Materials Research Laboratory

X-ray analysis

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AMC2024

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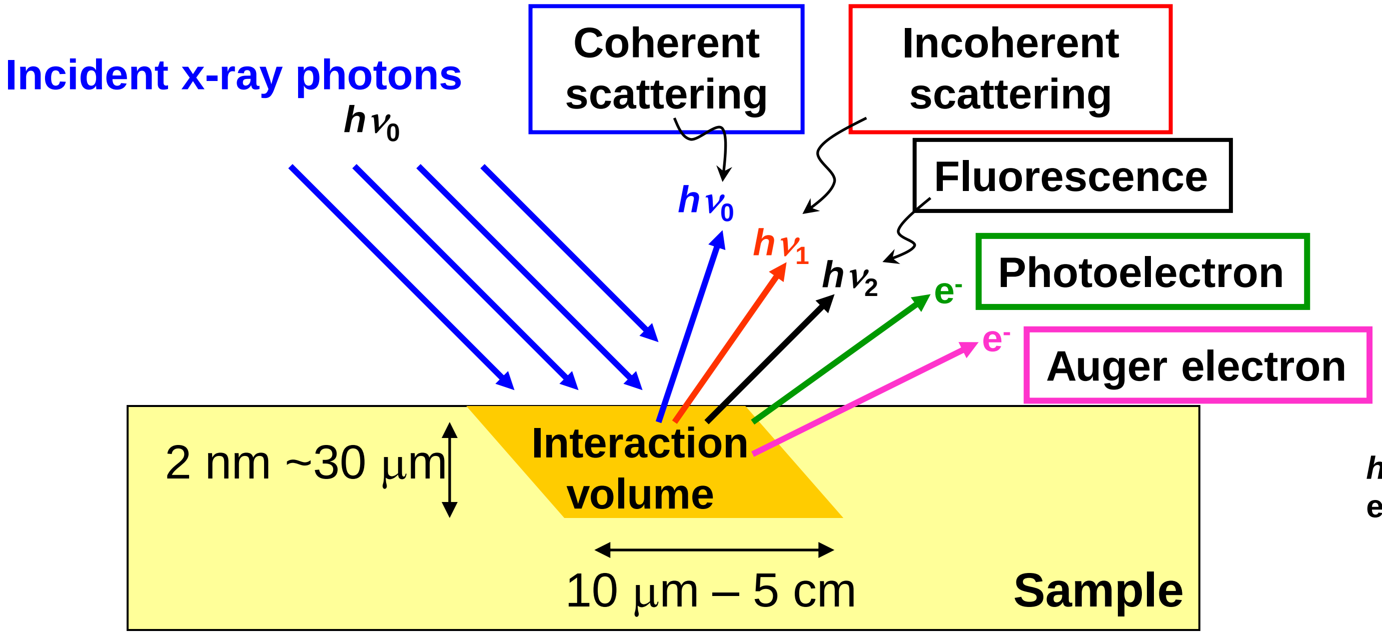
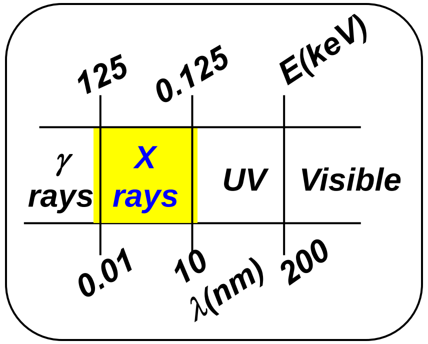
X-ray interactions with matter



$h\nu$: photon
e^-: electron



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

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

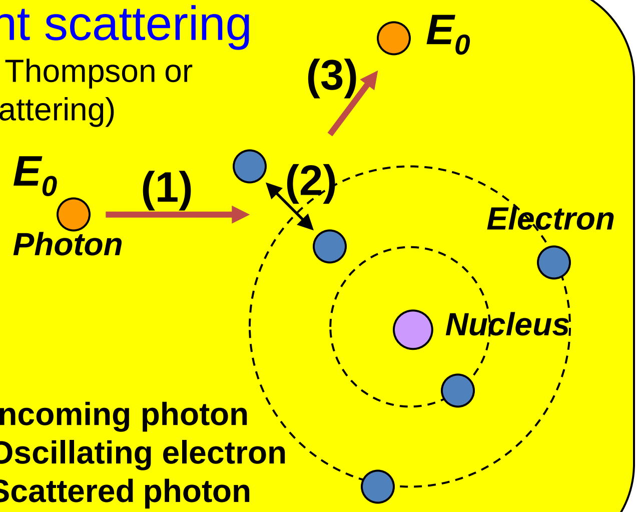
- ***Cu*** **Kα1: (λ= 0.15056 nm (high resolution)**

Anode	Cr	Fe	Co	Cu	Mo	Ag
Kα (nm)	0.229	0.194	0.179	0.154	0.071	0.056
Energy (keV)	5.41	6.39	6.93	8.05	17.46	22.14

X-ray interactions with matter

Coherent scattering

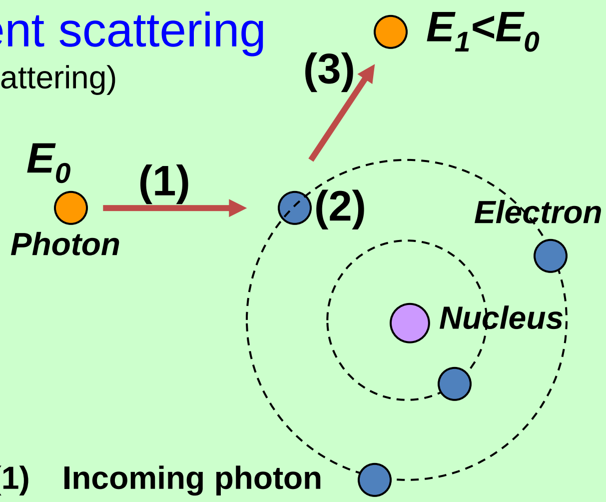
(Diffraction, Thompson or Rayleigh scattering)



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

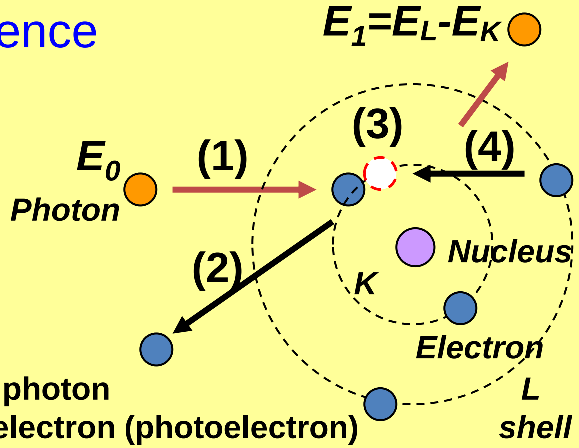
Incoherent scattering

(Compton scattering)



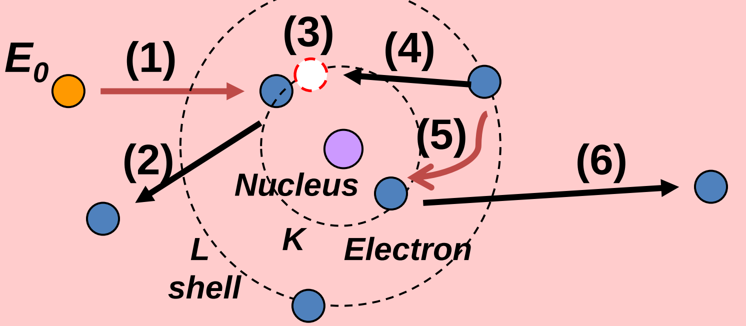
(1) **Incoming photon**
(2) **Energy is partially transferred to electron**
(3) **Scattered photon (energy loss).**

Fluorescence

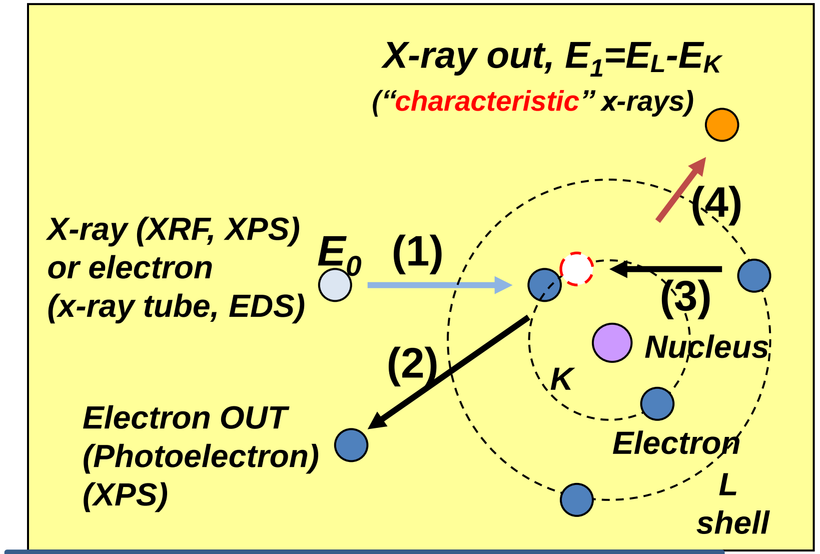


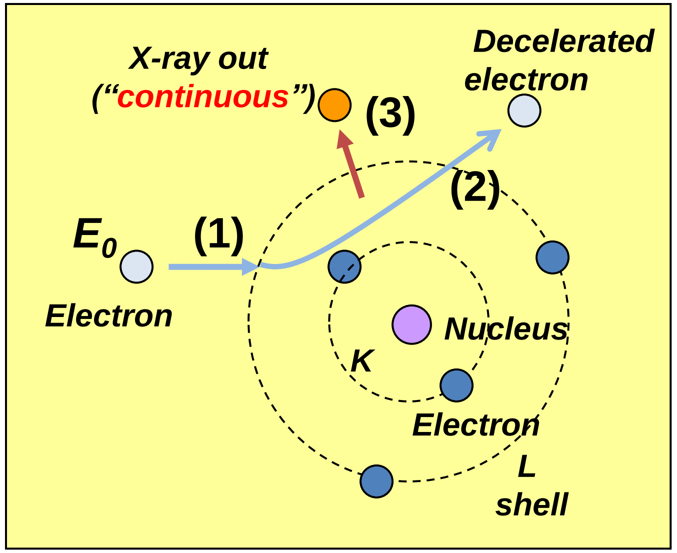
(1) **Incoming photon**
(2) **Expelled electron (photoelectron)**
(3) **Hole is created in the shell**
(4) **Outer shell electron moves to the inner shell hole**
(5) **Energy excess emitted as *characteristic photon*.**

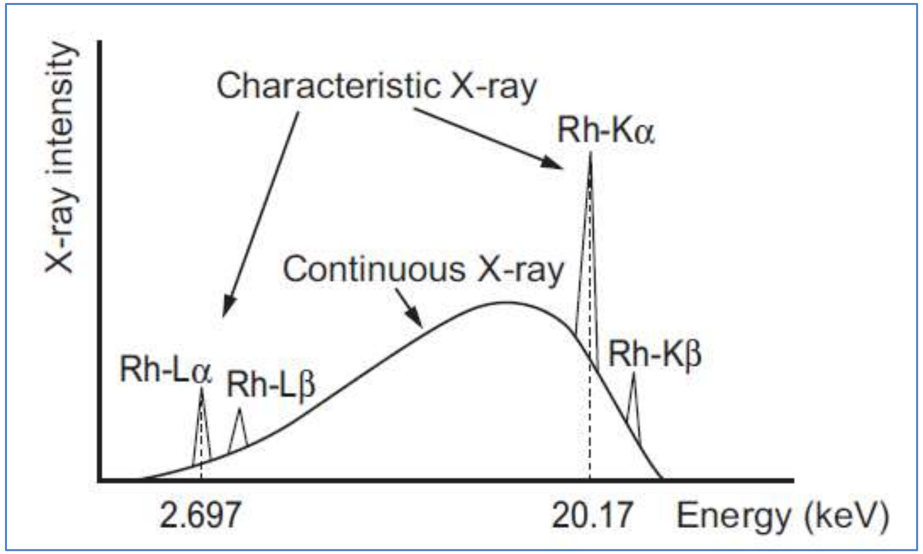
Auger electron



(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)**

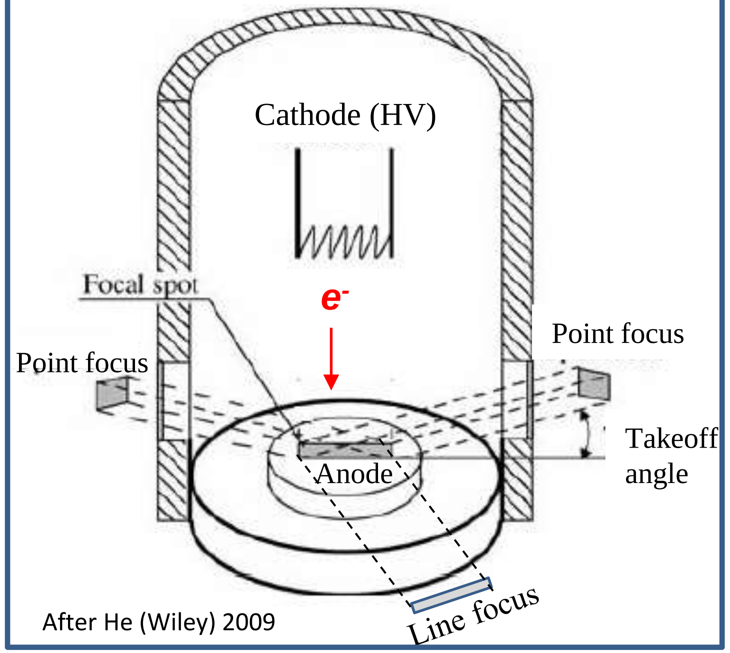






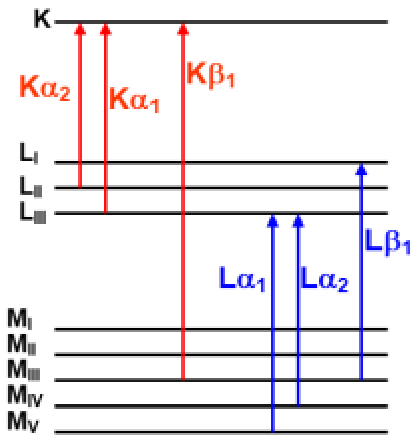
X-ray generation from sealed tubes:

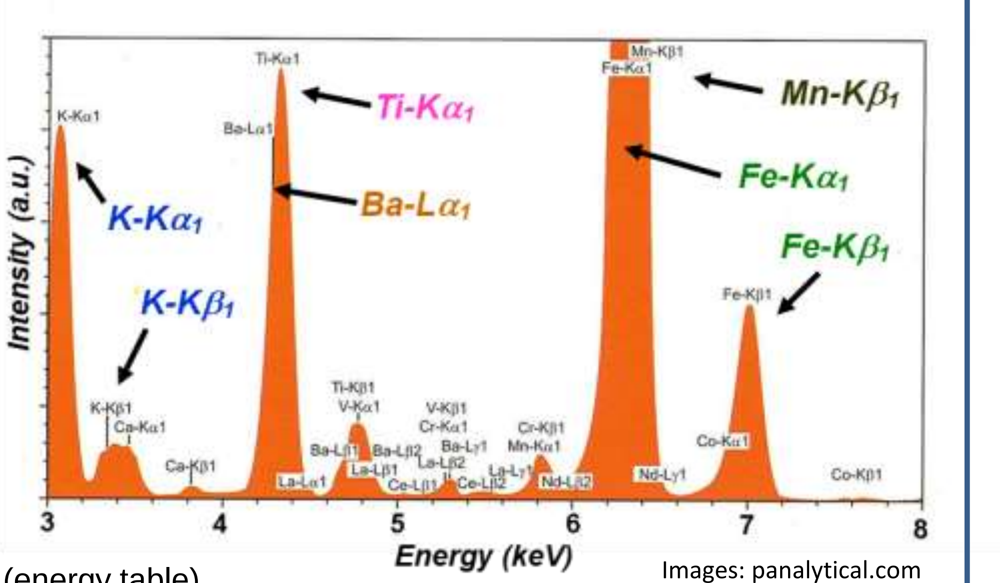
electrons from W filament accelerate under HV and hit a metal target (Cu, Mo, …) generating continuous and characteristic x-ray lines used in X-ray analytical instruments (Cu Kα, …)



After He (Wiley) 2009

X-ray characteristic lines x-ray fluorescence (XRF) for quantitative elemental chemical analysis

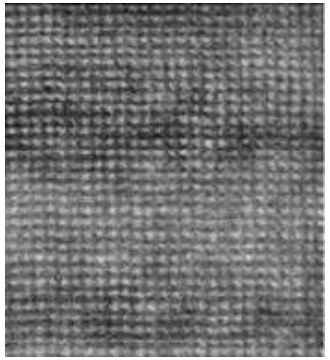




Images: panalytical.com

- E ~ Z^2 chemical fingerprinting
- Energy is known for each element transition (energy table)
- Energy resolution: 150-300 eV (EDXRF), 5-20 eV (WDXRF)
- Detection limits: 10% C, 0.5% O, 100 ppm F, 10 ppm Si, 0.1 ppm Pt – U
- Solids, liquids – non destructible technique, some tools are handheld.
- Use reference samples for calibration, or fundamental parameters method.

Fundamentals of diffraction



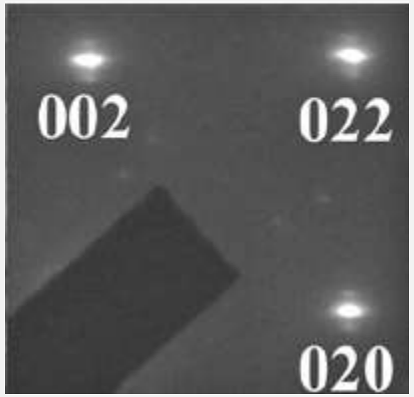
“Real” space

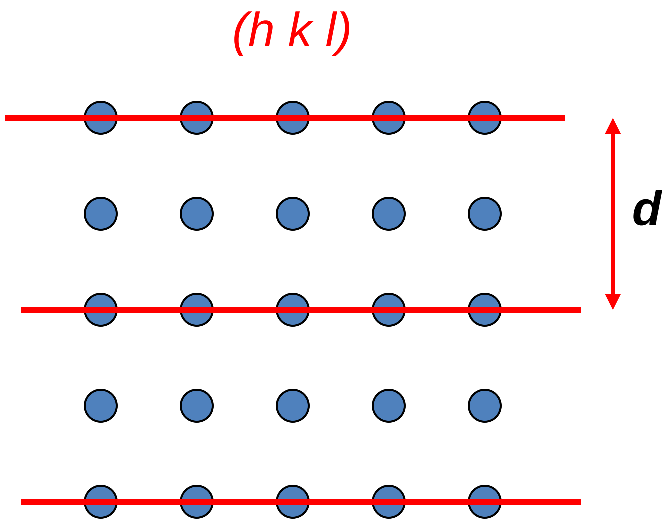
Set of planes

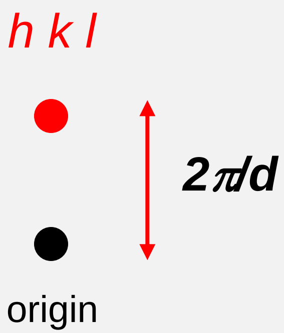
$\mathcal{F}$ →

Reciprocal space

Point



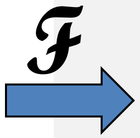




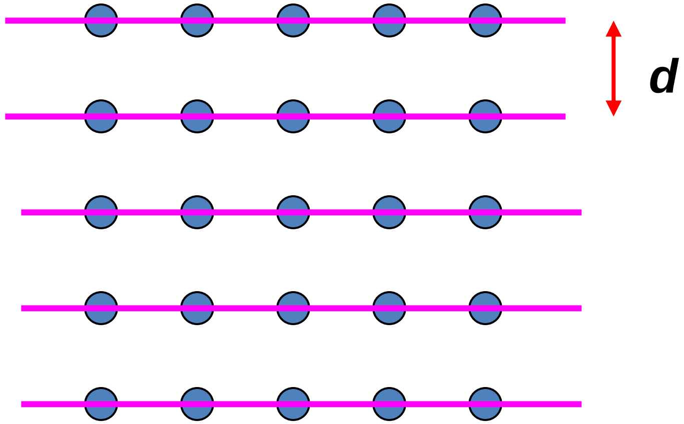
M. von Laue 1879-1960
X-rays from crystals, 1912.

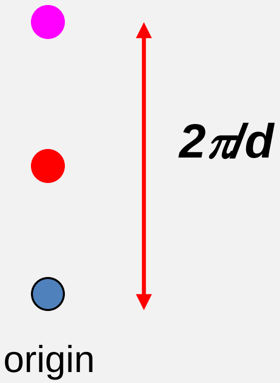
EM images: Howe et al, Acta Materialia 59 (2011) 421-428.

"Real" space

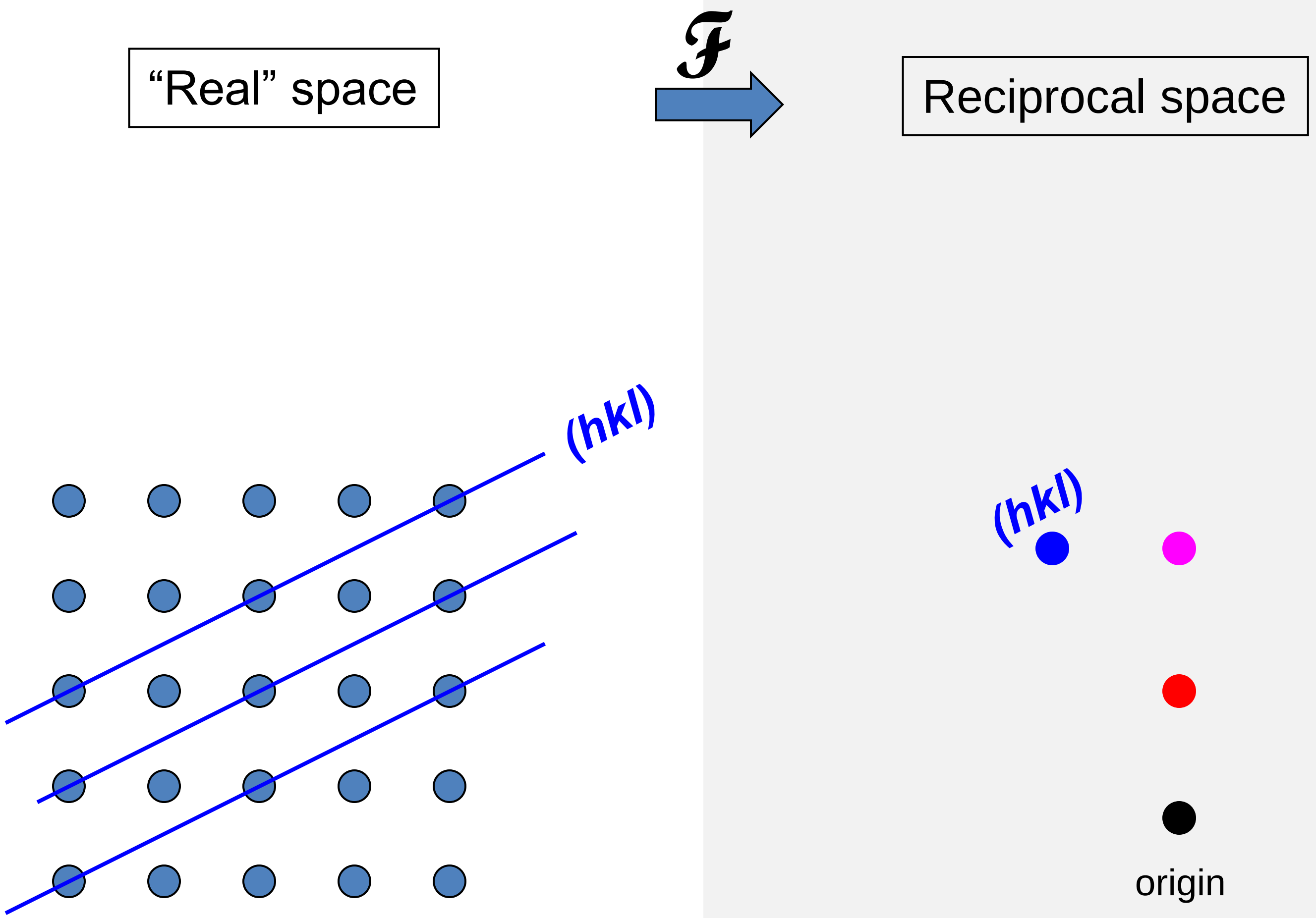


Reciprocal space

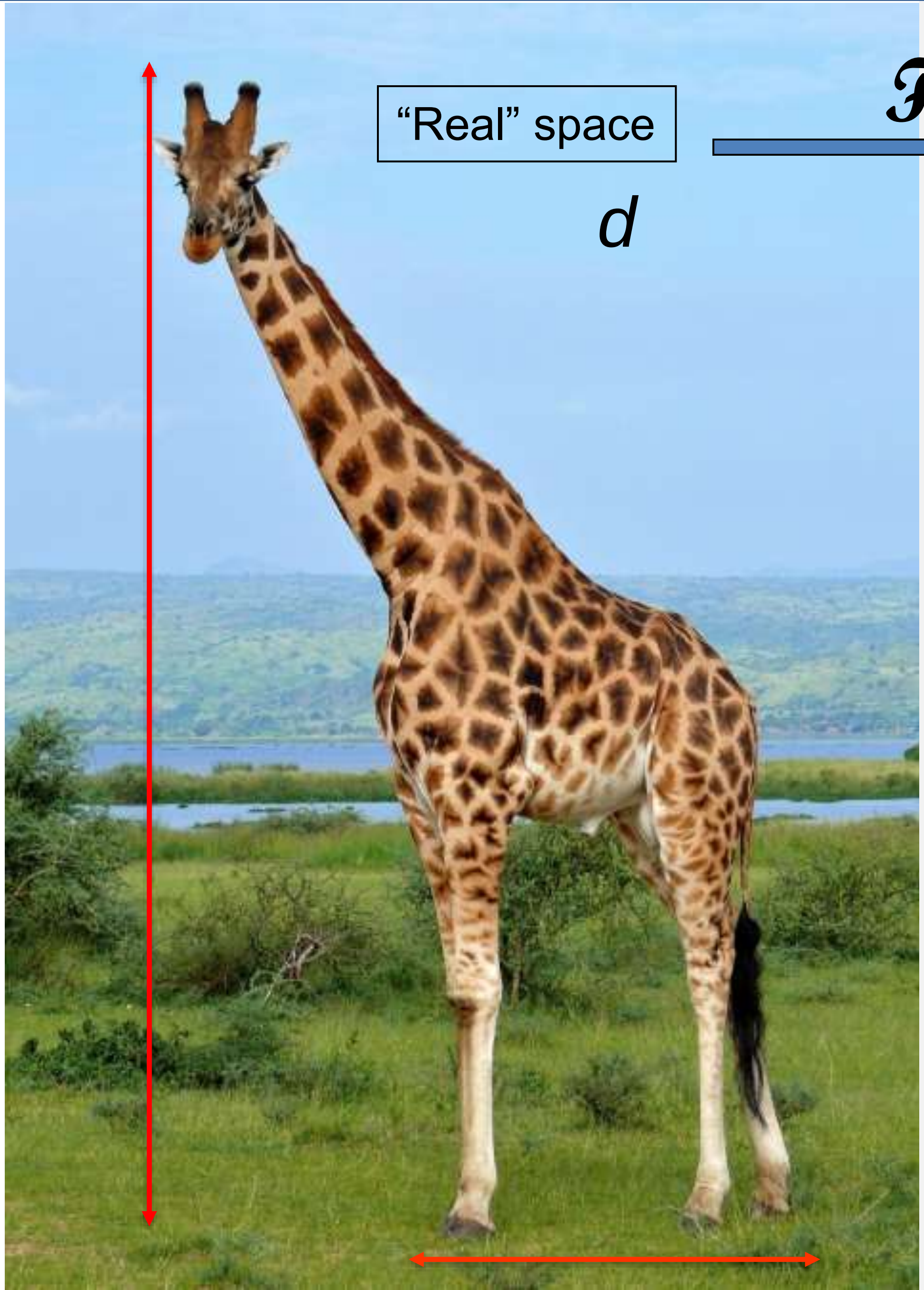




Fundamentals of diffraction



Fundamentals of diffraction



"Real" space

$\mathcal{F}$ →

Reciprocal space

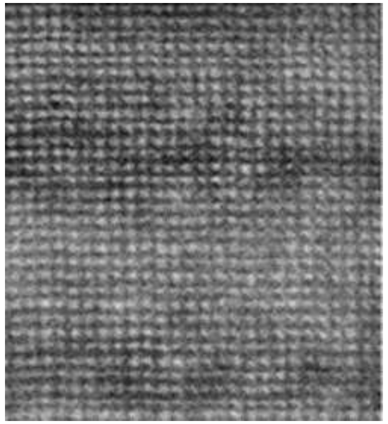
d

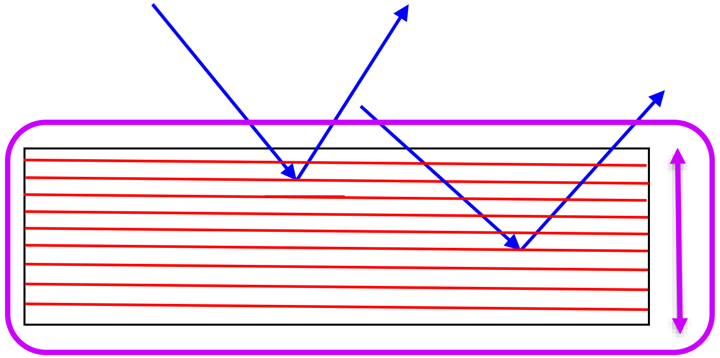
$\frac{1}{d}$

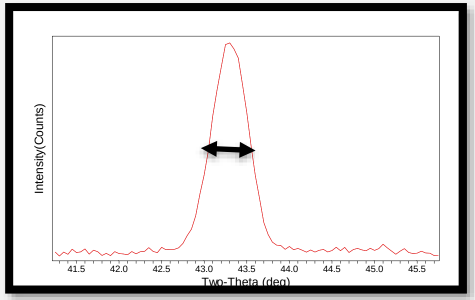
Fundamentals of diffraction

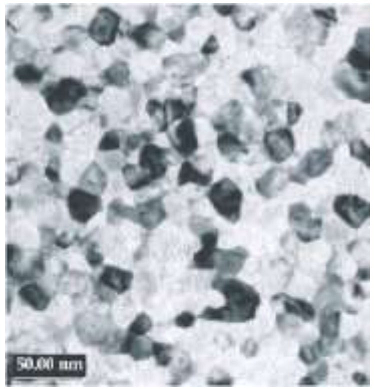
"Real" space → $\mathcal{F}$ → Reciprocal space

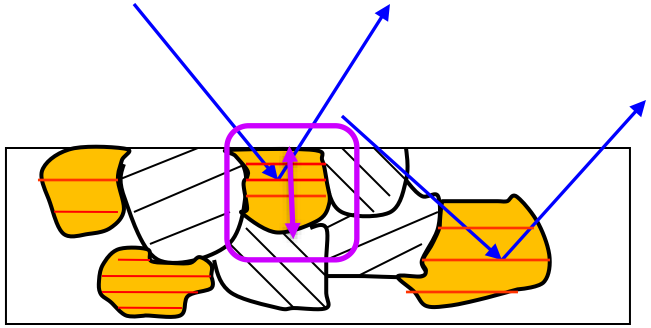
d $\qquad\qquad$ $\frac{1}{d}$

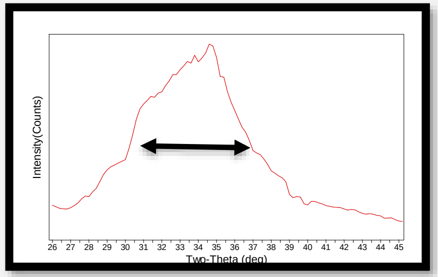






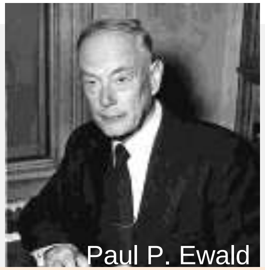






EM images: B. Howe, and MRL

Bragg's law and Ewald's spere



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

Bragg's law | **Ewald's sphere**

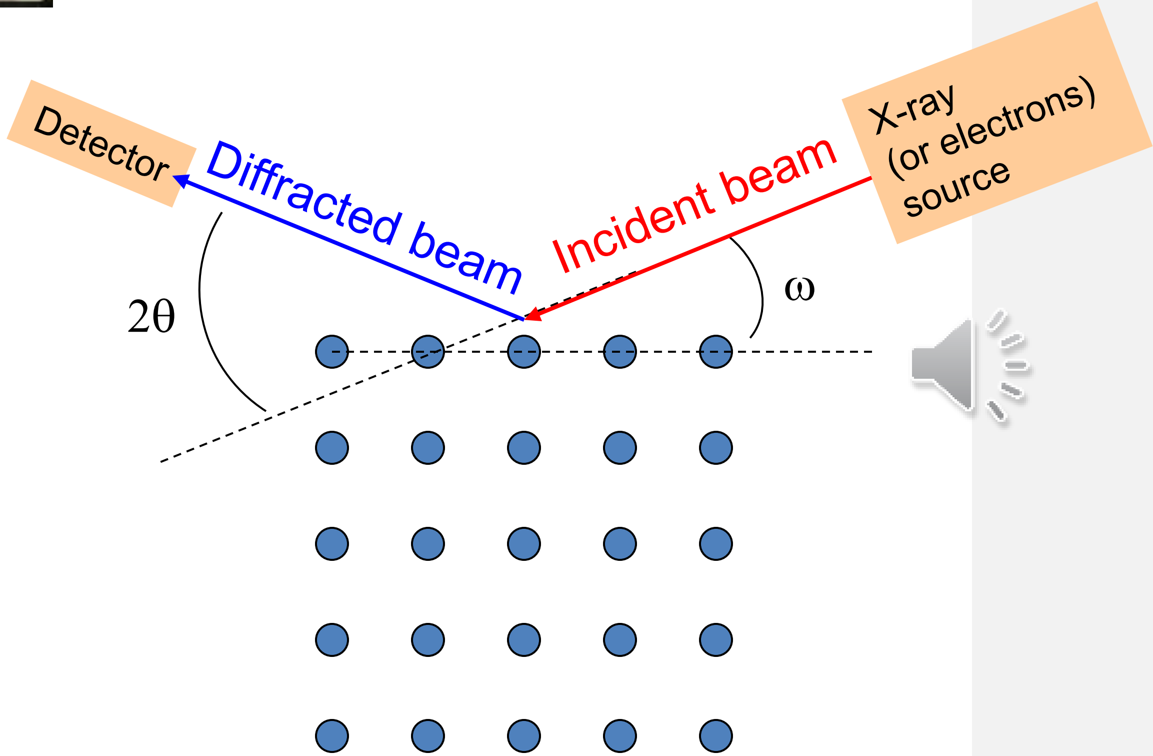
k_0 ~ 6.5 nm^{-1} (*Cu* kα x-rays)

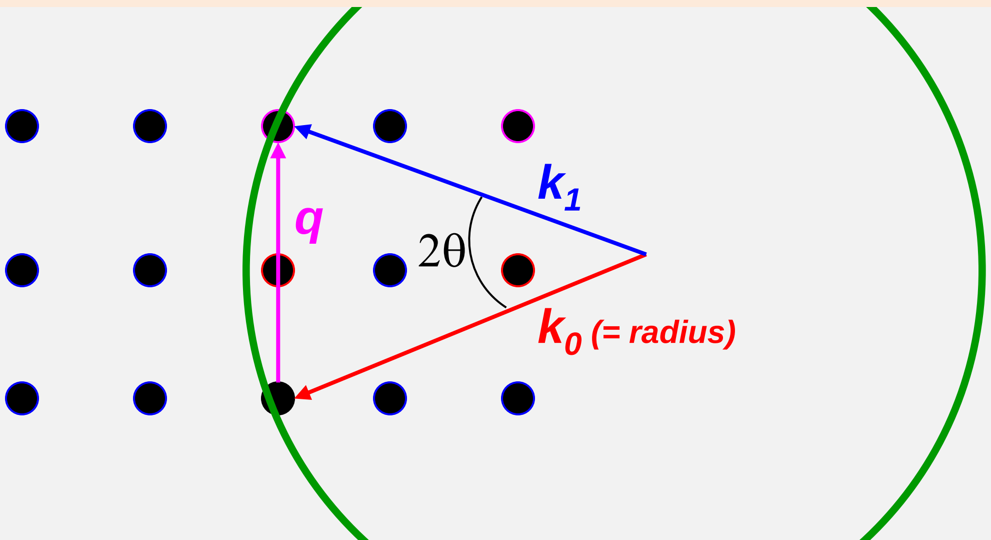
k_0 ~ 398 nm^{-1} (200 kV *e*-)

1/d ~ 2.78 nm^{-1} (d~ 0.36 nm, example for a metal)

e- k_0 much larger: *e*- diffraction from multiple plans

X-rays k_0 ~ 1/d: XRD sensitive to changes in crystal structure





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

Elastic scattering

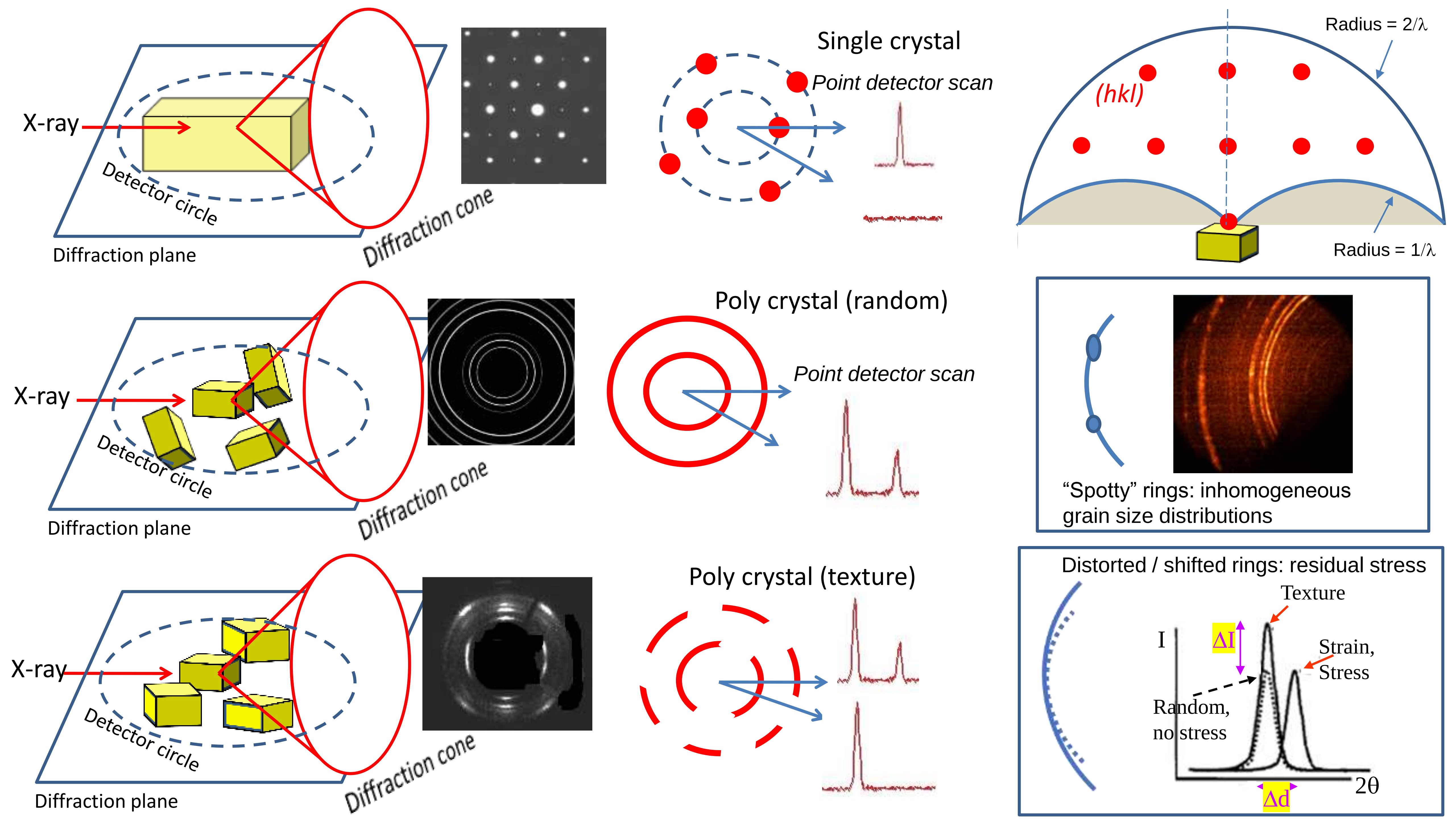
$$q = k_1 - k_0$$

Measure 2θ ⇨ *d*

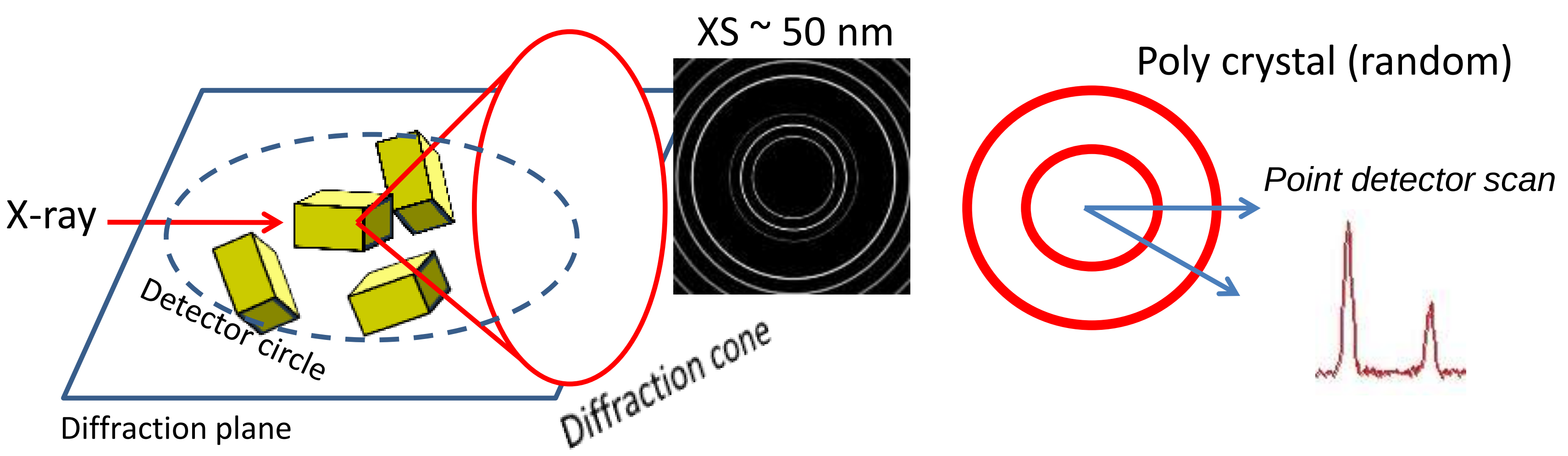
d ~ 1/sinθ

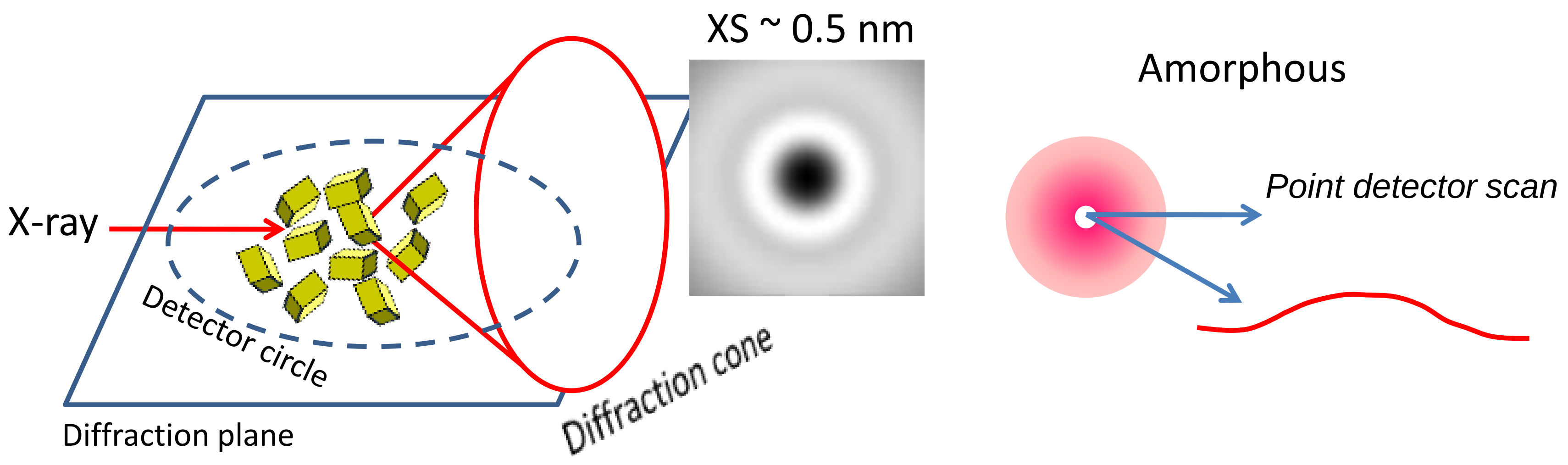
***q*: scattering vector**

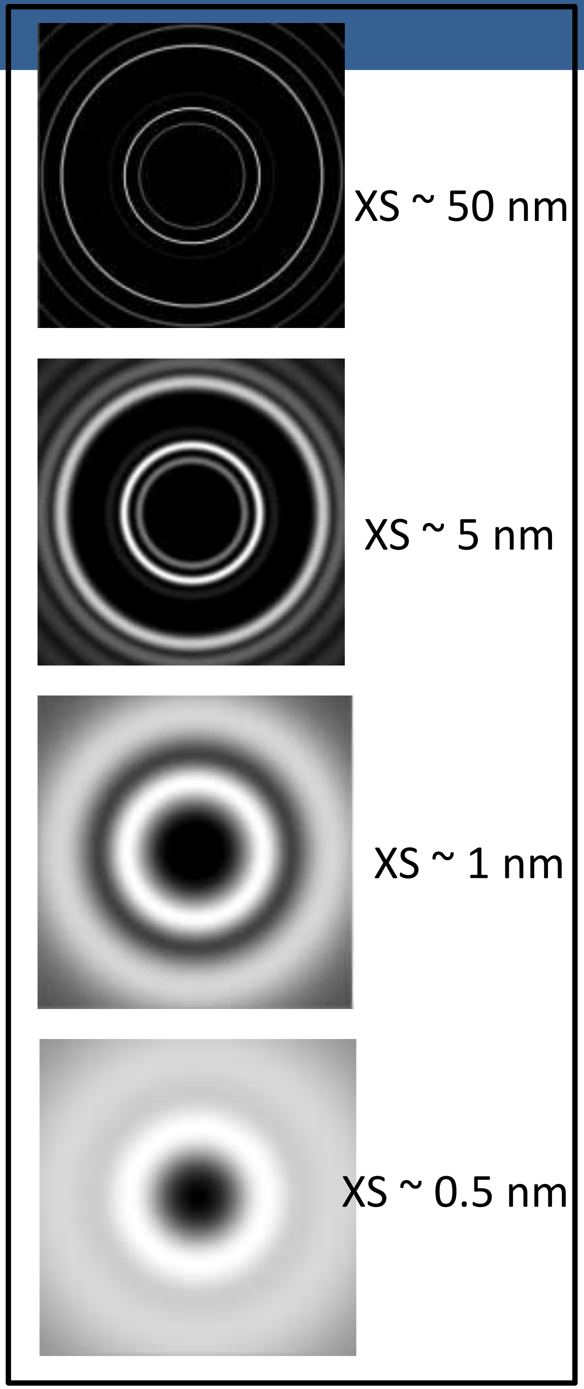
$q = (4\,\pi/\lambda)\sin\theta$


X-ray
Detector circle
Diffraction plane
Diffraction cone
Single crystal
Point detector scan
Radius = 2/λ
(hkl)
Radius = 1/λ
Poly crystal (random)
Point detector scan
"Spotty" rings: inhomogeneous grain size distributions
Poly crystal (texture)
Distorted / shifted rings: residual stress
Texture
I
ΔI
Strain, Stress
Random, no stress
2θ
Δd

Amorphous and polycrystalline phases



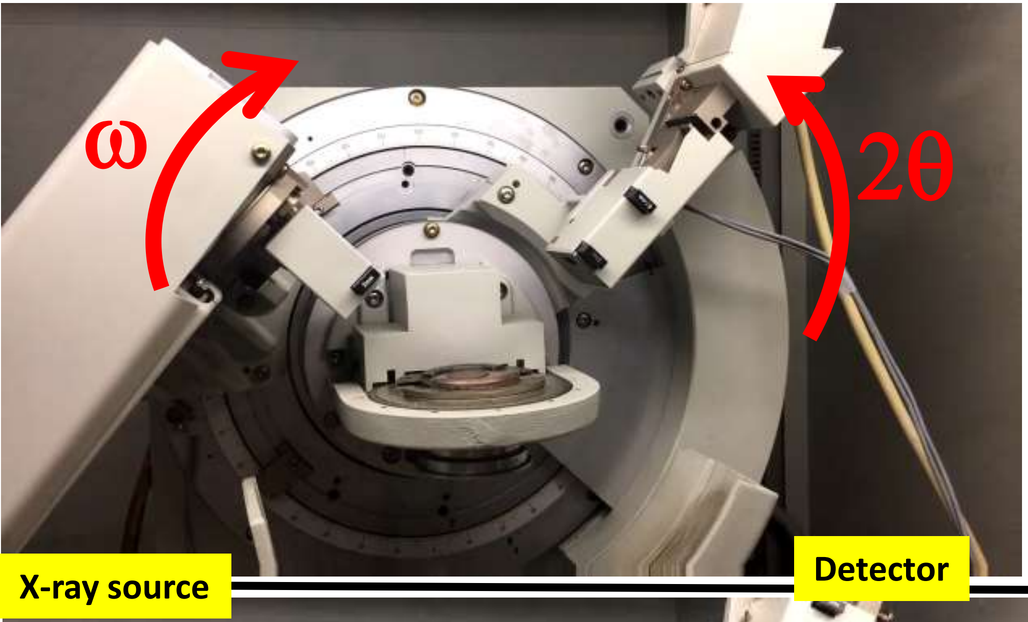


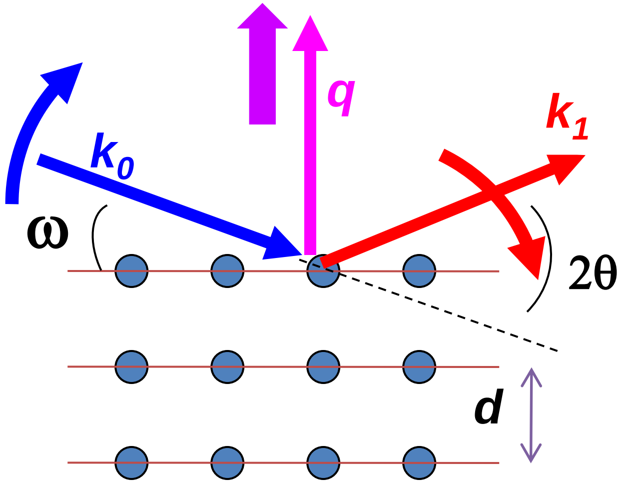


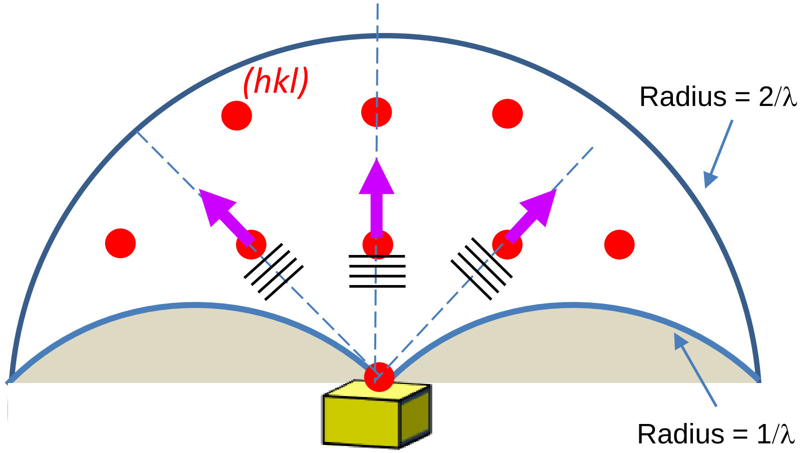
XS: crystallite size

2theta/omega scan *vs.* omega scan in XRD analysis

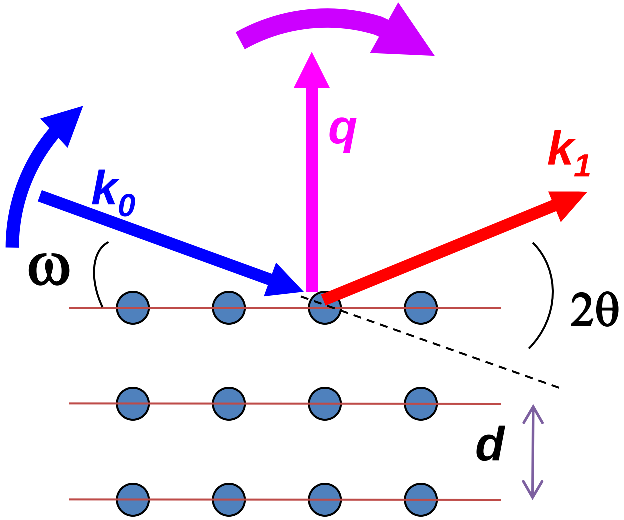
2theta/omega scan

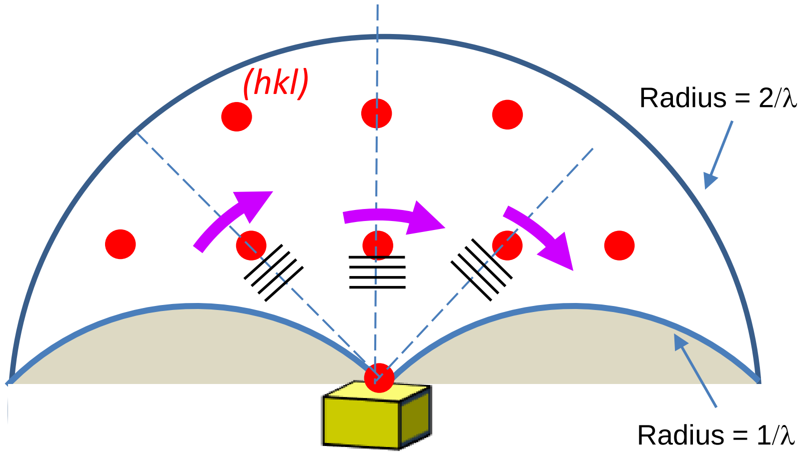






2θ/ω scan: radial scan, parallel to ***q***





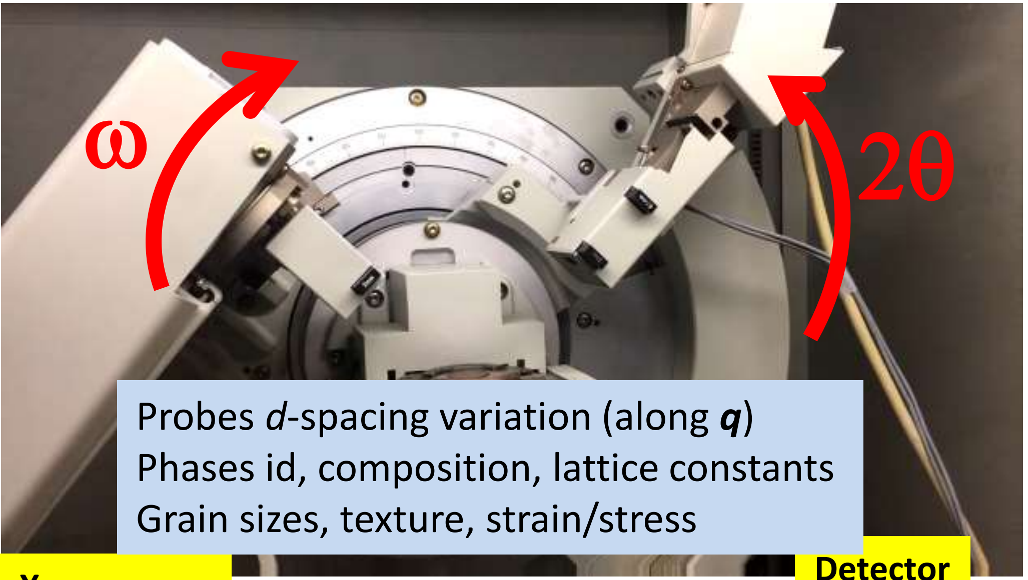
ω scan: circumferential scan, perpendicular to ***q***

omega scan

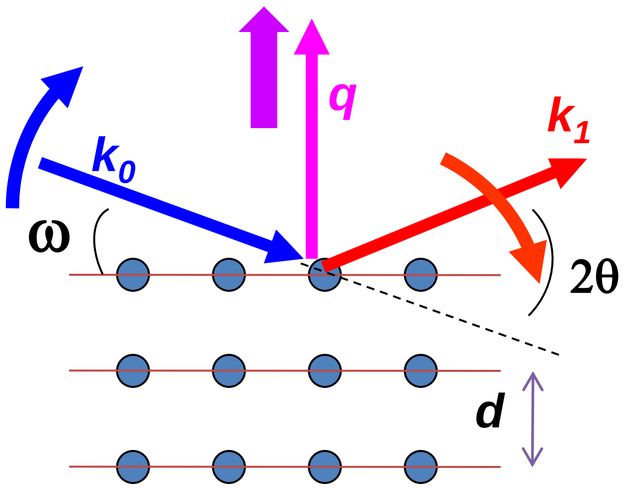
(rocking curve)

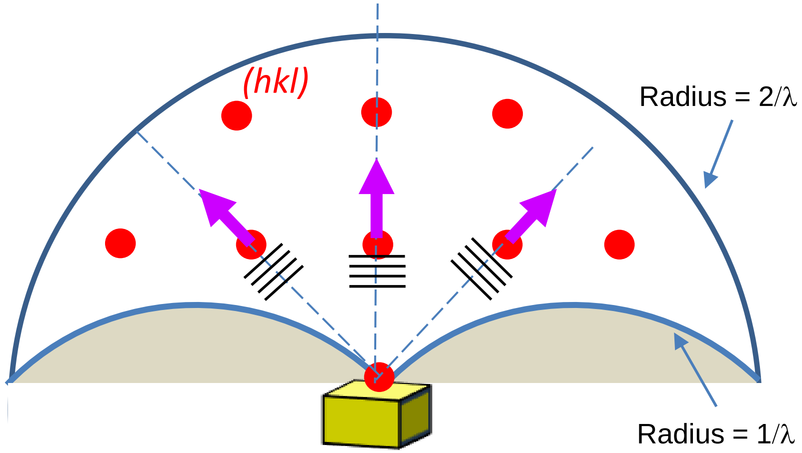
2theta/omega scan *vs.* omega scan in XRD analysis

2theta/omega scan



Probes *d*-spacing variation (along ***q***)
Phases id, composition, lattice constants
Grain sizes, texture, strain/stress

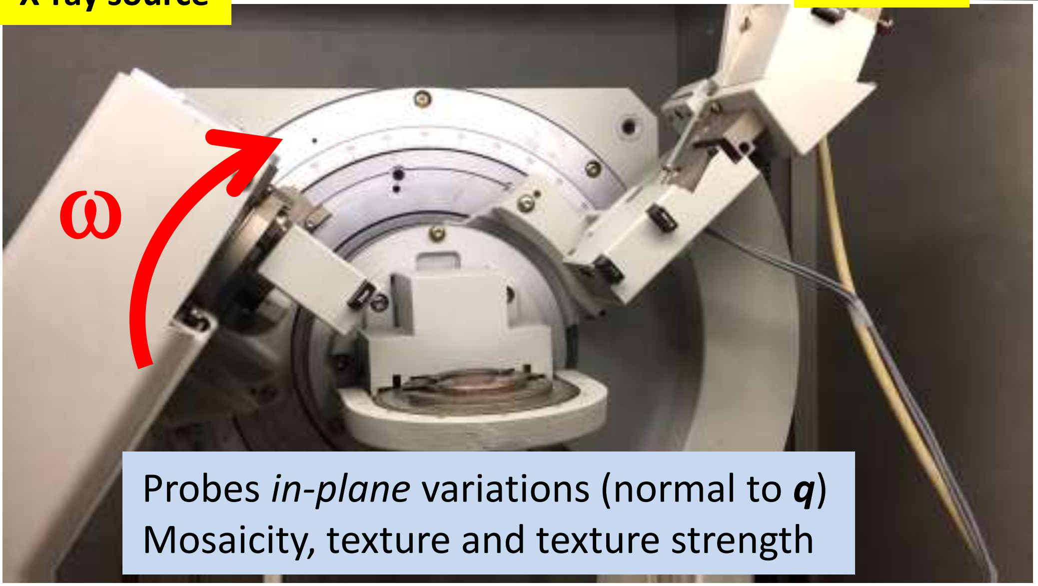




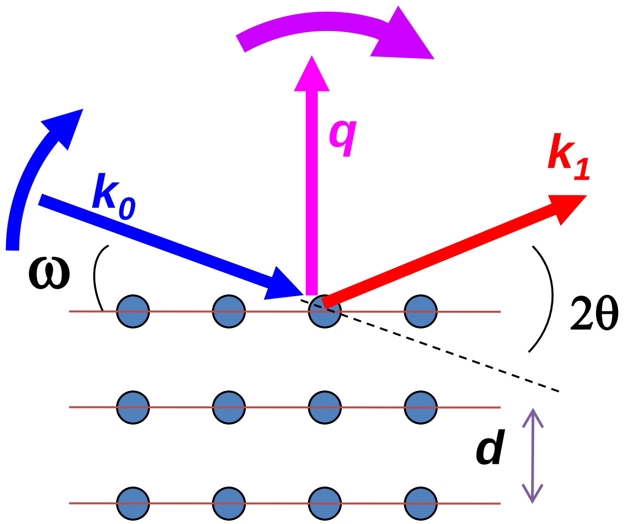
2θ/ω scan: radial scan, parallel to ***q***

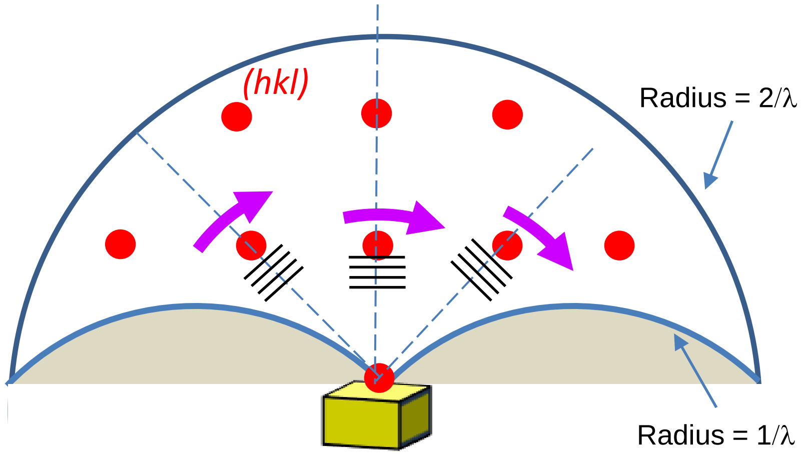
X-ray source

Detector



Probes *in-plane* variations (normal to ***q***)
Mosaicity, texture and texture strength



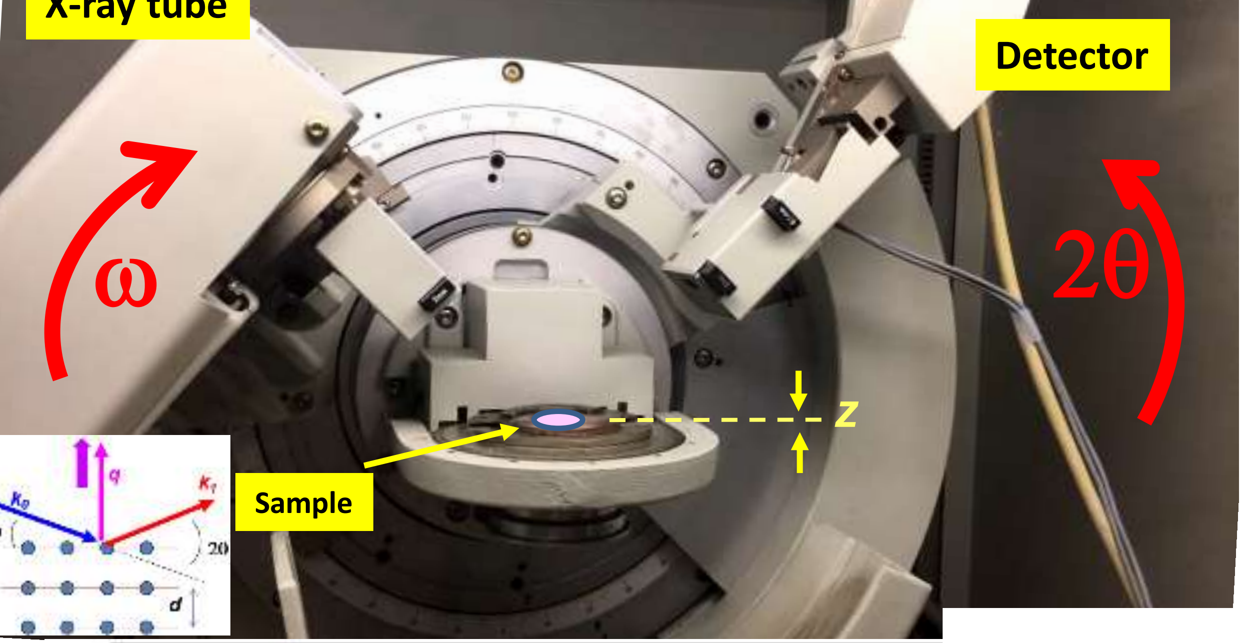


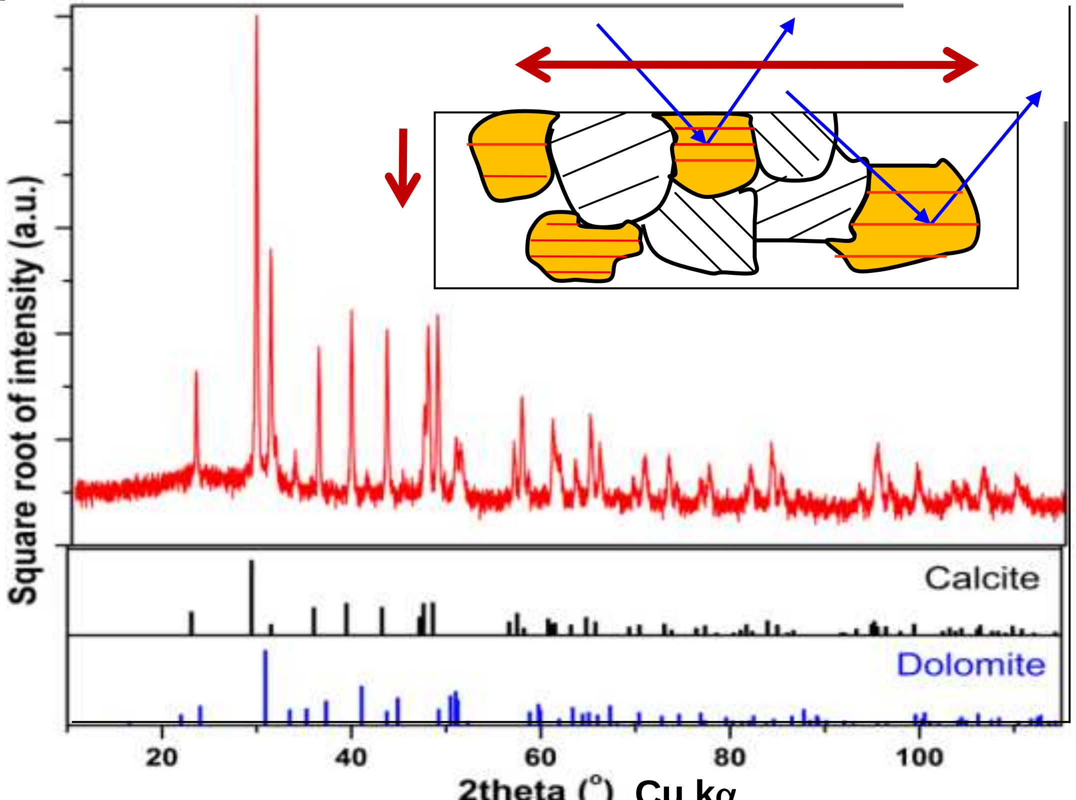
ω scan: circumferential scan, perpendicular to ***q***

omega scan

(rocking curve)

Information from typical XRD data





Grain orientations for planes parallel to surface (directional)
Not all grain orientations are seen in this scan

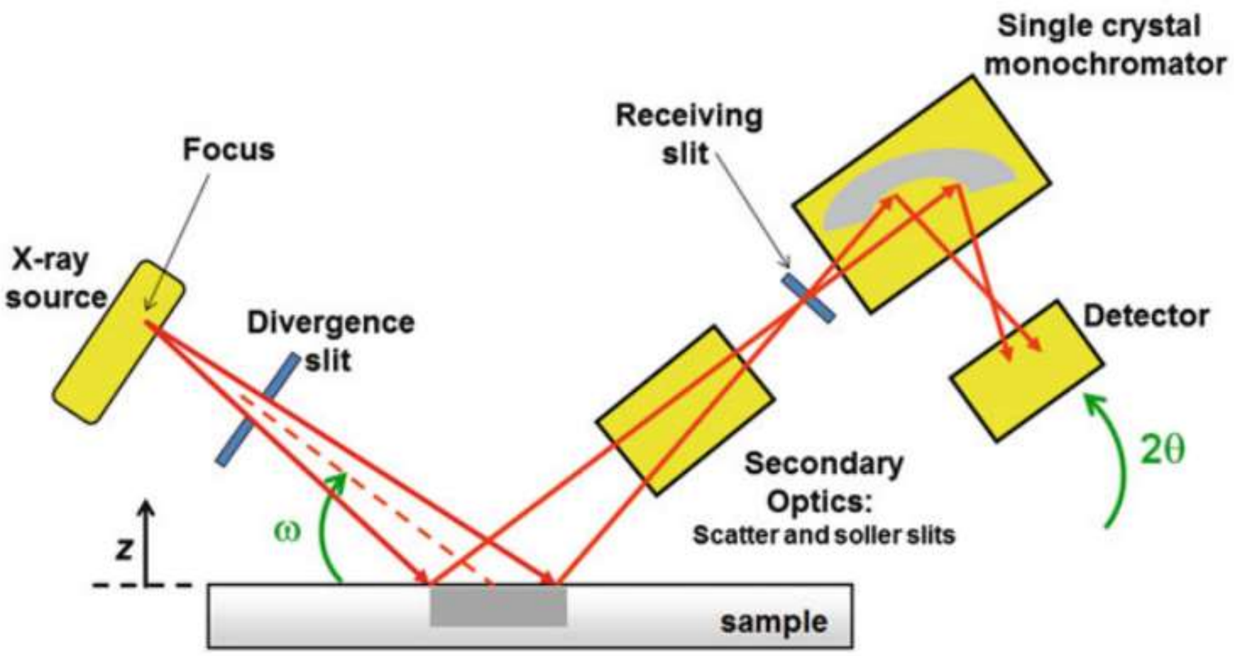
Irradiated volume may change:
surface area decreases, depth increases with increasing ω

2θ peak position: Z is critical (sample displacement error)
Parallel beam vs. Bragg Brentano configuration

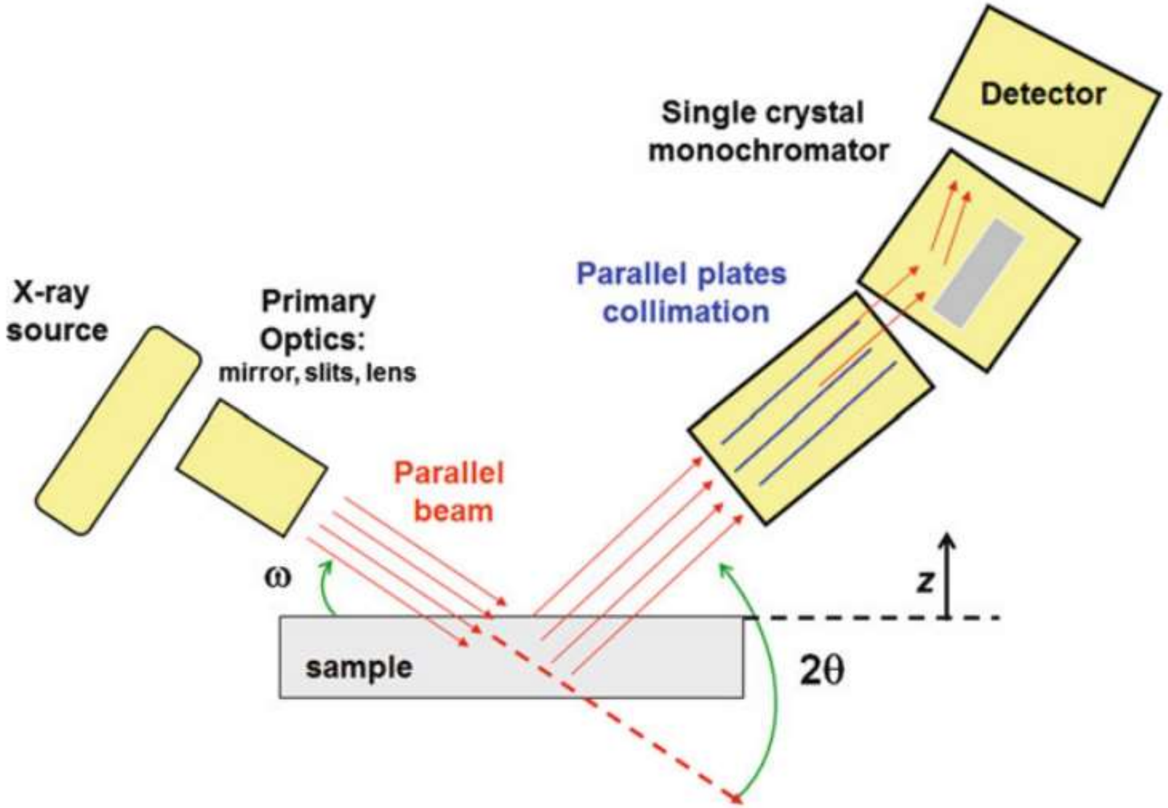
Peak shapes: optics, configuration, surface shape, fine vs coarse grains during powder prep.

Bragg-Brentano vs. parallel beam configurations

Bragg-Brentano or focusing configuration

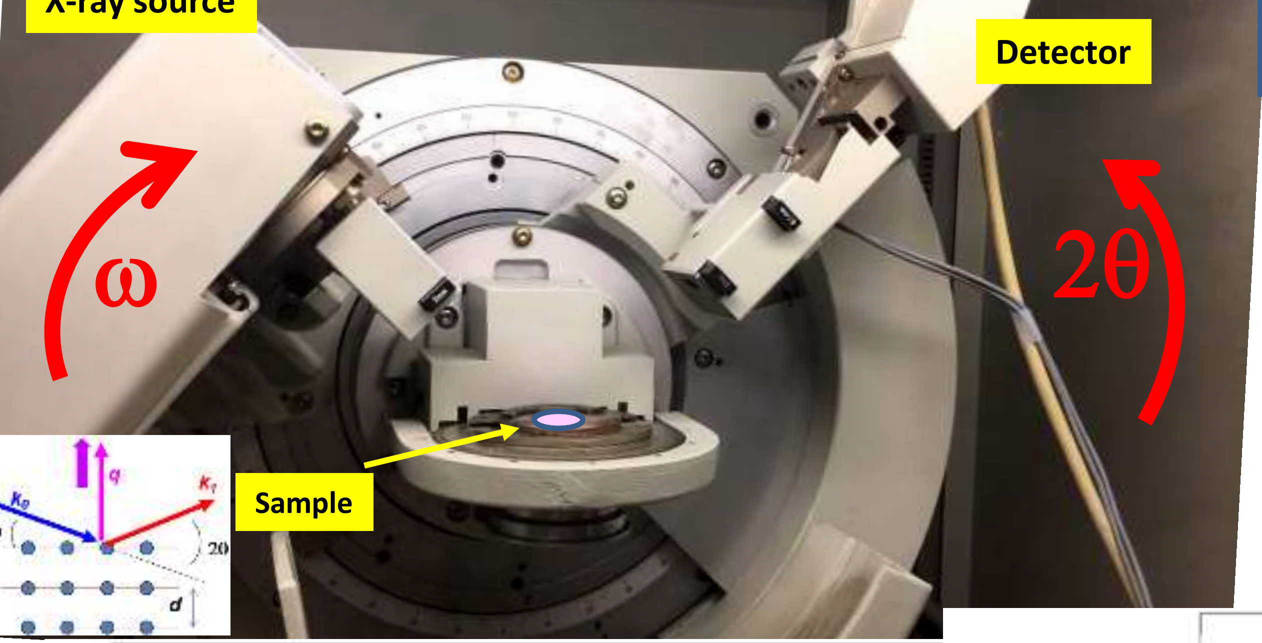


Parallel beam configuration

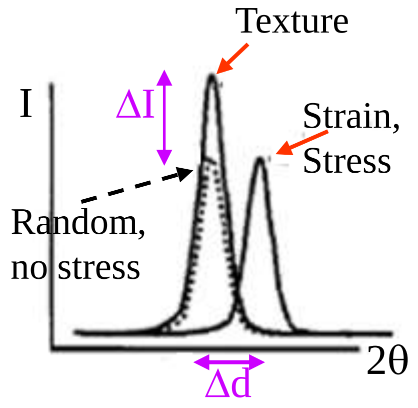


Simpler peak shape

Less sensitive to sample displacement error (Z error)
Better for non-flat surfaces
Better for GI-XRD, XRR

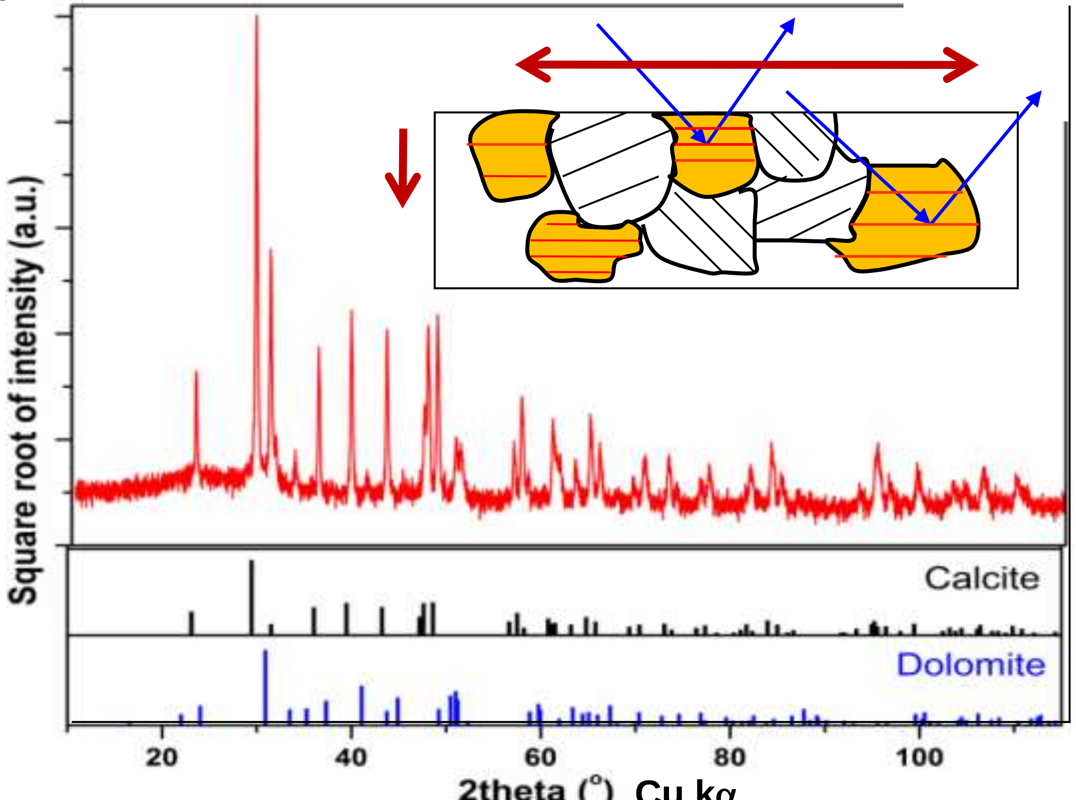


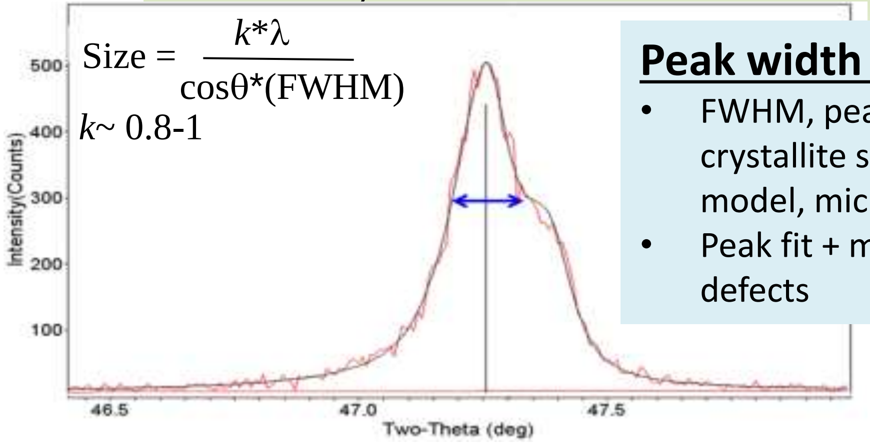
Information from typical XRD data



Peak position:

- 2θ, Bragg's law, *d*-spacing, crystalline phase identification, *(hkl)* for each peak, structure determination, lattice parameters (*a, b, c,* α, β, γ)
- Δd, lattice mismatch, strain (compressive or tensile stress), alloy composition
- Can identify elements, compounds, polymorphs (ex: *Ti* vs. *TiO_2* rutile vs. *TiO_2* anatase)





Peak width (peak shape analysis):

- FWHM, peak fit, Scherrer's equation, crystallite size, grain size, Williamson-Hall model, microstrain
- Peak fit + modeling, extended and point defects

Data background:

Amorphous (short range order) contents

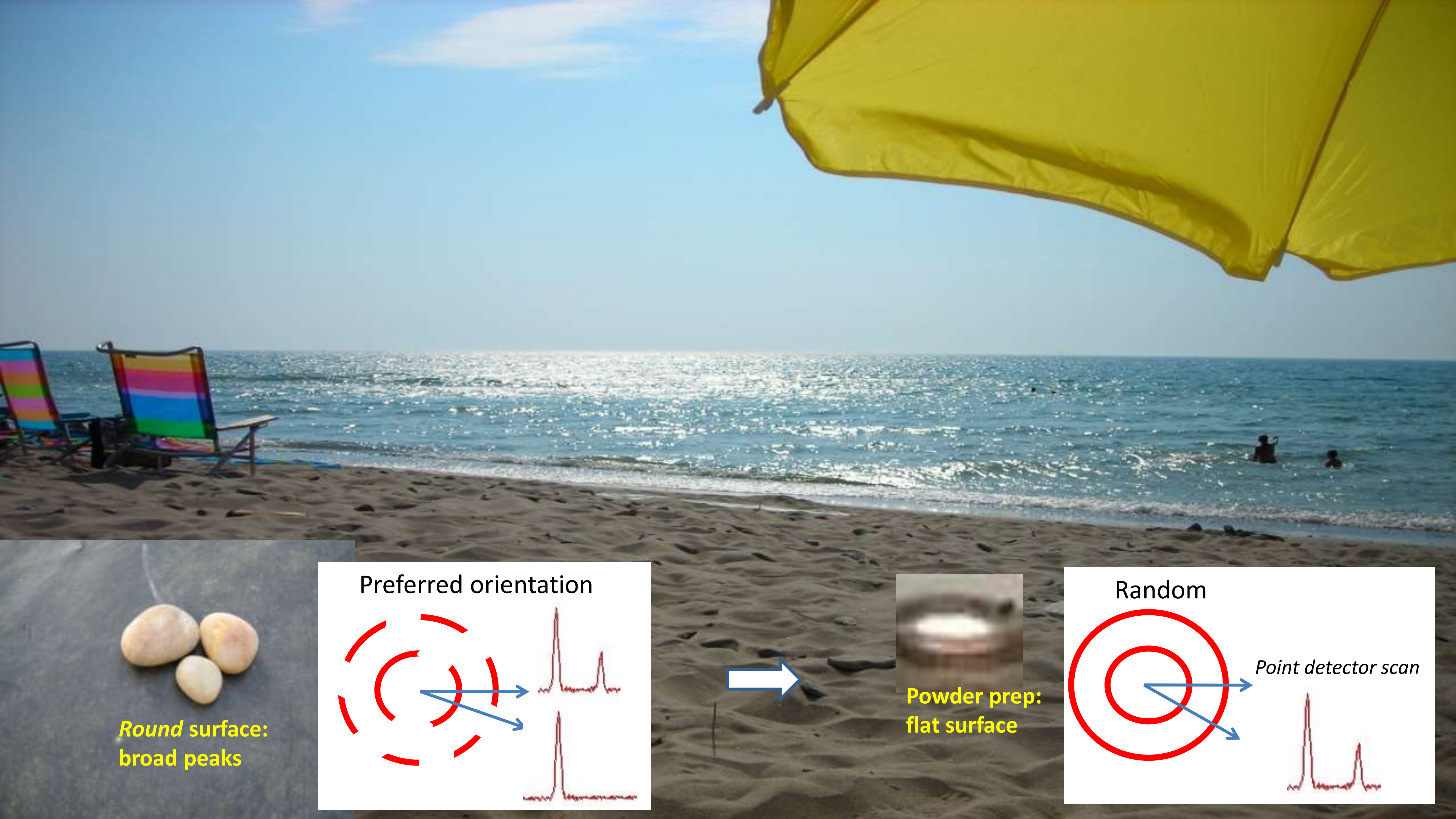
Peak area ratio:

Quantitative analysis of multiple phases (> 0.1 w%)

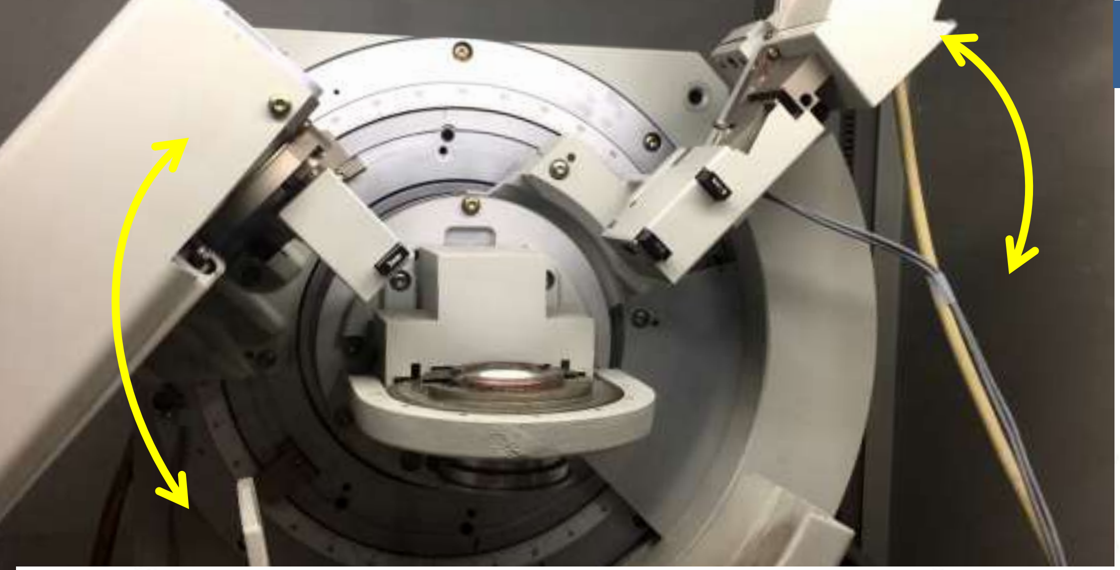
Preferred orientation / texture (type and quantification of texture)

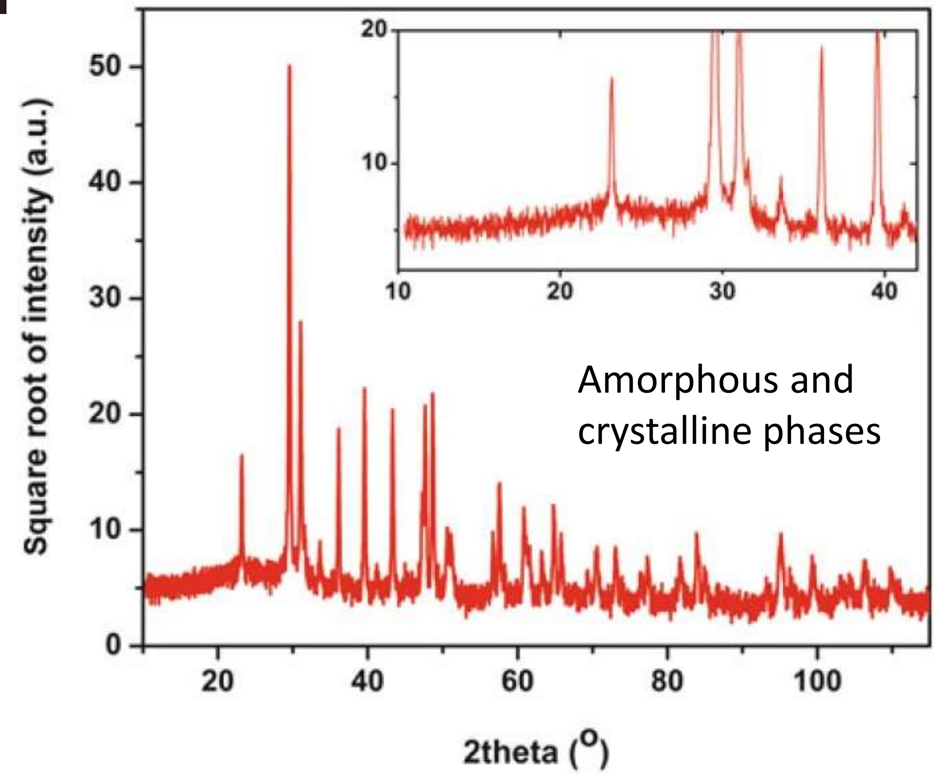
Whole pattern fitting:

Rietveld structure refinement, accurate quantification of phases, size analysis, atomic position, etc.


Round surface:
broad peaks
Preferred orientation
Powder prep:
flat surface
Random
Point detector scan

XRD analysis walkthrough: phase identification





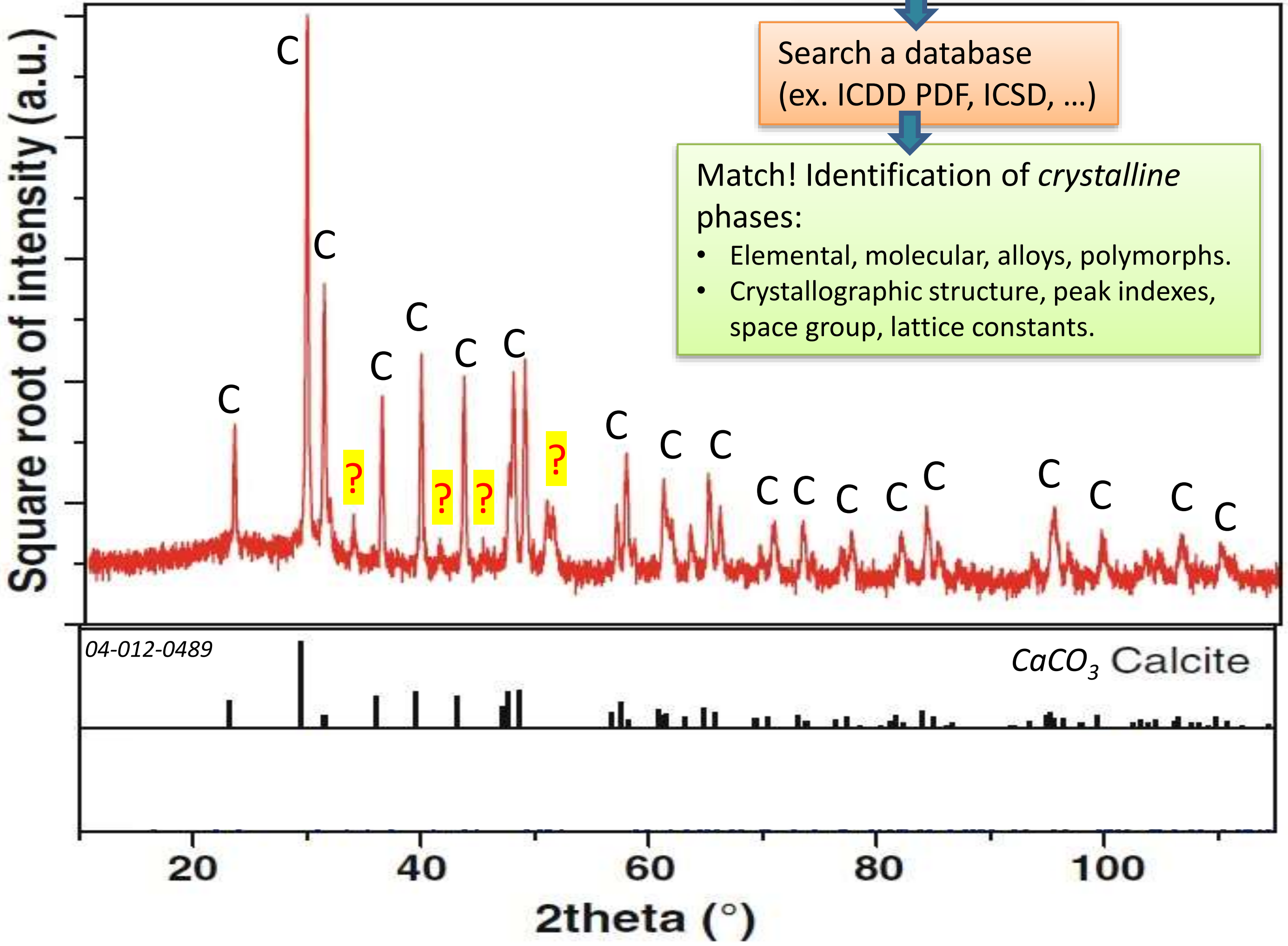
Use a *low-background* sample holder in order to identify and quantify amorphous contents.

Peak position & intensity ratio (peak fit)

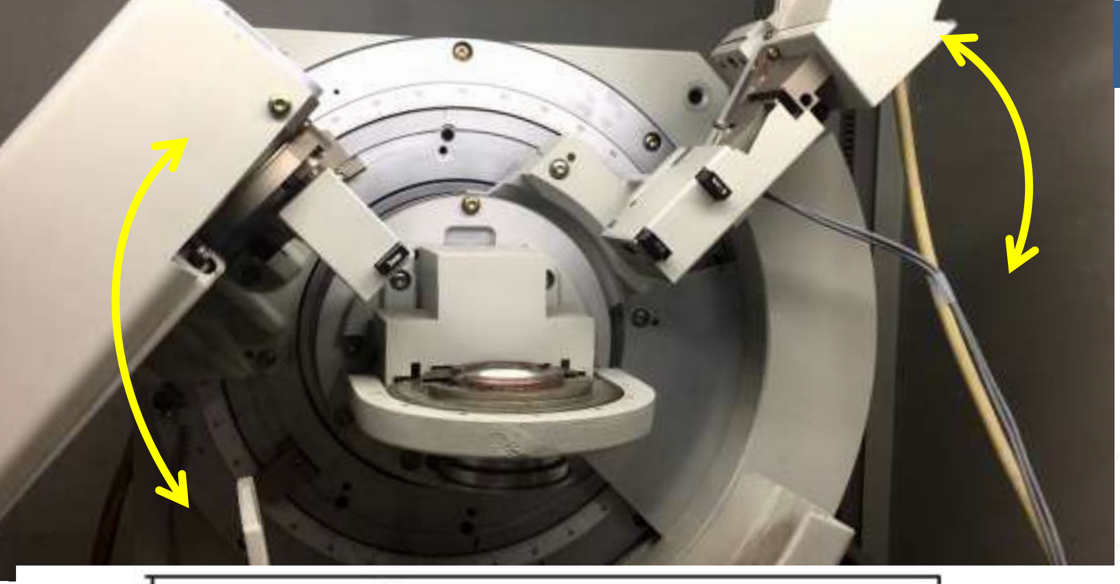
Search a database (ex. ICDD PDF, ICSD, …)

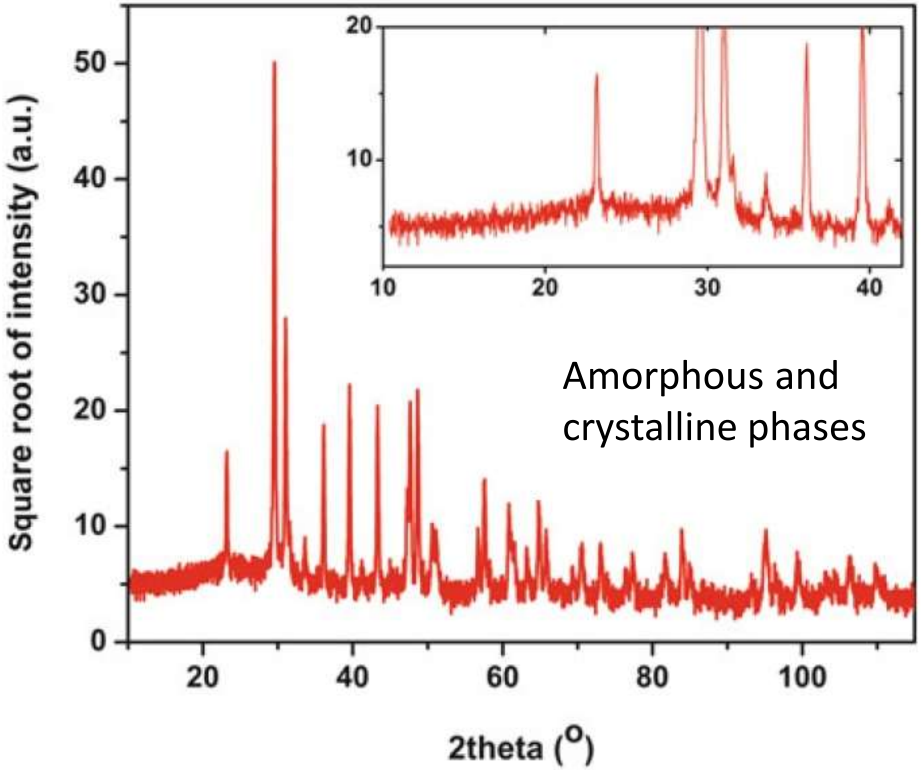
Match! Identification of *crystalline* phases:

- Elemental, molecular, alloys, polymorphs.
- Crystallographic structure, peak indexes, space group, lattice constants.



XRD analysis walkthrough: phase identification





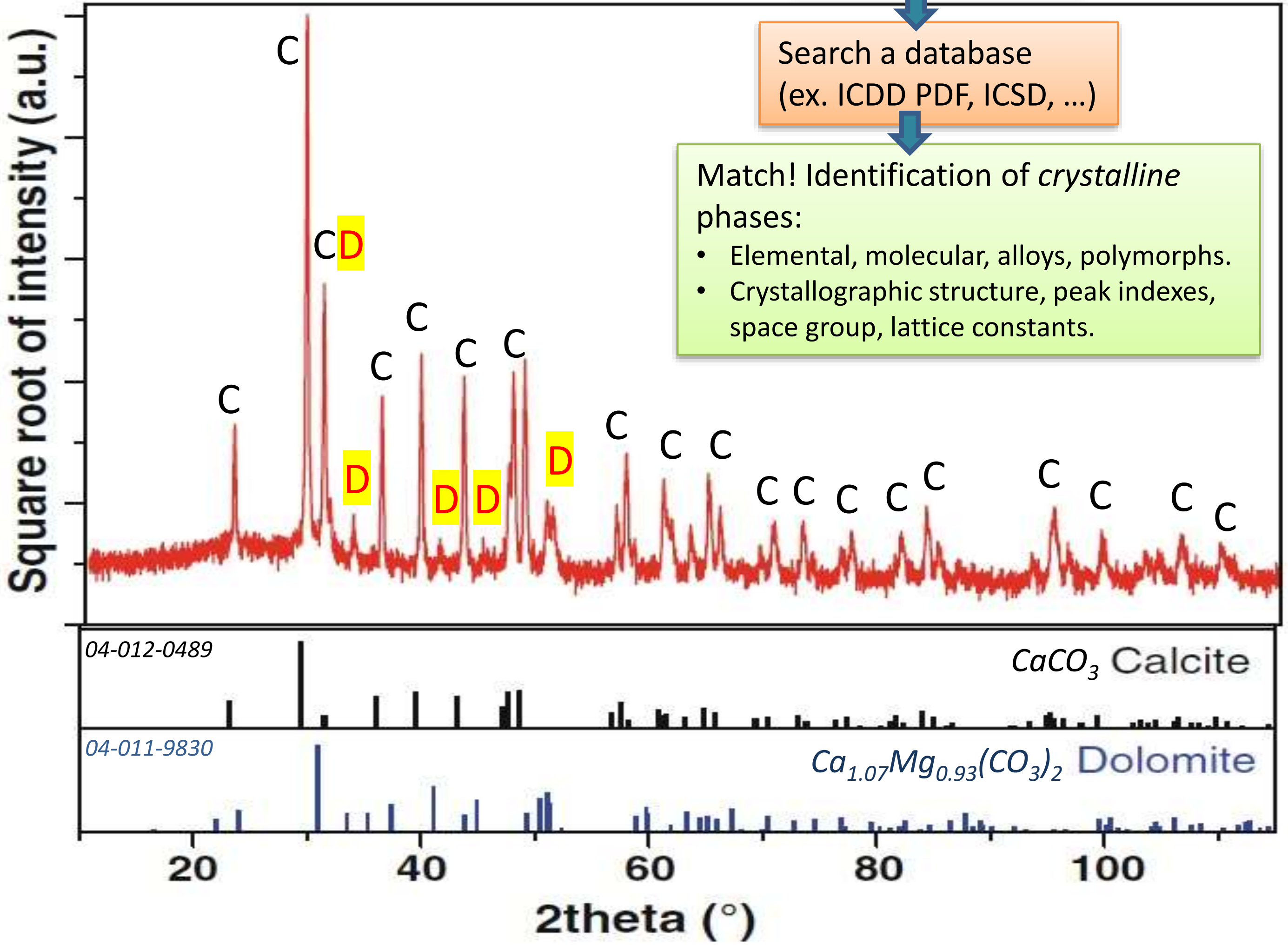
Use a *low-background* sample holder in order to identify and quantify amorphous contents.

Peak position & intensity ratio (peak fit)

Search a database (ex. ICDD PDF, ICSD, …)

Match! Identification of *crystalline* phases:

- Elemental, molecular, alloys, polymorphs.
- Crystallographic structure, peak indexes, space group, lattice constants.



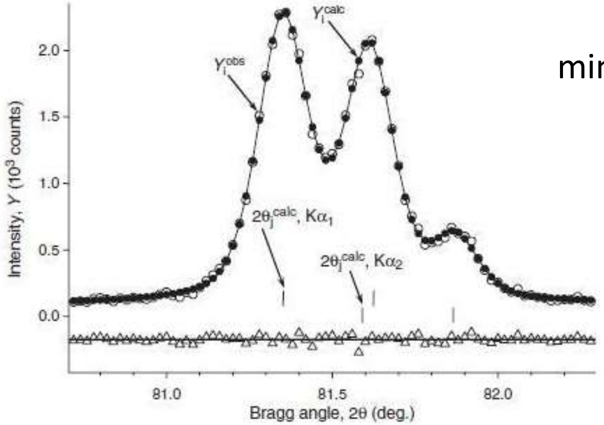
XRD analysis walkthrough: quantitative analysis

H. Rietveld
(1932-2016)

Input:

- **Data**
- **Peaks and background fit**
- **Phases and crystalline structures**
- **Instrument resolution function (peak shape)**

Rietveld refinement:



Non-linear least square minimization of this function for each data point i:

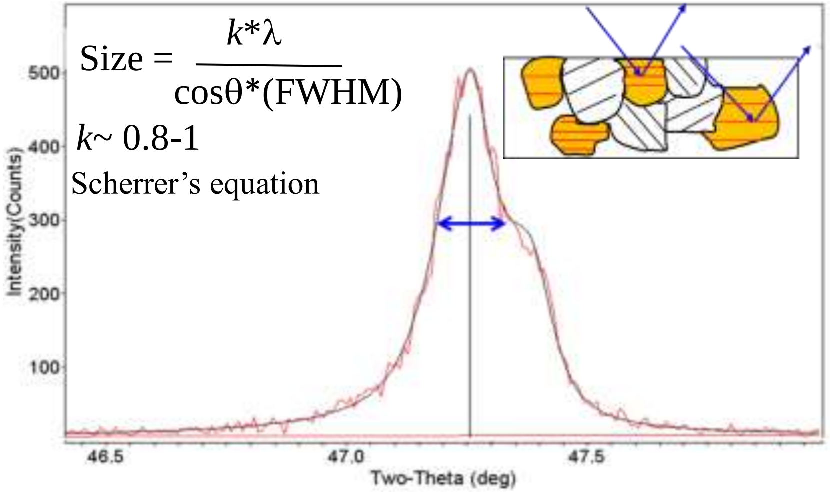
$$\Phi = \sum_{i=1}^{n} w_i (Y_i^{obs} - Y_i^{calc})^2$$

Data fitting with a model: minimize figure of merit "*R*"

Output:

- ***Quantitative analysis***: **% of each phase and % of amorphous**
- **Crystallite size**
- **Unit cell and lattice parameters**
- **Preferred orientation**
- **Scale factors**
- **Atomic positions/displacements in the structure**
- **…**

Crystalline size:



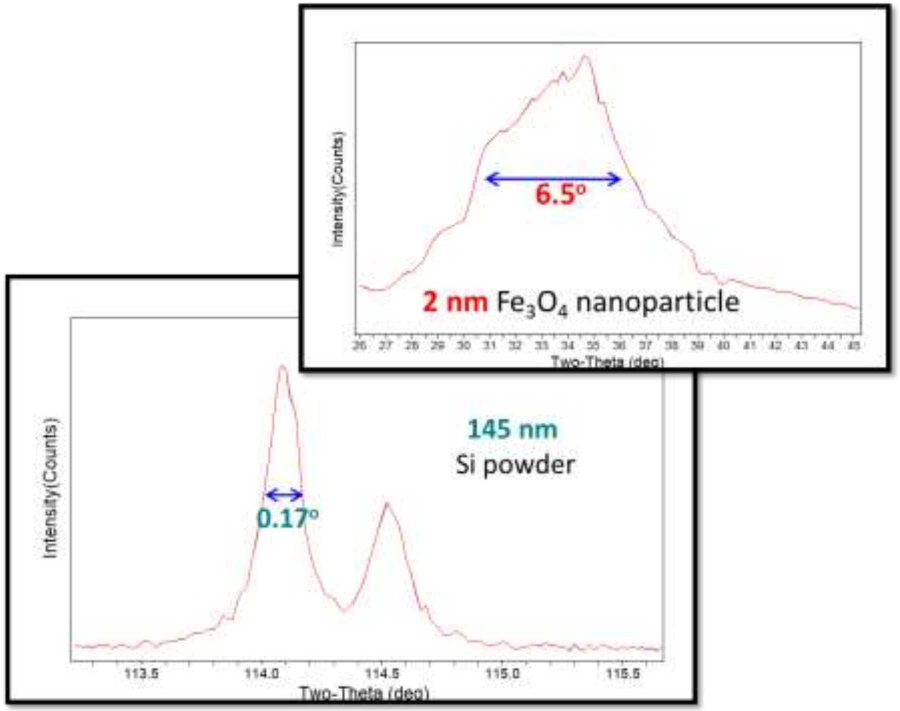
Domain (volume) of diffraction

Peak fit
Choice of peak shape function:
Pseudo-Voigt, Lorentzian, Gaussian,…

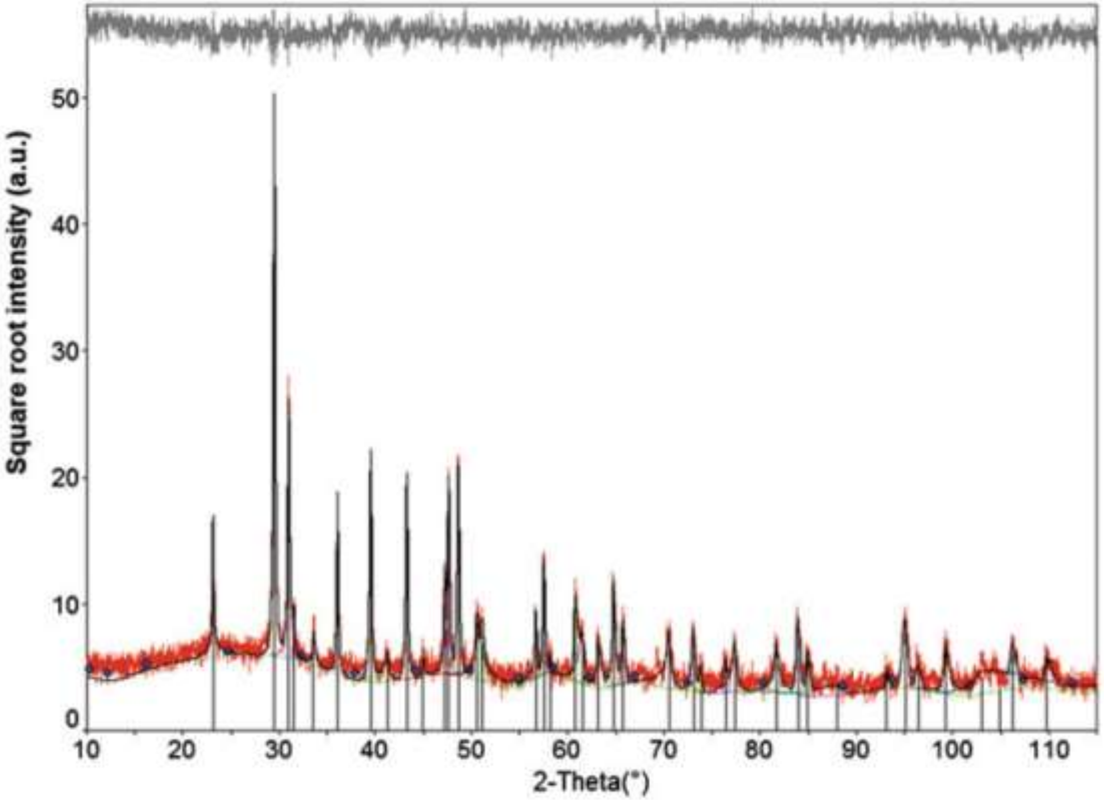
Choice of instrument peak shape function
Need standard (NIST LaB6, …)

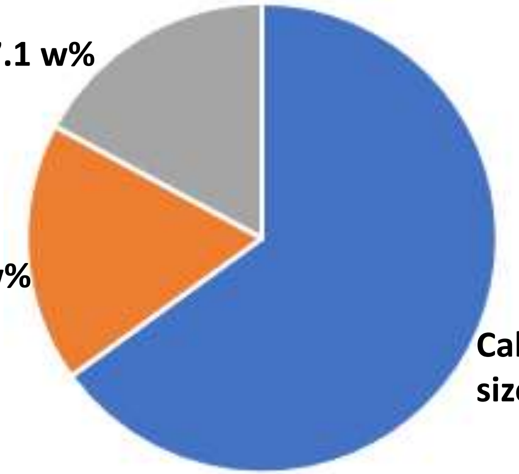
Scherrer's equation limitations
***Directional* size information**
***Volume* average (SEM is number average)**
Crystallite size ≤ grain size ≤ particle size

Range < ~ 500 nm



XRD analysis walkthrough: Rietveld analysis

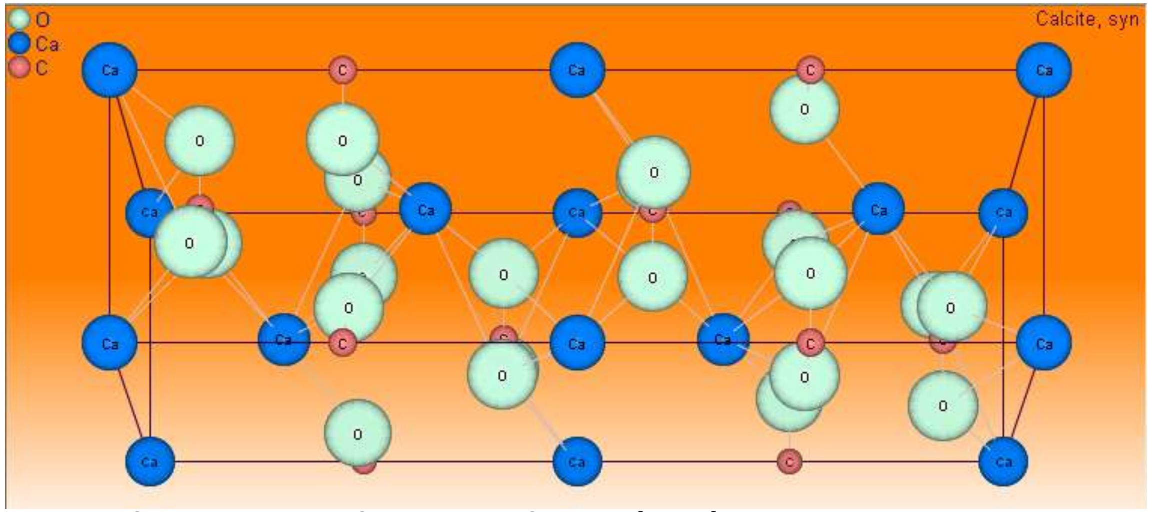




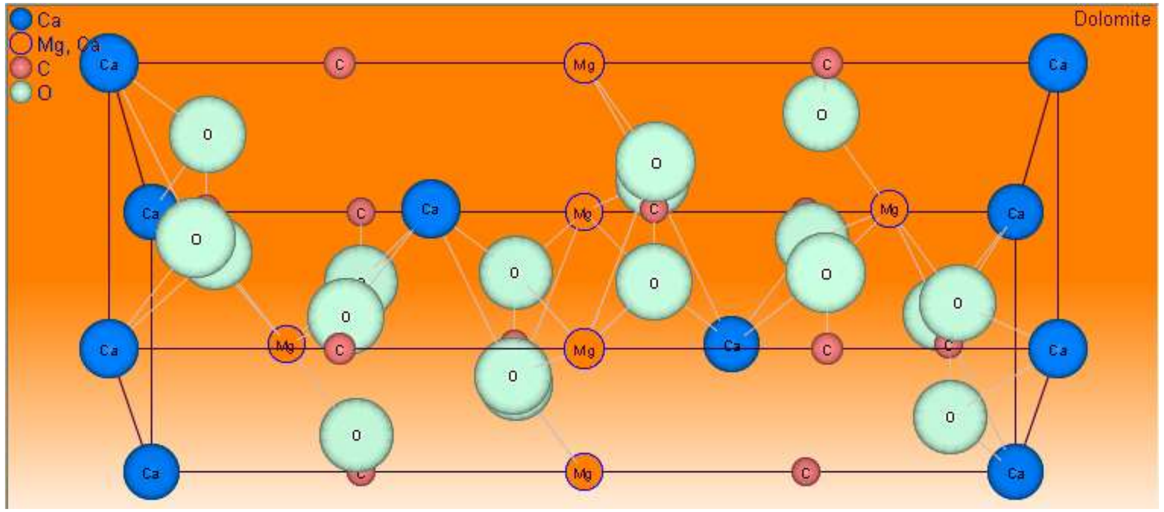
Amorphous 17.1 w%

Dolomite 17.9 w%
size 35.6 nm

Calcite 65.0 w%
size 56.8 nm

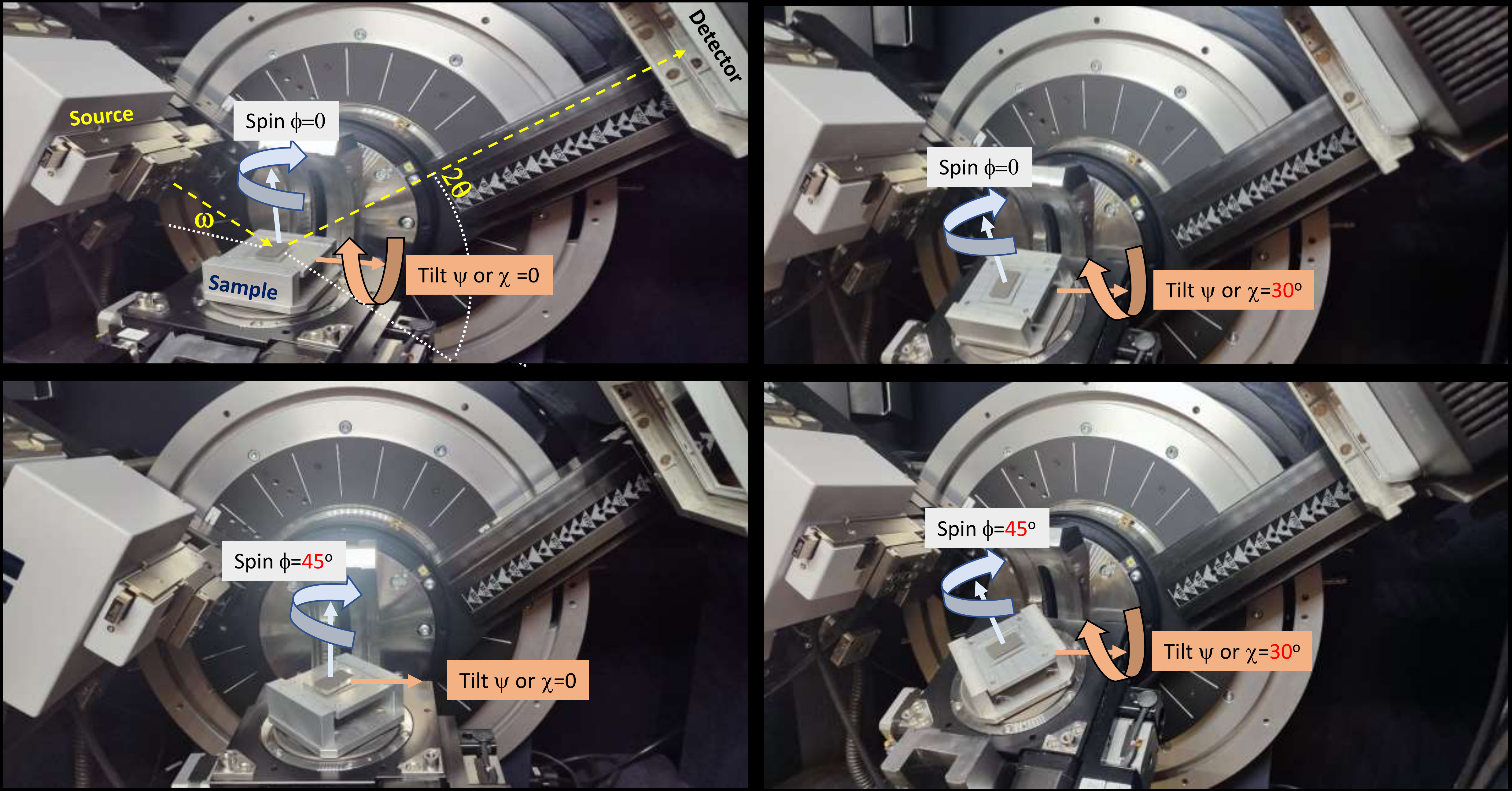


Calcite, $CaCO_3$, hexagonal, R3c (167)
0.499 nm/ 0.499 nm / 1.705 nm <90.0/90.0/120.0>



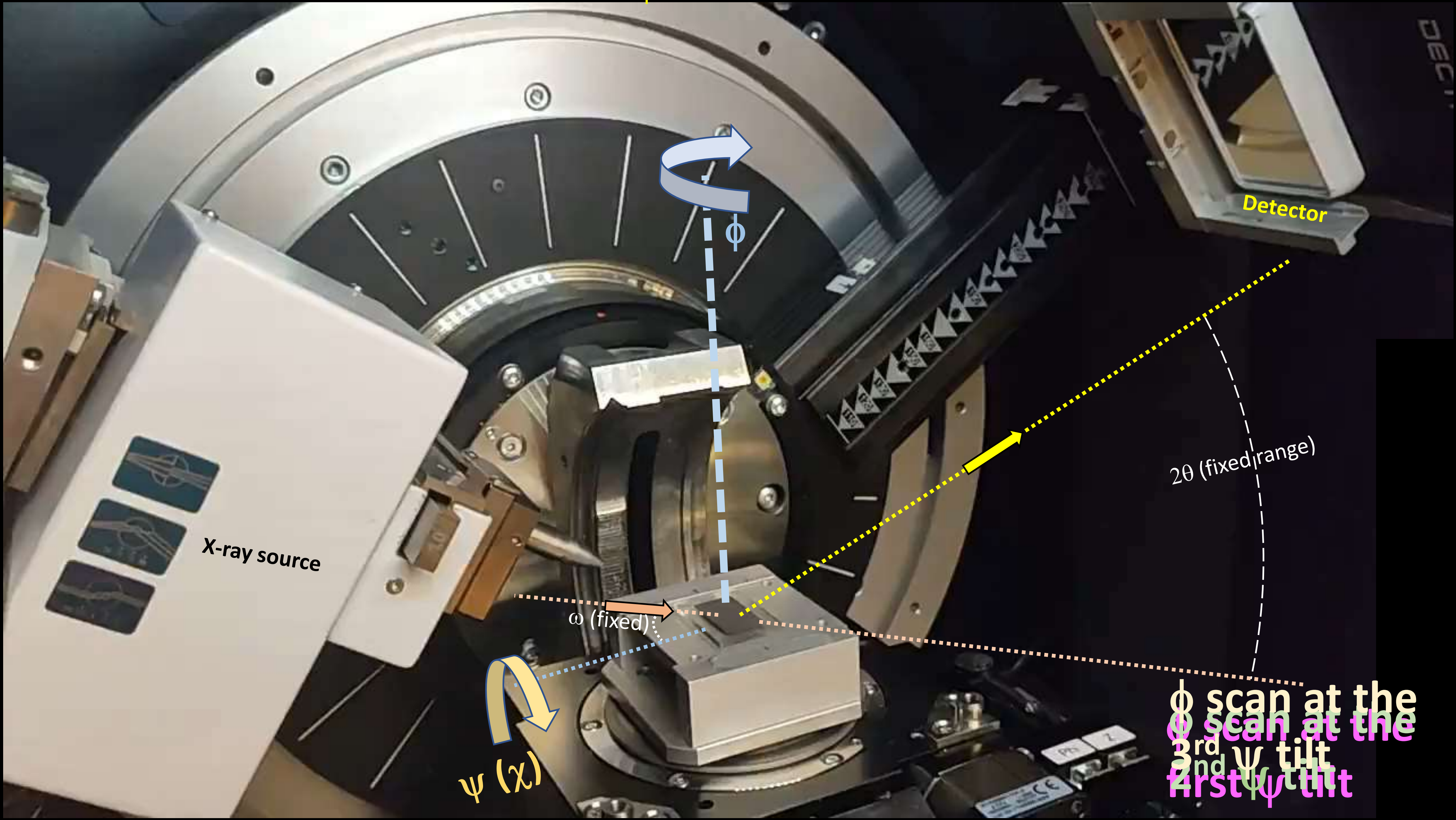
Dolomite, $Ca_{1.07}Mg_{0.93}(CO_3)_2$, hexagonal, R3 (148)
0.481 nm/ 0.4819 nm / 1.602 nm <90.0/90.0/120.0>

Tilt and spinning rotations



Pole figure measurement using a theta/theta XRD system with point focus and 2D detector with full ROI

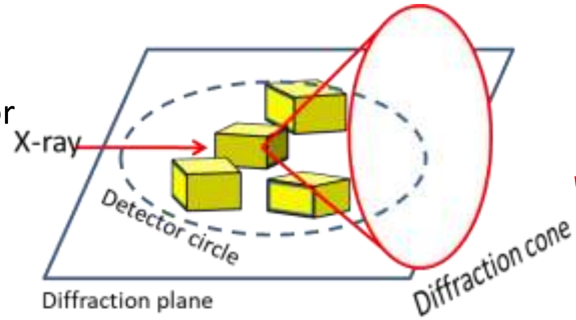
Video speed 5X than normal

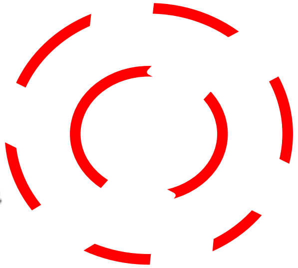


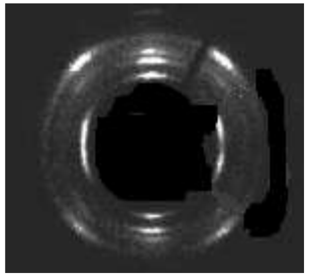
Texture / preferred orientation

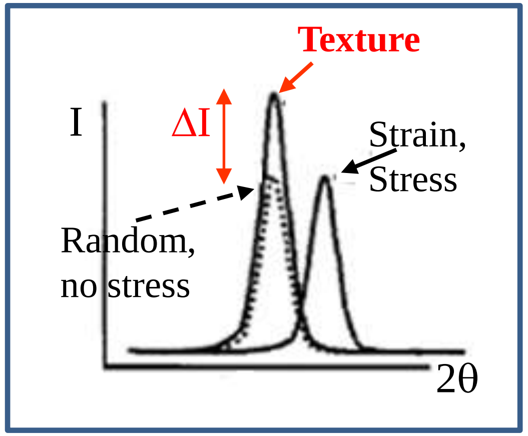
- What is the preferred (hkl) orientation? What is the **texture type and its strength**?
- How is a *(hkl)* orientation distributed in the material? Use **pole figure** measurements for a certain *(hkl)*.
- Use a combination of pole figures to determine the **orientation distribution function** (ODF).
- ODF describe the plans, directions and volume of each orientation present.

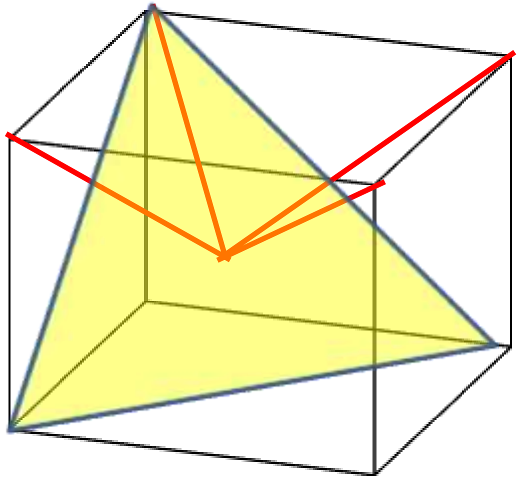
Poly crystal (texture)

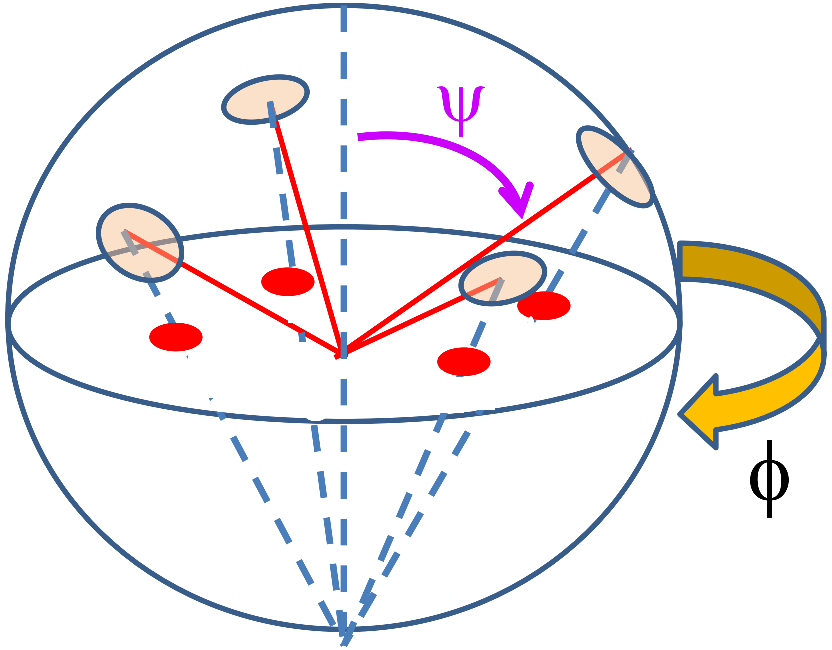


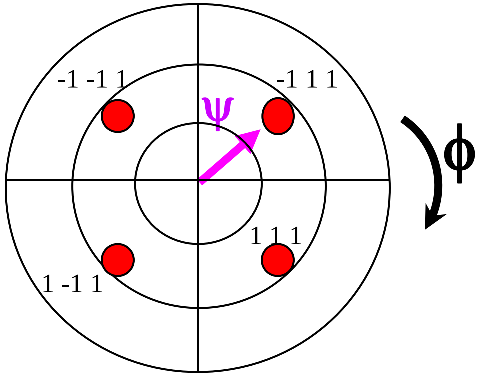










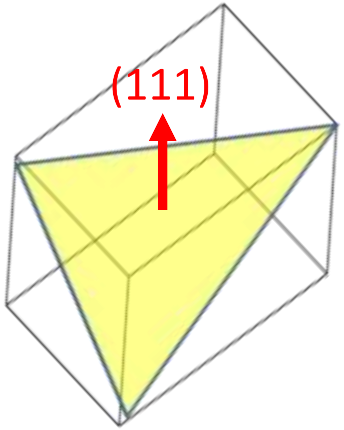


Azimuth
$\phi = 45^o, 135^o, 225^o, 315^o$

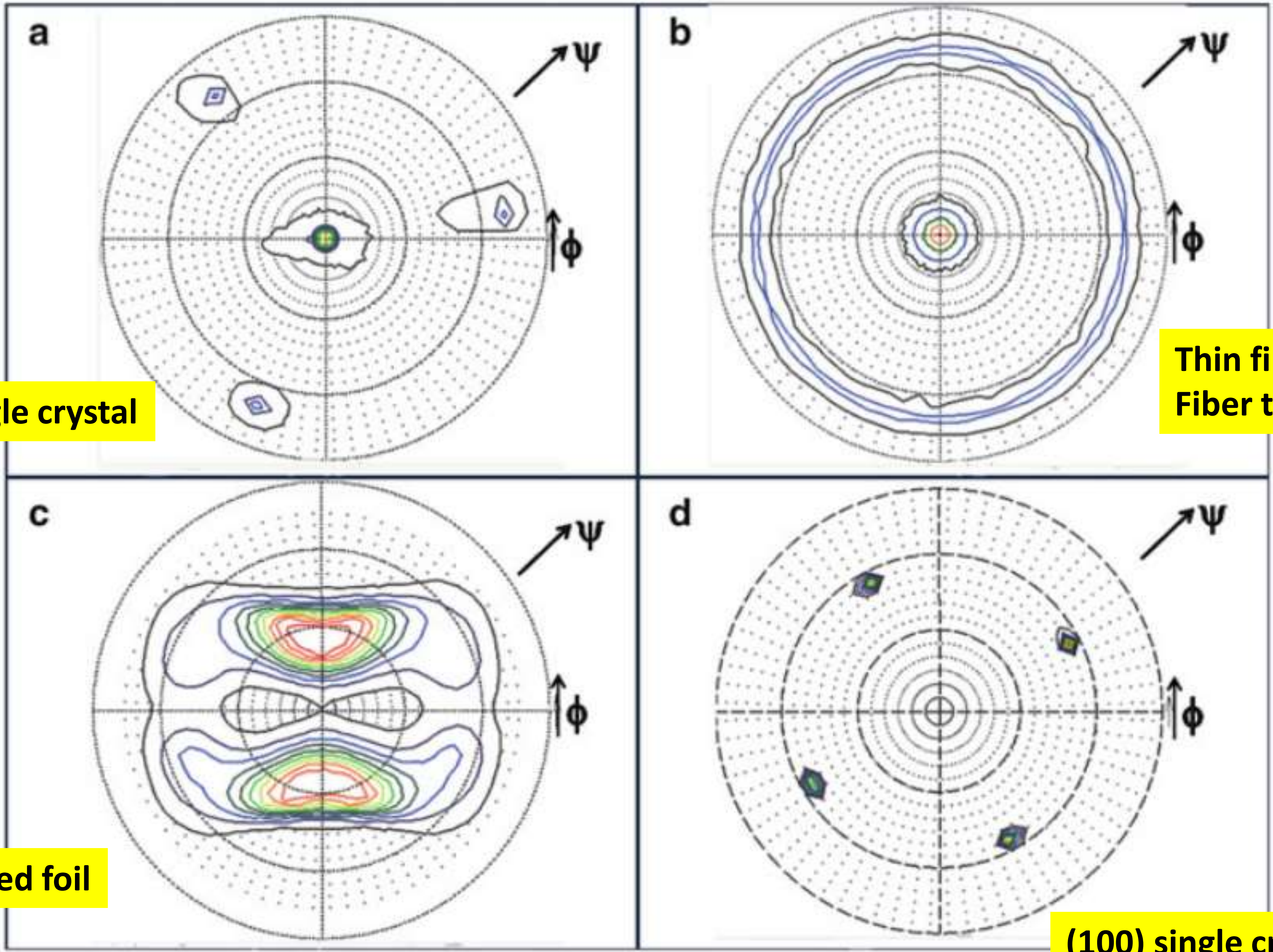
Tilt $\psi = 54.7^o$

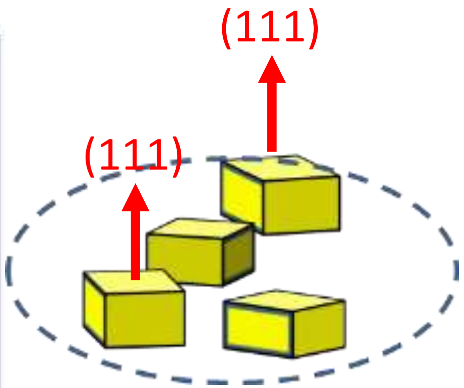
ψ: [100],[111]

(111) pole figures from 4 Cu samples: thin film, rolled foil and two types of single crystal



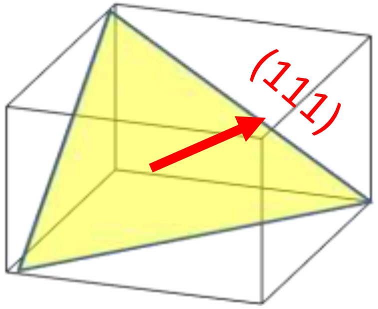
(111) single crystal





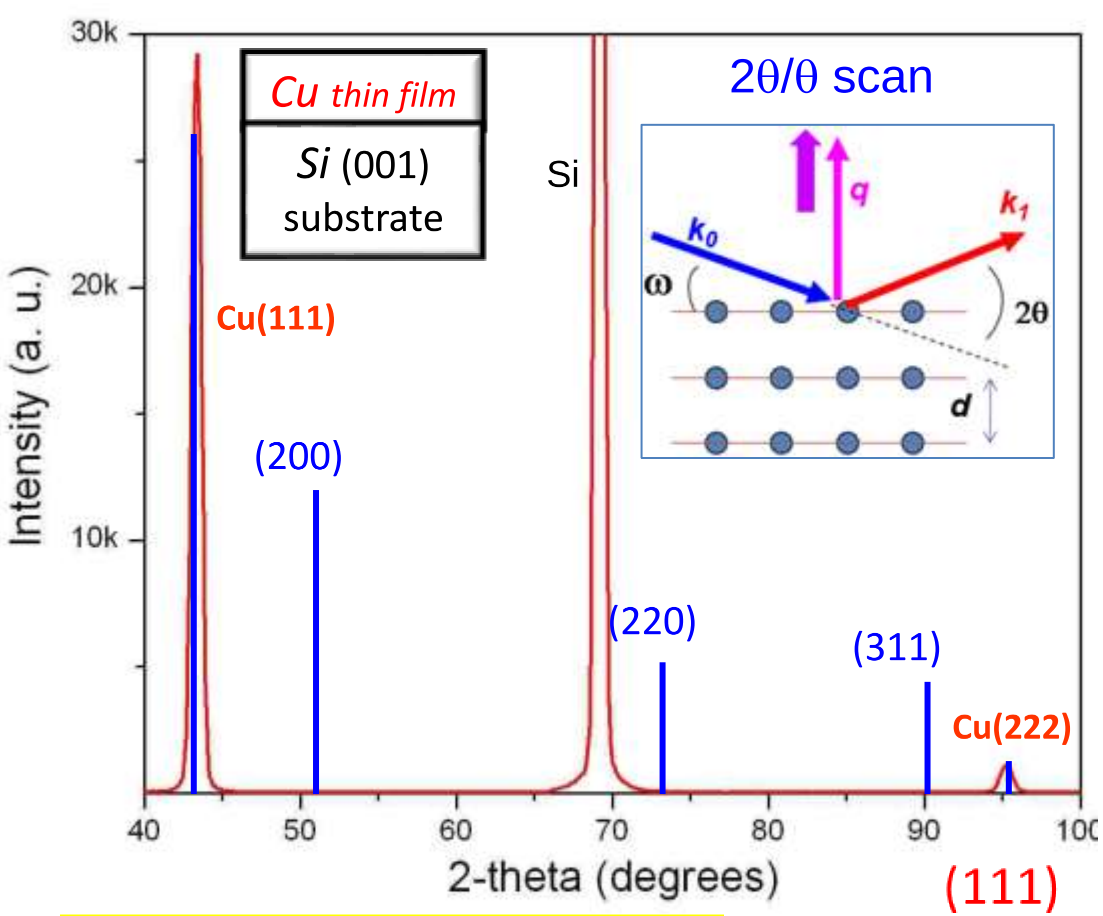
Thin film
Fiber texture

Rolled foil

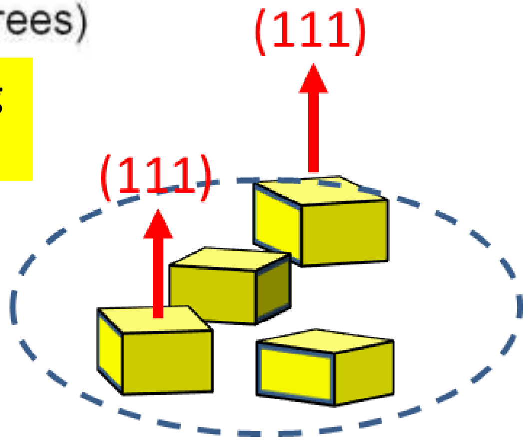


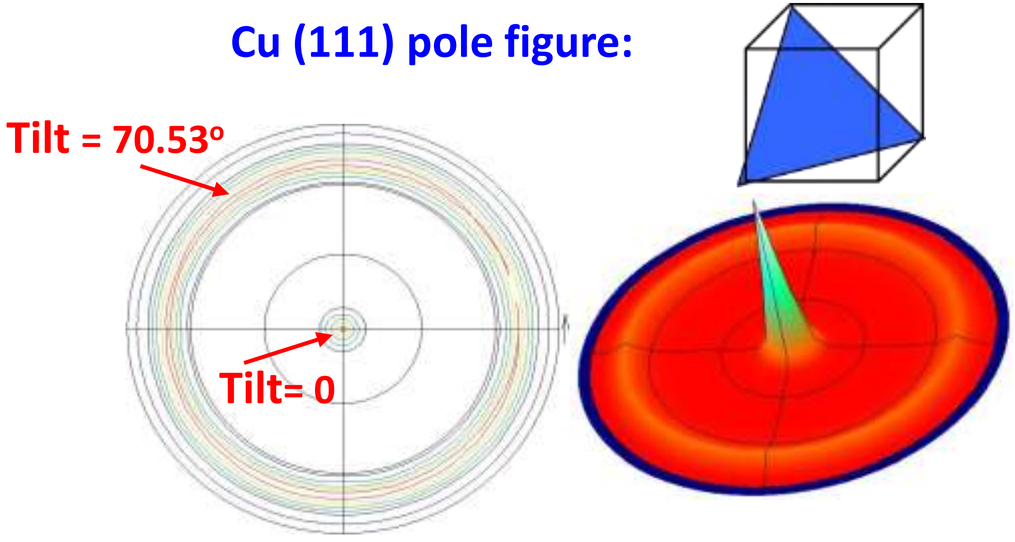
(100) single crystal

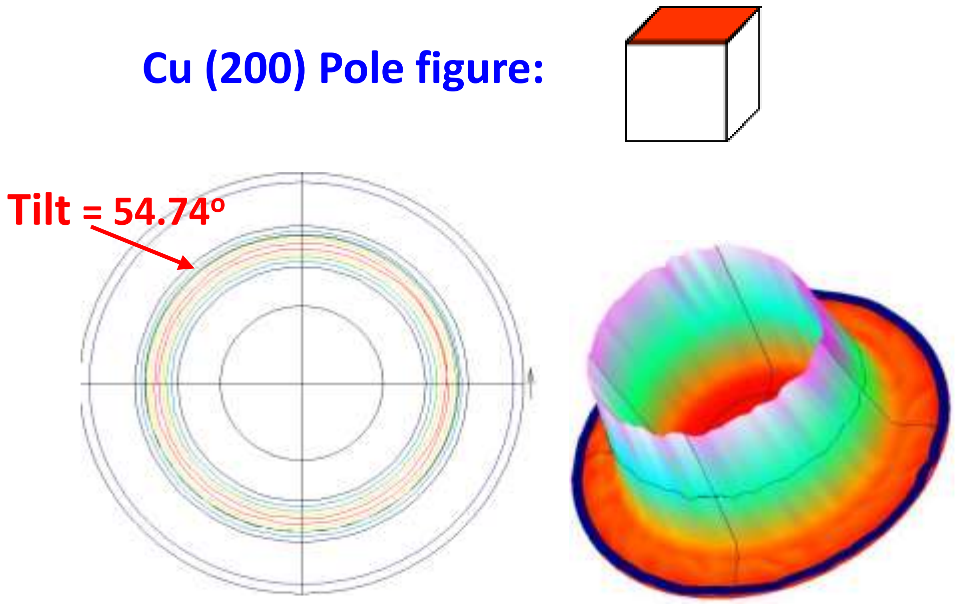
Preferred orientation in a thin film



All grains are <111> oriented along the film growth direction.

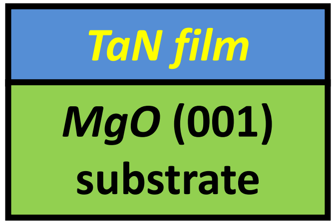


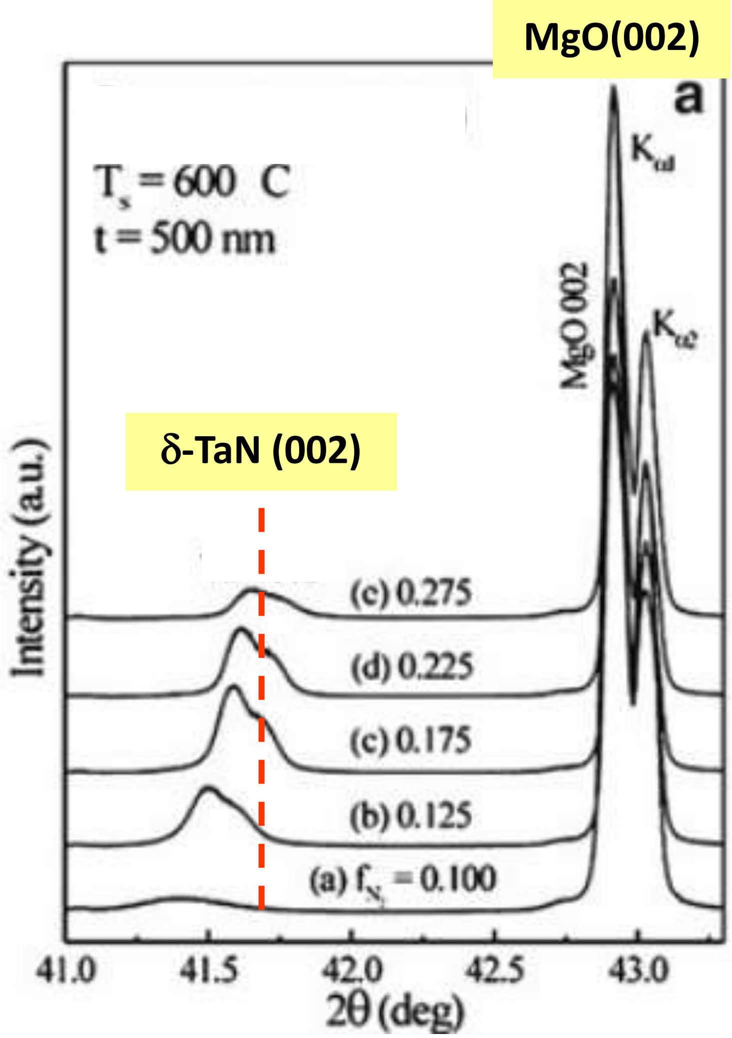


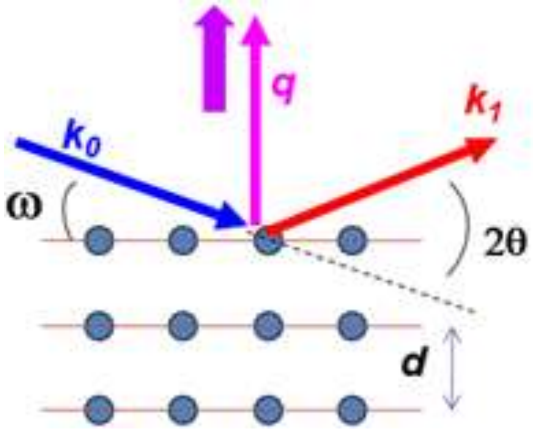


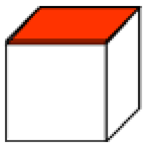
Grains are randomly oriented along the surface

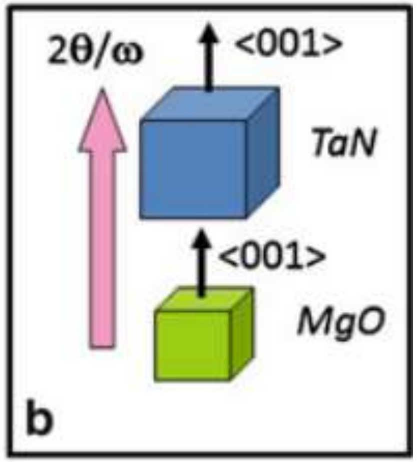
Thin film XRD analysis walkthrough

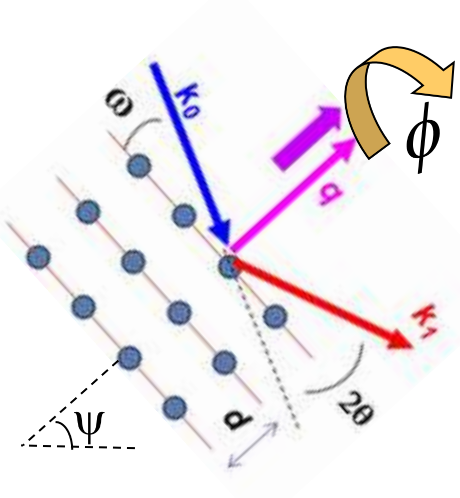


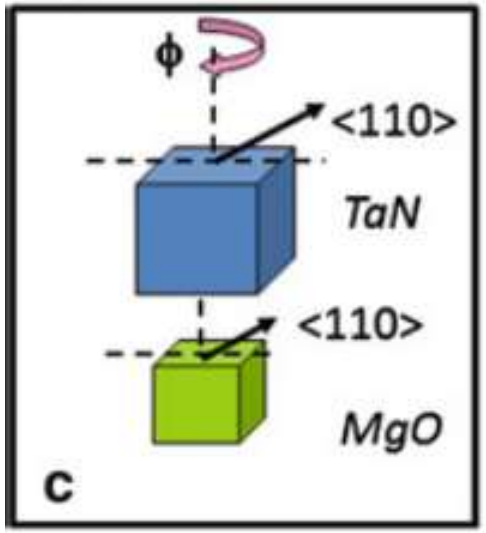


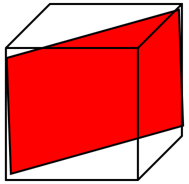


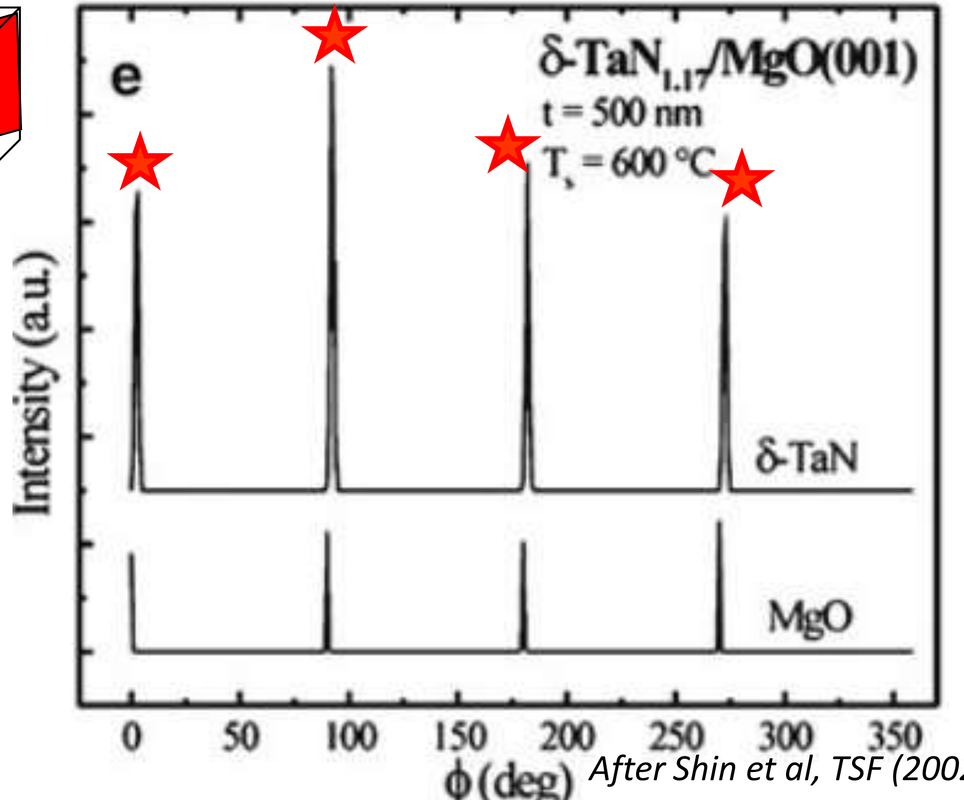






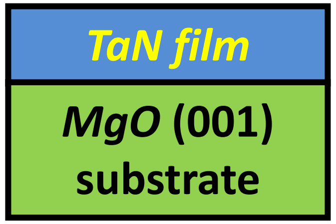


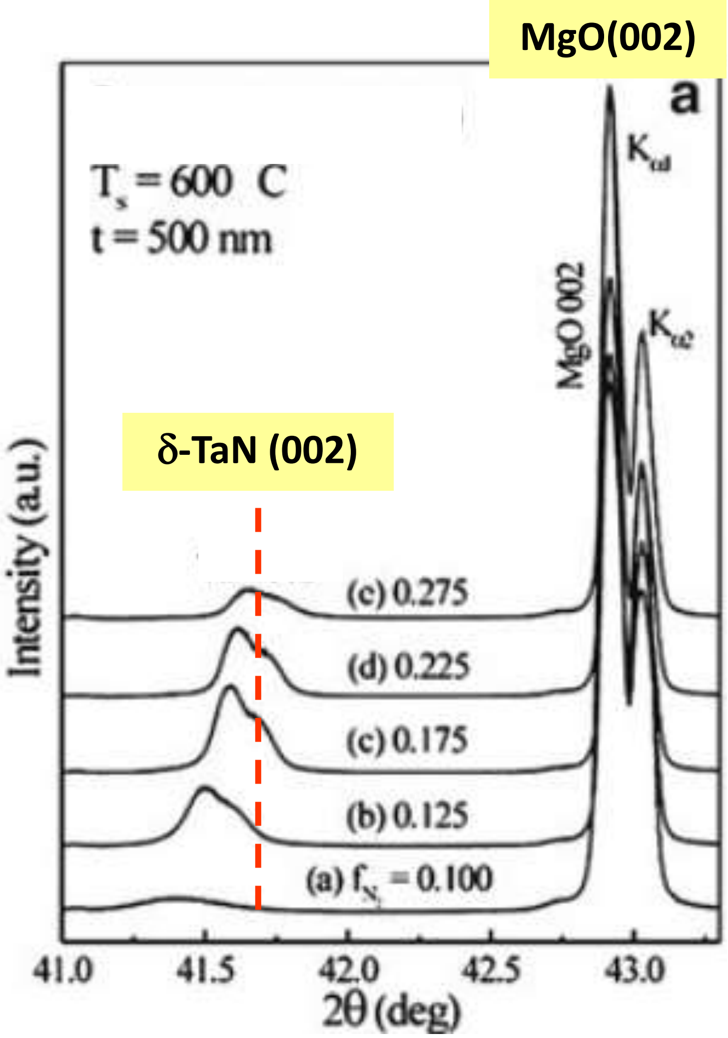


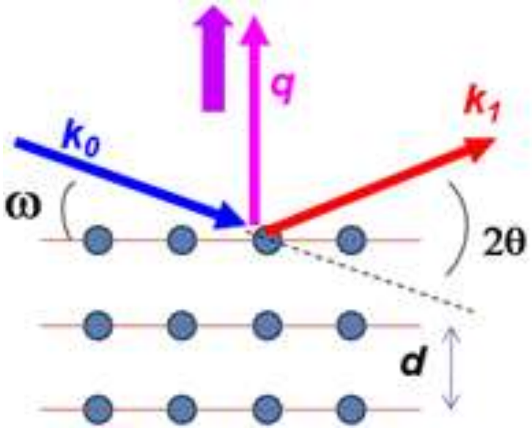


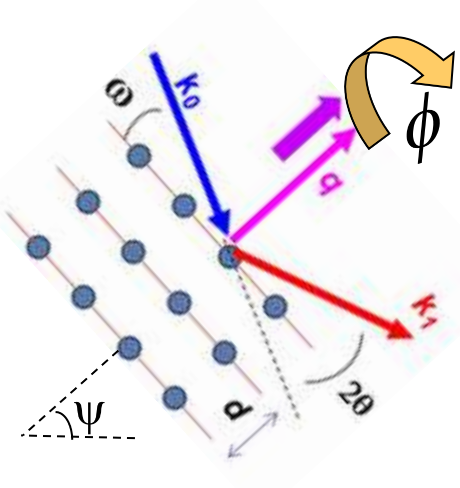
After Shin et al, TSF (2002)

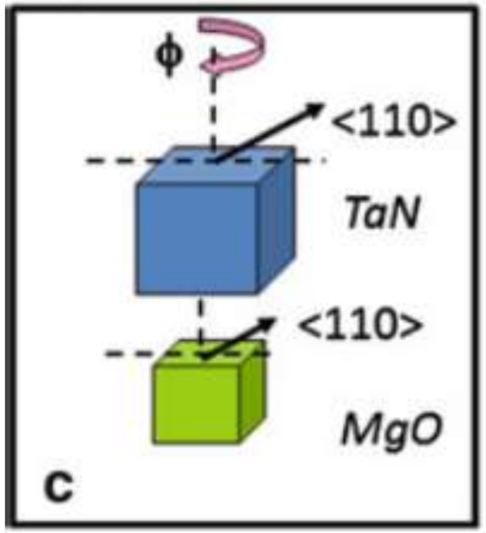
Thin film XRD analysis walkthrough

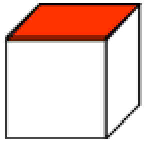








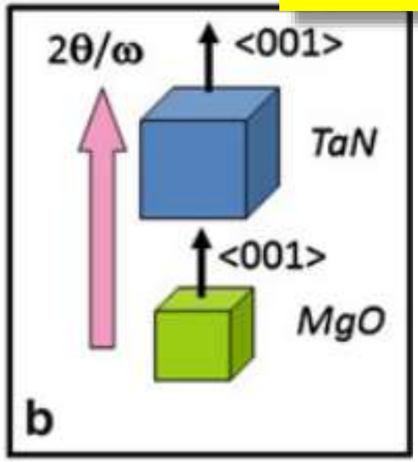


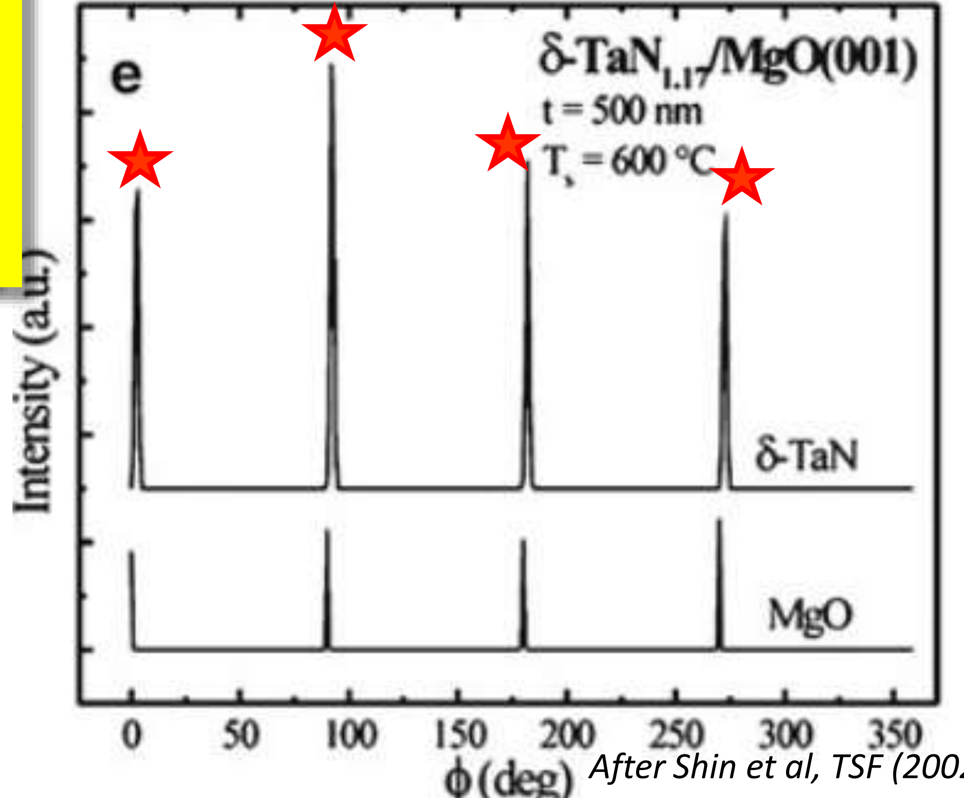


Cube on cube epitaxy:

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

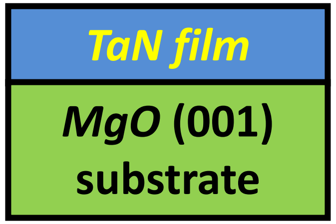
$(100)_{TaN}//(100)_{MgO}$



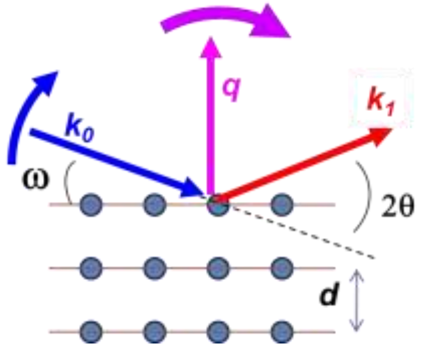


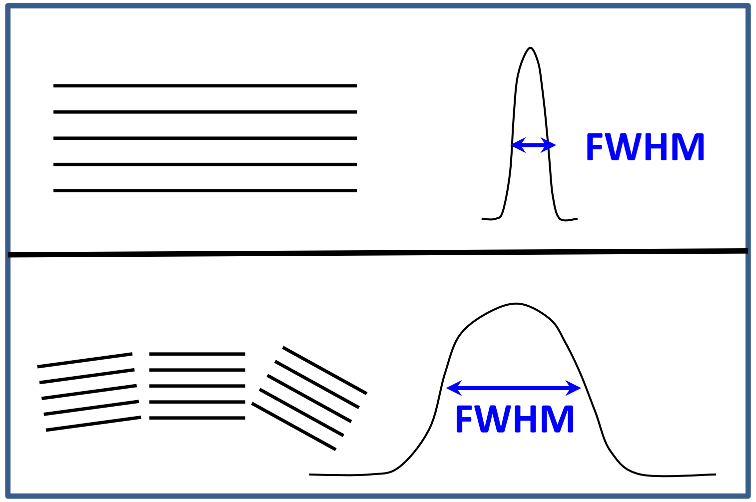
After Shin et al, TSF (2002)

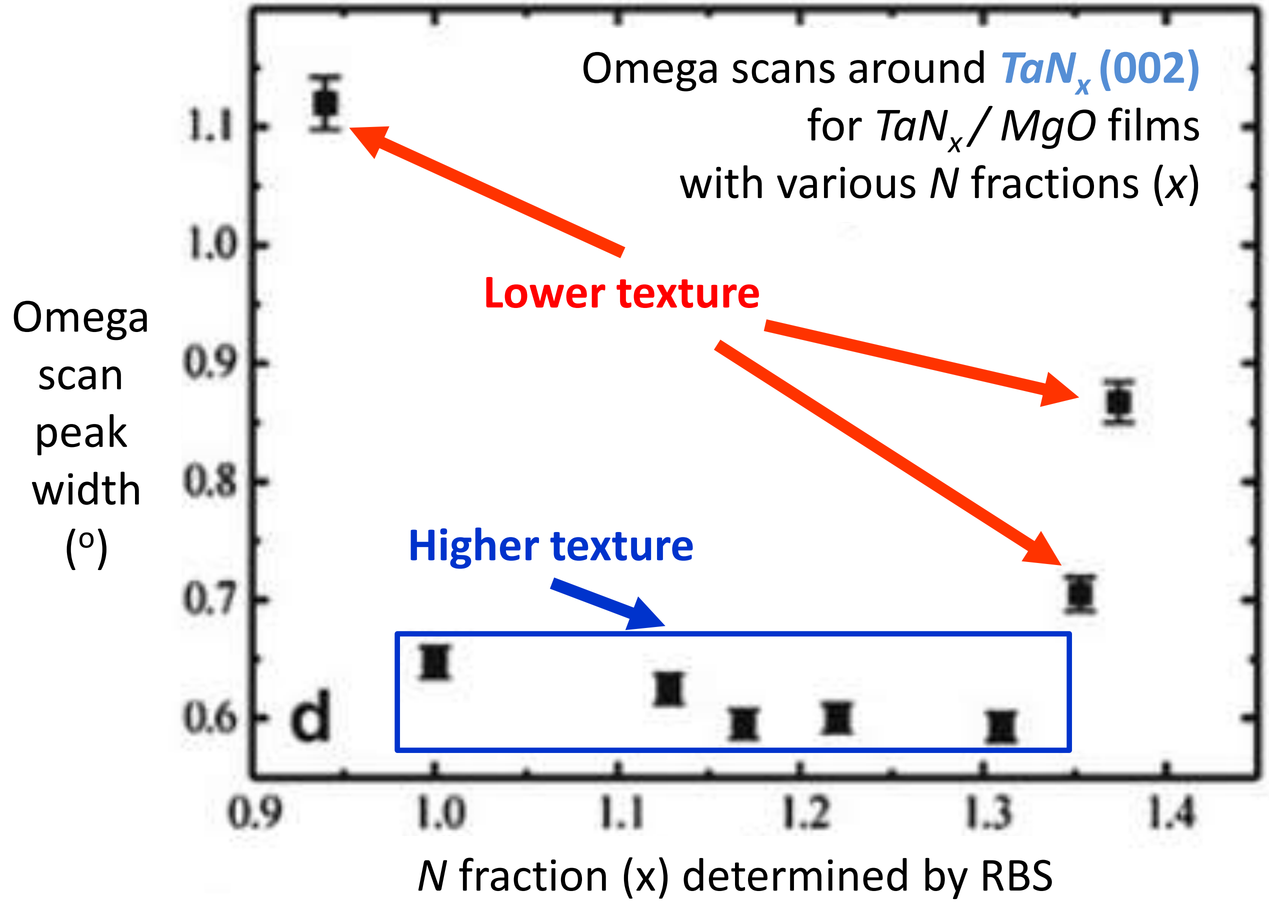
Thin film XRD analysis walkthrough



Omega scan around a *(hkl)* peak
preferred orientation analysis

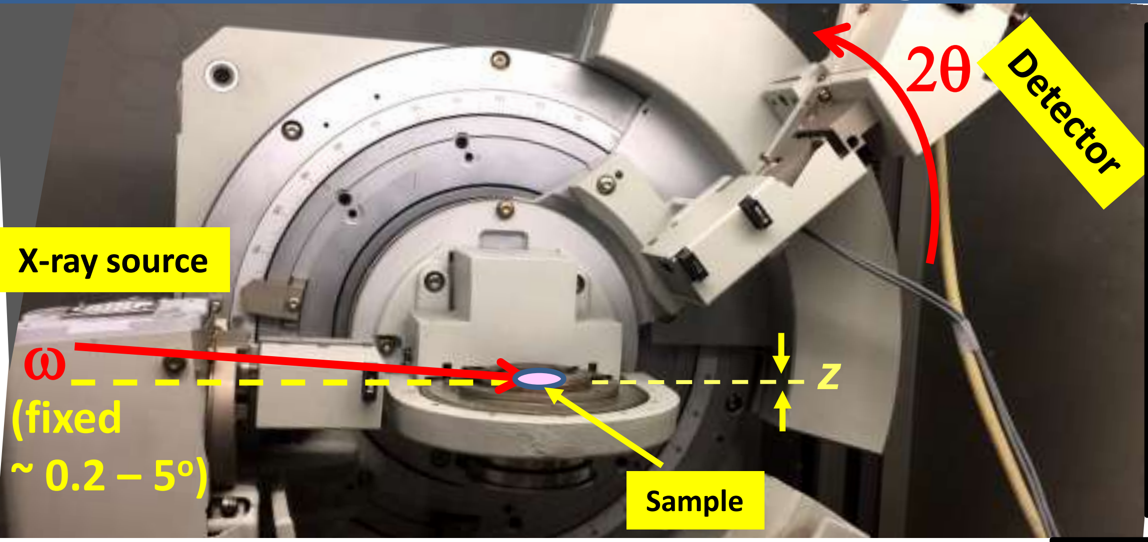


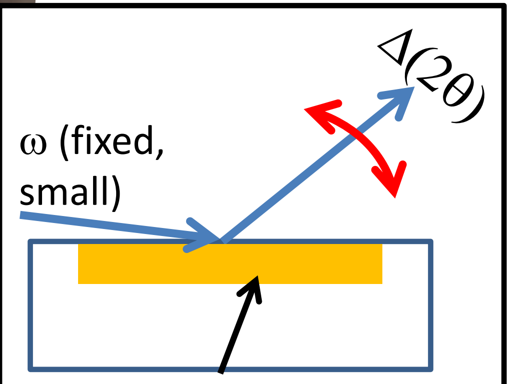




After Shin et al, TSF (2002)

Glancing incidence x-ray diffraction (GI-XRD)



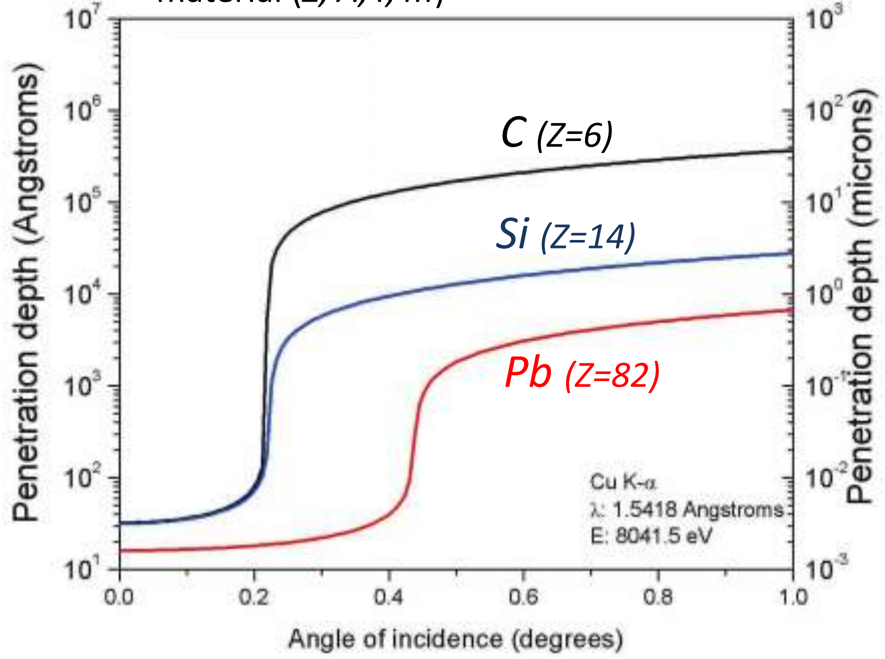


Shallow, wide *constant* probed volume

- Enhances intensities from surface, near surface regions.
- Phases and grain orientations in multiple directions also not parallel to the surface (2θ only scan).
- Change ω to probe different depth (“depth profiling”)
- Sample heigh (*z*) critical: use parallel

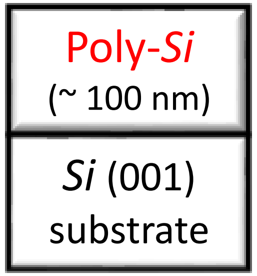
X-ray penetration depth:

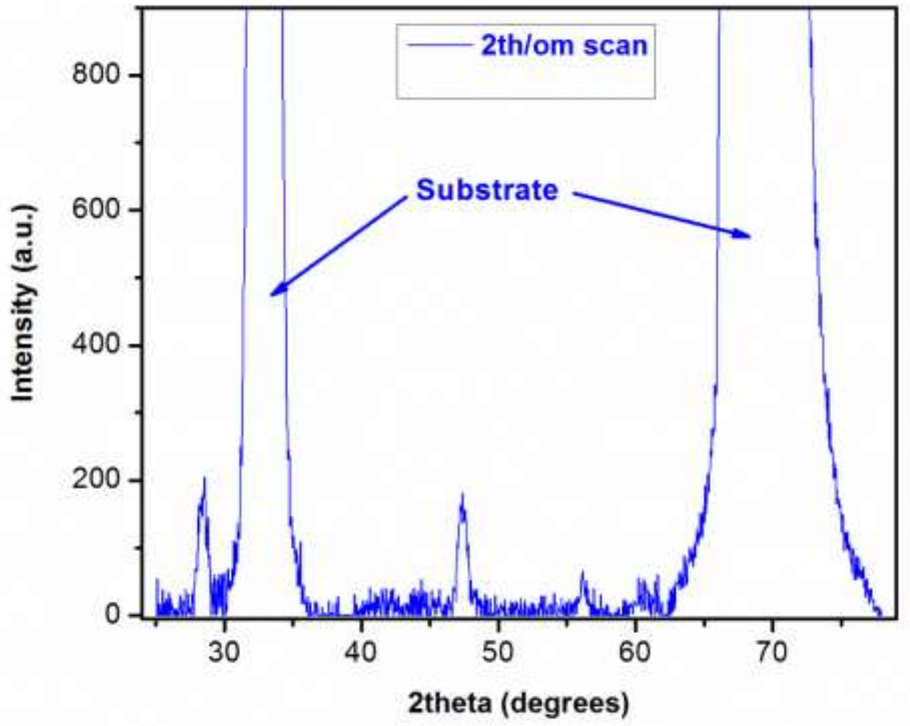
Type of radiation, angle of incidence, material (*Z, A, r, m*)



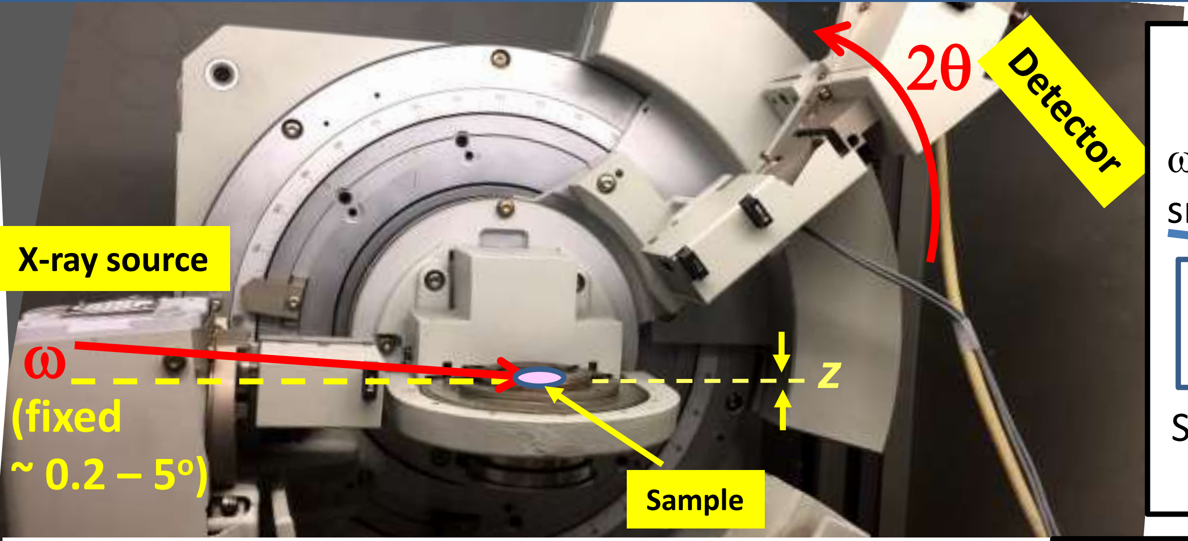
Example:

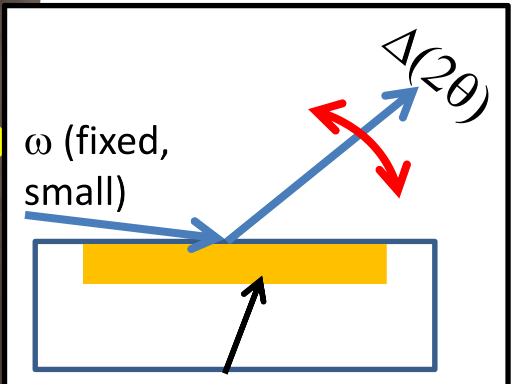
Poly-*Si* gate in CMOS





Glancing incidence x-ray diffraction (GI-XRD)

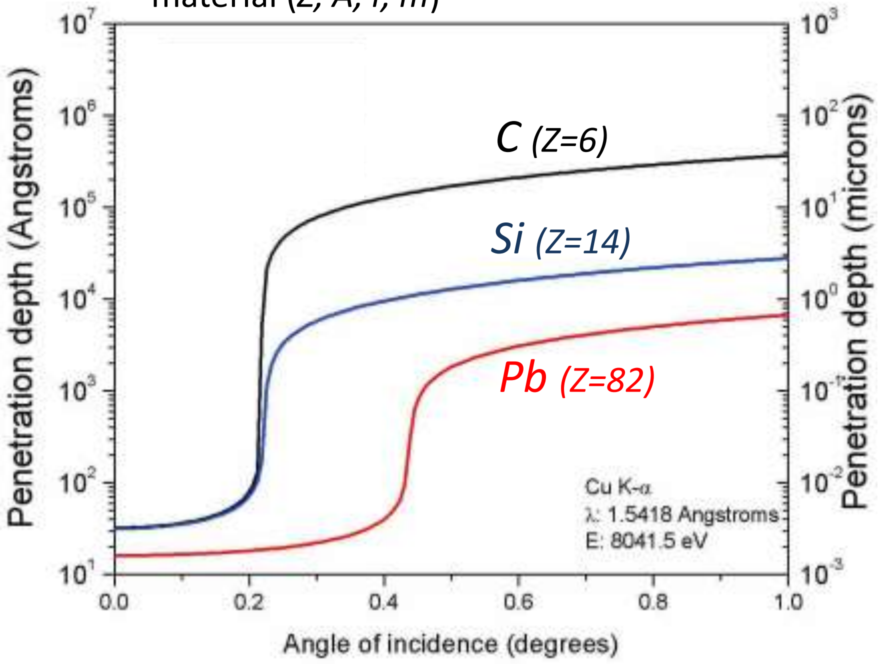




- Enhances intensities from surface, near surface regions.
- Phases and grain orientations in multiple directions also not parallel to the surface (2θ only scan).
- Change ω to probe different depth ("depth profiling")
- Sample heigh (*z*) critical: use parallel beam configuration.

X-ray penetration depth:

Type of radiation, angle of incidence, material (*Z, A, r, m*)

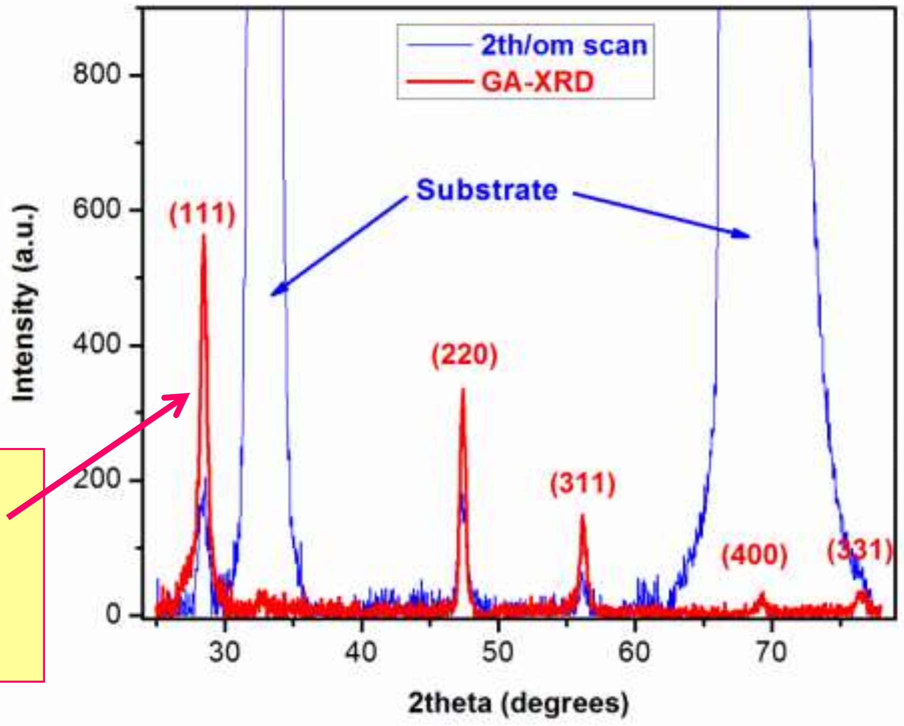


Example:

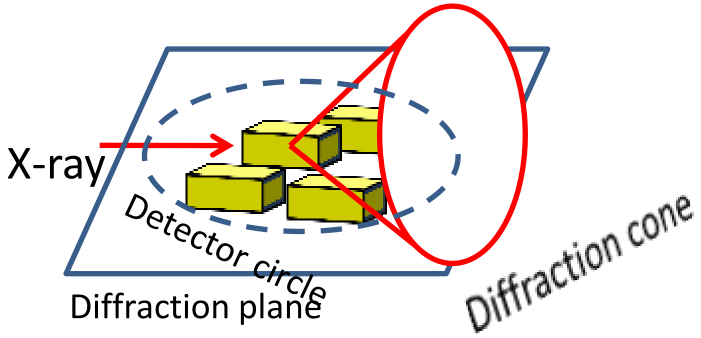
Poly-*Si* gate in CMOS

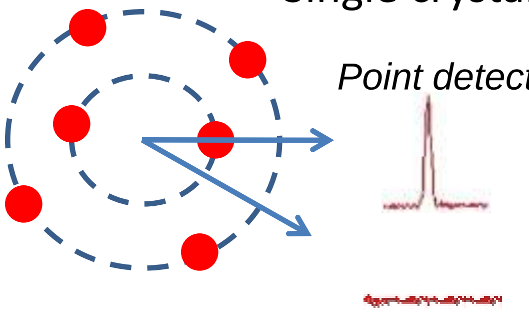
Poly-*Si* (~ 100 nm)
Si (001) substrate

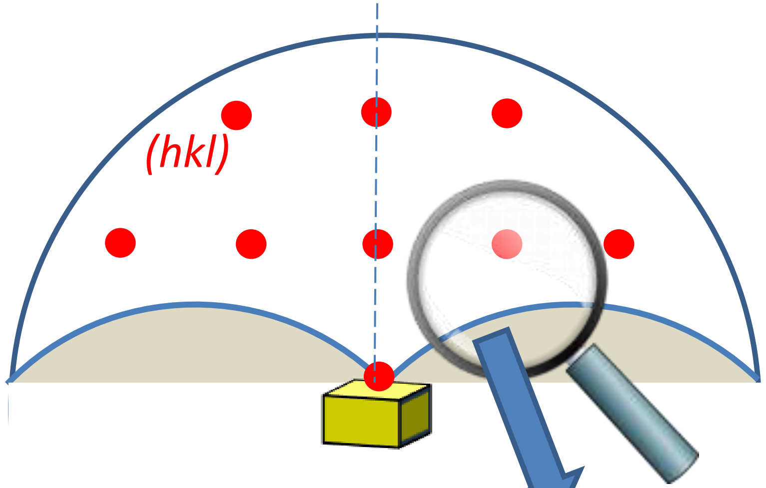
GI-XRD:
more accurate phase id, texture and grain size analysis

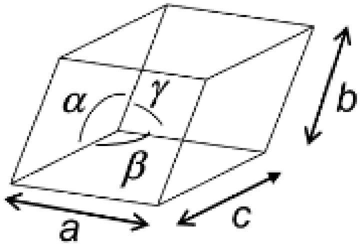
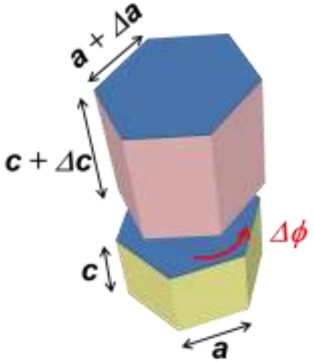


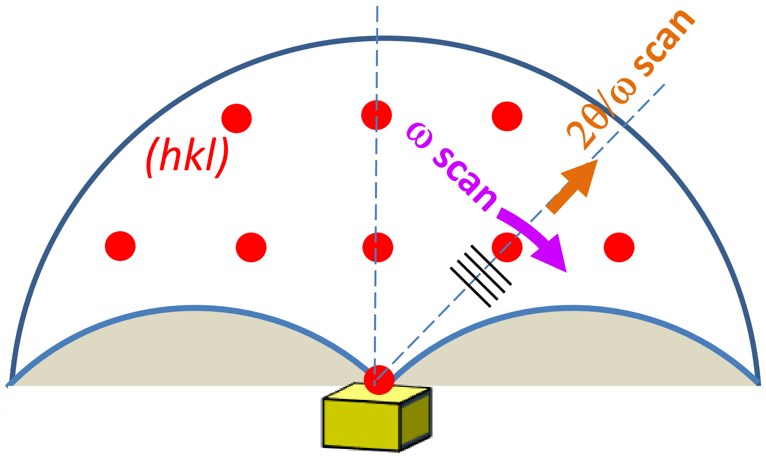
High-resolution x-ray diffraction (HR-XRD)





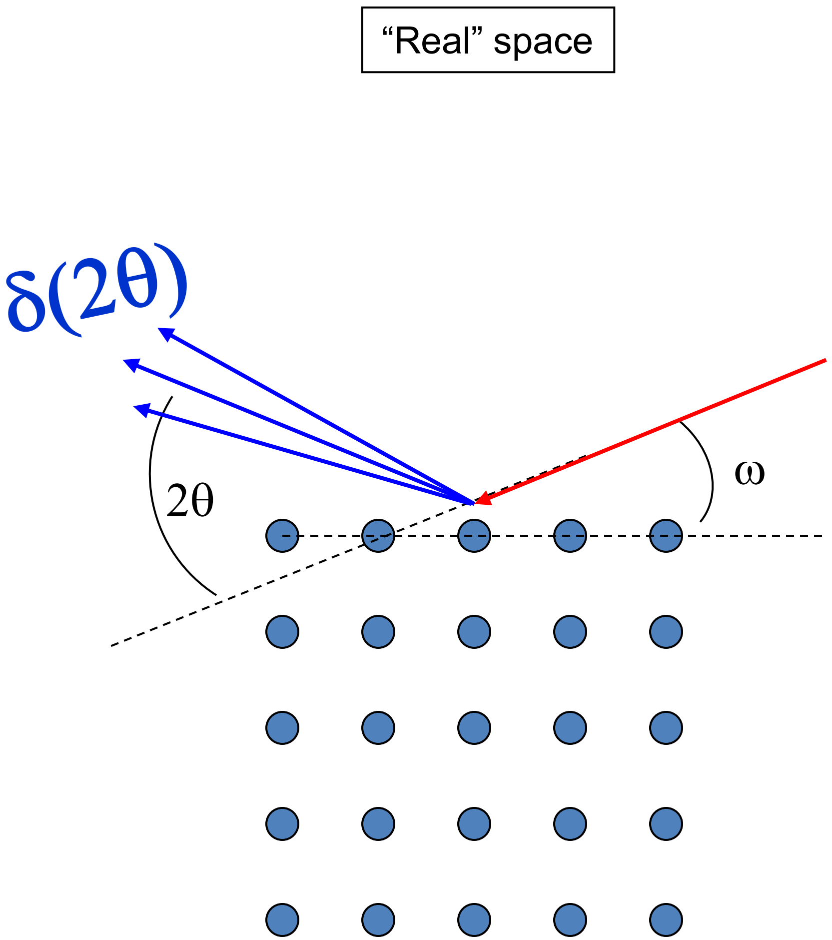


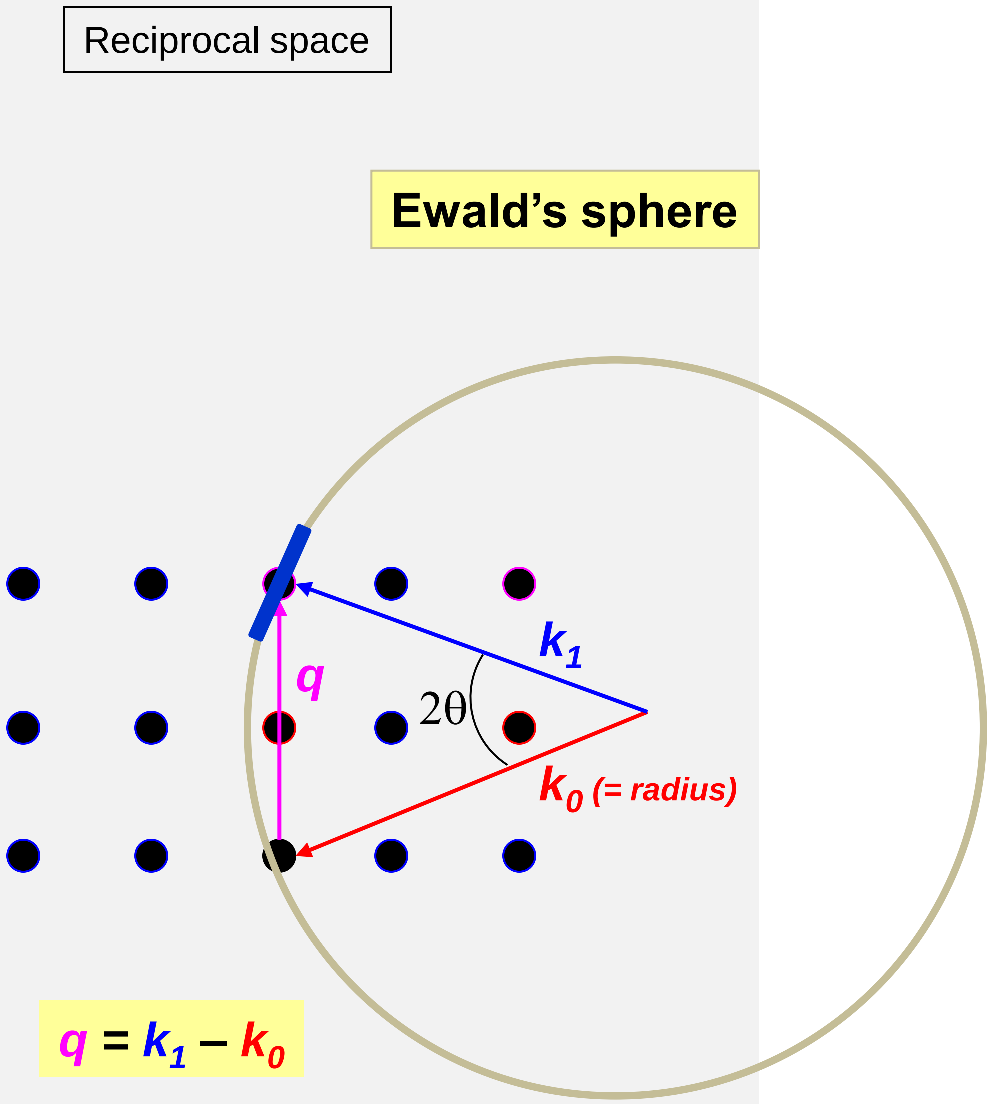
Single crystals 	• Accurate lattice parameter measurements. • Accurate peak shape analysis: defects, mosaicity.
Epitaxial thin films on substrates 	• Measure small lattice distortions (Δa, Δc ~ 10^{-5}). • Layer tilts $\Delta\phi$ • Accurate peak shape analysis: defects, strain, mosaicity



Multiple RLP's
(Reciprocal Lattice Points)
Relative position
Orientation
Shape

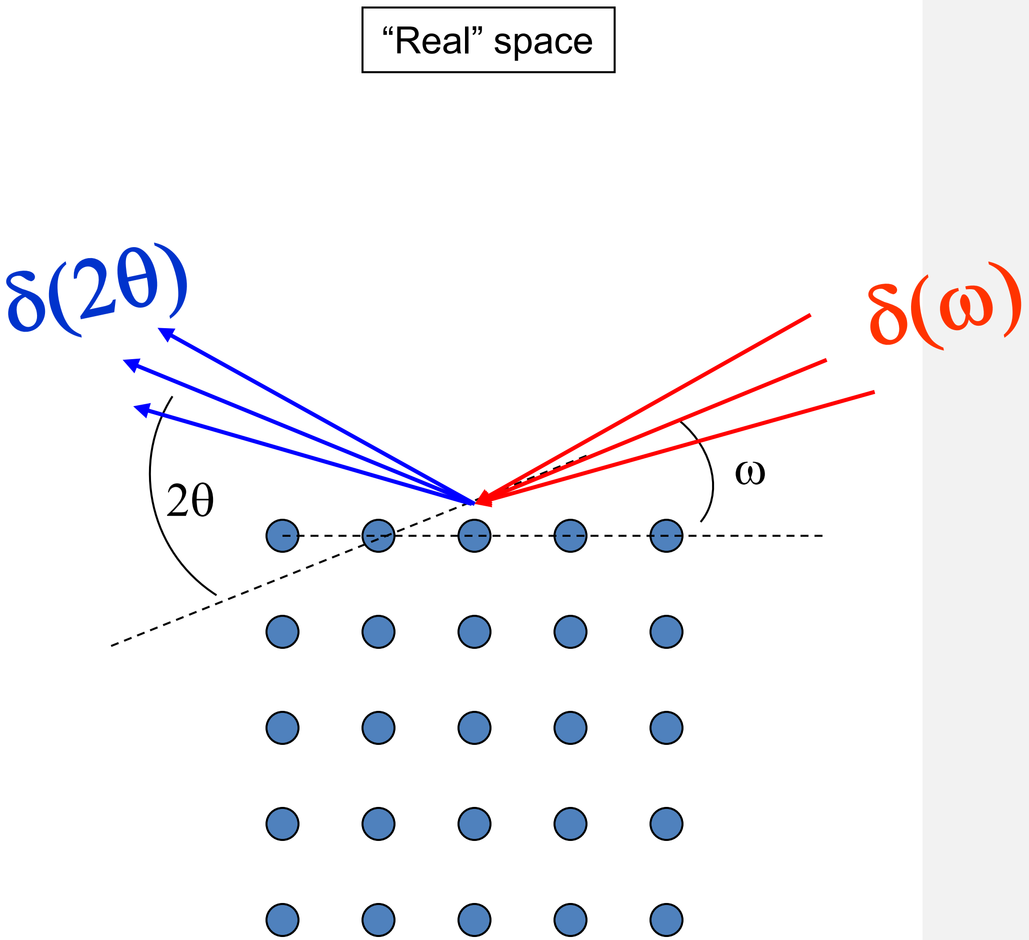
Instrumental resolution in reciprocal space

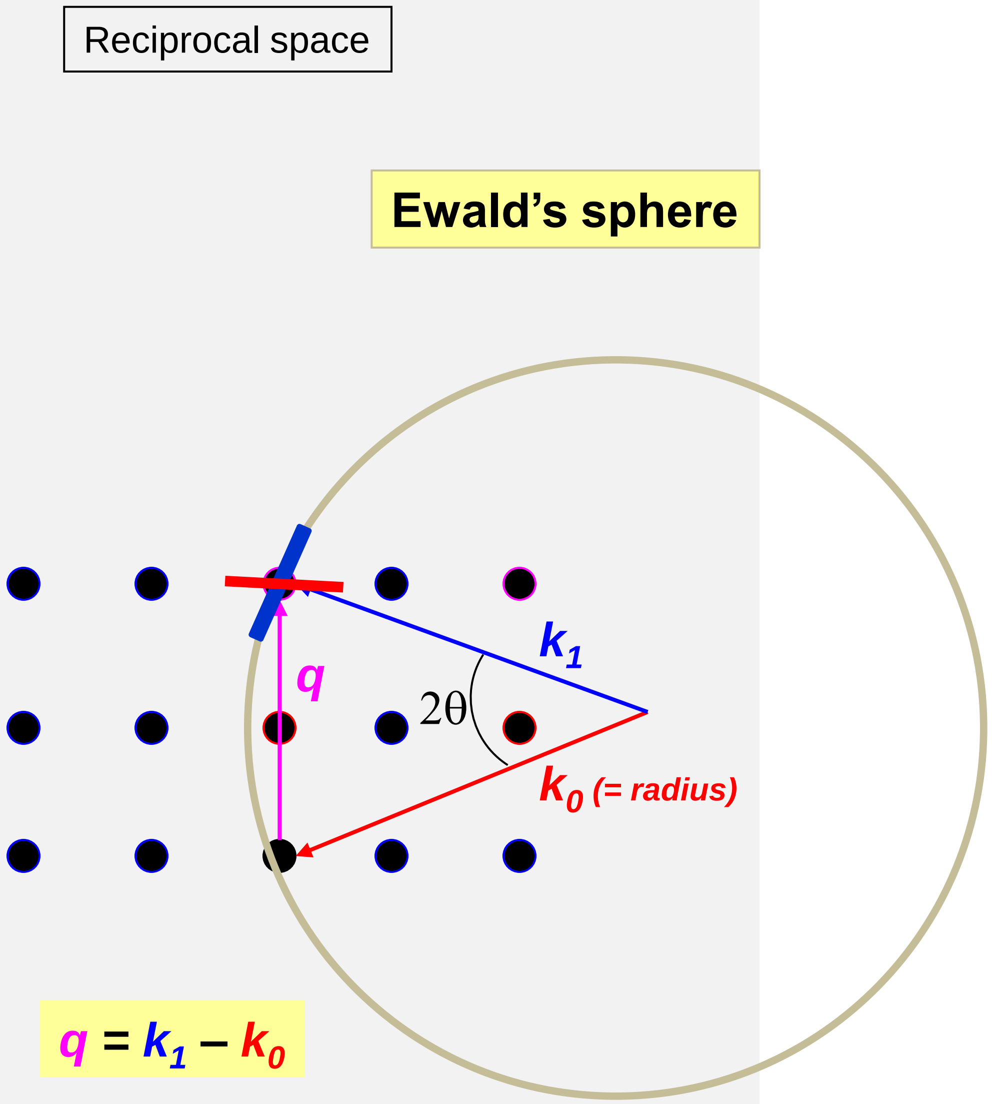




$\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_0$

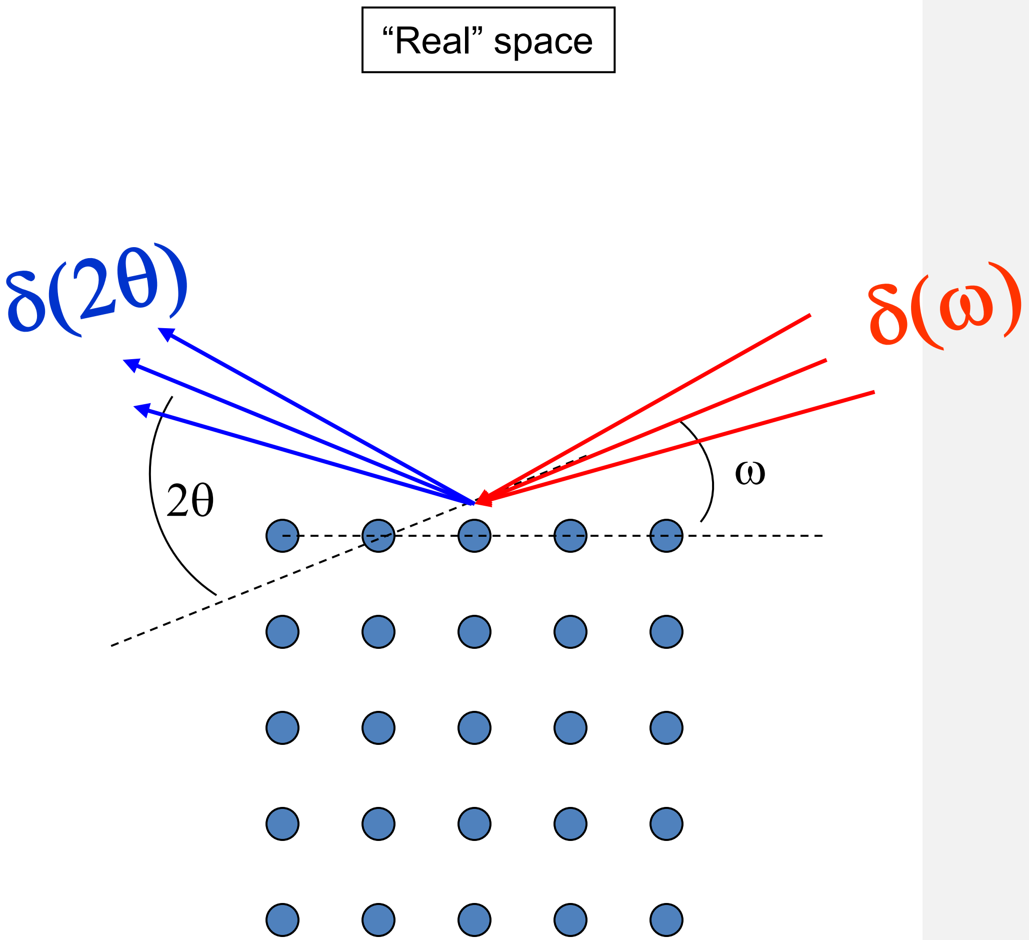
Instrumental resolution in reciprocal space

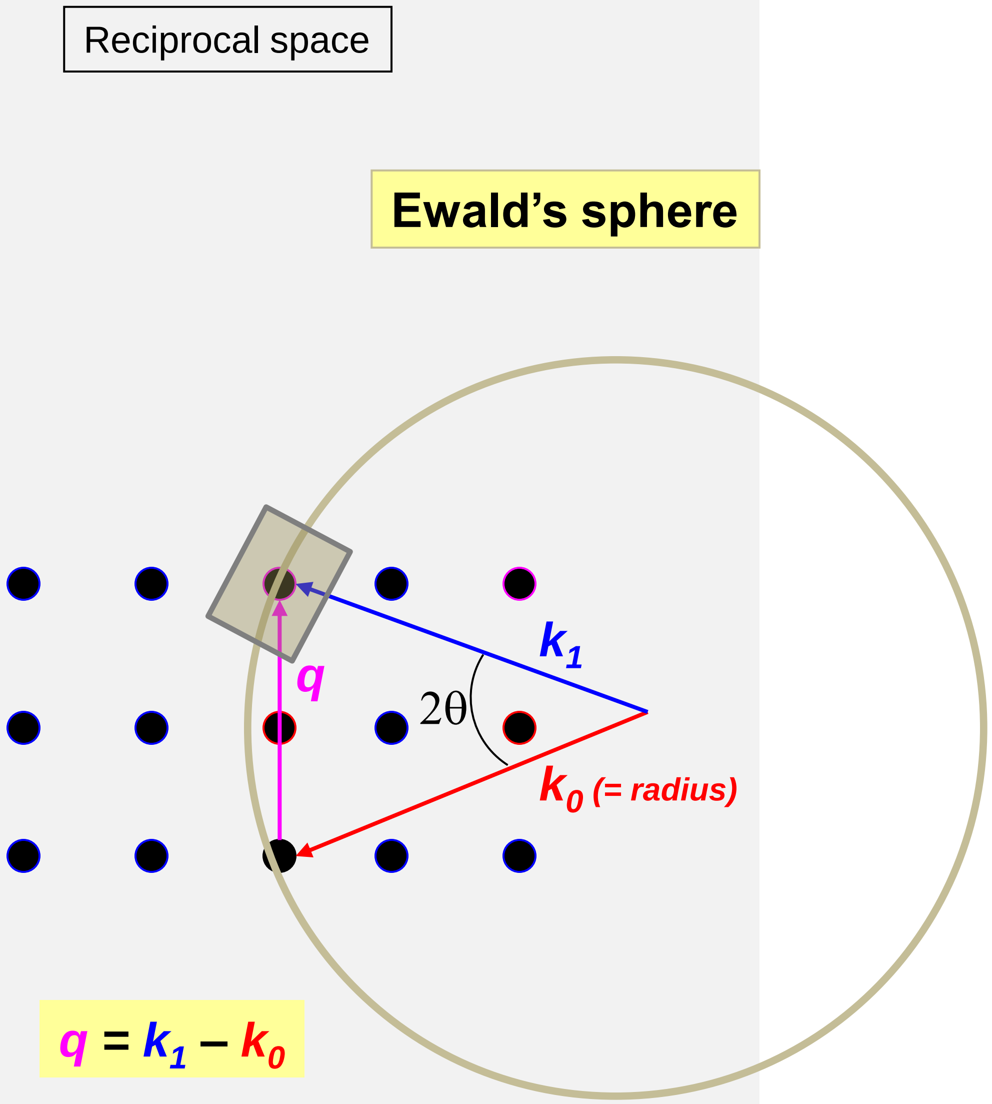




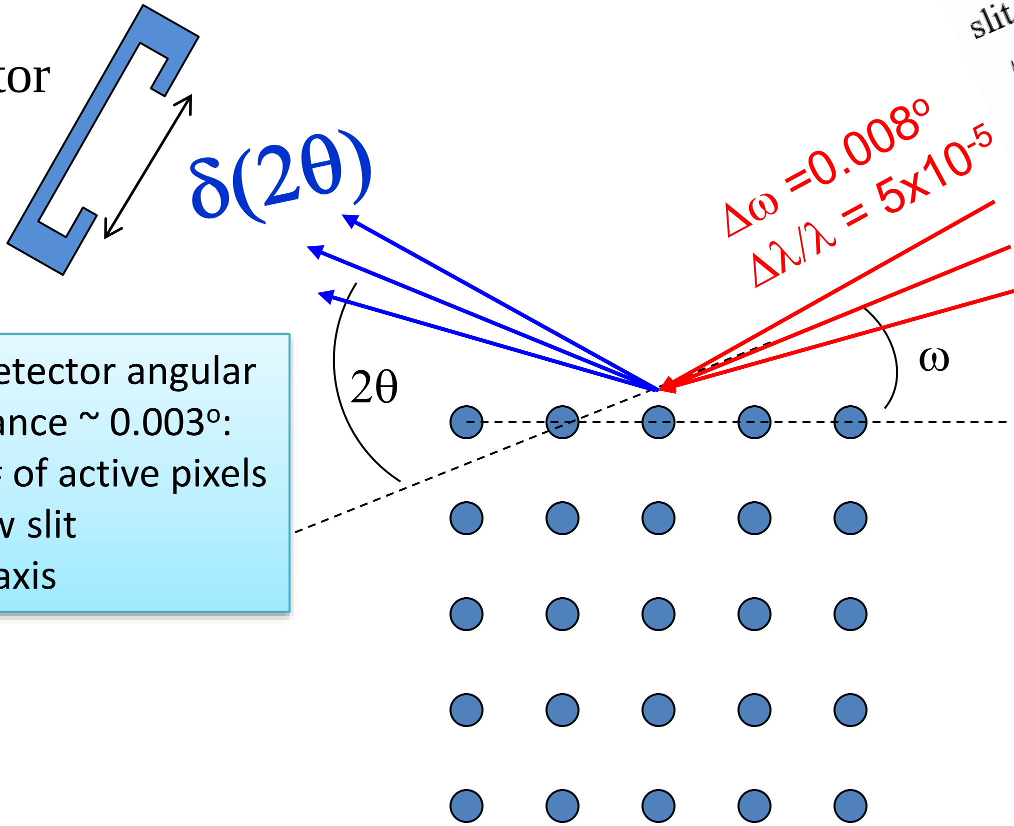
$q = k_1 - k_0$

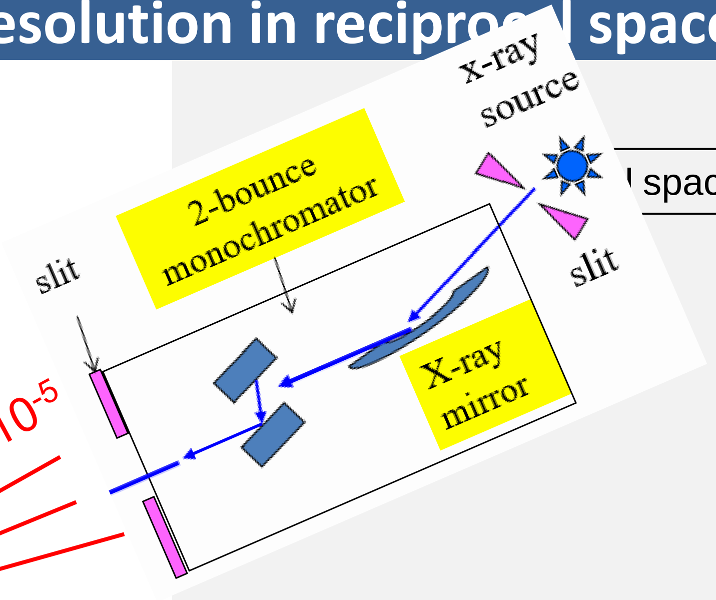
Instrumental resolution in reciprocal space





"Real" space

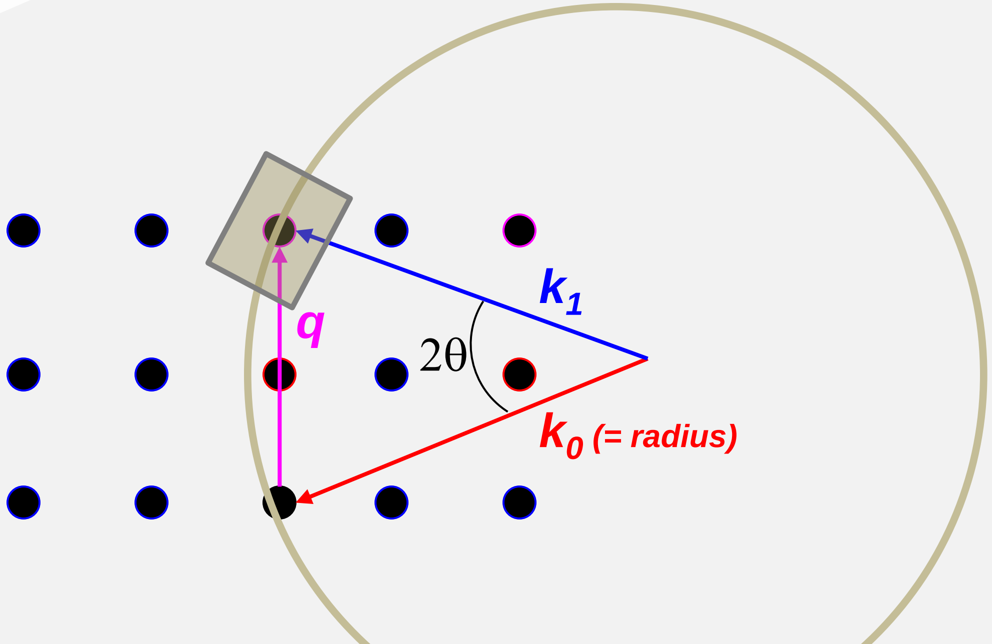




Limit detector angular acceptance ~ 0.003°:
- Limit # of active pixels
- Narrow slit
- Triple axis

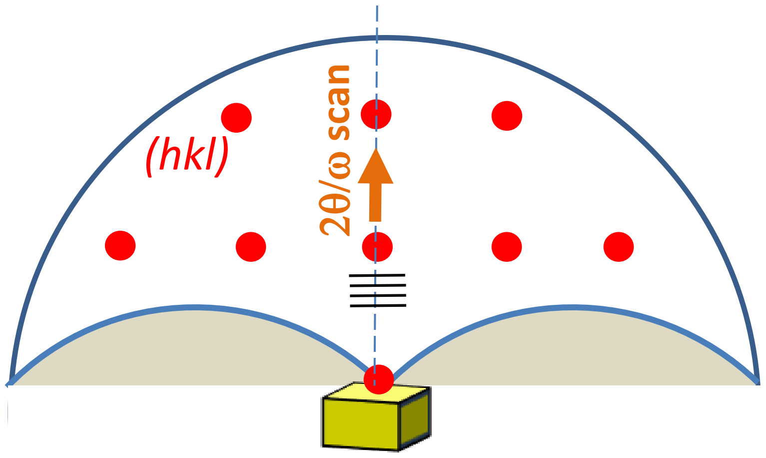
l space

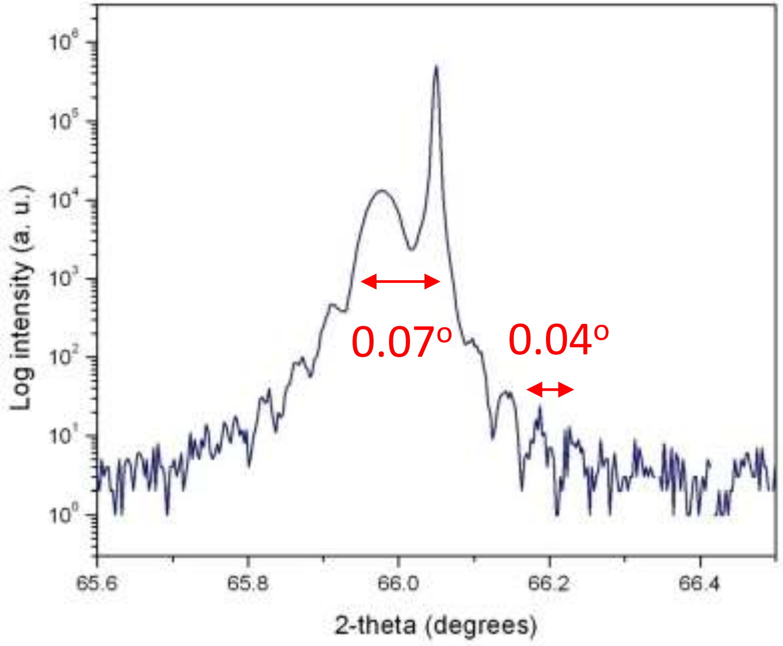
Ewald's sphere



$q = k_1 - k_0$

High-resolution x-ray diffraction (HR-XRD)





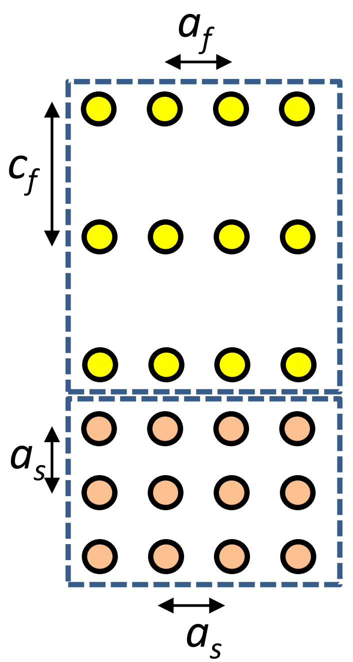
HR-XRD 2θ/ω scan near GaAs(004)

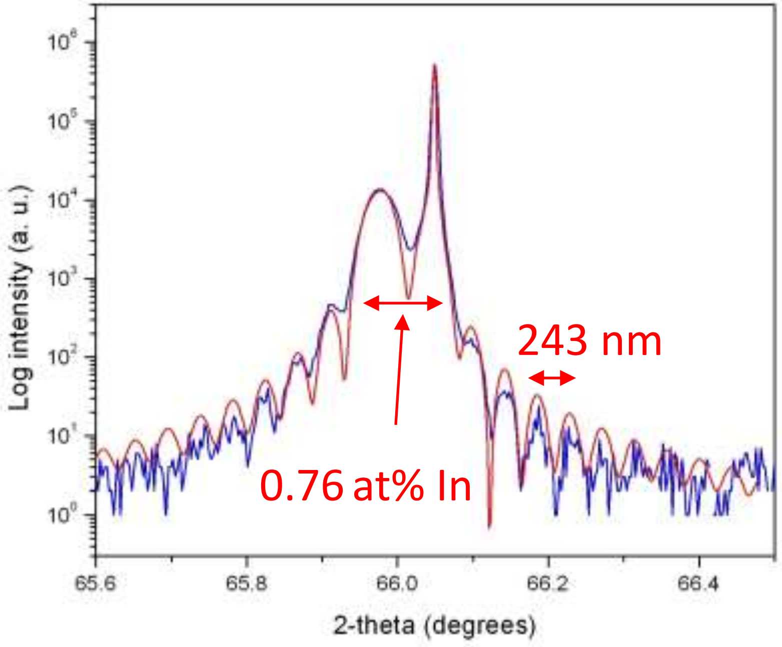
$$\frac{\Delta a}{a} = \frac{\sin\theta(\text{substrate})}{\sin\theta(\text{film})} - 1$$

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

Atomic radius:
In > Ga

Lattice constants:
$a_f = a_s$
$c_f > a_s$

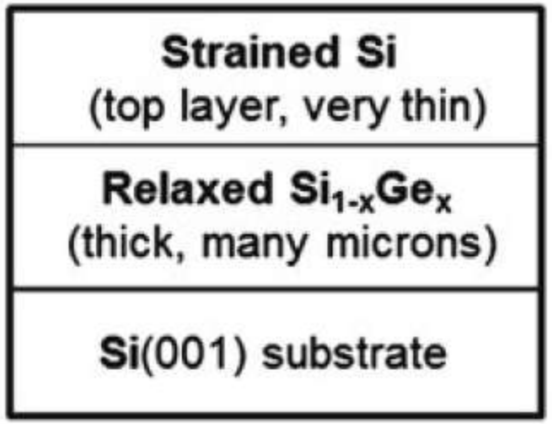


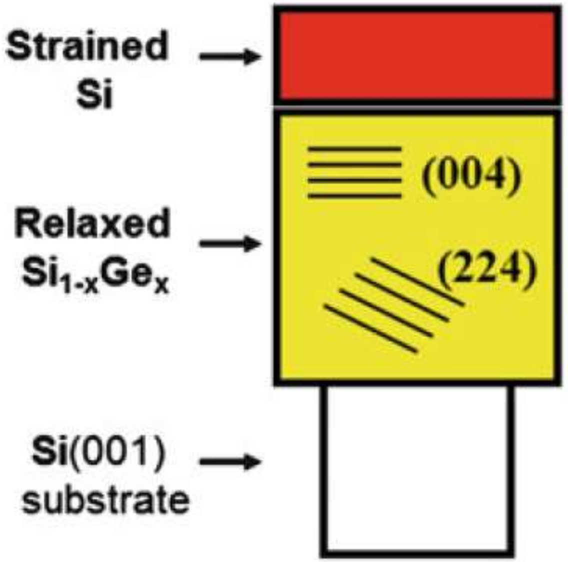


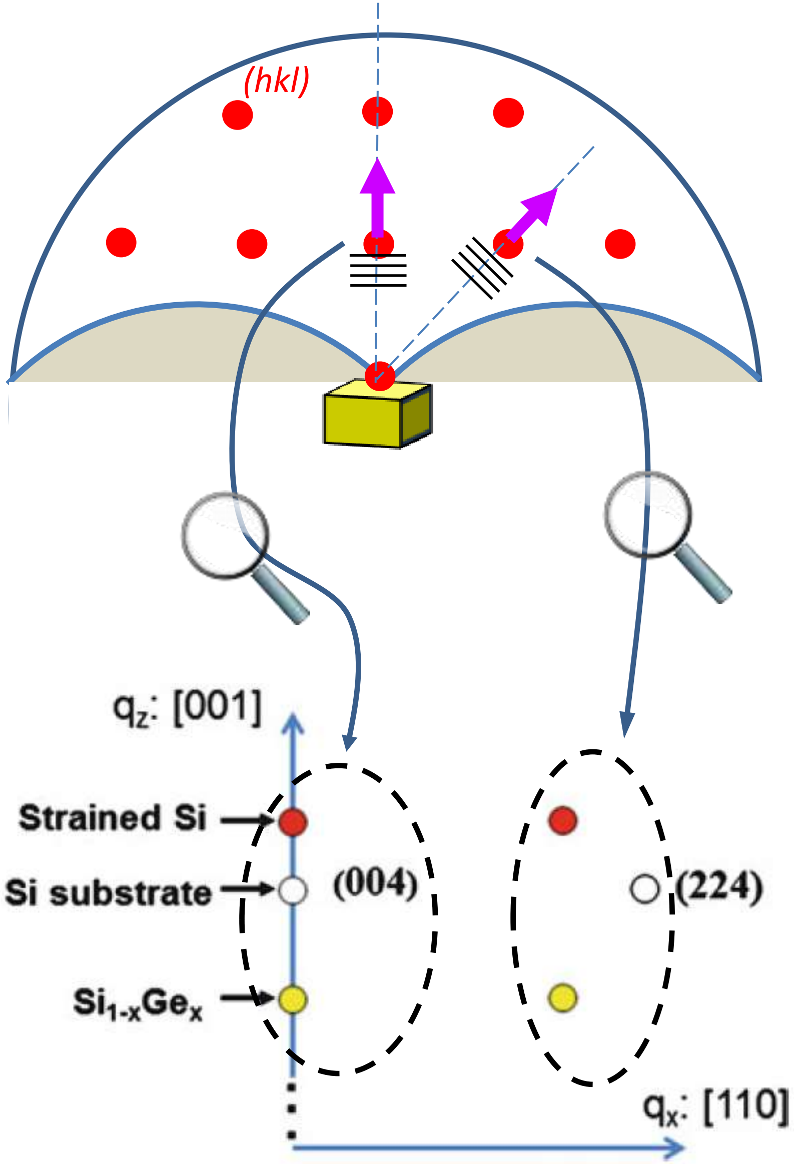
Takagi-Taupin dynamical scattering simulation

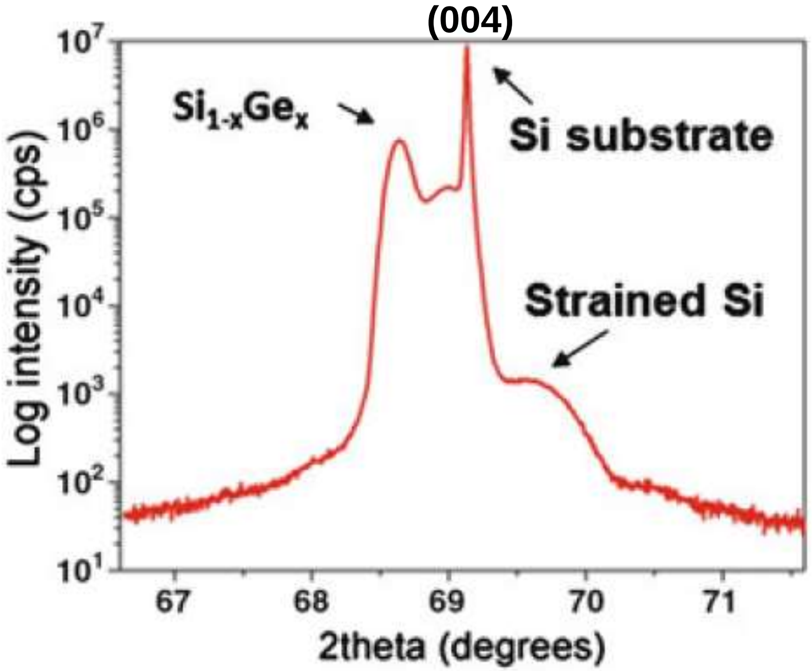
Data: Sardela
Sample: Highland, Cahill, Coleman et at, UIUC

Reciprocal space mapping RSM (reciprocal lattice mapping RLM)



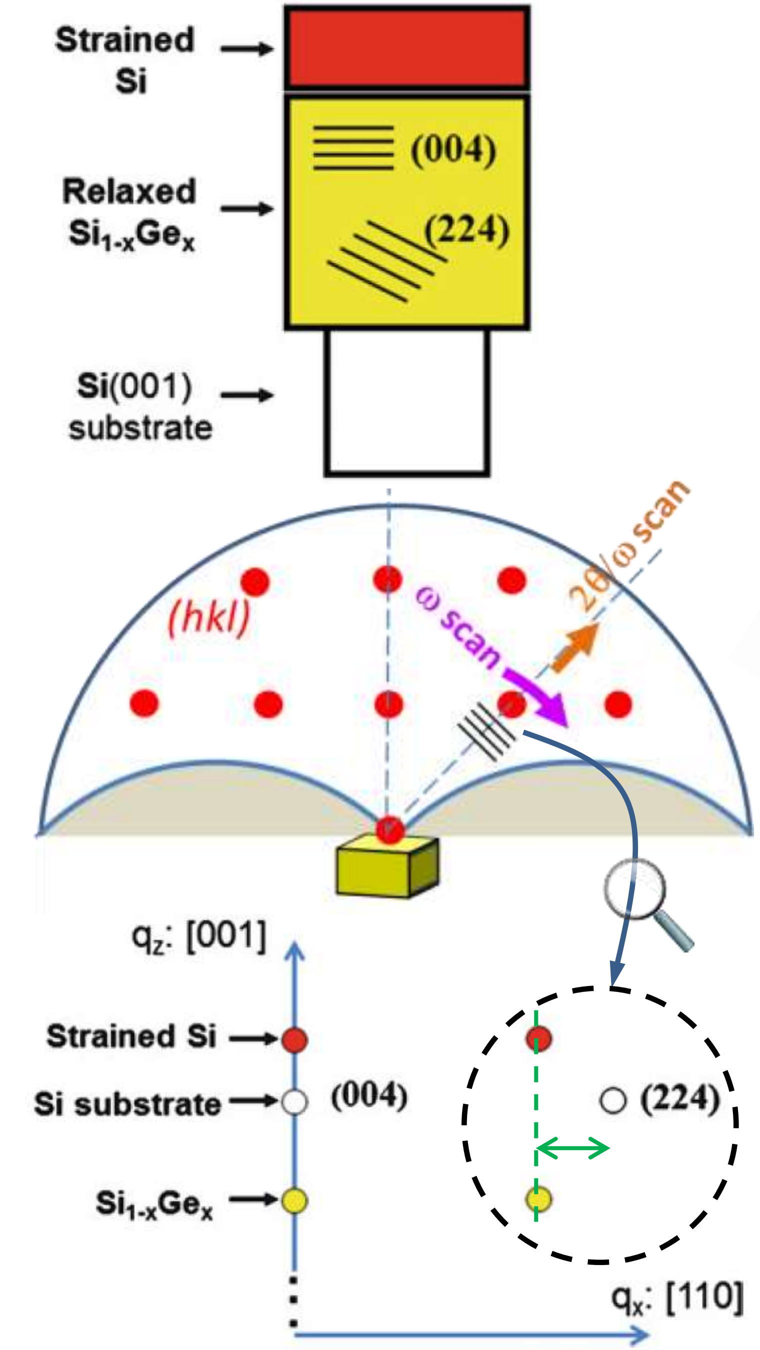


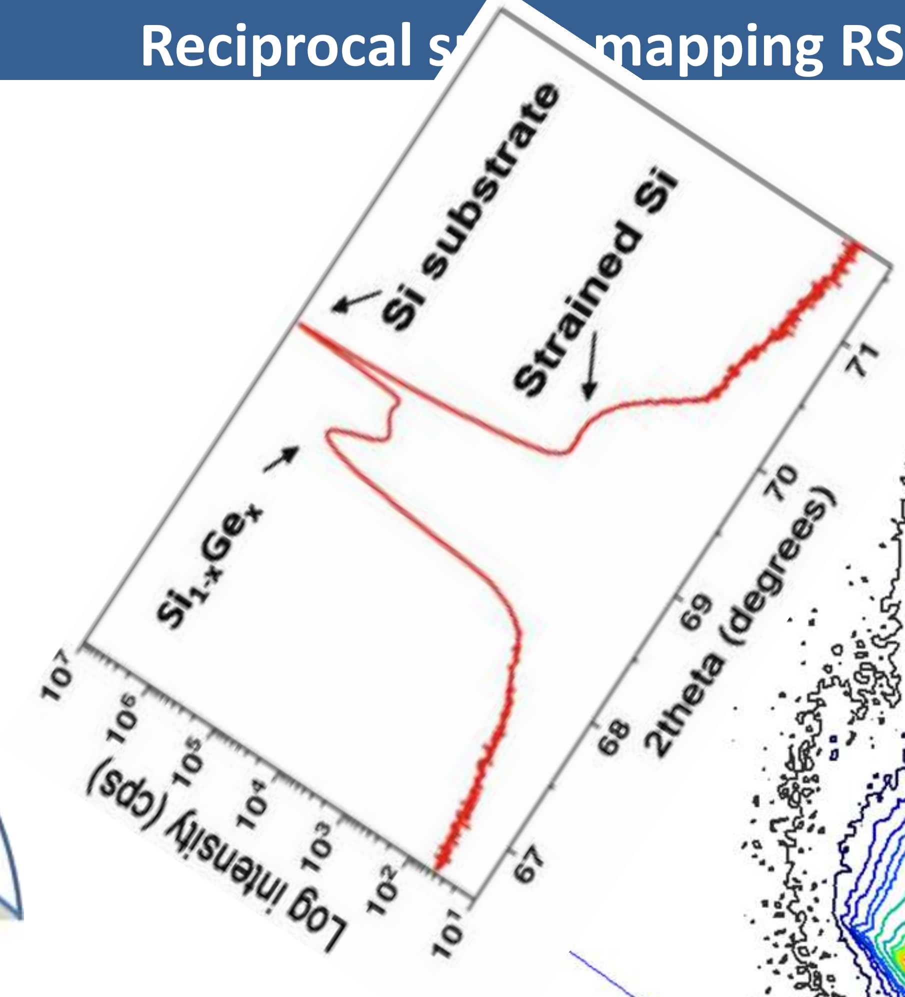


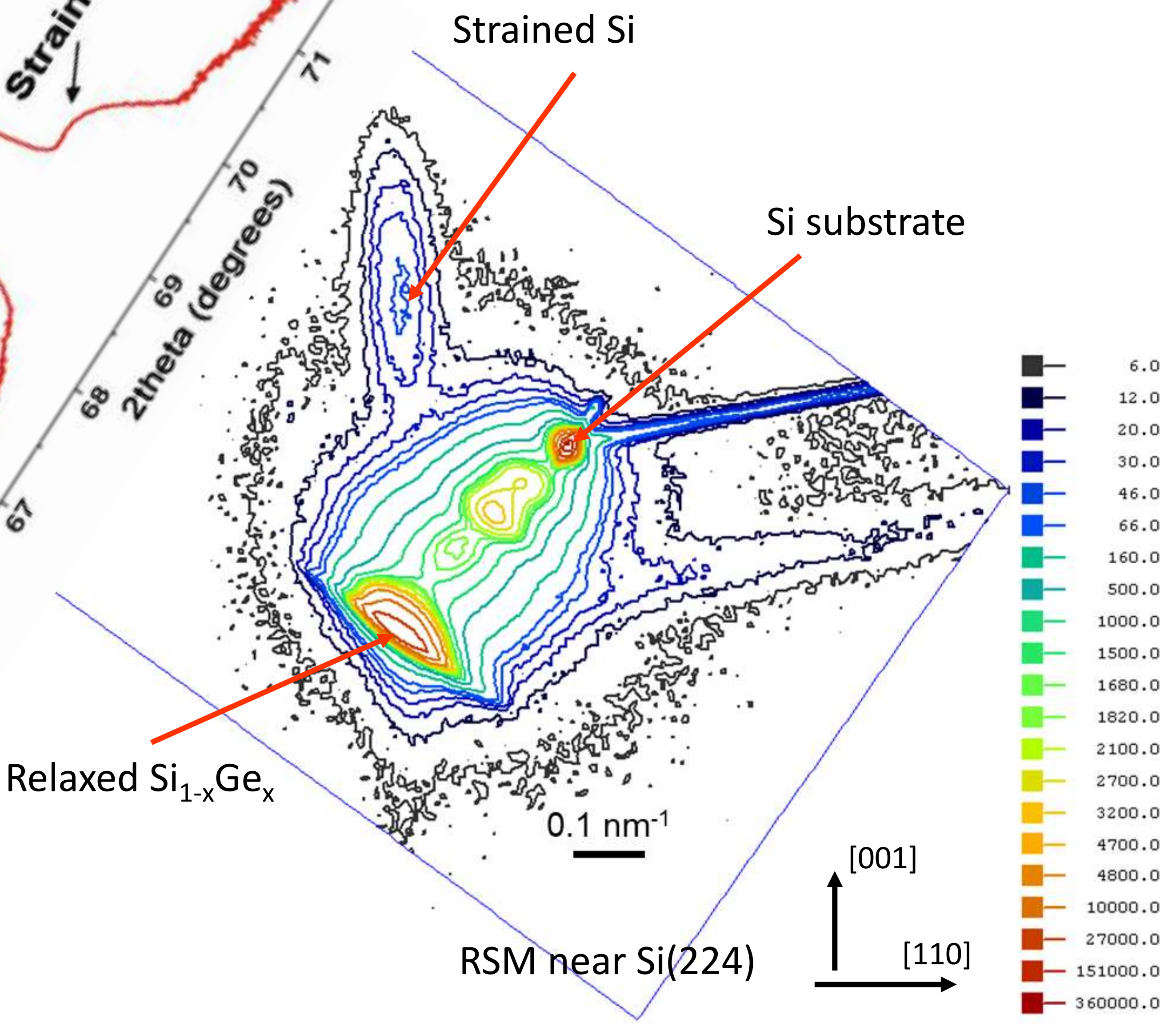


In-plane lattice constants?
Strain relaxation?
Broad peaks?

Reciprocal s mapping RSM







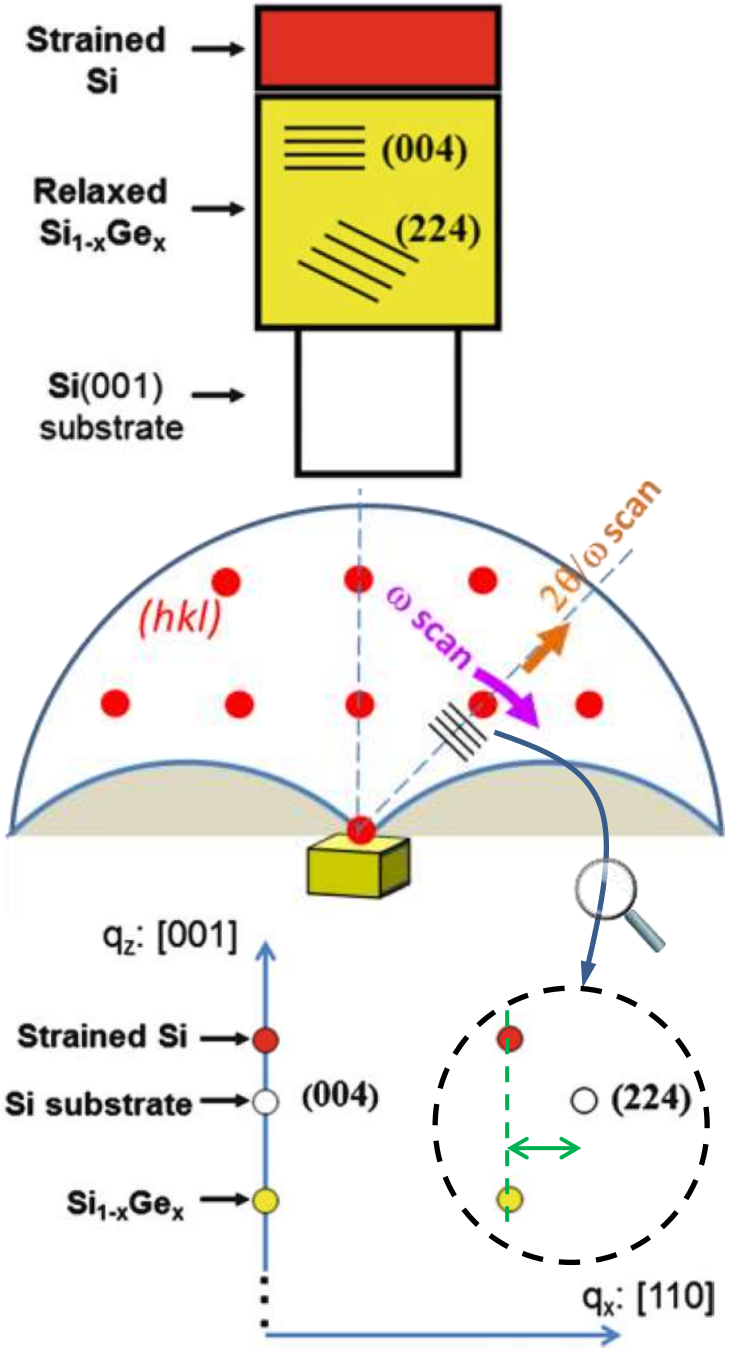
Reciprocal space mapping RSM: peak position

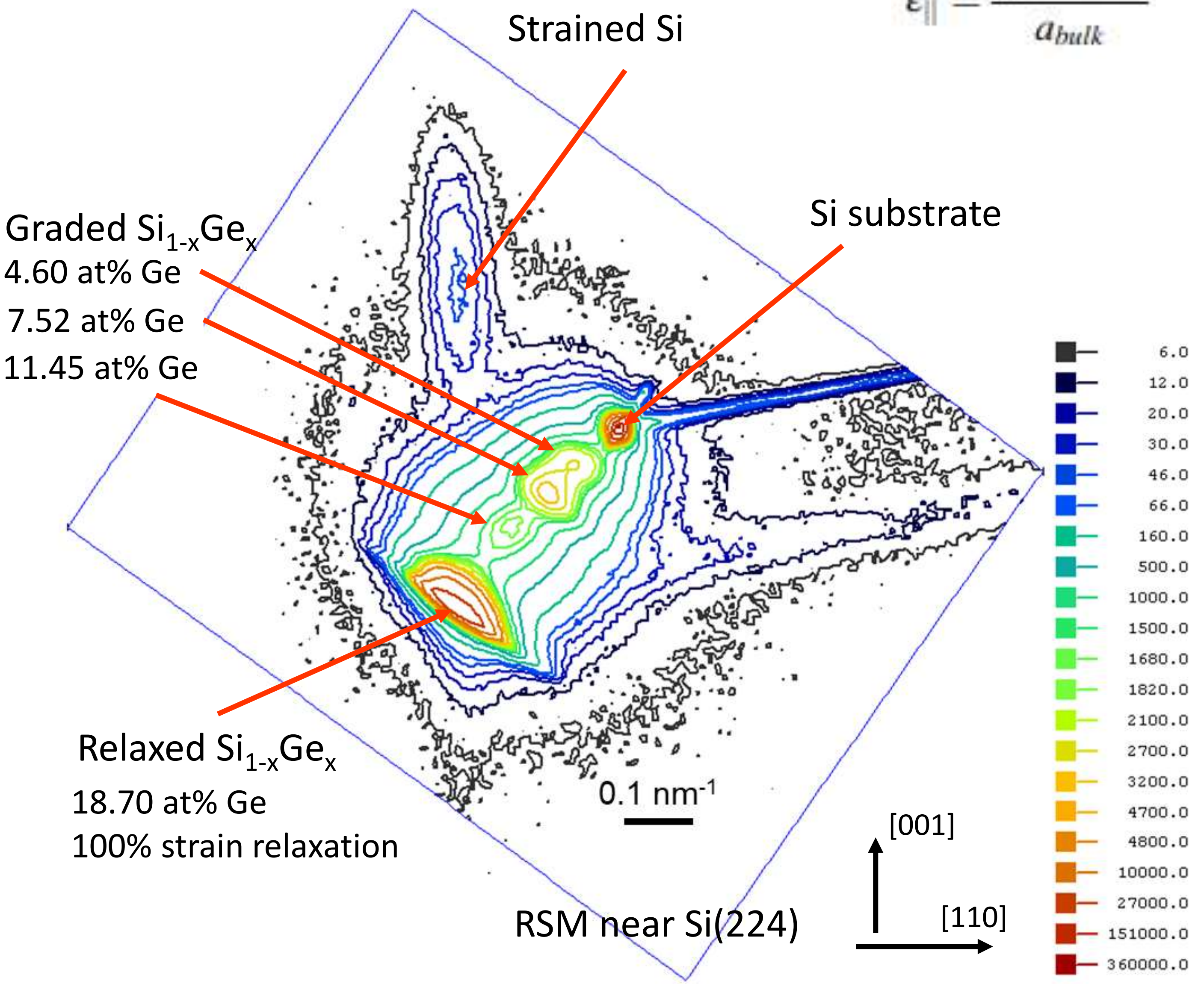
$$\varepsilon_{\perp} = \frac{a_{\perp} - a_{bulk}}{a_{bulk}}$$

$$\varepsilon_{\parallel} = \frac{a_{\parallel} - a_{bulk}}{a_{bulk}}$$

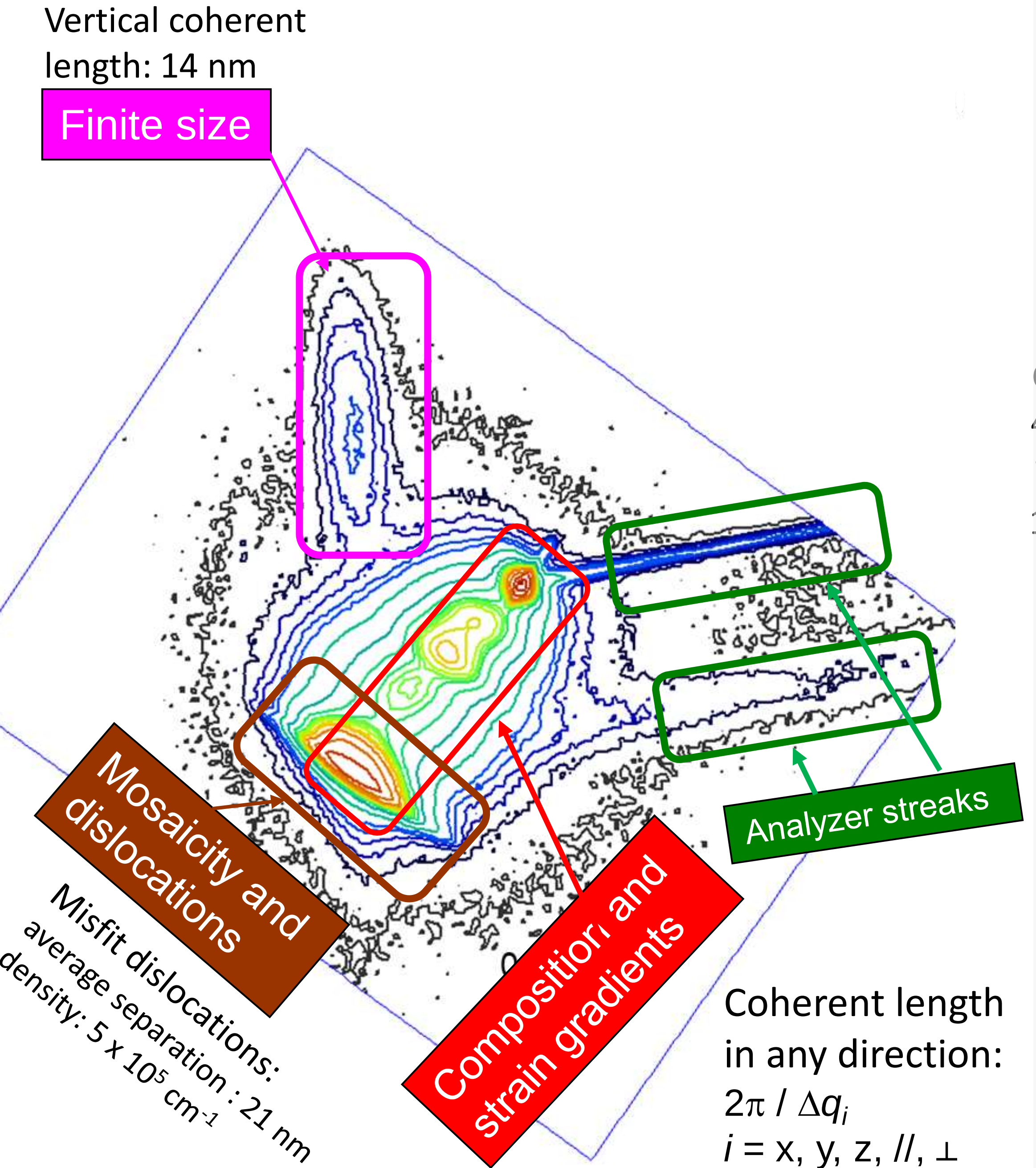
$\varepsilon_{\perp}$ = - 0.77%

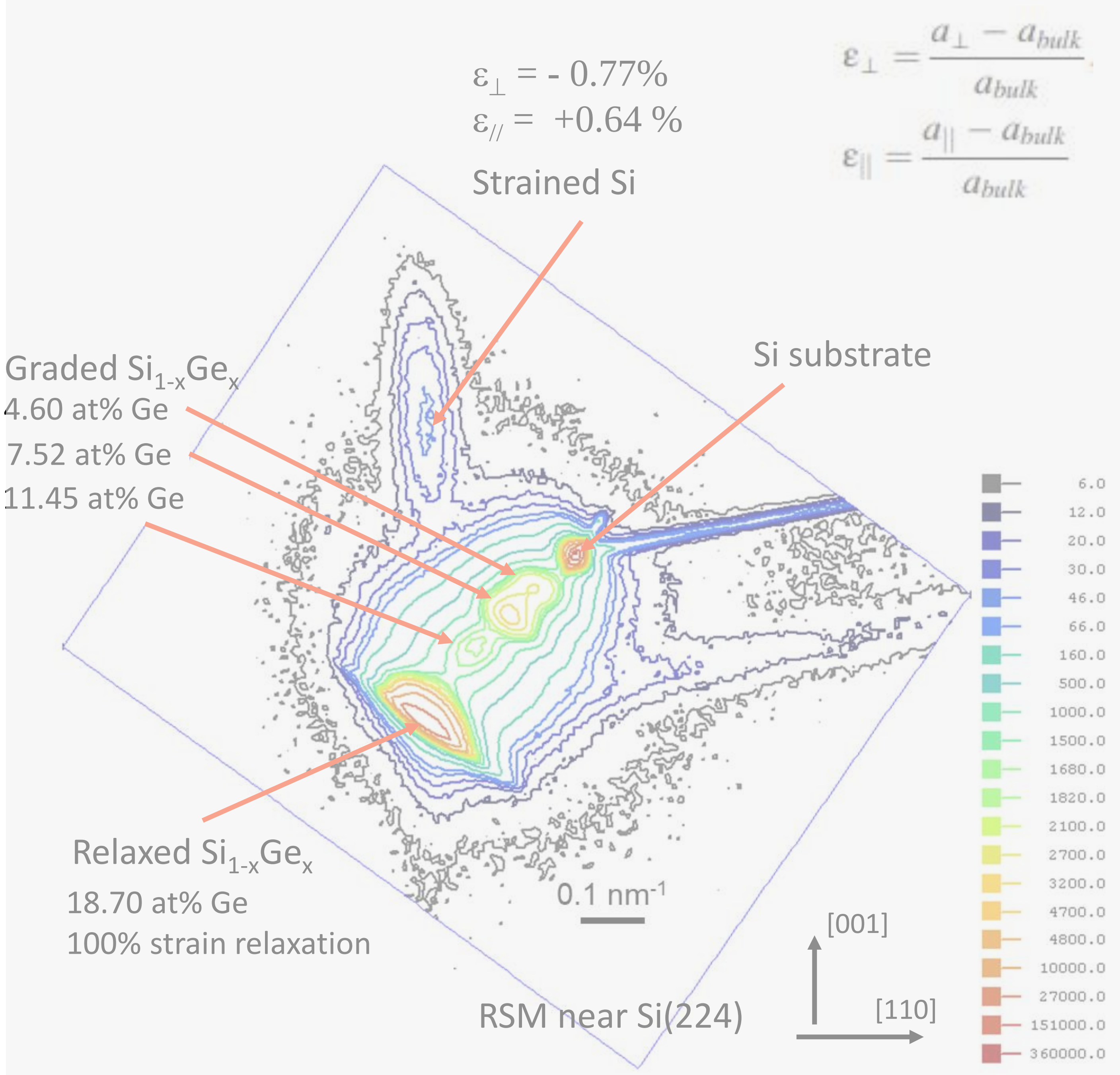
$\varepsilon_{//}$ = +0.64 %





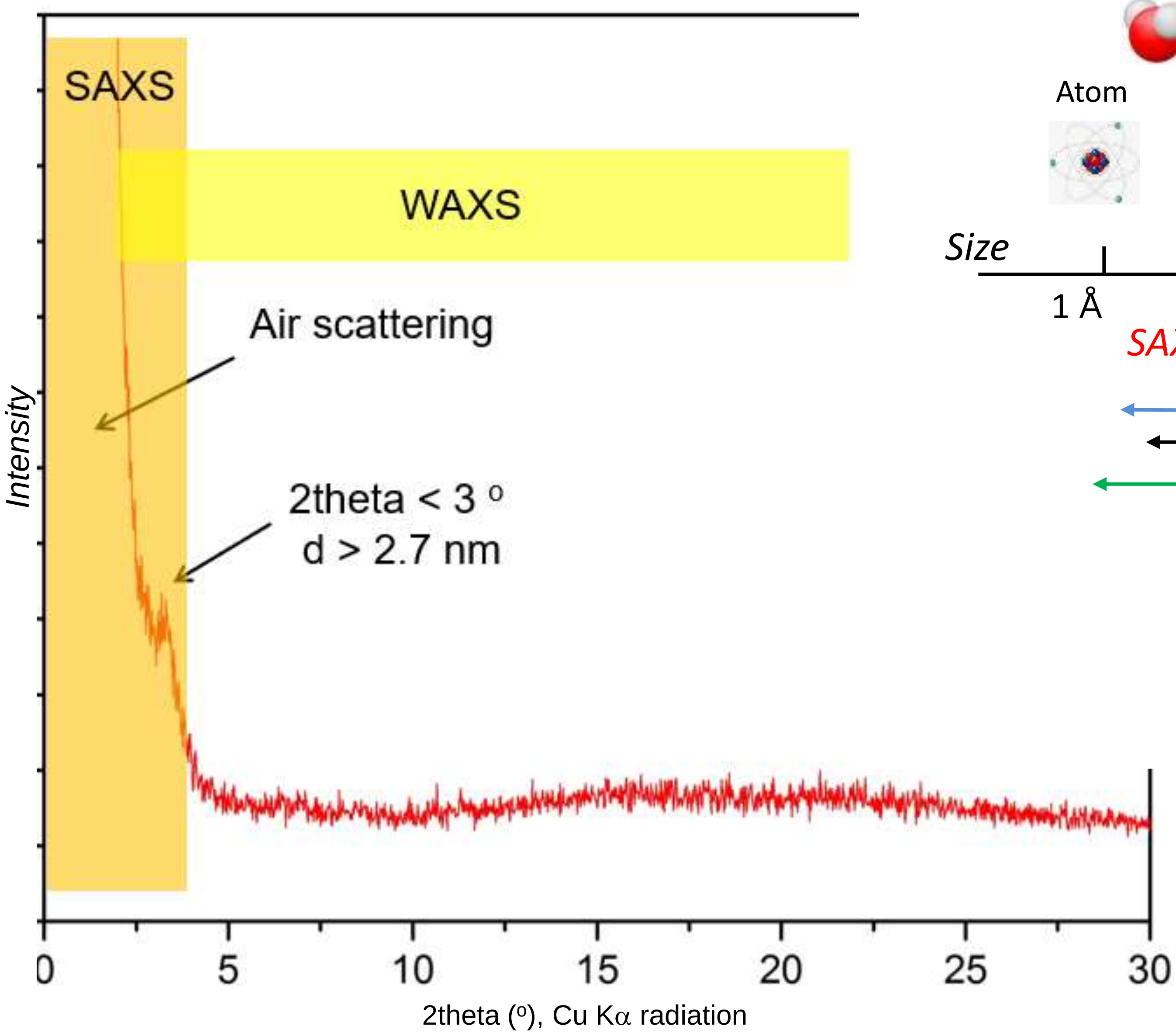
Reciprocal space mapping RSM: peak shape

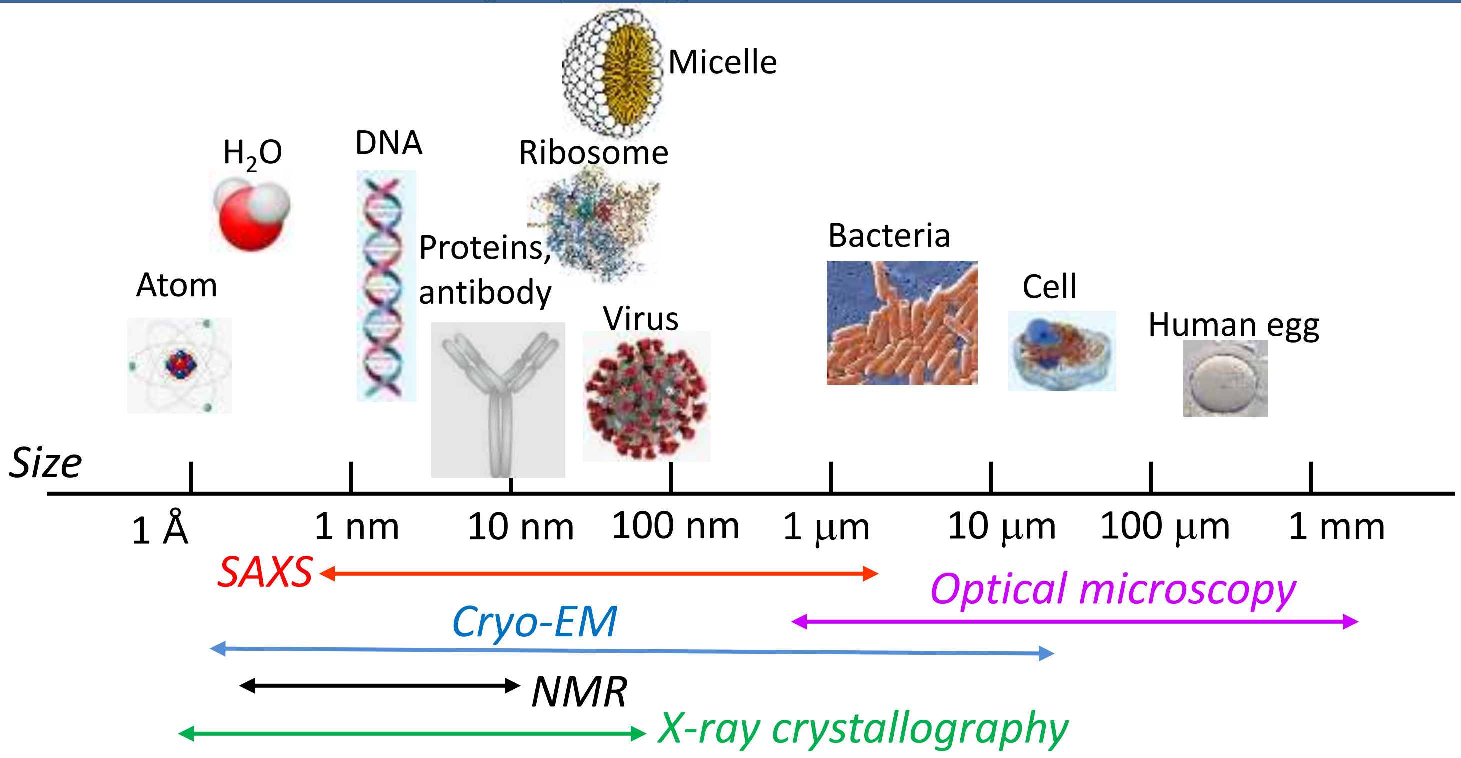




Small angle x-ray diffraction (SAXS) and wide angle x-ray diffraction (WAXS)

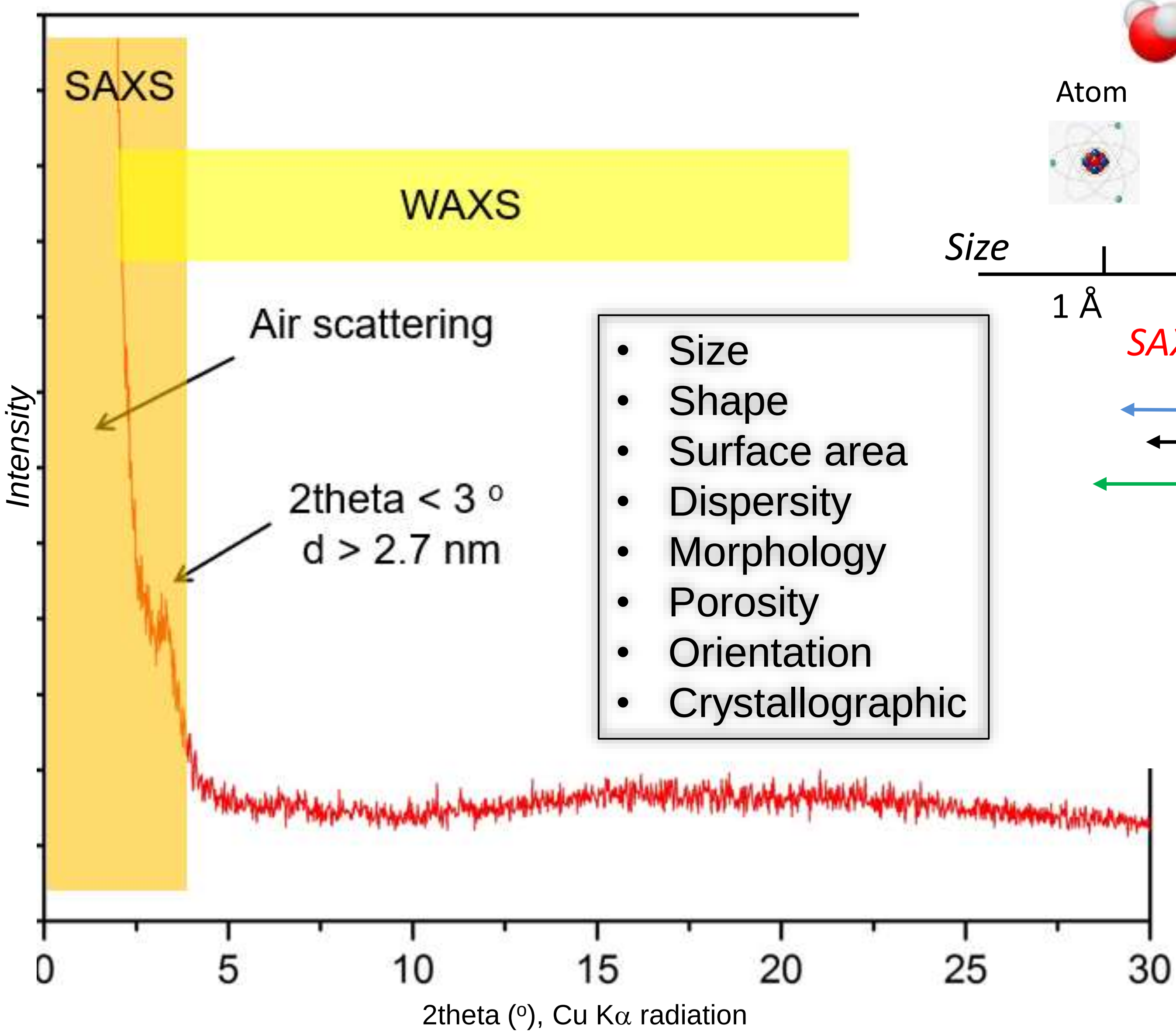
Small angles… large things…



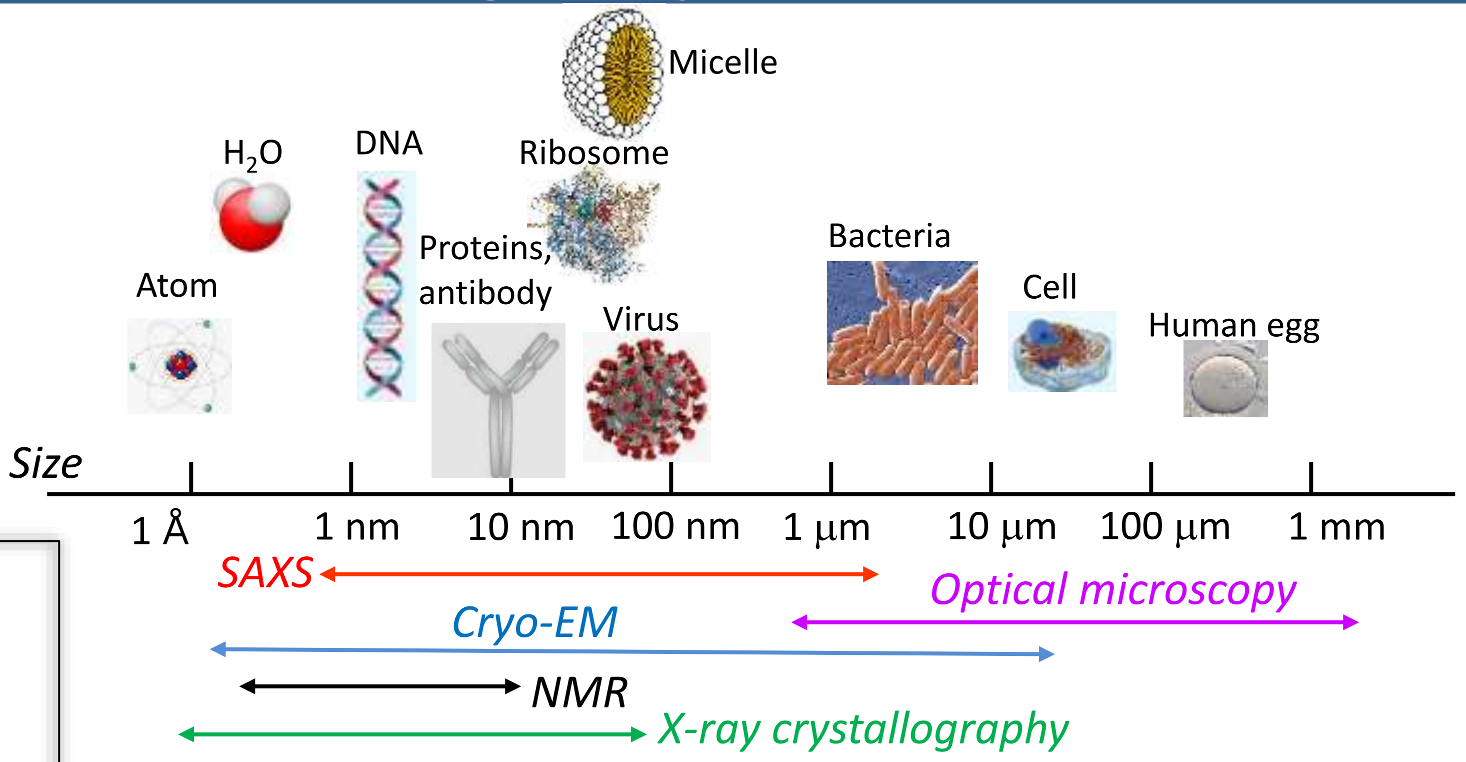


Small angle x-ray diffraction (SAXS) and wide angle x-ray diffraction (WAXS)

Small angles… large things…



- Size
- Shape
- Surface area
- Dispersity
- Morphology
- Porosity
- Orientation
- Crystallographic



Large feature sizes: very low scattering angles

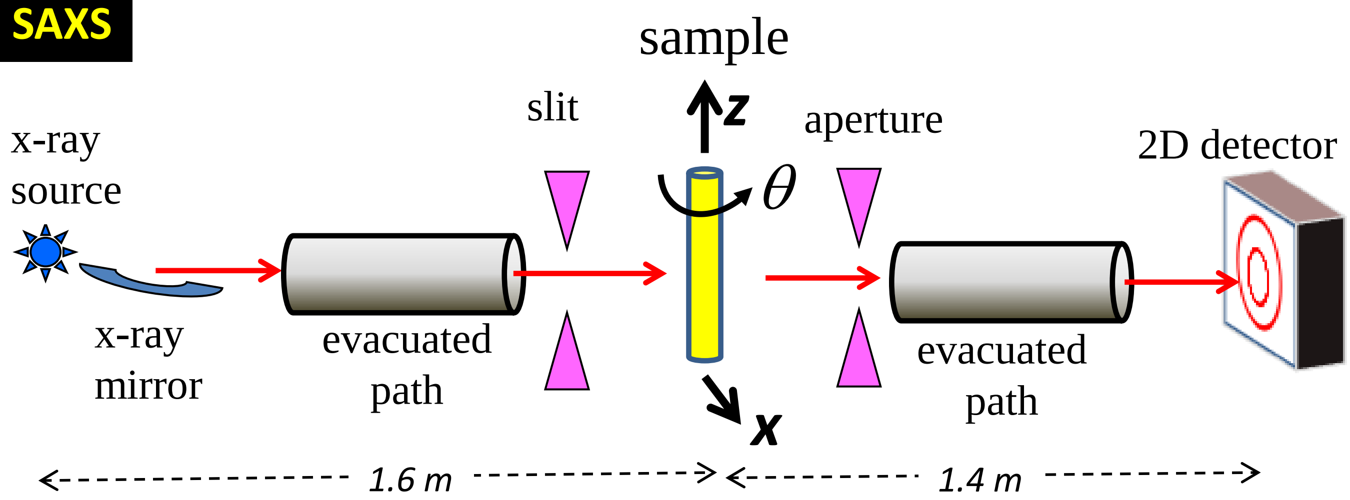
Air scattering at low scattering angles

Low scattering intensities. Subtle features in data.

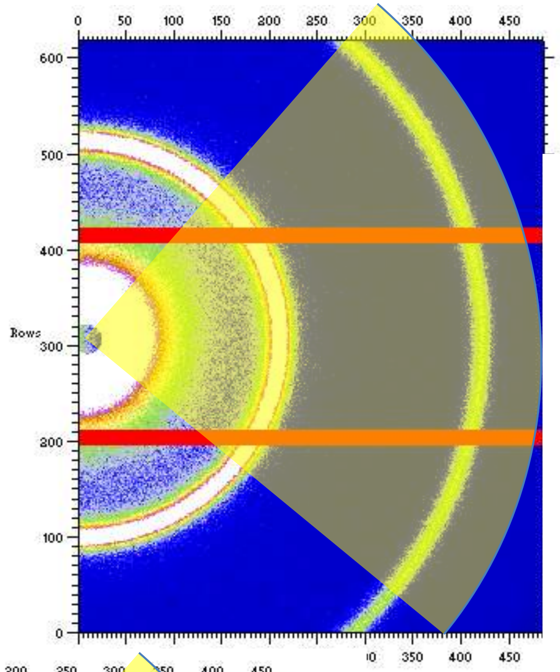
Contrary to hard materials, soft materials may be damaged by the x-ray radiation: need fast data collection

SAXS and WAXS configurations

SAXS

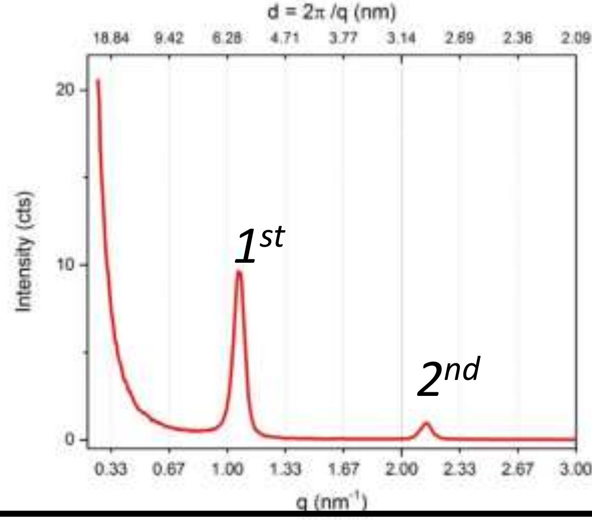


q ~ 0.3 – 3 nm^{-1}, d ~ 24 - 4 nm

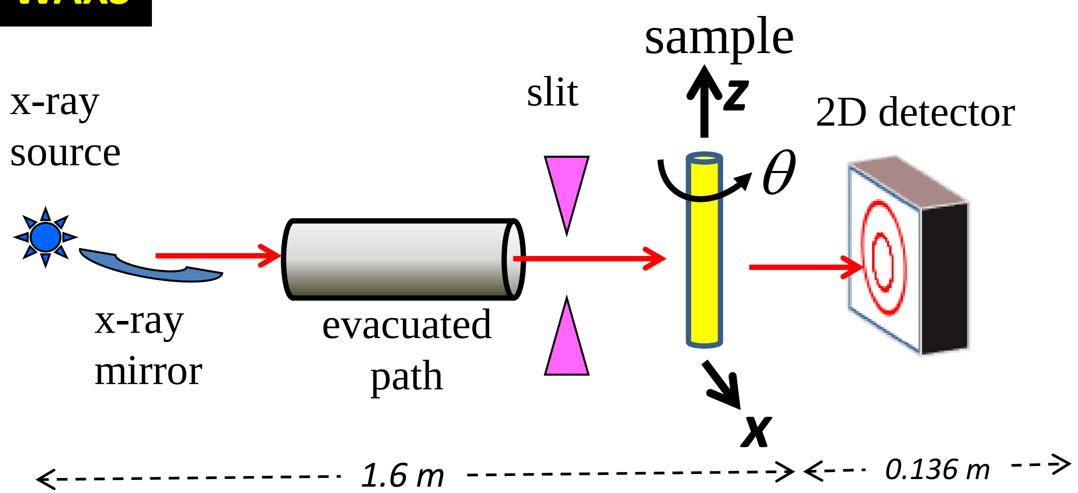


Silver behenate $AgC_{22}H_{43}O$

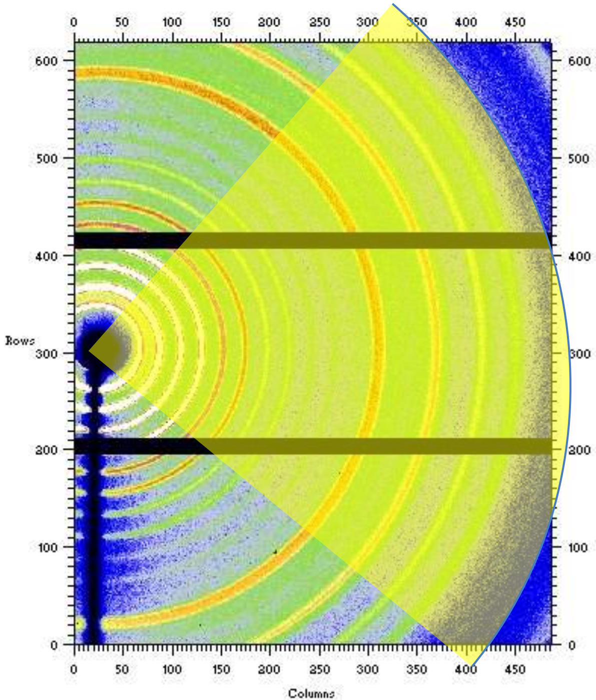
$$\frac{q_n}{q_1} = 1,2,3,4\ldots \text{ (lamella)}$$

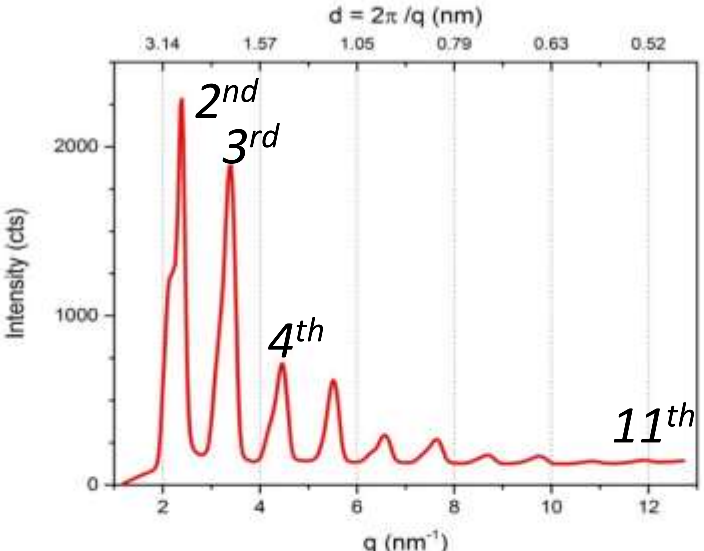


WAXS



q ~ 1.3 – 13 nm^{-1}, d ~ 5 – 0.5 nm





Typical SAXS data ranges

The slope in a graph of Ln(I) vs. Q^2 gives the **radius of gyration** (R_g) (effective size of the scattering particle, ex. a polymer chain, micelle, domain in a multiphase system, etc.)

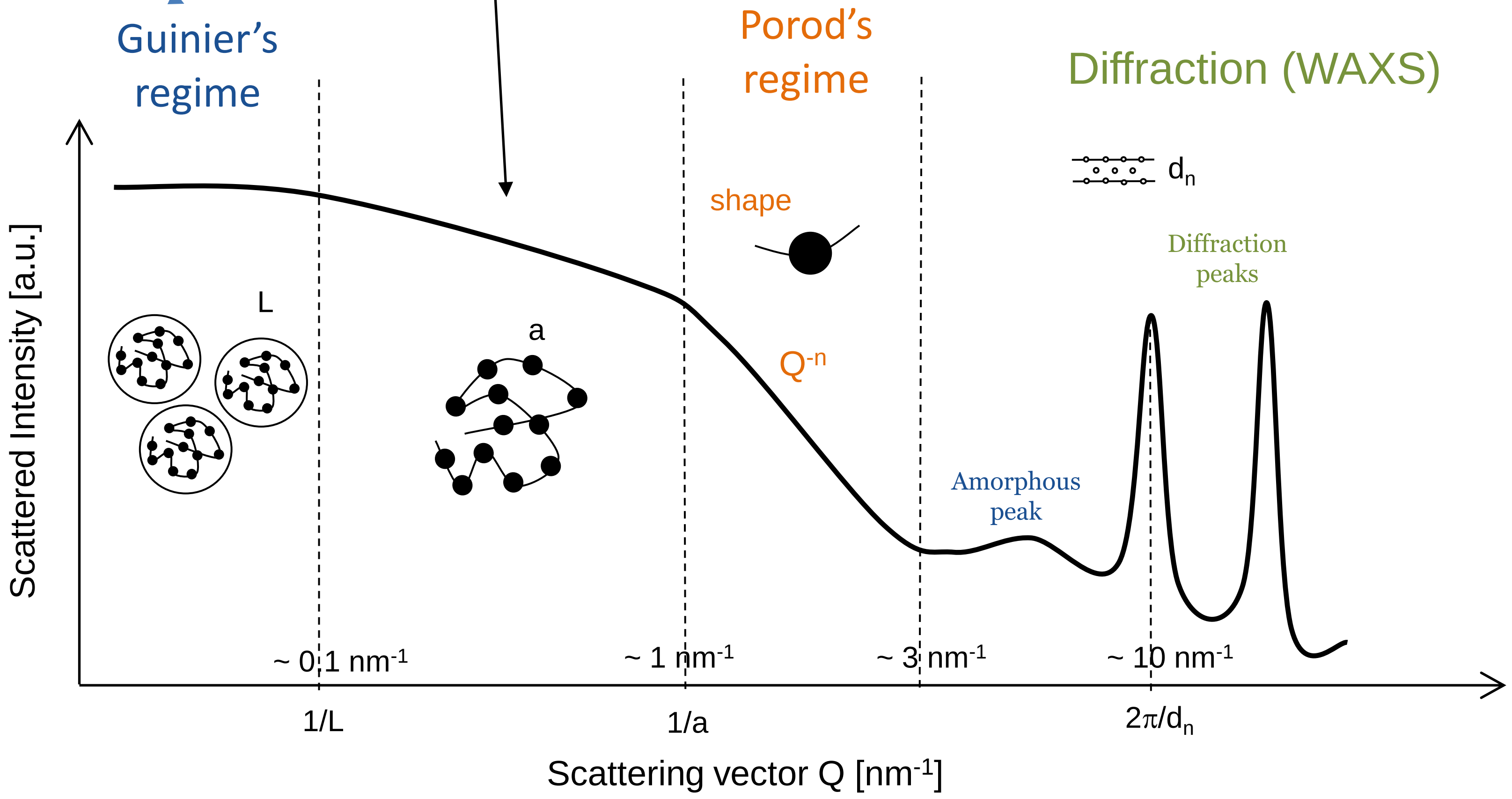
$$I(Q) = I_0 \exp\left(-\frac{Q^2 R_g^{\ 2}}{3}\right)$$

$$\mathrm{Ln}[I(Q)] = \mathrm{Ln}[I_0] - \frac{Q^2 R_g^{\ 2}}{3}$$

Intermediate range, different dependence on Q (elongated objects)

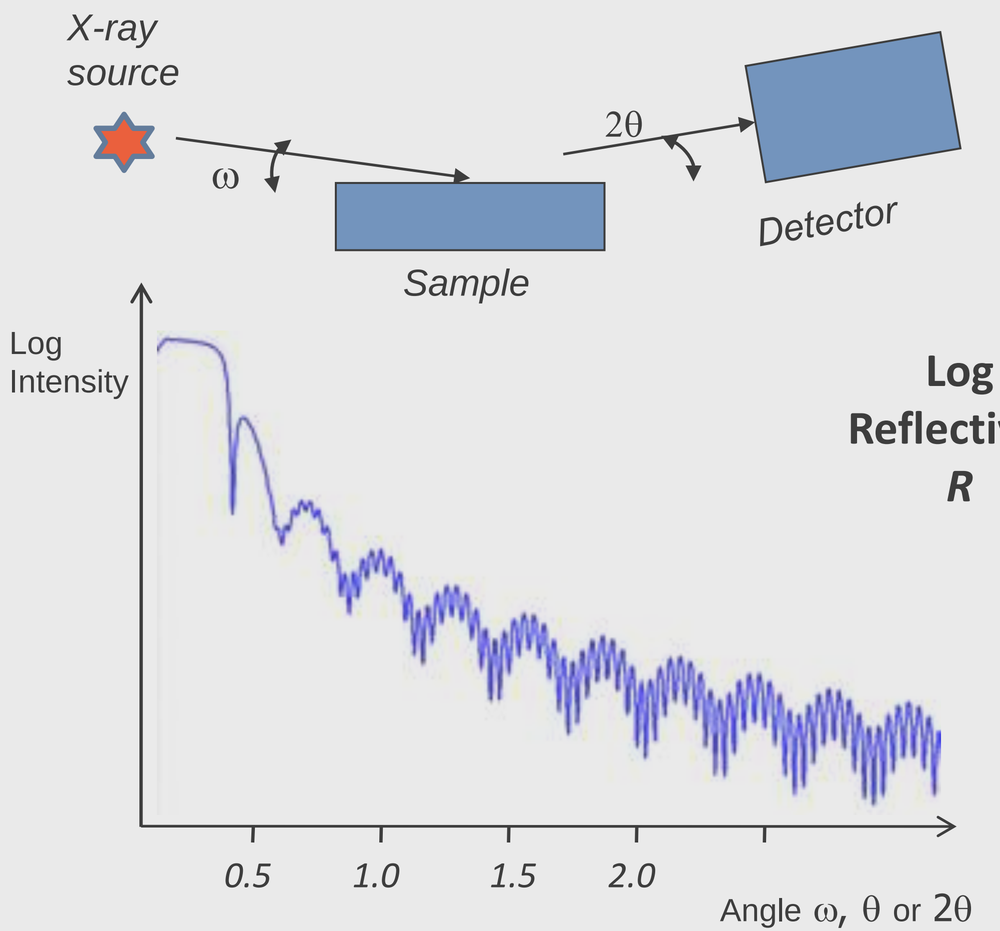
$$I(Q) = \frac{I(0)}{Q} \exp\left(-\frac{Q^2 R_g^{\ 2}}{2}\right)$$

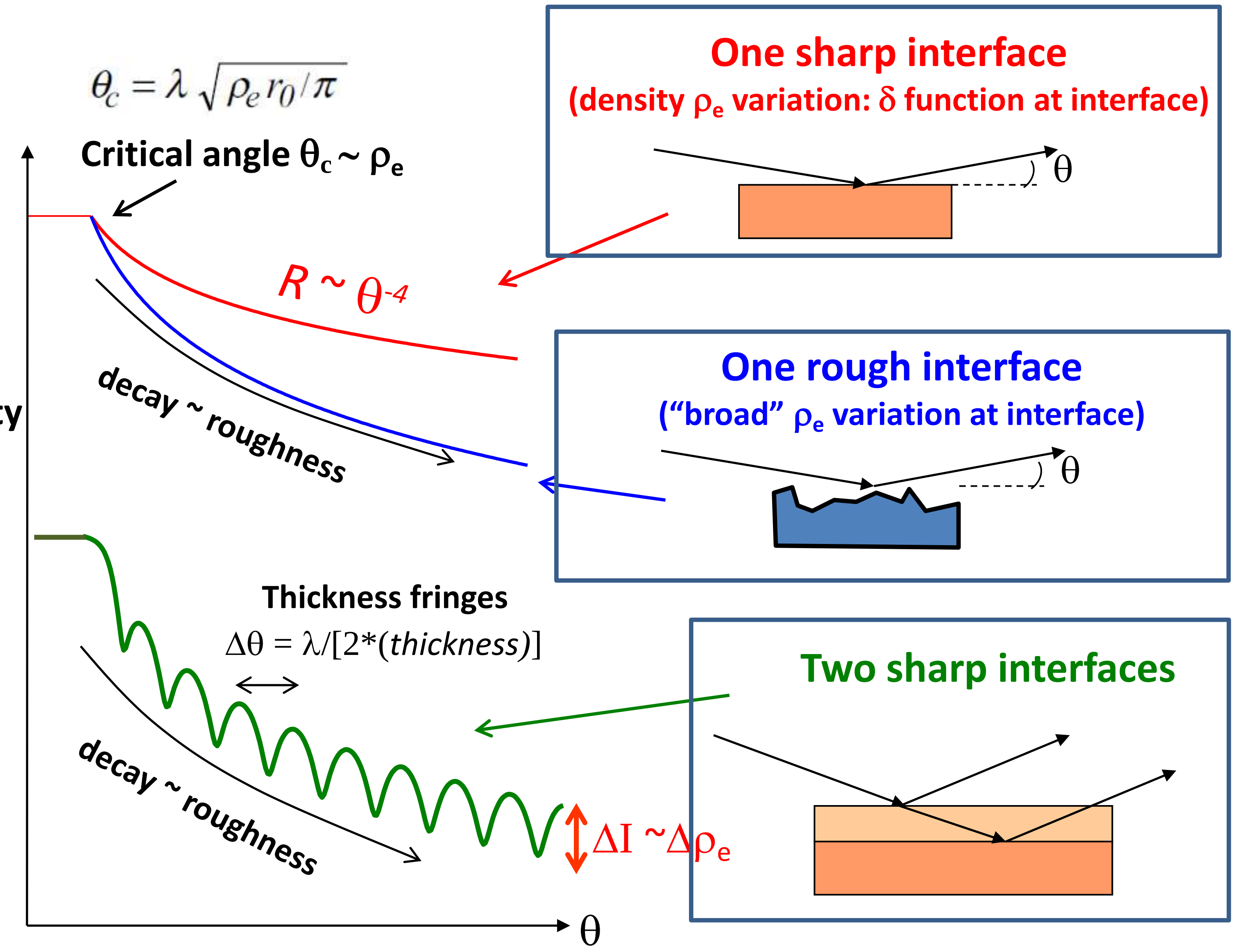
Plot Log(I) vs Log(Q), Porod's slope n from $\boldsymbol{Q^n}$
n: rigid rods, n: 3-4 rough interfaces of fractal dimension $D = 6 - n$
n: 4, smooth surface



After J.L Brousseau, Xenocs

X-ray reflectivity (XRR)



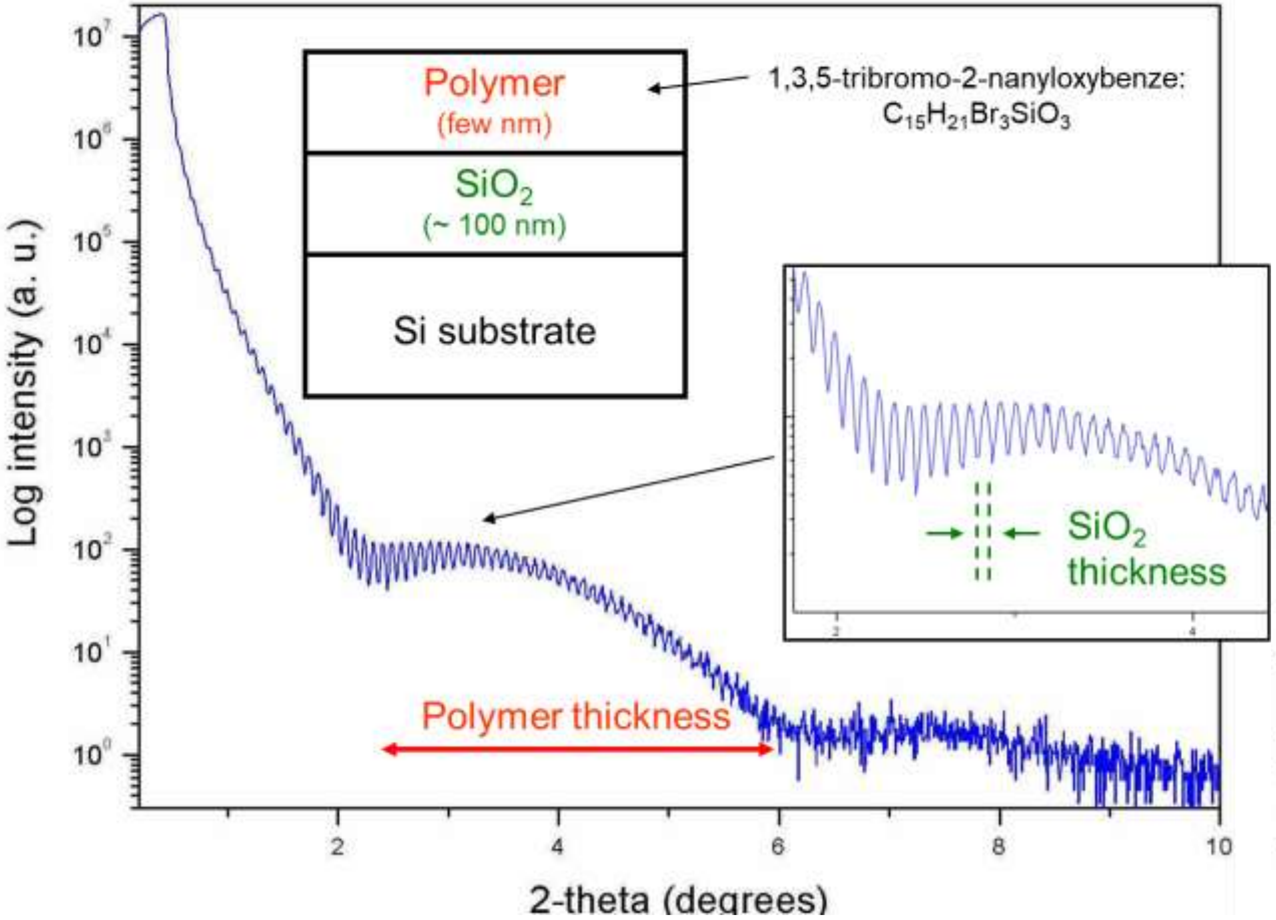


XRR measures *changes in electron density* near surface and over a depth up to ~ 100-200 nm: density, porosity, density profile, surface and interface roughness, layer thickness.

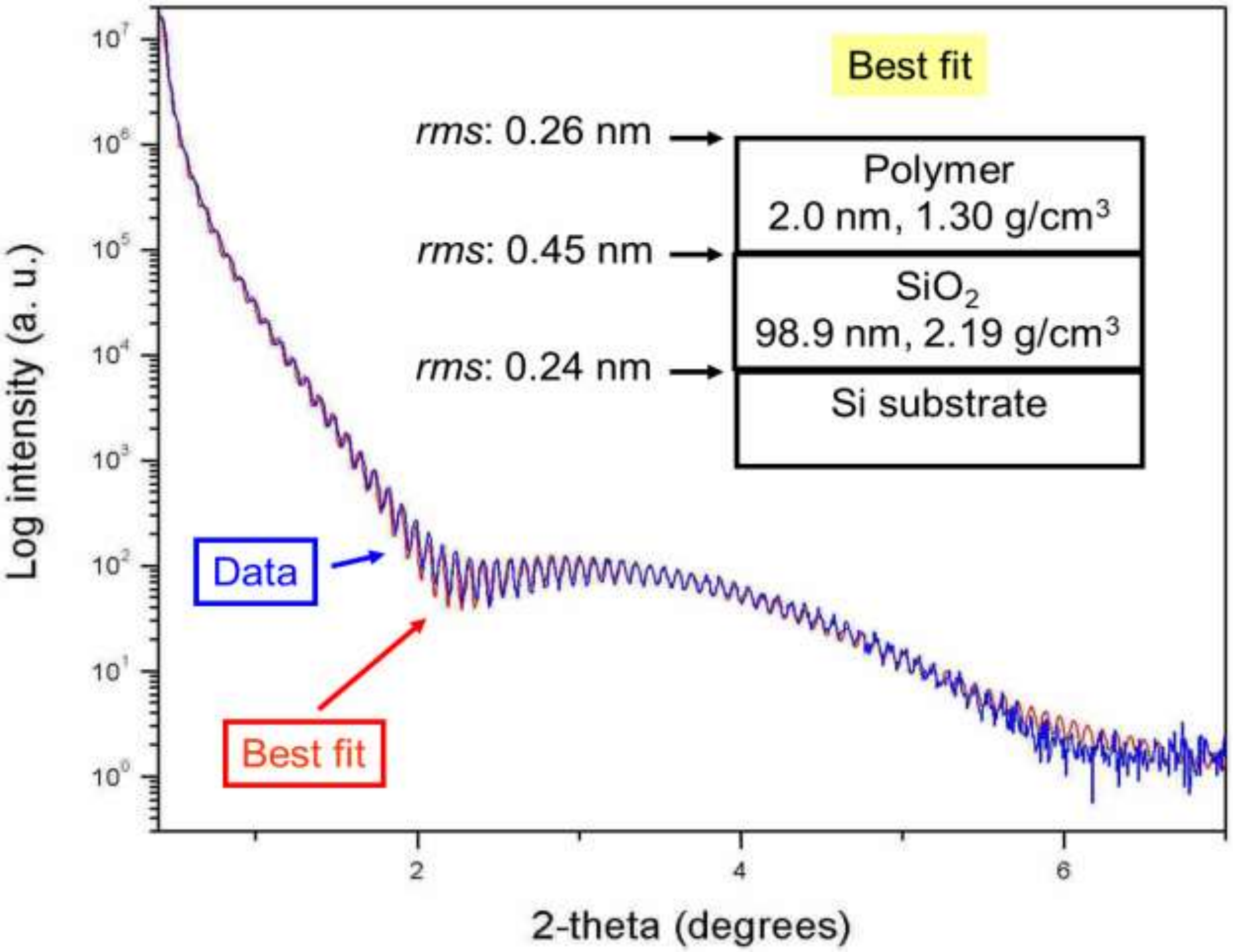
Amorphous, crystalline, layered, solids, liquids.

~ sharp surface and interfaces required for layer thickness determination

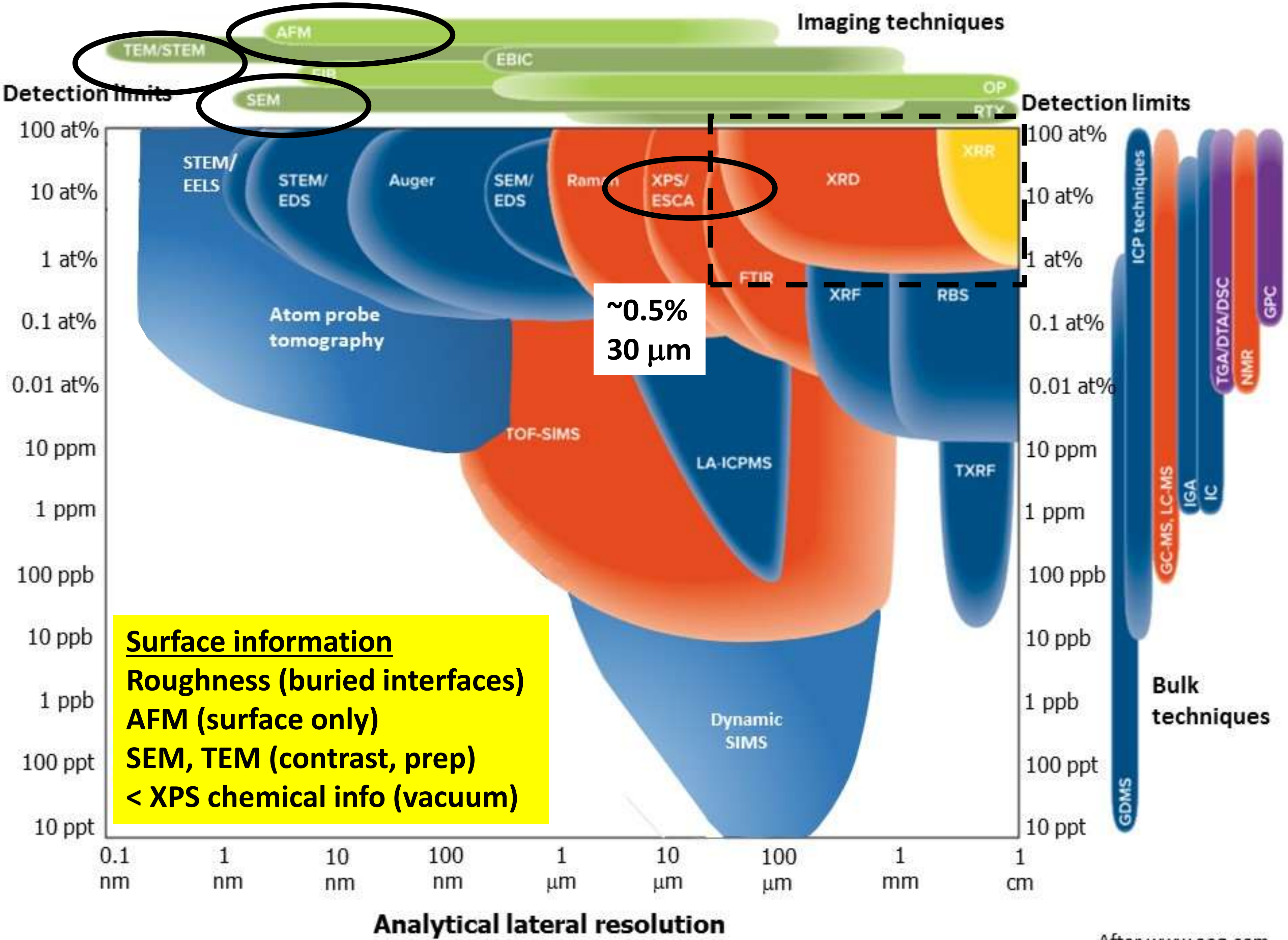
X-ray reflectivity of ultra-thin films



Simulation using Parrat's formalism
and generic algorithm fitting

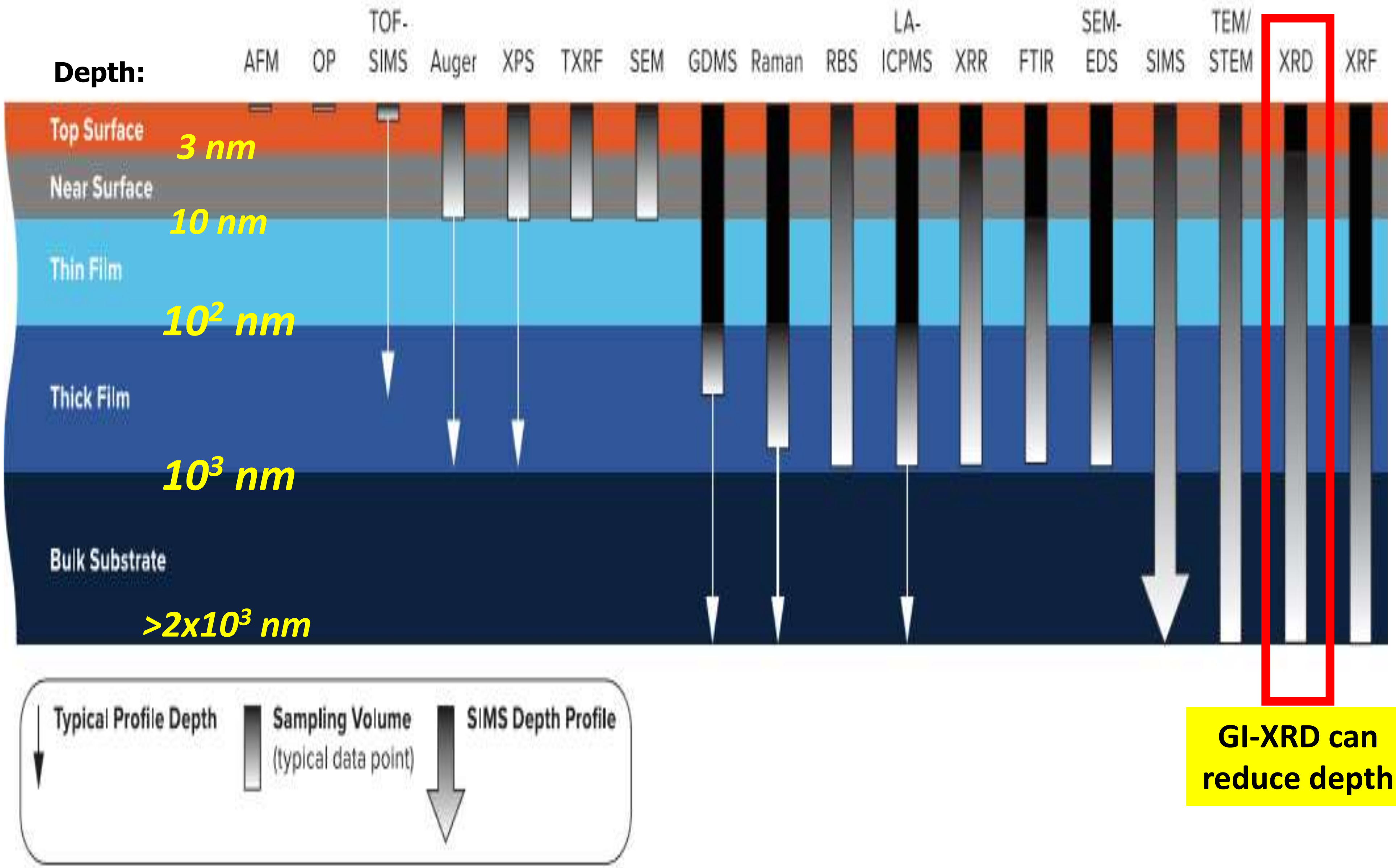


Data: Sardela
Sample: Zhang, Rogers et al, UIUC



After www.eag.com

Typical analysis depth for common analytical techniques



GI-XRD can reduce depth

www.eag.com

X-ray analysis: summary, pros and cons

(+)

Non destructive

No vacuum requirement
Optional sample prep

Crystalline phases identification and quantification
Element, molecules, polymorphs (structural fingerprinting)

Crystallite / grain size: easy to measure (be careful)

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

Multiple levels of complexity: simple to complex

Easy integration to in situ HT, LT, pressure, humidity controls

Microdiffraction, pair distribution function, microfocus sources, fast areal detectors

(-)

No localized information:

Areal spatial resolution not better than 100 um

Depth resolution down to tens of nm only with special techniques

Defects identification and quantification requires simulation and data fitting

No direct info or image of microstructure

X- ray analysis methods

Based on the book…

"PRACTICAL MATERIALS CHARACTERIZATION"

Editor Mauro Sardela
Published by Springer
Hardcover and e-book editions