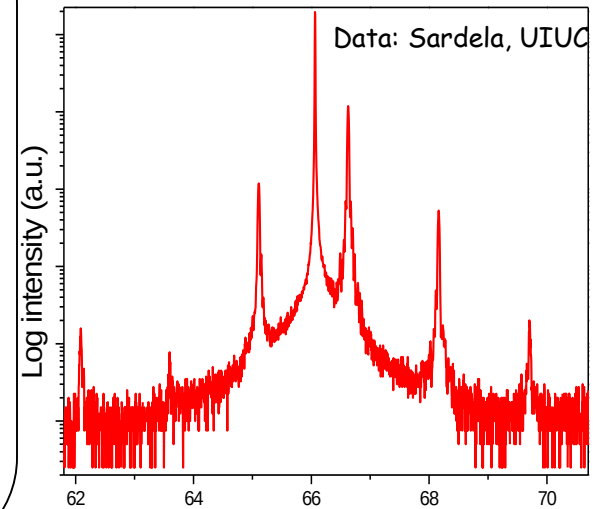
- Lattice distortions within 10^{-5}.
- Rocking curve analysis.
- Film thickness.
- Strain relaxation and lattice parameter measurements.
- Alloy composition and superlattice periods.
- Interface smearing in heterostructures (dynamical simulation).

Single crystals
Epitaxial films
Heterostructures
Superlattices
Quantum dots

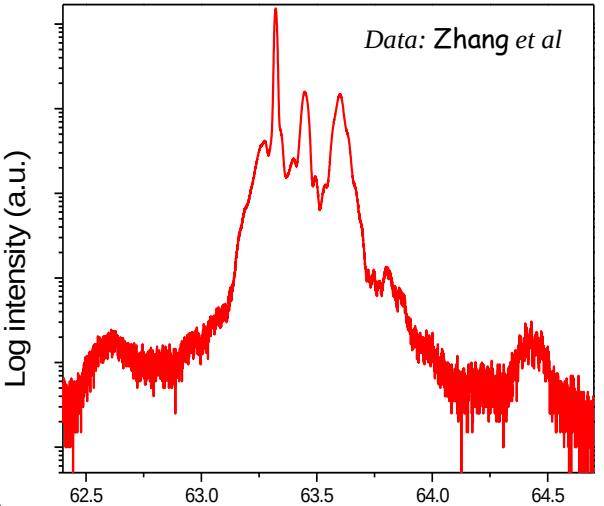
InAs / GaAs multilayer



SiGe / Ge superlattice



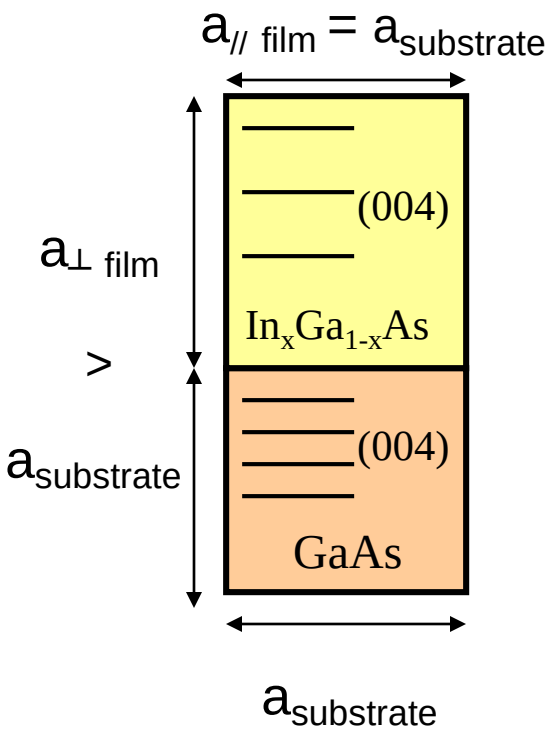
InAs quantum dots on GaAs



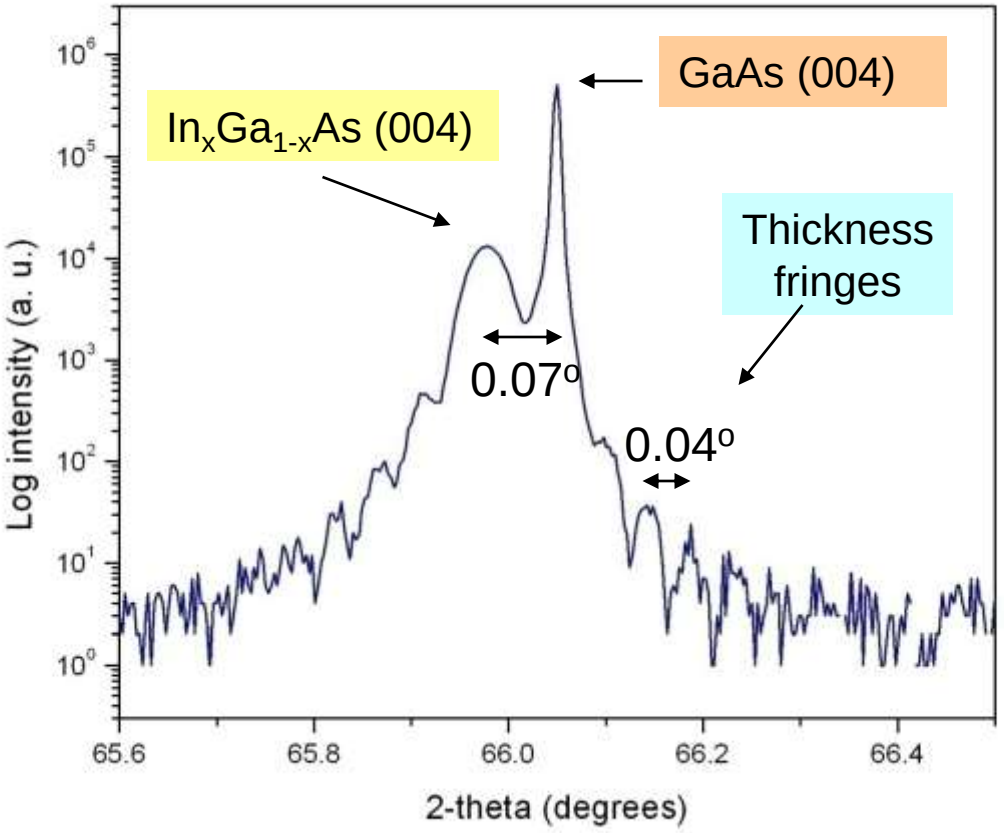
High resolution x-ray analysis

Example: strained $In_xGa_{1-x}As$ on GaAs (001) substrate

Lattice structure



High resolution 2θ/θ scan near GaAs(004)



$$\frac{\Delta a}{a} = \frac{\sin\theta(\text{substrate})}{\sin\theta(\text{film})} - 1$$

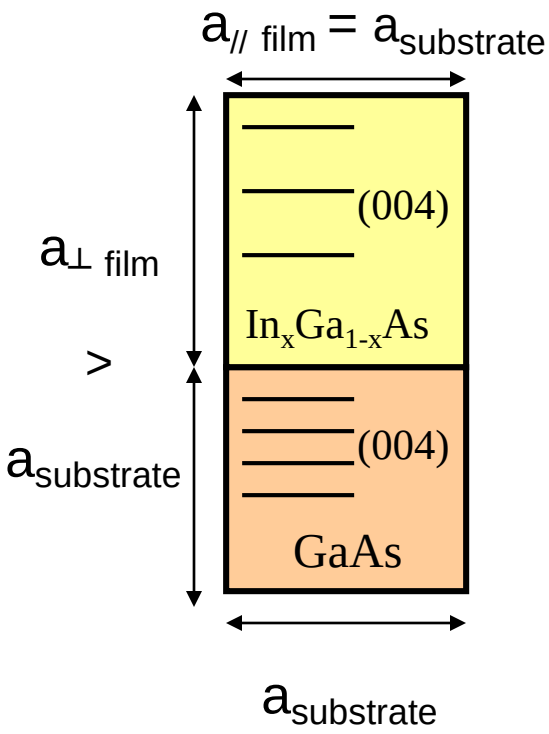
$$\text{Thickness} = \frac{\lambda}{2\,\Delta\theta\cos\theta}$$

Data: Sardela
Sample: Highland, Cahill, Coleman et at, UIUC

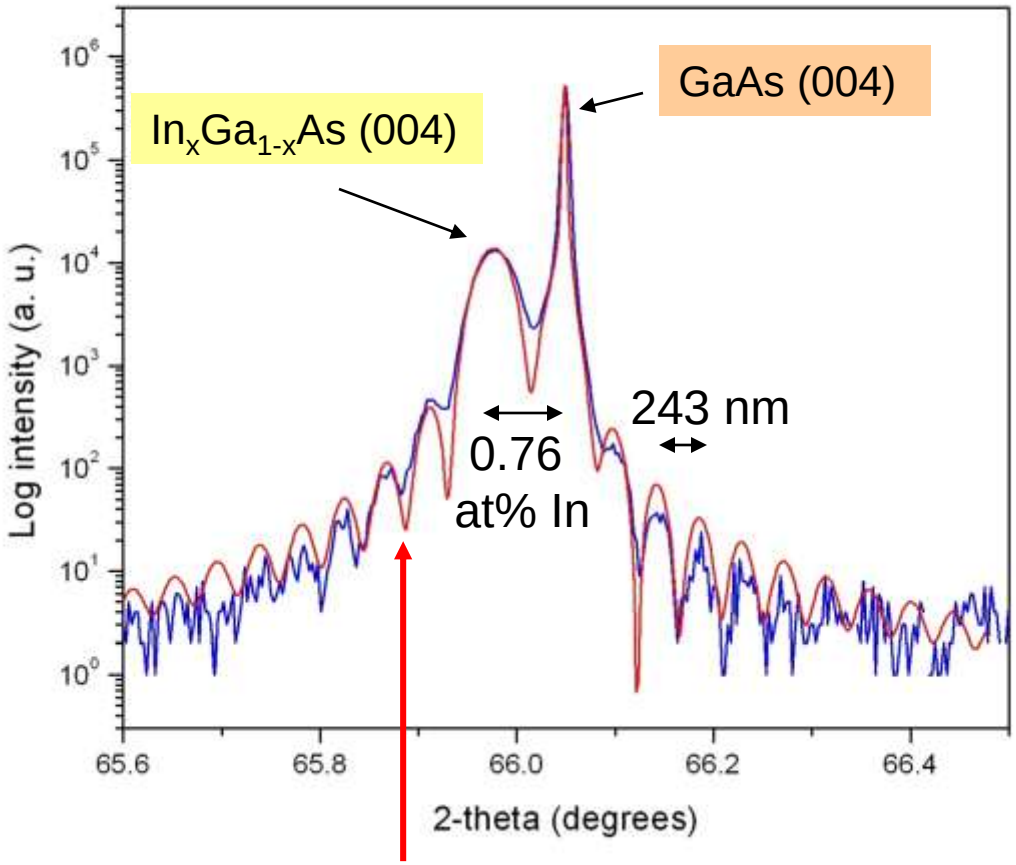
High resolution x-ray analysis

Example: strained $In_xGa_{1-x}As$ on GaAs (001) substrate

Lattice structure



High resolution 2θ/θ scan near GaAs(004) and dynamical scattering simulation

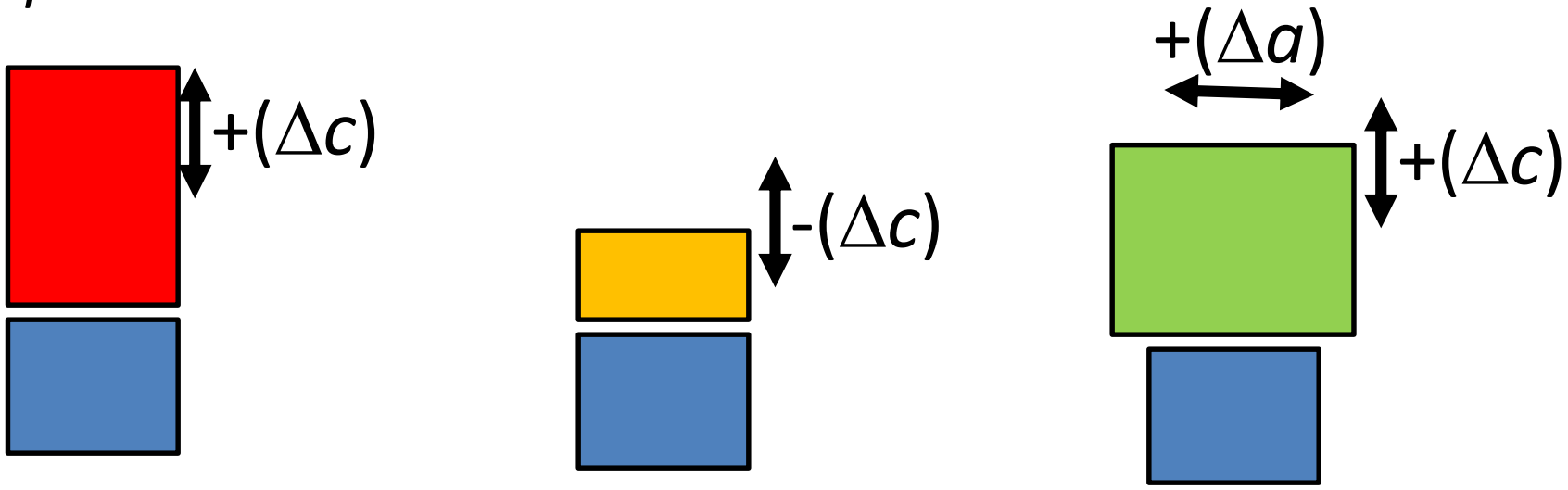


Takagi-Taupin dynamical scattering simulation

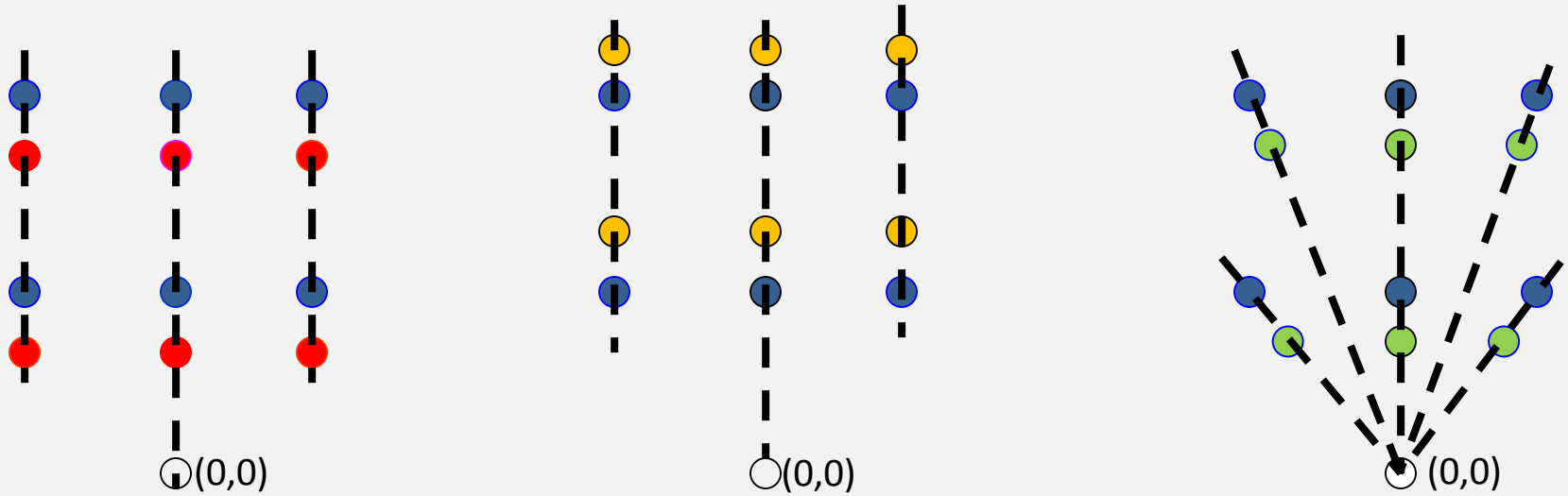
Data: Sardela
Sample: Highland, Cahill, Coleman, et al, UIUC

Reciprocal space mapping

Direct space:



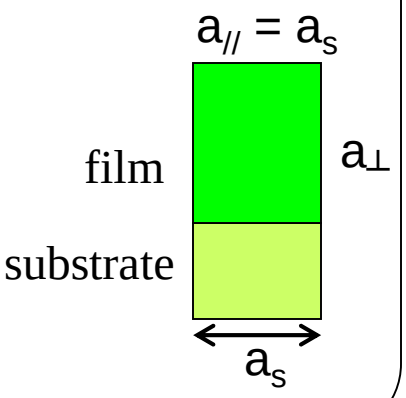
Reciprocal space:



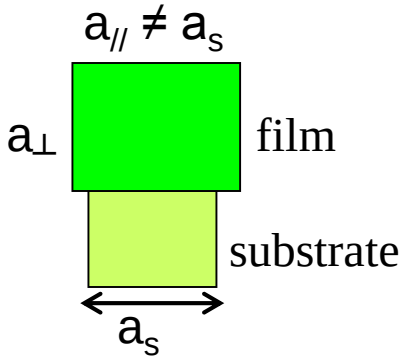
Reciprocal space mapping

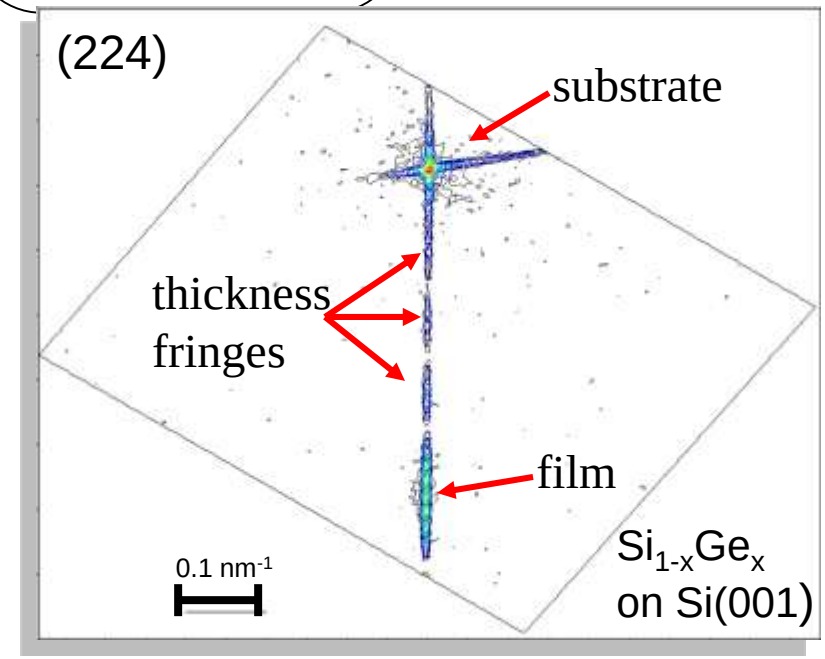
- Separation of strain and mosaicity
- Lattice distortions within 10^{-5}.
- Accurate lattice parameters in and out of plane
- Strain and composition gradients
- Strain relaxation
- Mosaic size and rotation
- Misfit dislocation density
- Nanostructure dimensions,
- Lattice disorder and diffuse scattering.

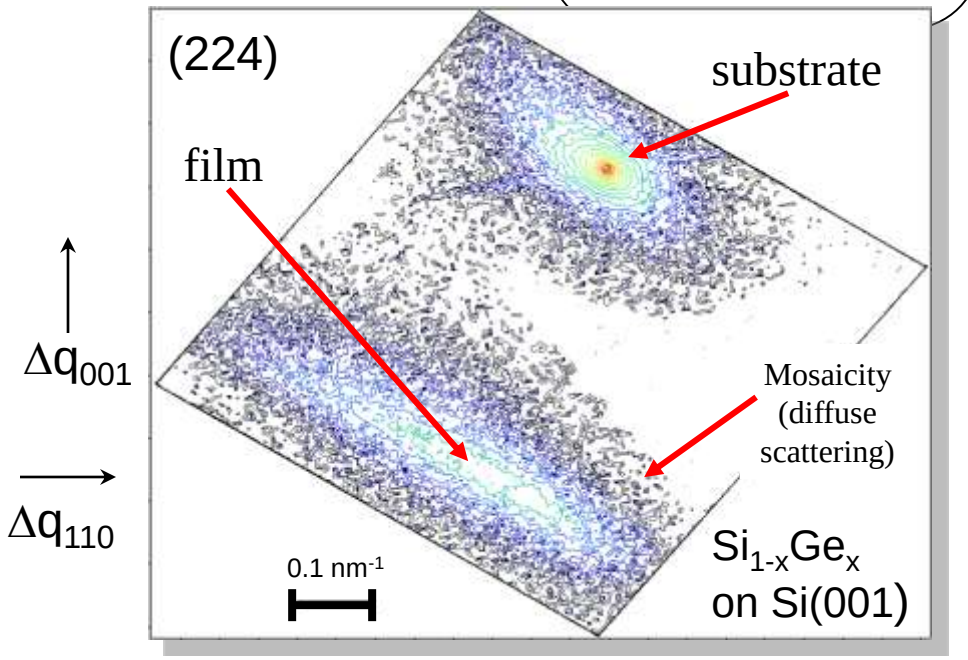
No strain relaxation:



Strain relaxation:



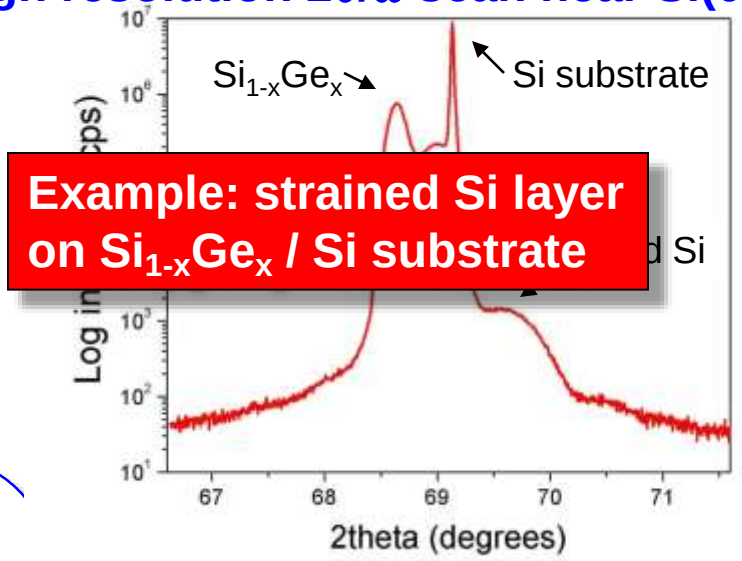




Data: Sardela et al

High resolution reciprocal space mapping

High resolution 2θ/ω scan near Si(004)



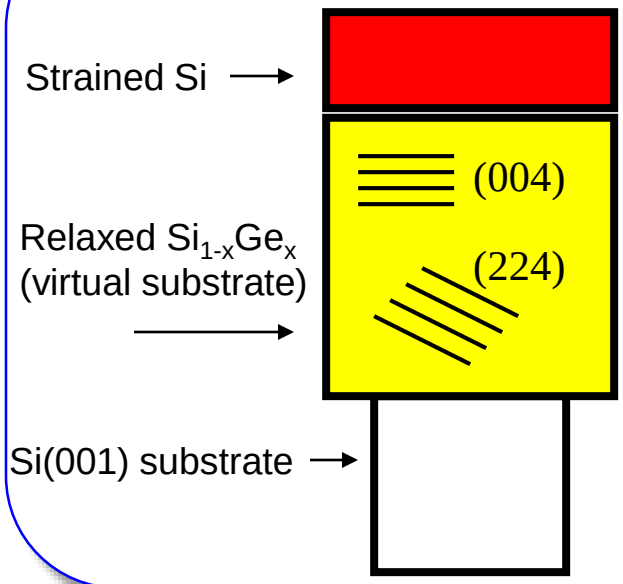
Layer structure

Strained Si (top layer, very thin)

Relaxed $Si_{1-x}Ge_x$ (thick, many microns)

Si(001) substrate

Lattice structure



Strain?

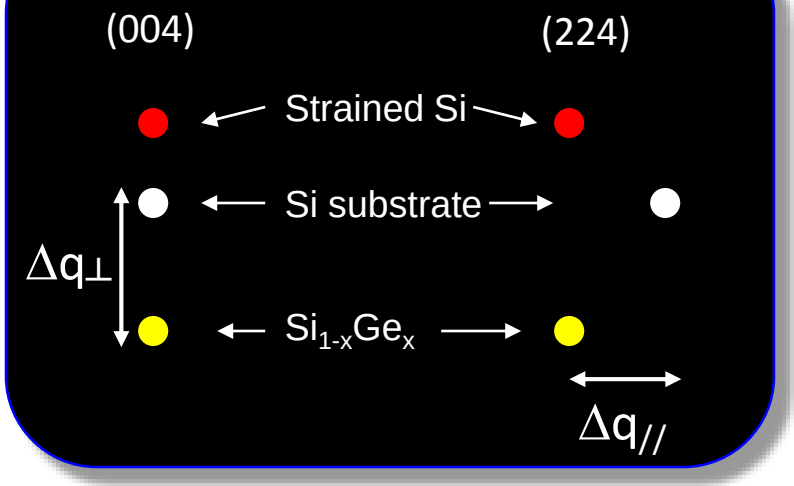
Lattice distortion?

% of relaxation?

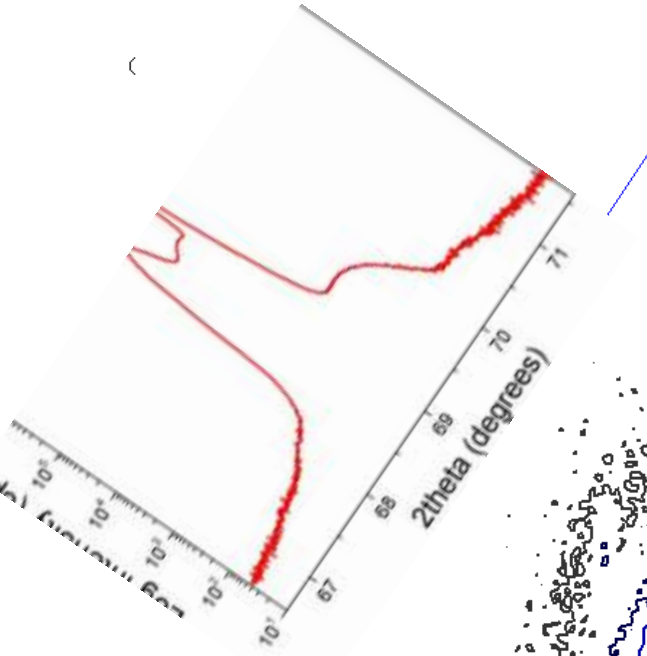
% of *Ge*?

Defects?

Reciprocal lattice

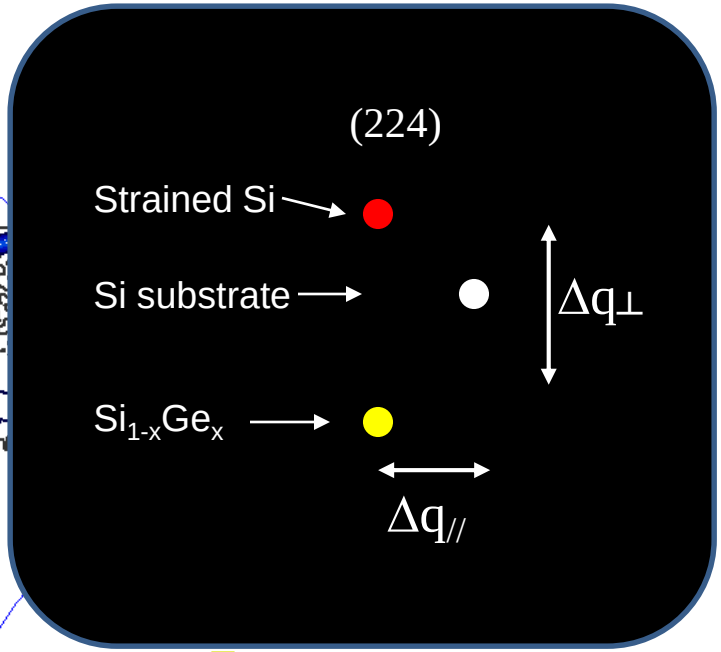


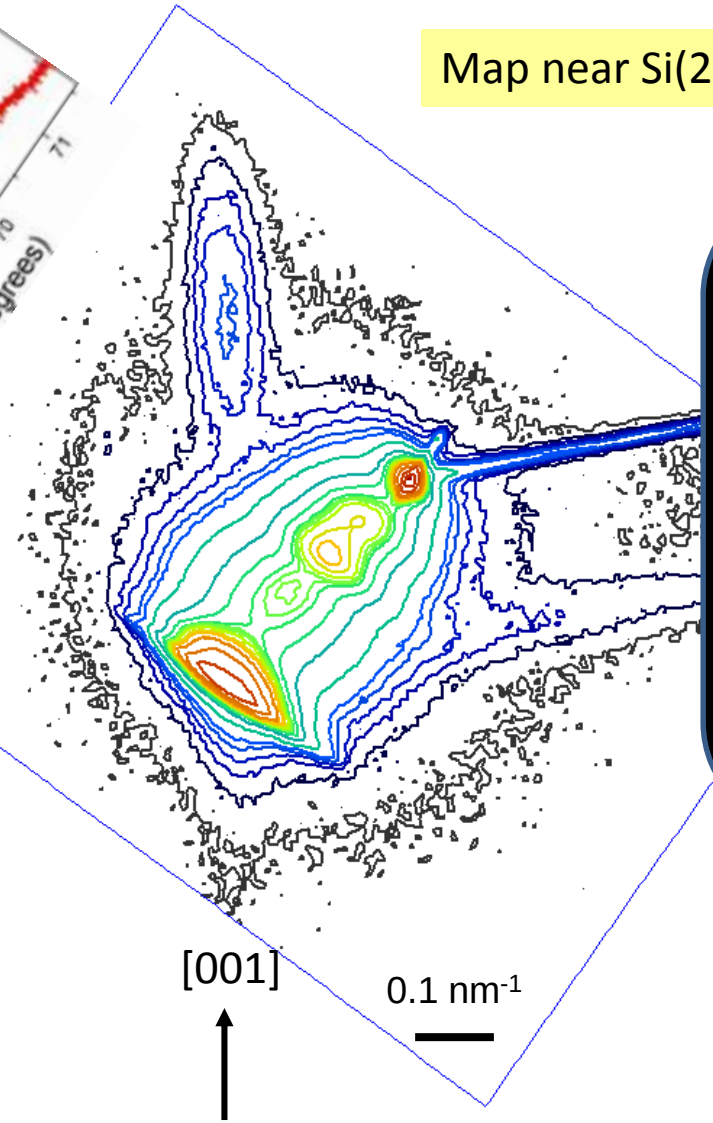
High resolution reciprocal space mapping

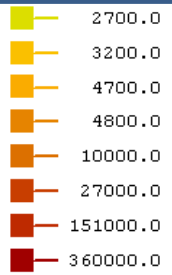


Map near Si(224)

Strained Si (top layer)
Relaxed $Si_{1-x}Ge_x$
Si(001) substrate

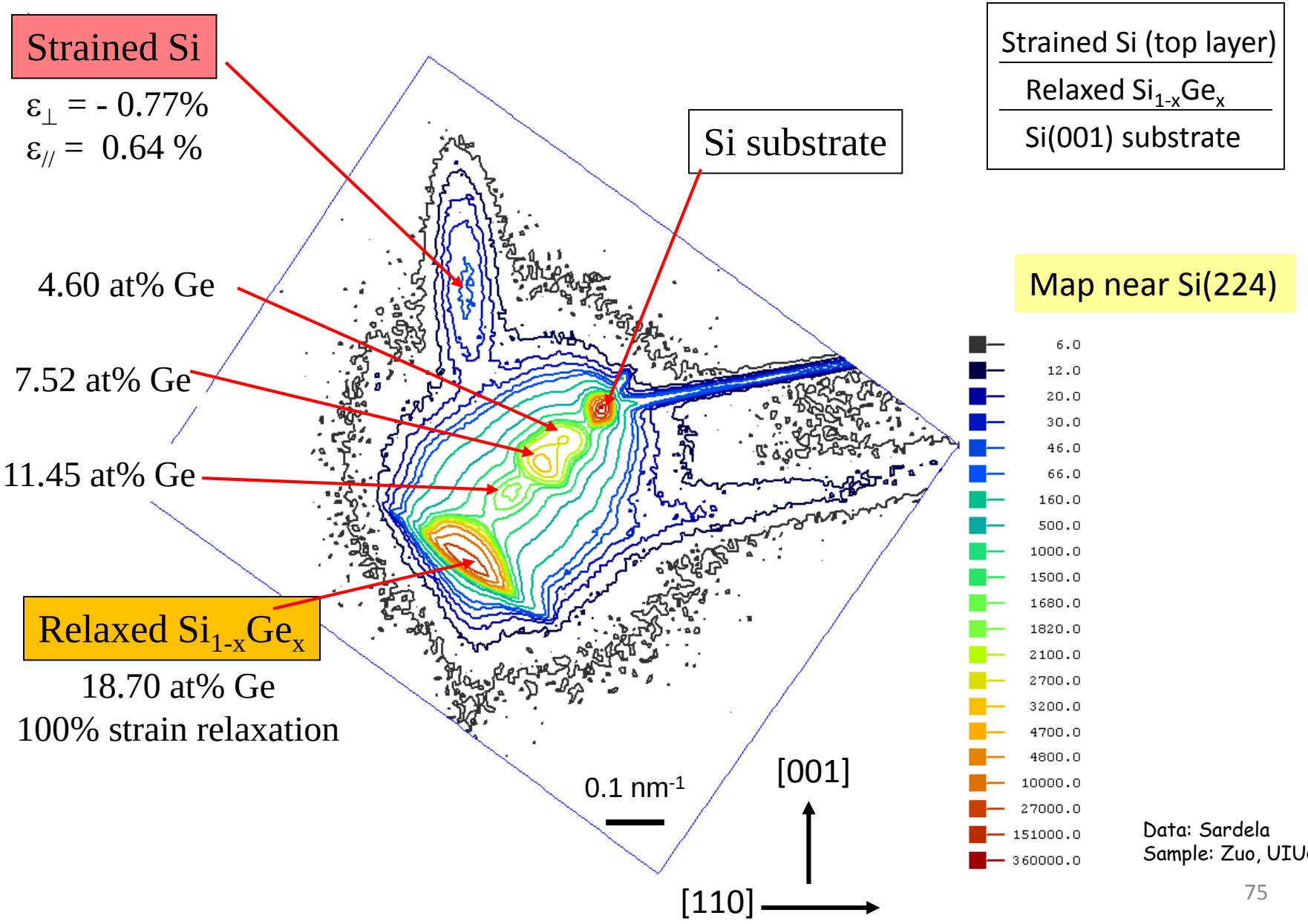




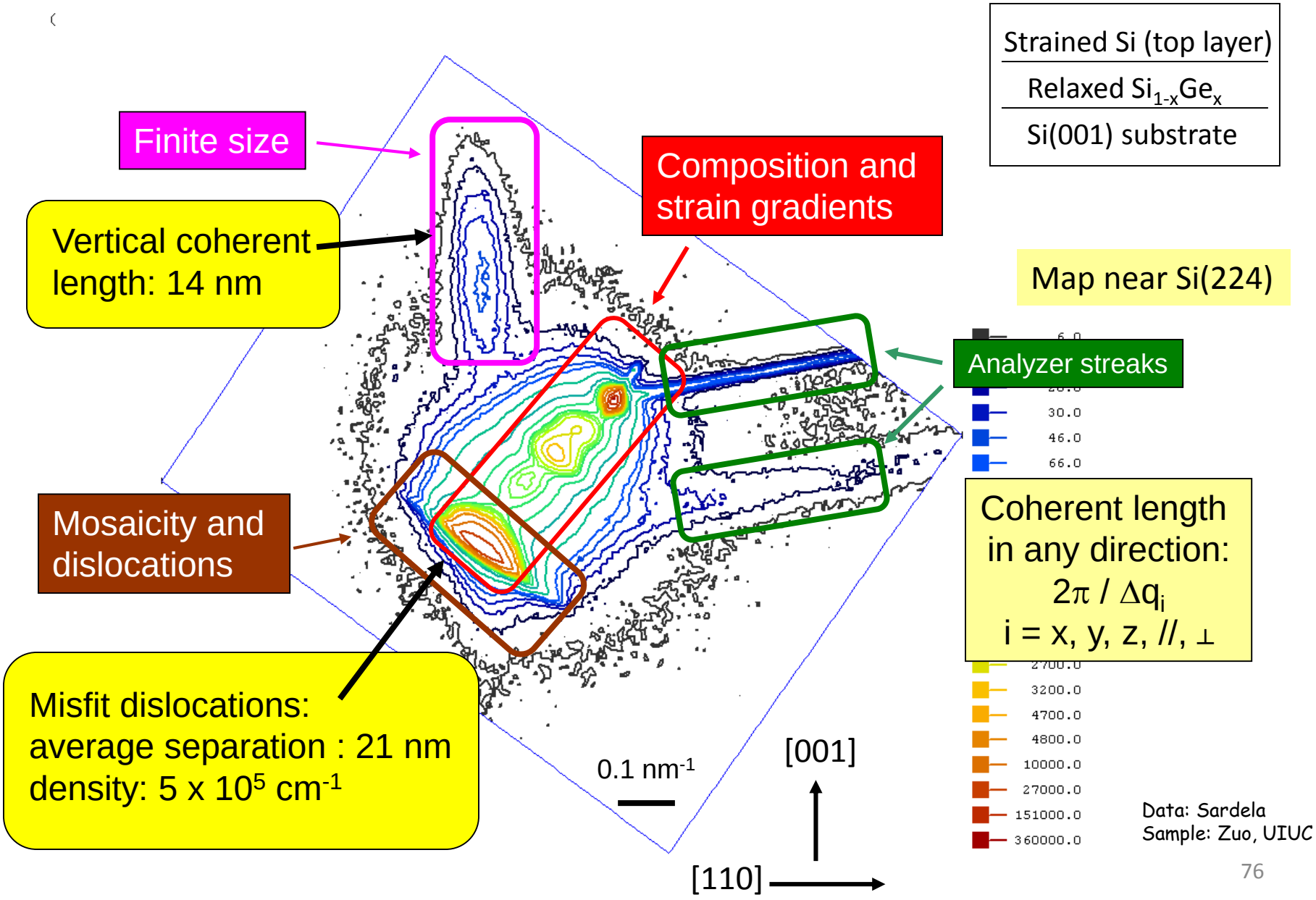


Data: Sardela
Sample: Zuo, UIUC

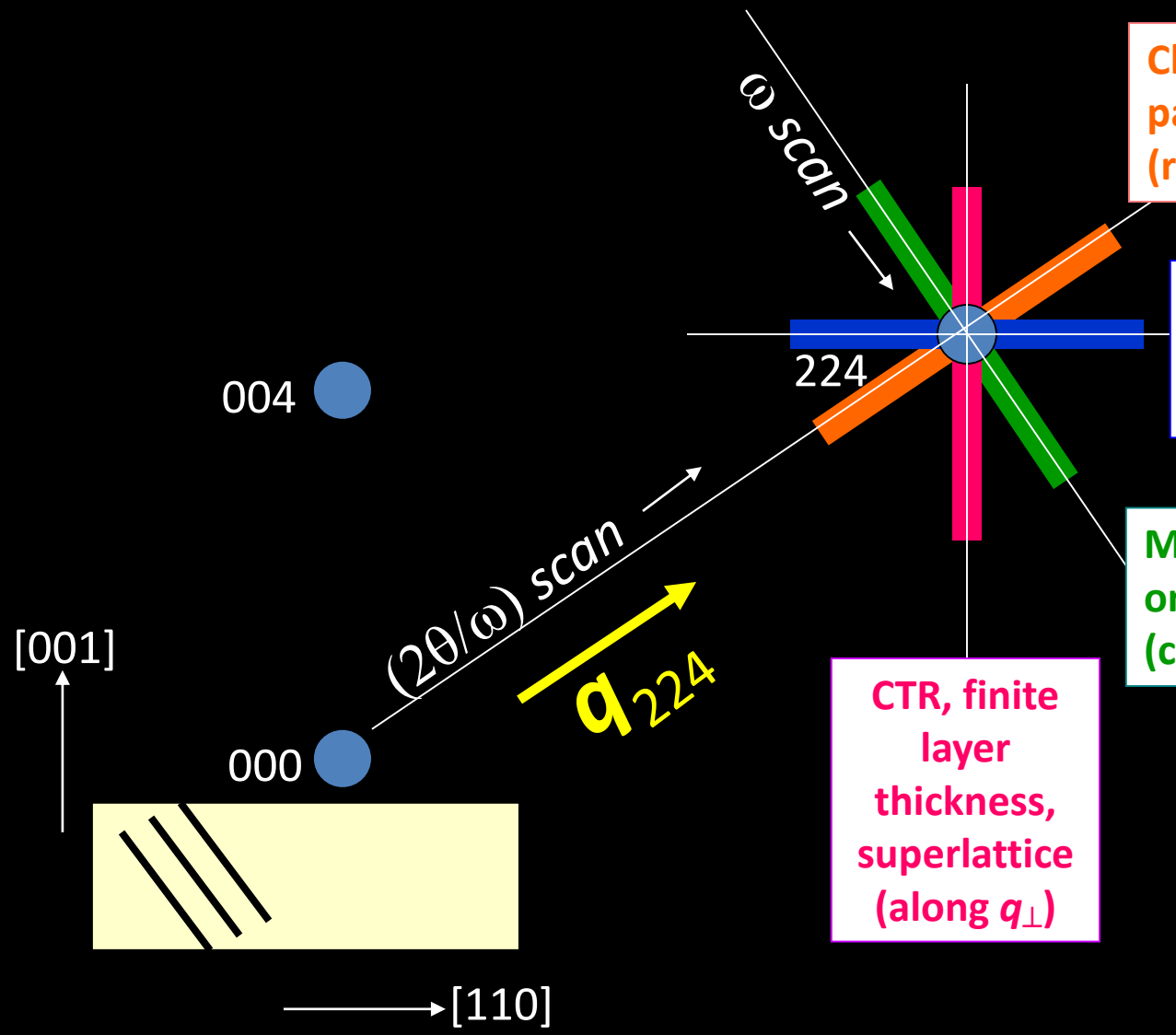
High resolution reciprocal space mapping



High resolution reciprocal space mapping



The “shape” of the reciprocal lattice point



Changes in lattice parameter (radial direction)

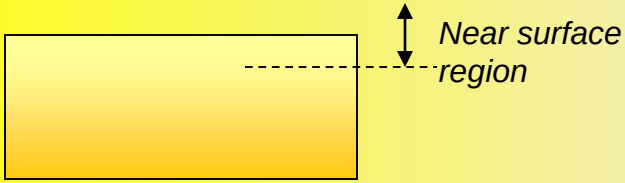
Lateral sub-grain boundaries (along $q_{//}$)

Mosaicity, curvature, orientation (circumferential direction)

CTR, finite layer thickness, superlattice (along $q_{\perp}$)

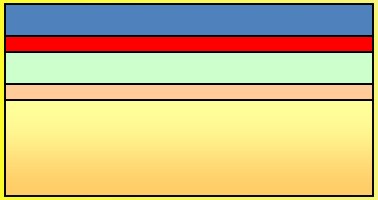
X-ray reflectivity

Bulk materials:



Liquids:

Multilayered systems:



Near surface and interface information on:

Density

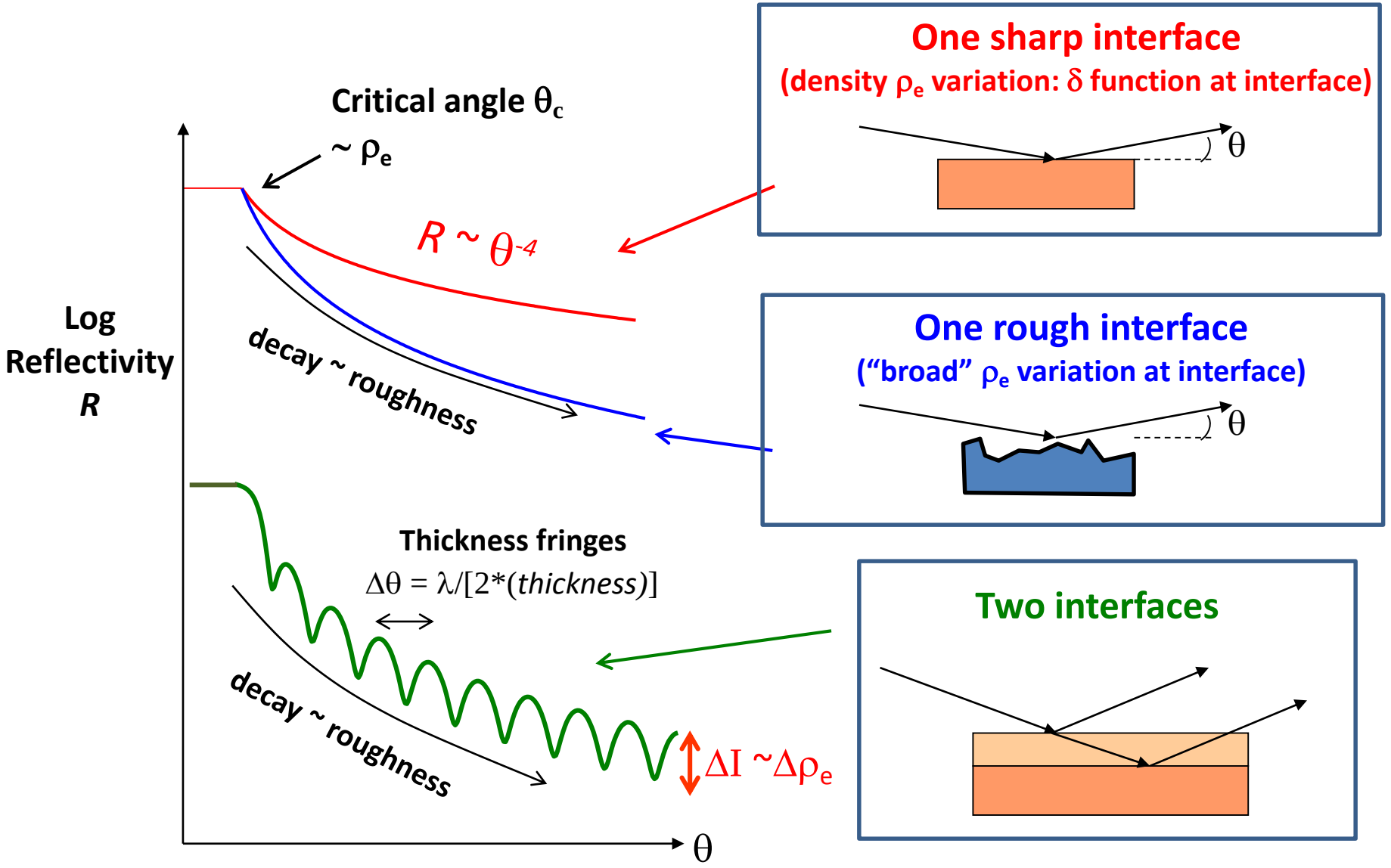
Porosity

Roughness

Thickness in films (ultra thin to thick)

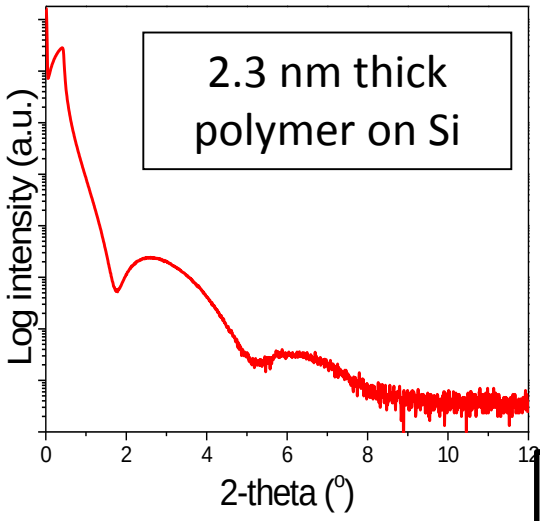
Amorphous or crystalline materials

X-ray reflectivity



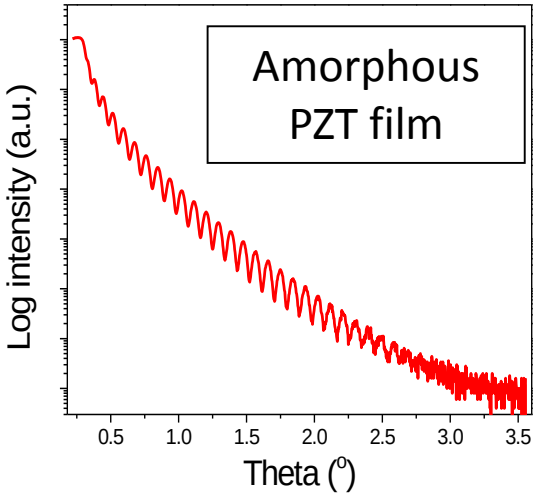
X-ray reflectivity analysis of thin films

Ultra-thin film



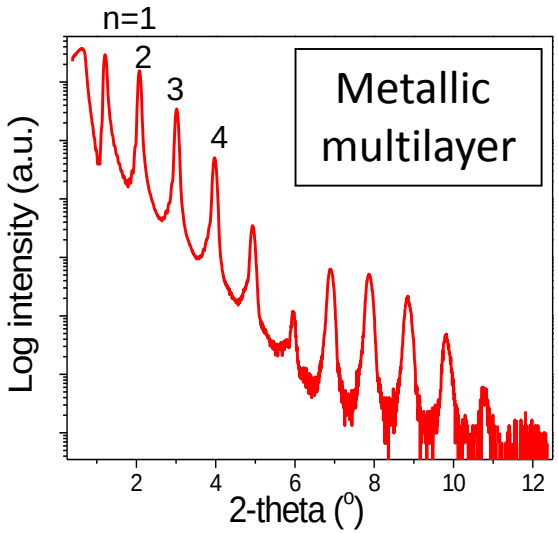
Data: Heitzman et al, UIUC

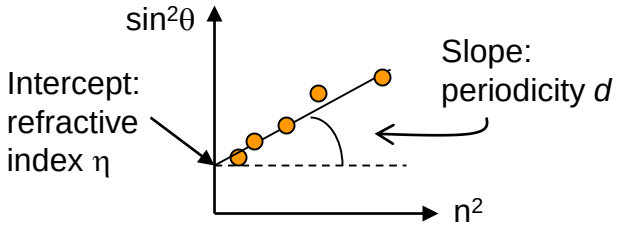
Non crystalline



Data: Mikalsen et al, UIUC

Multilayers



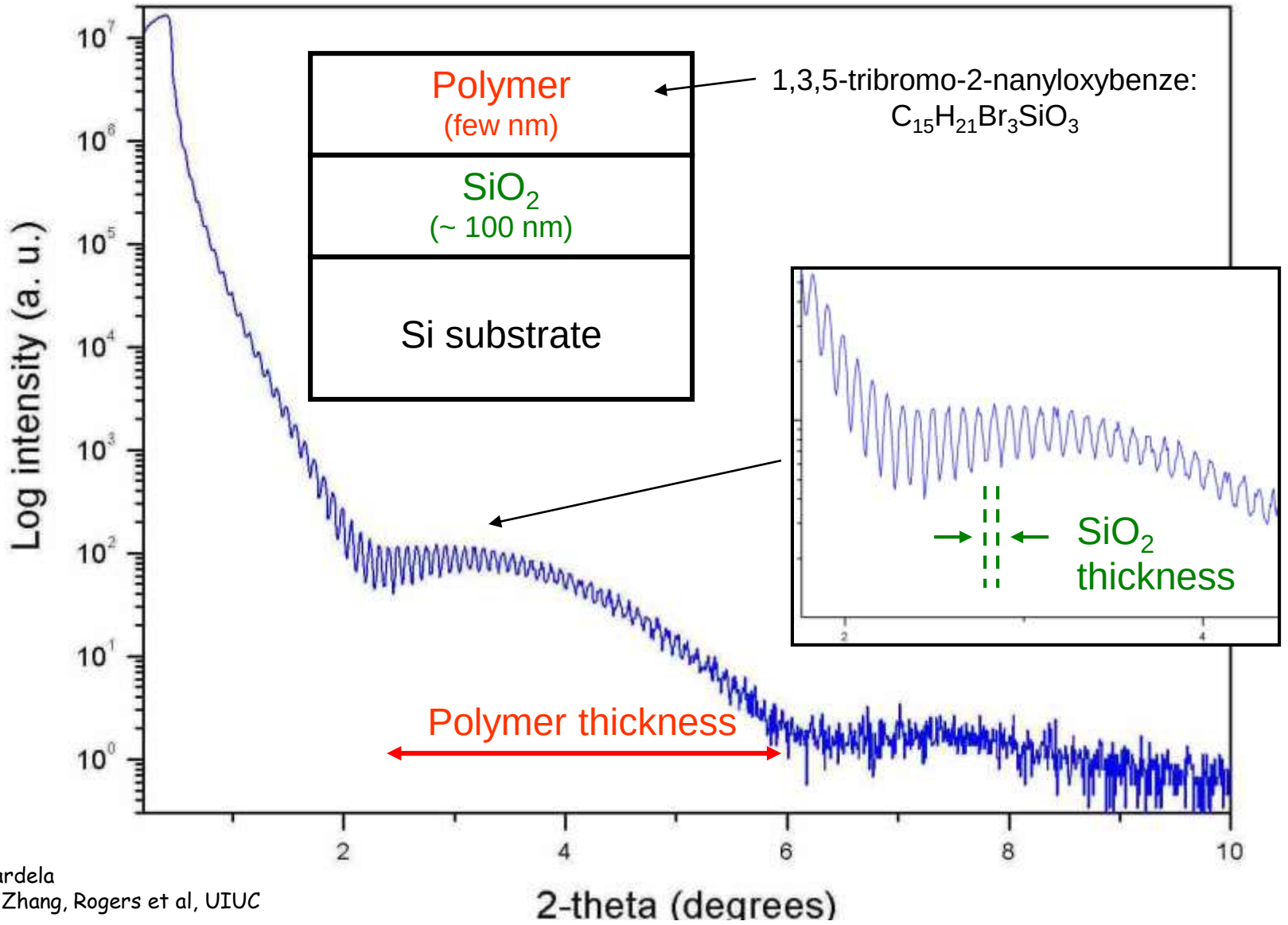


$\sin^2\theta = (\lambda^2/2d)^2\, n^2 - (\eta^2 - 1)$

(modified Bragg's law to include refractive index)

Data: Sardela, UIUC
Sample: Auoadi et al, SIU

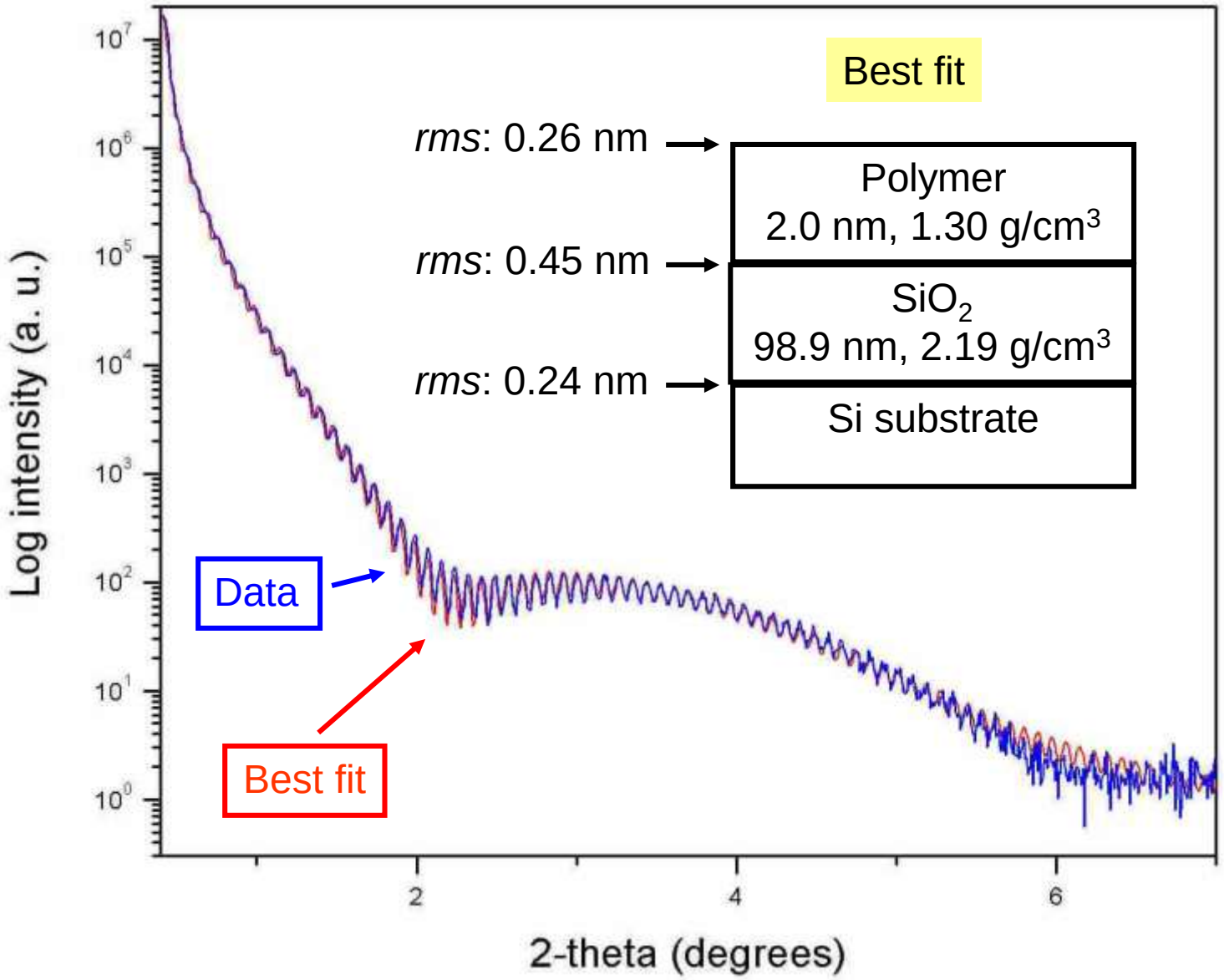
X-ray reflectivity data fitting in ultra-thin films



Data: Sardela
Sample: Zhang, Rogers et al, UIUC

X-ray reflectivity data fitting

Simulation using Parrat's formalism and generic algorithm fitting



X-ray reflectivity: summary

* Non destructive method
* Applicable to whole wafers (wafer mapping option)
* Fast method (in most cases)
* Do not depend on crystalline quality of the films
  (can also be used in amorphous layers).

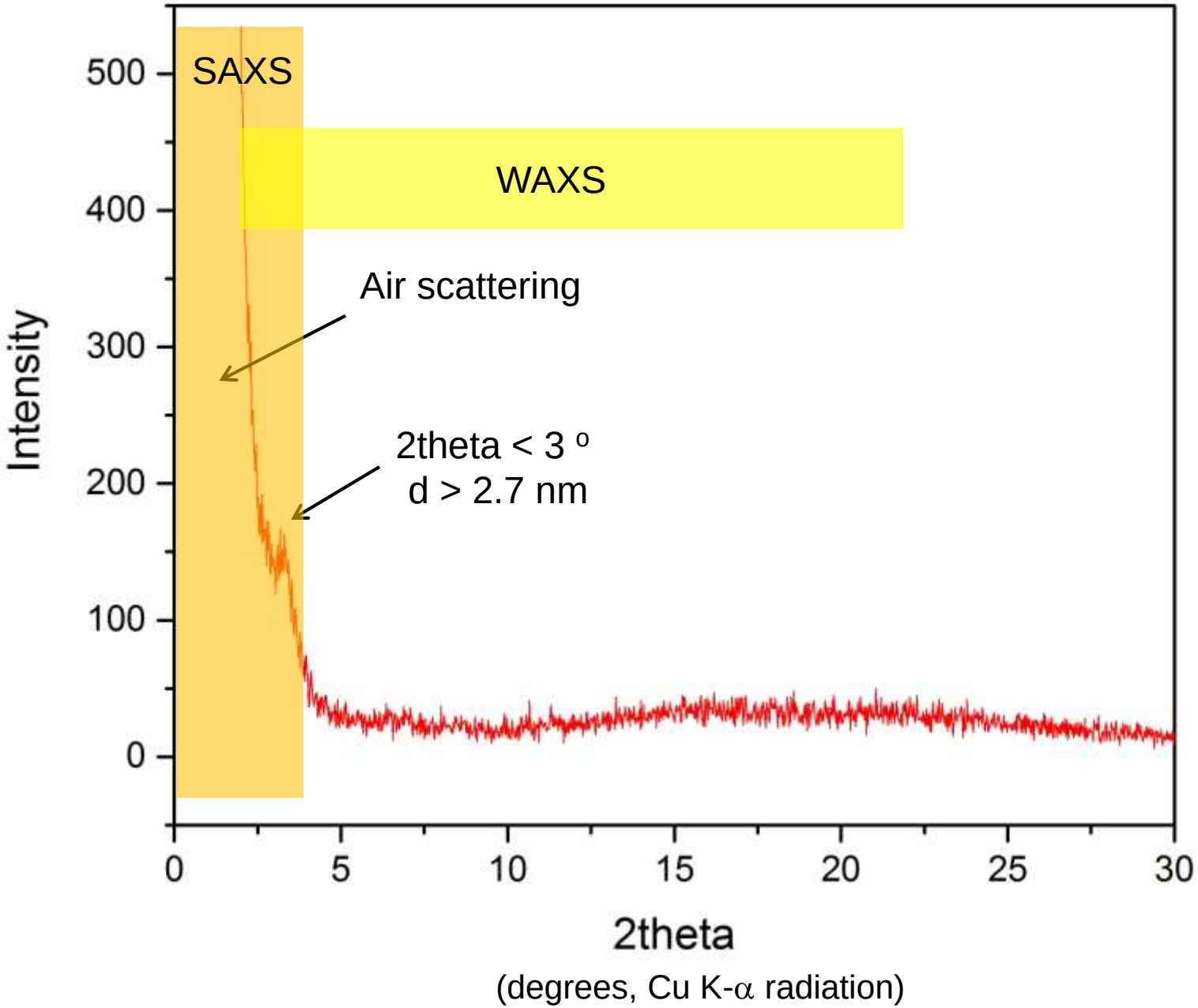
Quantification of:

* Layer thickness in thin films and superlattices: 1 nm ~ 1 μm (± 0.5-1%).
* Layer density and porosity (± 1-2%).
* Interface roughness: 0.1 – 10 nm (model dependent; reproducibility ~ 3%).
* Layer density gradients (variations > 2%).
* Interface roughness correlation in superlattices and multilayers.

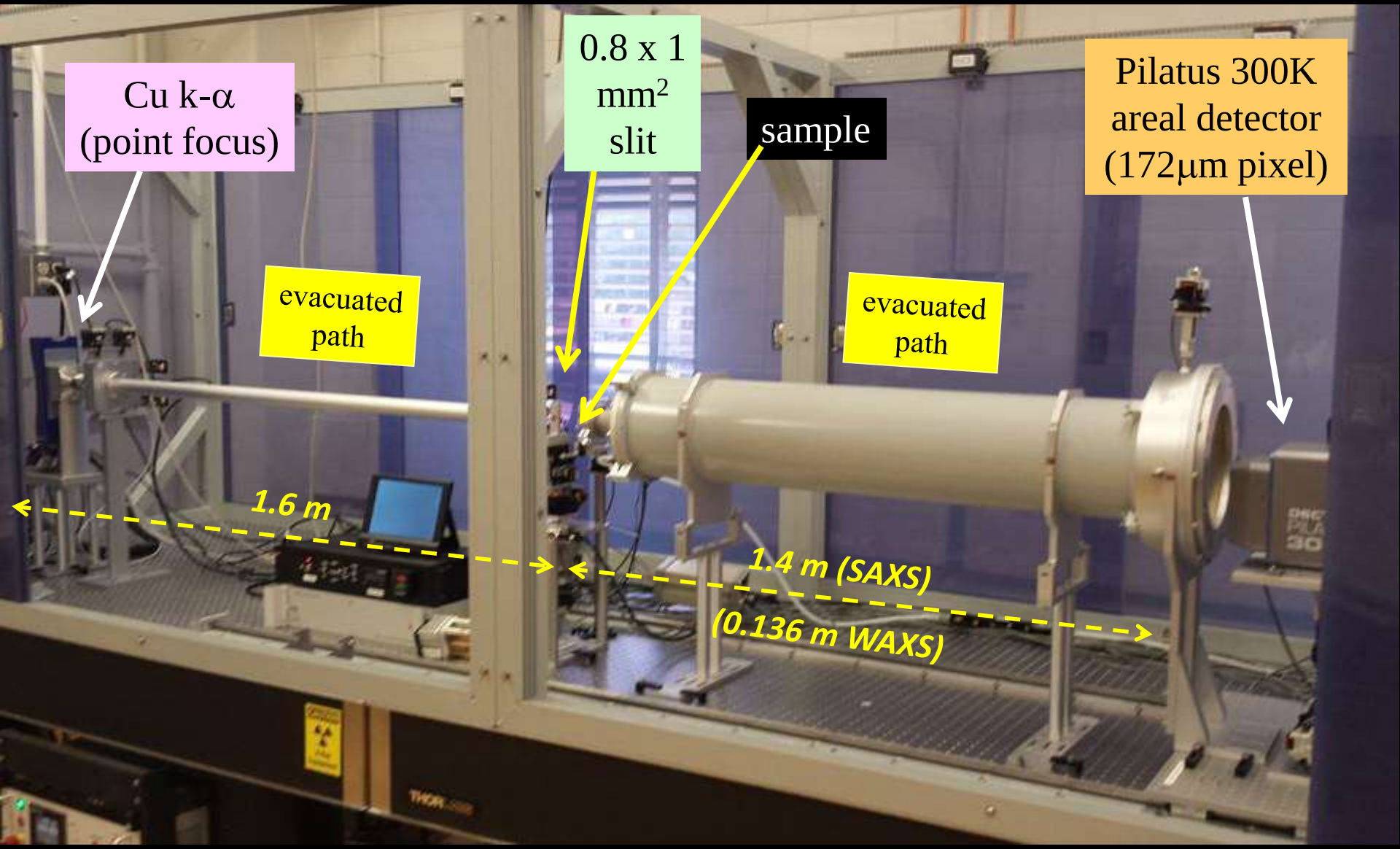
Alternative techniques:

* Thickness: optical methods (TEM, SEM) poor contrast issues.
* Density: RBS (issues for ultra thin layers).
* Interface roughness: AFM (surface only – not buried interfaces).

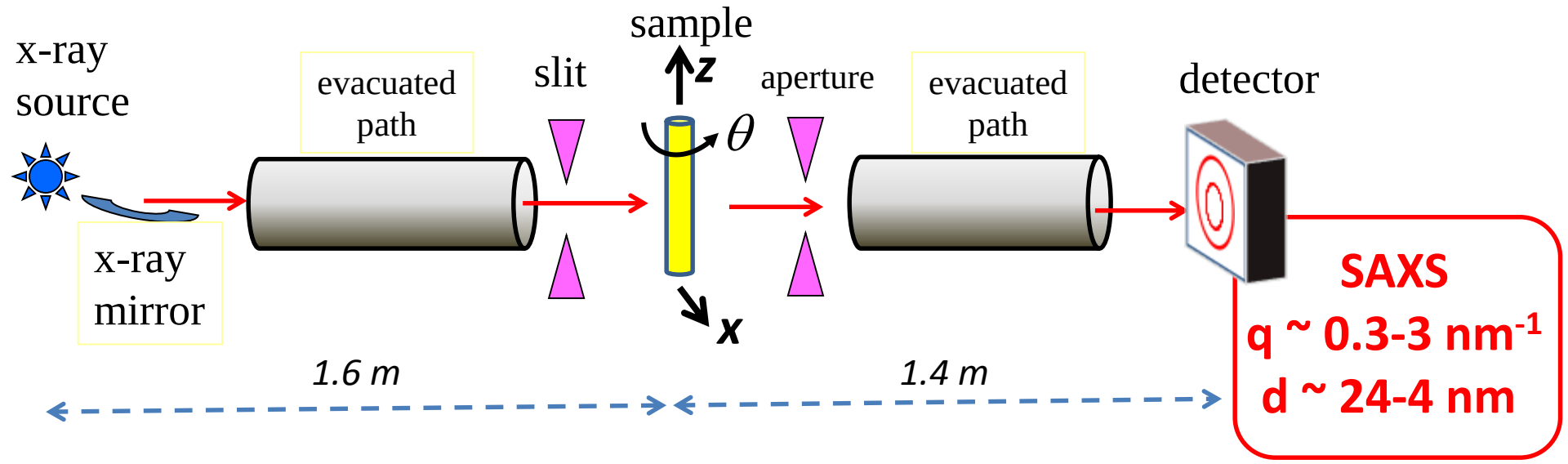
Small angles… large things…



SAXS instrument



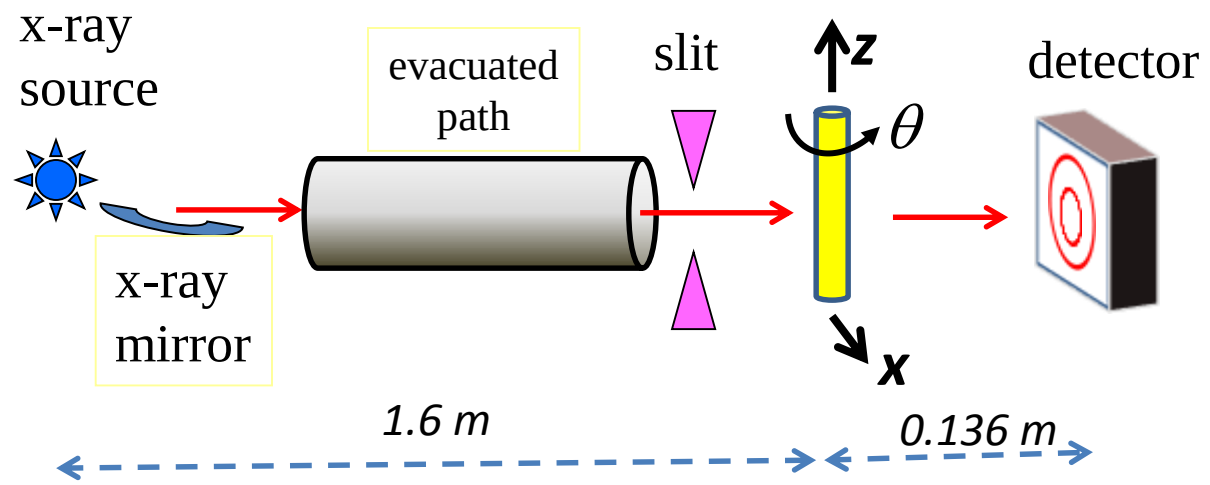
Small angle x-ray scattering



SAXS

q ~ 0.3-3 nm^{-1}

d ~ 24-4 nm



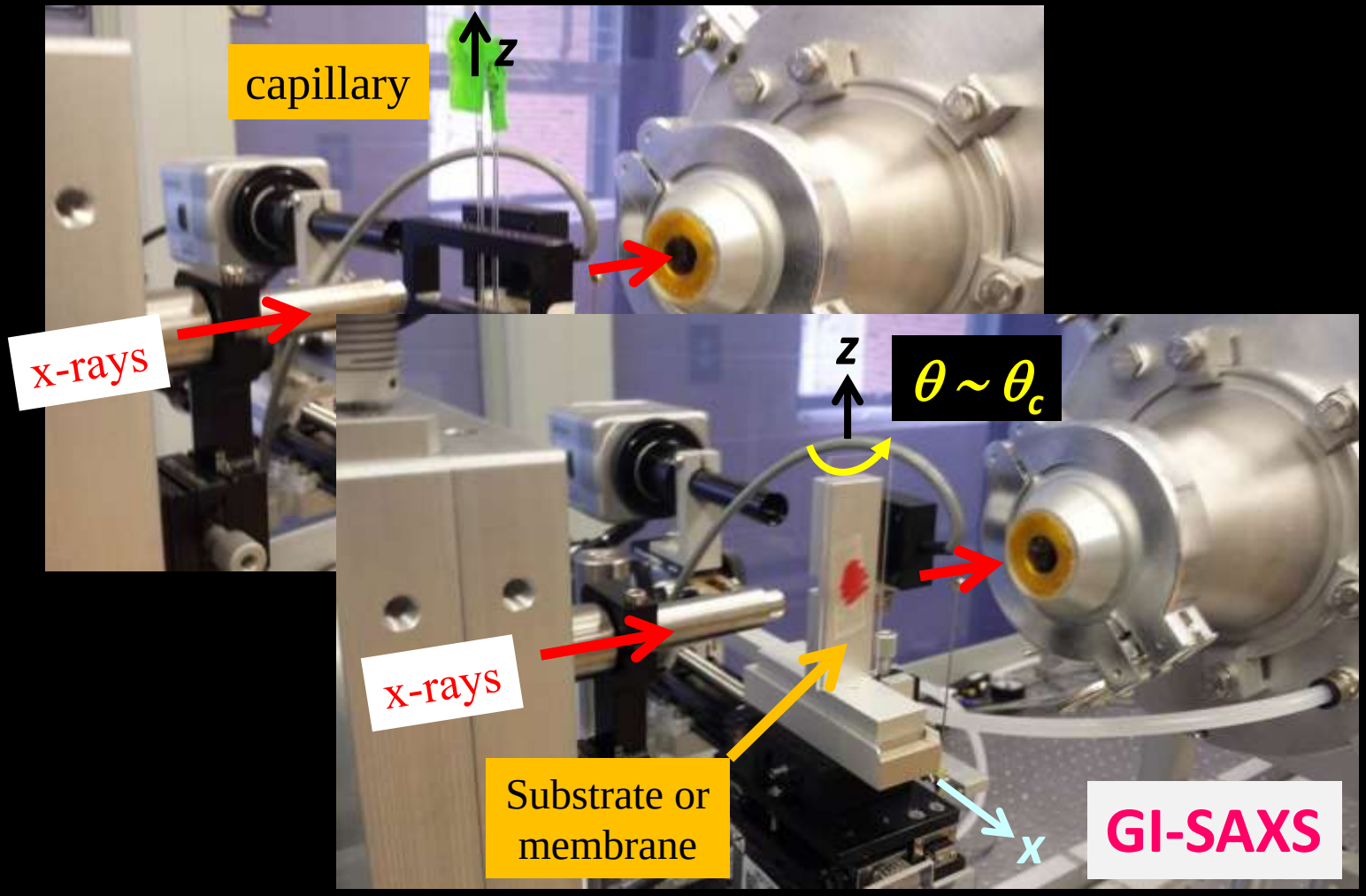
WAXS

(wide angle)

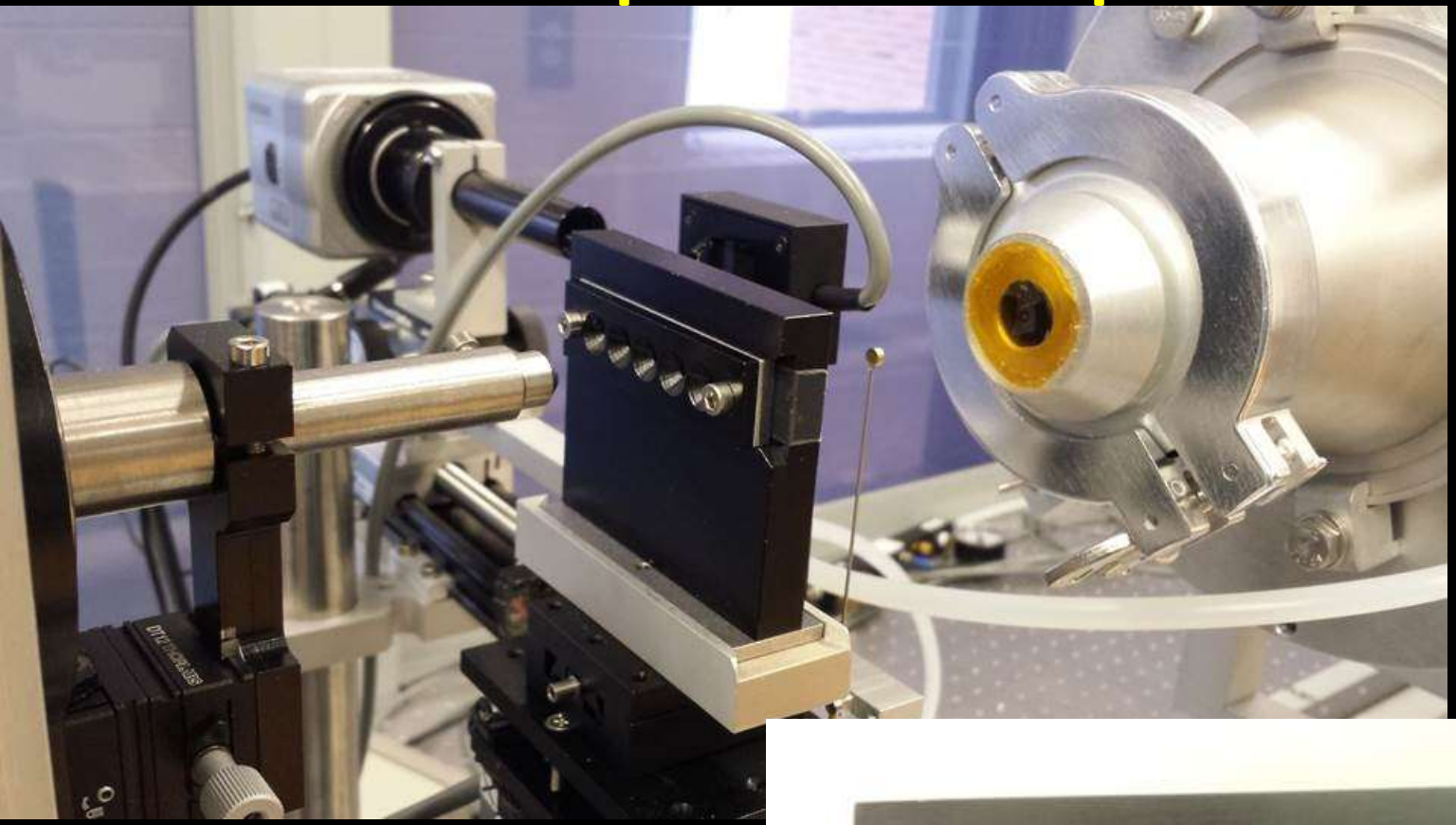
q ~ 1.3-13 nm^{-1}

d ~ 5-0.5 nm

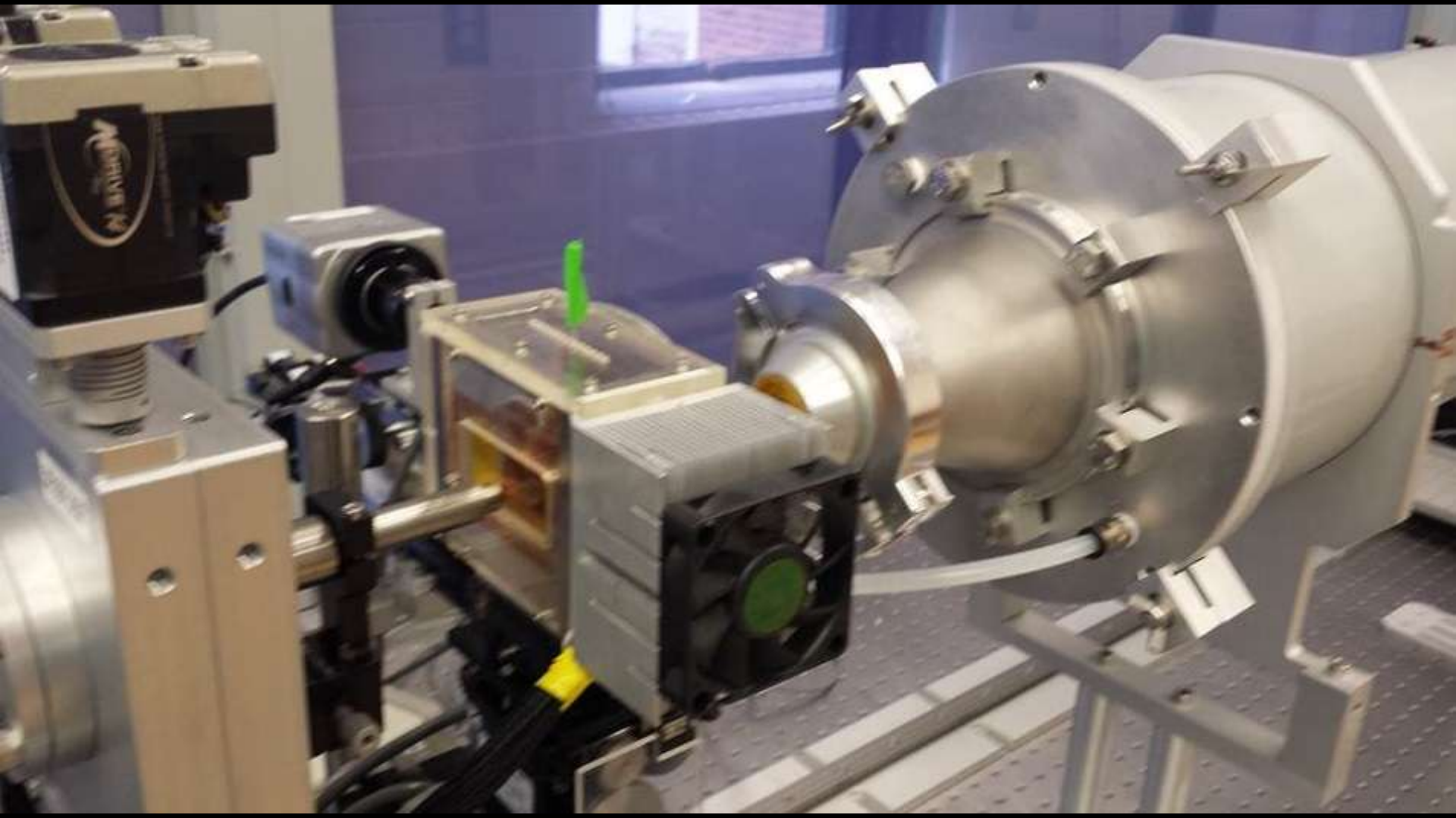
SAXS and GI-SAXS



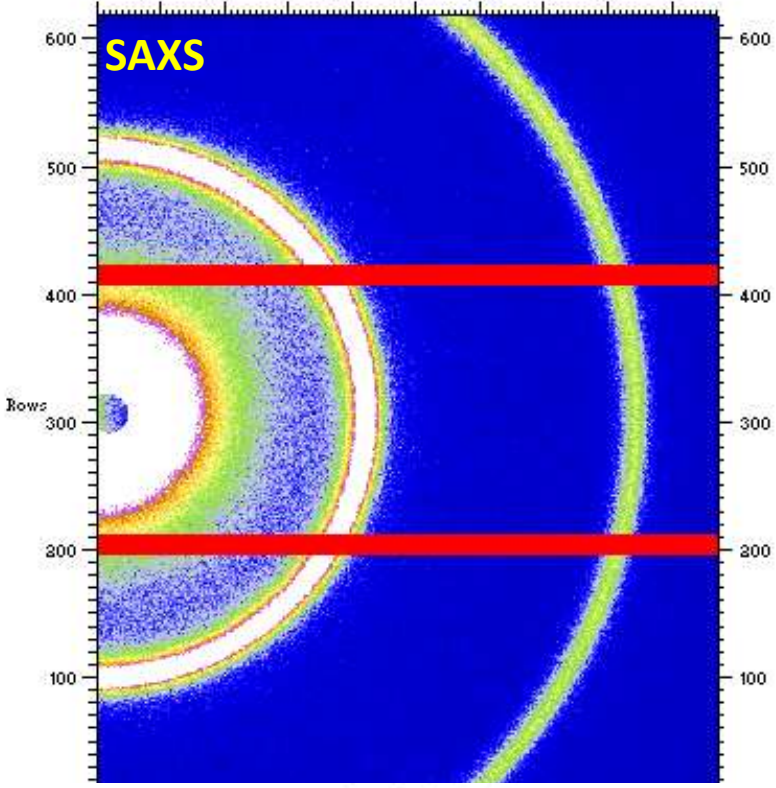
Sample holder for powders



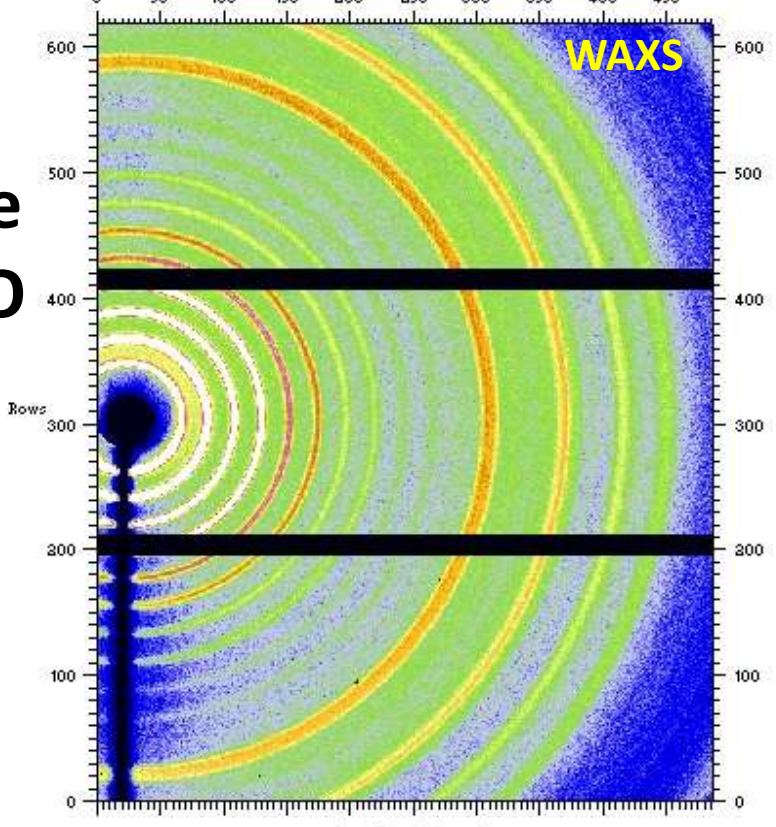
Temperature control stage for capillaries

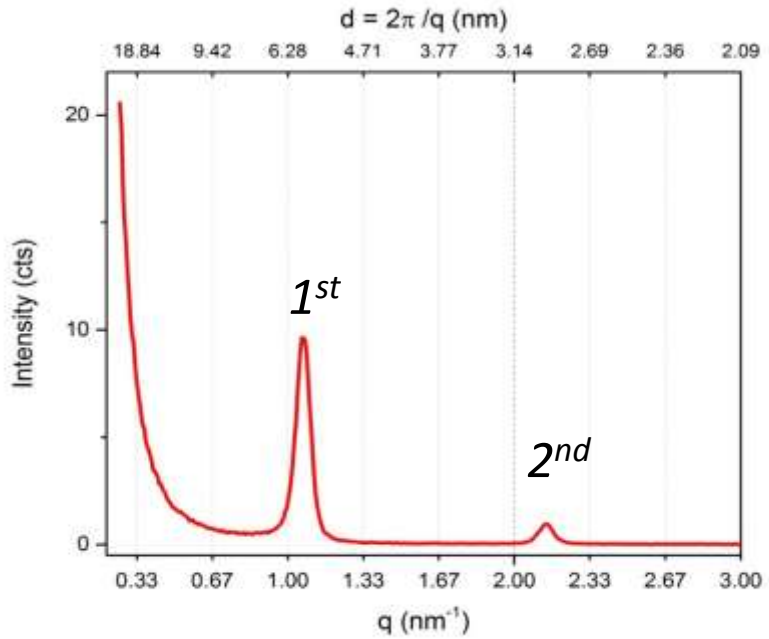


-20°C up to 120°C



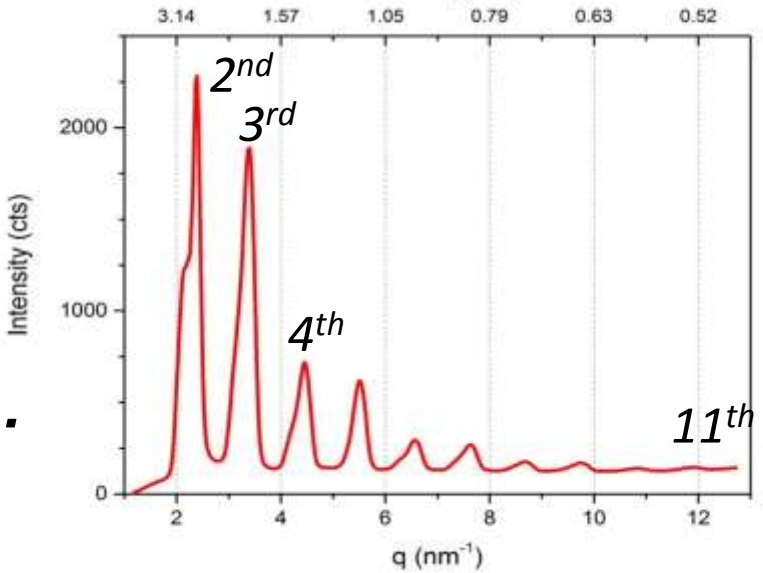
Silver behenate $AgC_{22}H_{43}O$



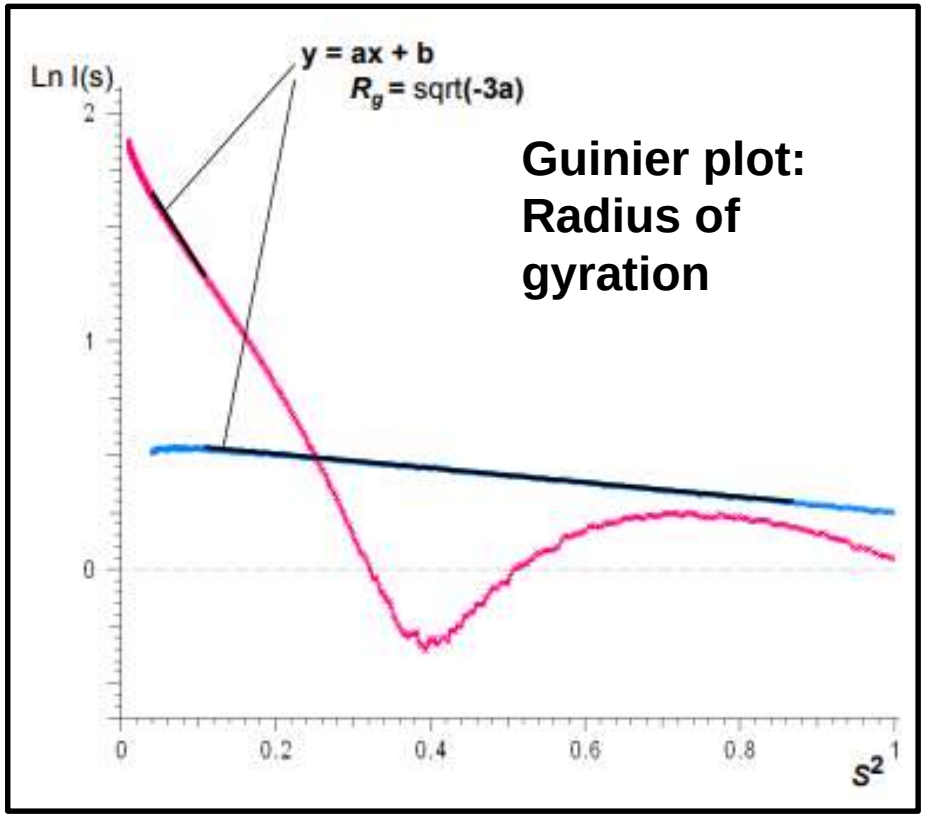


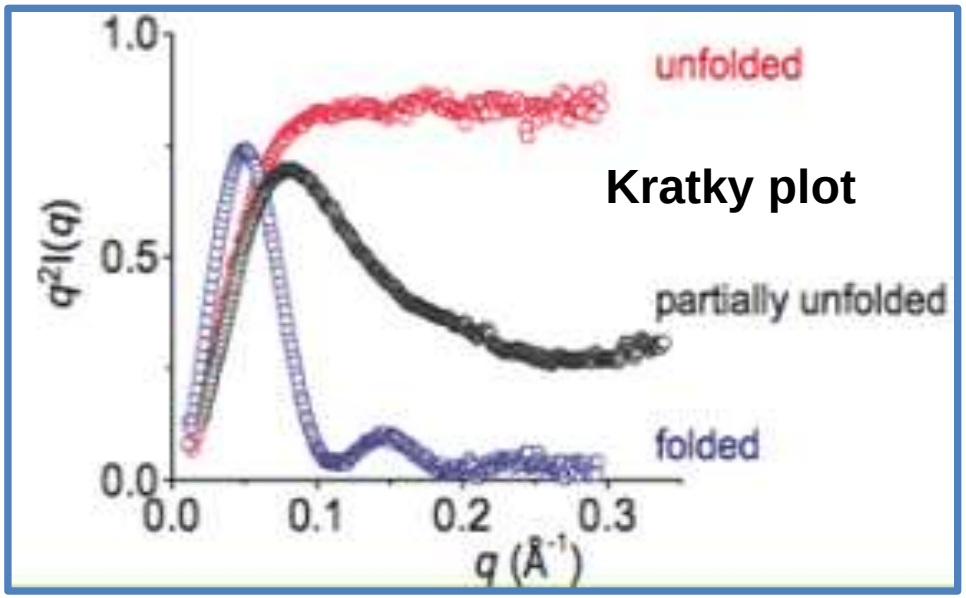
$$\frac{q_n}{q_1} = 1,2,3,4\ldots$$

lamellar



SAXS applications:





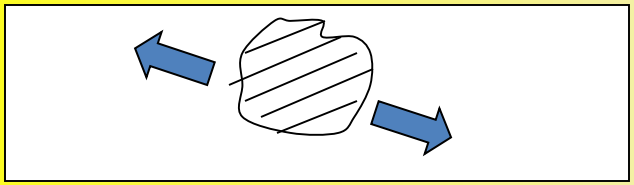
Analysis:

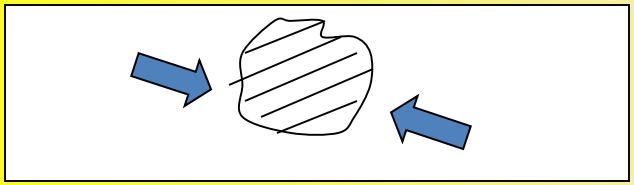
- Crystalline structure
- Degree of crystallinity and orientation
- Particle shape, size, distribution
- Radius of gyration
  Guinier plot *Ln I(q) vs. q^2*
- Folded, partially or unfolded proteins
  Kratky plot *$I(q)*q^2$ vs. q*
- Distance distribution function *p(r)*

Materials:

- Nanoparticles
- Membranes
- Lipids
- Polymers
- Proteins
- Solutions
- Nanocomposites
- Polymers
- Thin films …

Residual stress analysis methods





Residual stress?

How much? (MPa – GPa)

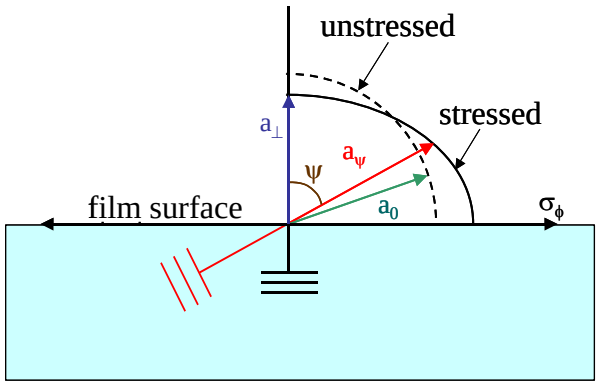
Type?

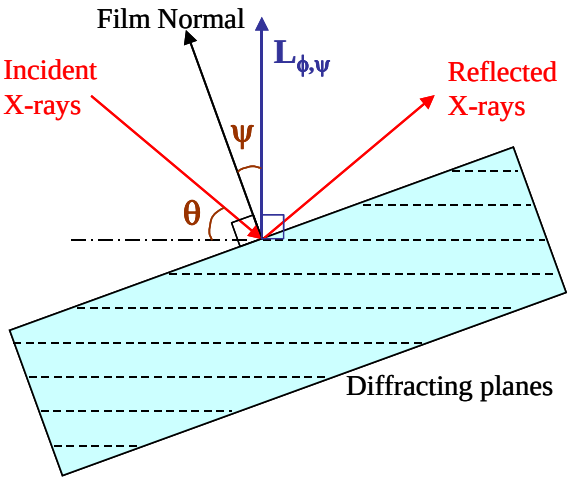
Direction (s)?

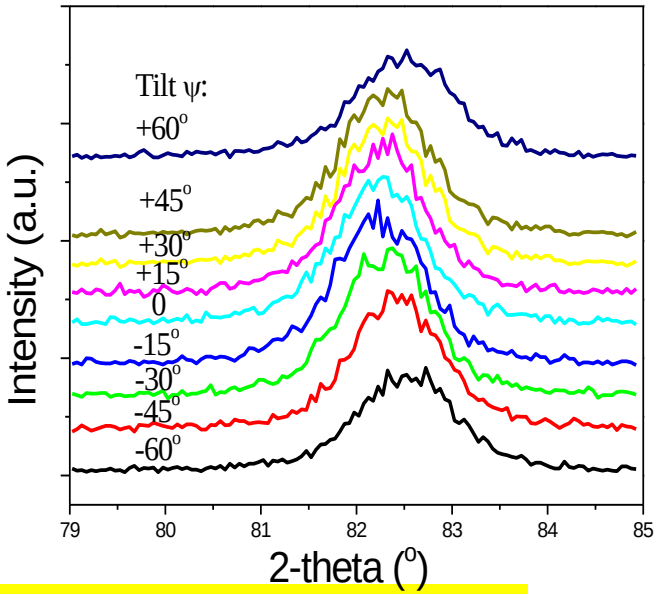
Stress gradients?

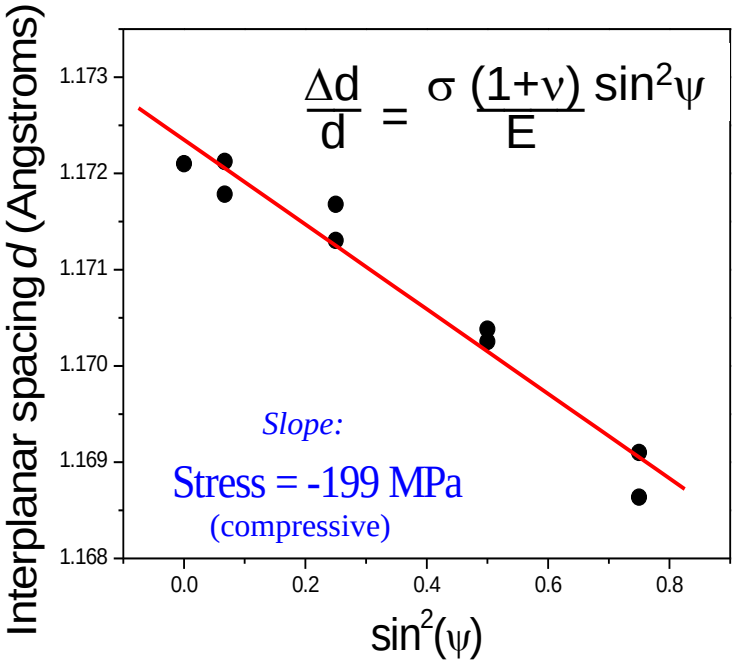
XRD measures strain (Δd) $\xrightarrow[\text{Elastic properties } (E, \nu)]{\text{Hooke's law}}$ Stress tensor

X-ray analysis of residual stress









Stress results from a steel sample

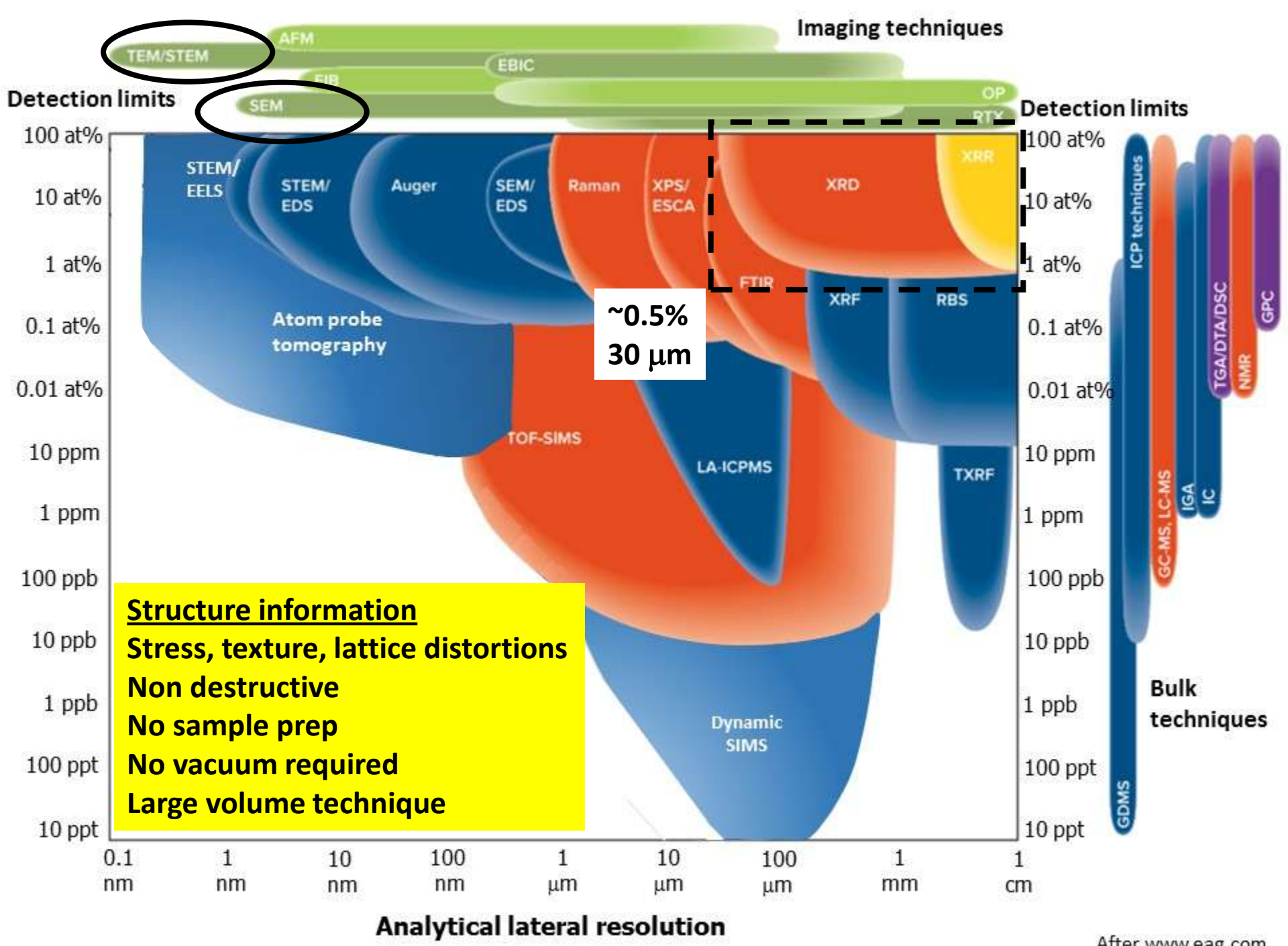
Data: Sangid et al, UIUC

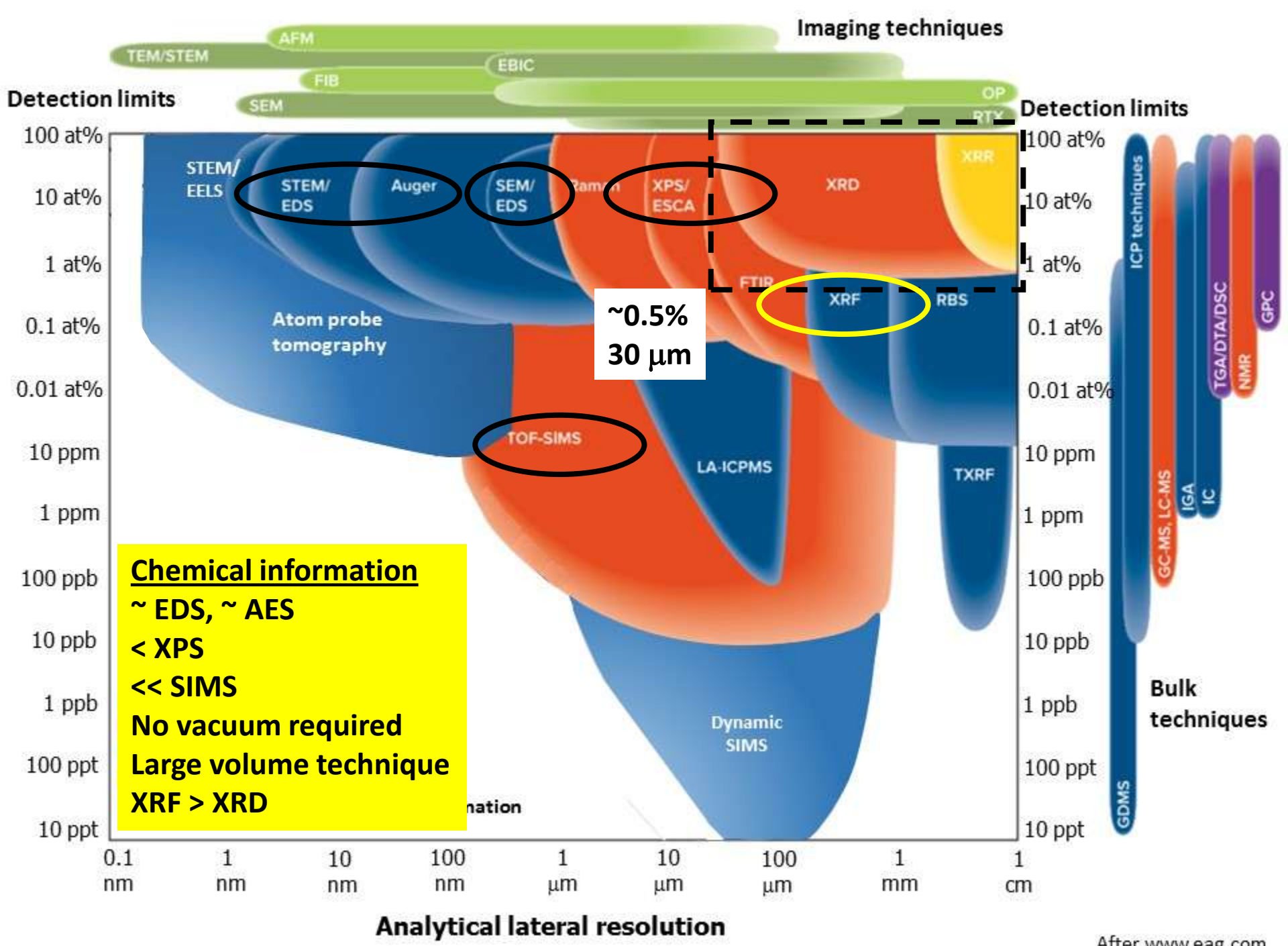
- Quantification of residual stress.
- Compressive (-) and tensile (+) stress.
- Crystallographic orientation of stress.

- $\sin^2\psi$ method. Linear for rotationally symmetric biaxial stress where the only non-zero components are $\sigma_{11} = \sigma_{22} = \sigma_{//}$
- ψ and ω scan methods.

- Glancing angle method (texture).
- Determination of stress tensor.

- Requires crystallinity (no amorphous).


Imaging techniques
TEM/STEM
AFM
EBIC
FIB
SEM
OP
RTX
Detection limits
Detection limits
100 at%
10 at%
1 at%
0.1 at%
0.01 at%
10 ppm
1 ppm
100 ppb
10 ppb
1 ppb
100 ppt
10 ppt
STEM/ EELS
STEM/ EDS
Auger
SEM/ EDS
Raman
XPS/ ESCA
XRD
XRR
FTIR
XRF
RBS
Atom probe tomography
~0.5%
30 µm
TOF-SIMS
LA-ICPMS
TXRF
Dynamic SIMS
ICP techniques
GC-MS, LC-MS
IGA
IC
TGA/DTA/DSC
NMR
GPC
GDMS
Bulk techniques
Structure information
Stress, texture, lattice distortions
Non destructive
No sample prep
No vacuum required
Large volume technique
0.1 nm
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm
1 mm
1 cm
Analytical lateral resolution
After www.eag.com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FIB
SEM
OP
RTX
Detection limits
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STEM/ EELS
STEM/ EDS
Auger
SEM/ EDS
XPS/ ESCA
XRD
XRR
FTIR
XRF
RBS
Atom probe tomography
~0.5%
30 µm
TOF-SIMS
LA-ICPMS
TXRF
Dynamic SIMS
Chemical information
~ EDS, ~ AES
< XPS
<< SIMS
No vacuum required
Large volume technique
XRF > XRD
ICP techniques
GC-MS, LC-MS
IGA
IC
TGA/DTA/DSC
NMR
GPC
GDMS
Bulk techniques
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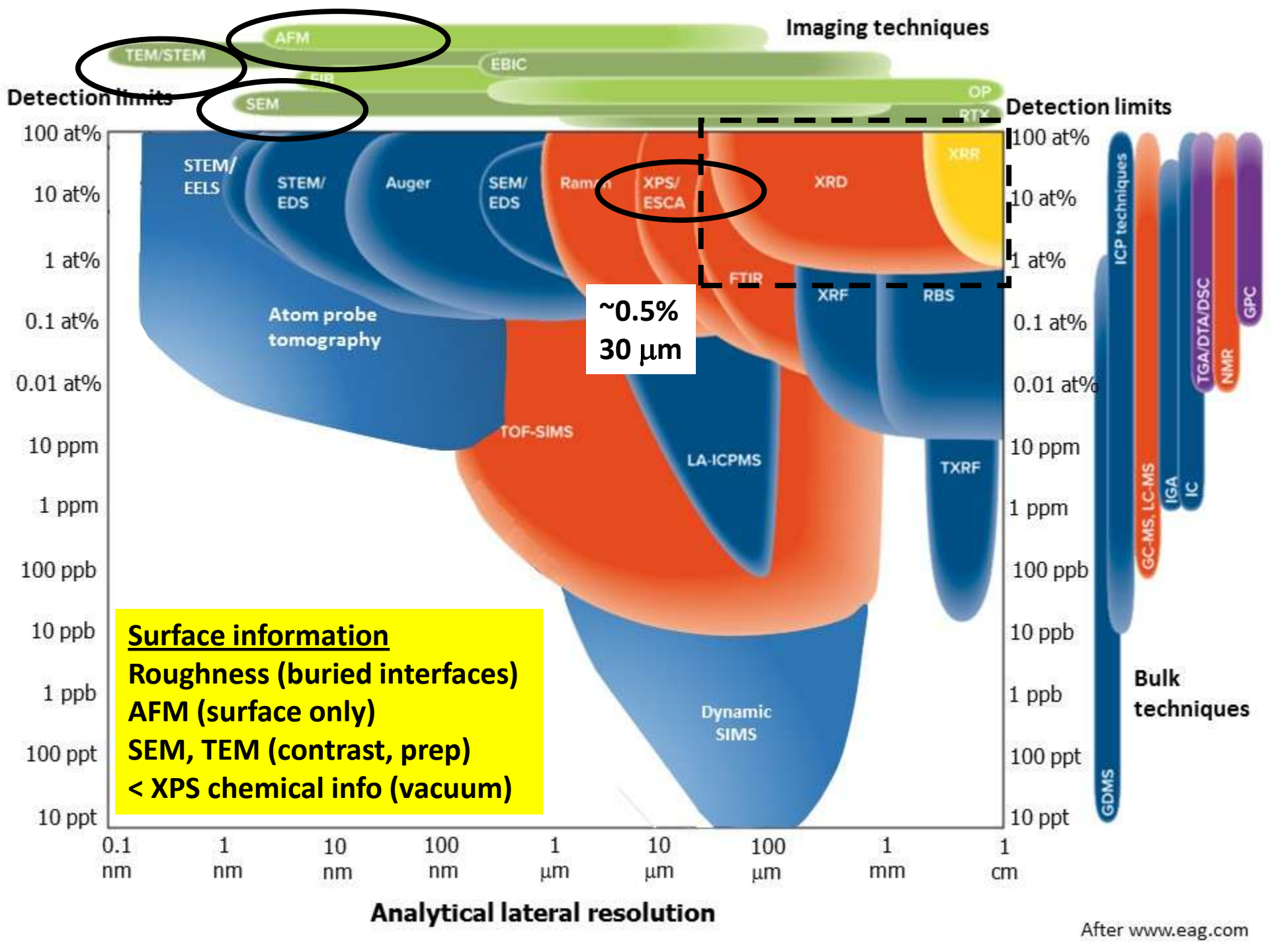
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm
1 mm
1 cm
Analytical lateral resolution
After www.eag.com


Imaging techniques
AFM
TEM/STEM
EBIC
FIB
SEM
OP
RTX
Detection limits
Detection limits
100 at%
10 at%
1 at%
0.1 at%
0.01 at%
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1 ppm
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STEM/ EELS
STEM/ EDS
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Raman
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30 µm
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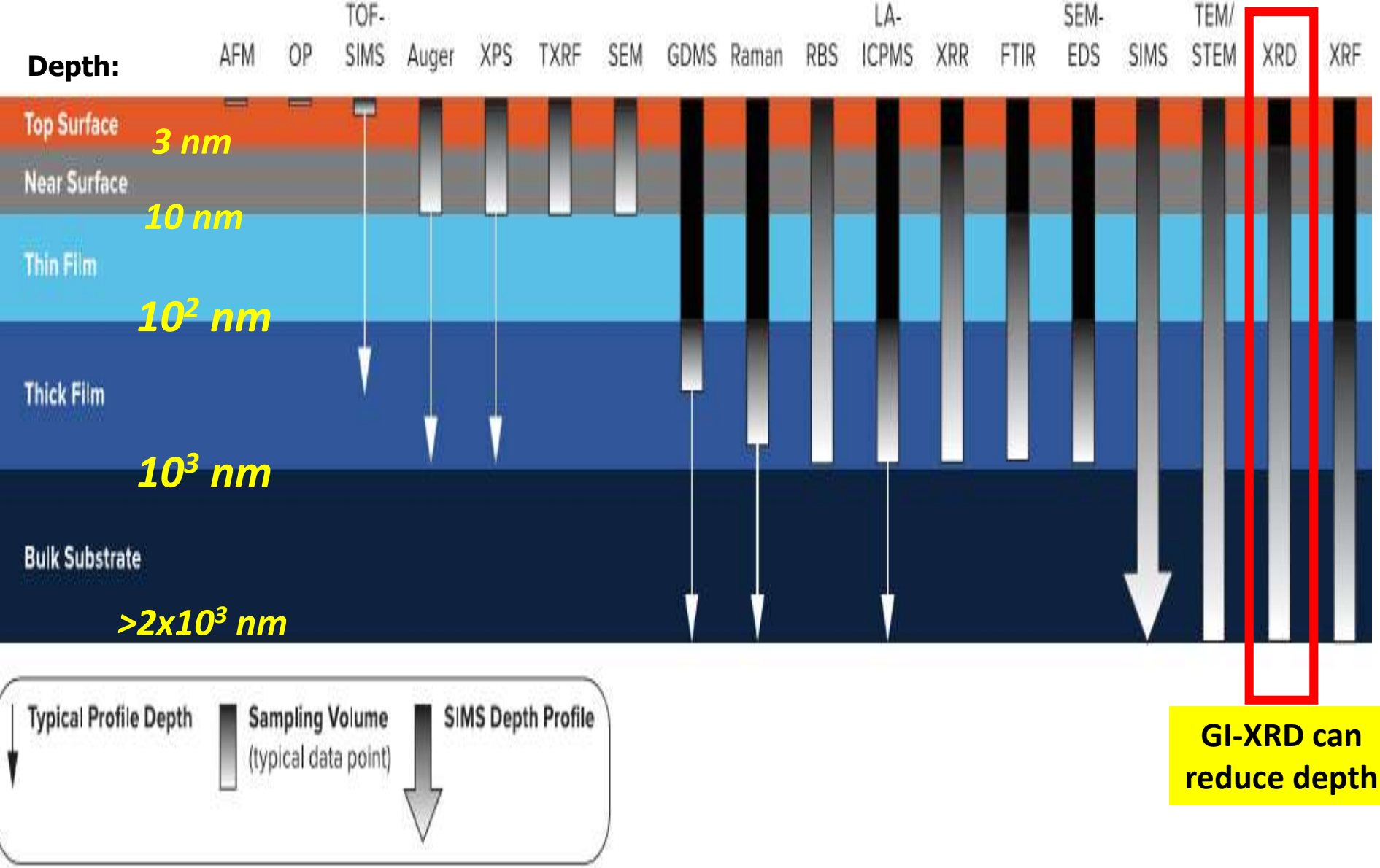
TXRF
Dynamic SIMS
ICP techniques
GC-MS, LC-MS
IGA
IC
TGA/DTA/DSC
NMR
GPC
GDMS
Bulk techniques
Surface information
Roughness (buried interfaces)
AFM (surface only)
SEM, TEM (contrast, prep)
< XPS chemical info (vacuum)
0.1 nm
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm
1 mm
1 cm
Analytical lateral resolution
After www.eag.com

Typical analysis depth for common analytical techniques



X-ray analysis summary

(+)

Non destructive

Quantitative

Finger printing (chemical info)

Very accurate crystalline structure info

Averages over large volume (~ 30 μm x 0.5-2 cm's)

Levels of complexity: simple to complex

Microdiffraction, pair distribution function, fast areal detectors

(-)

Localized info (below 100 μm)

Defects identification and quantification

Direct imaging