Lesson 3
Sample Preparation & Problems

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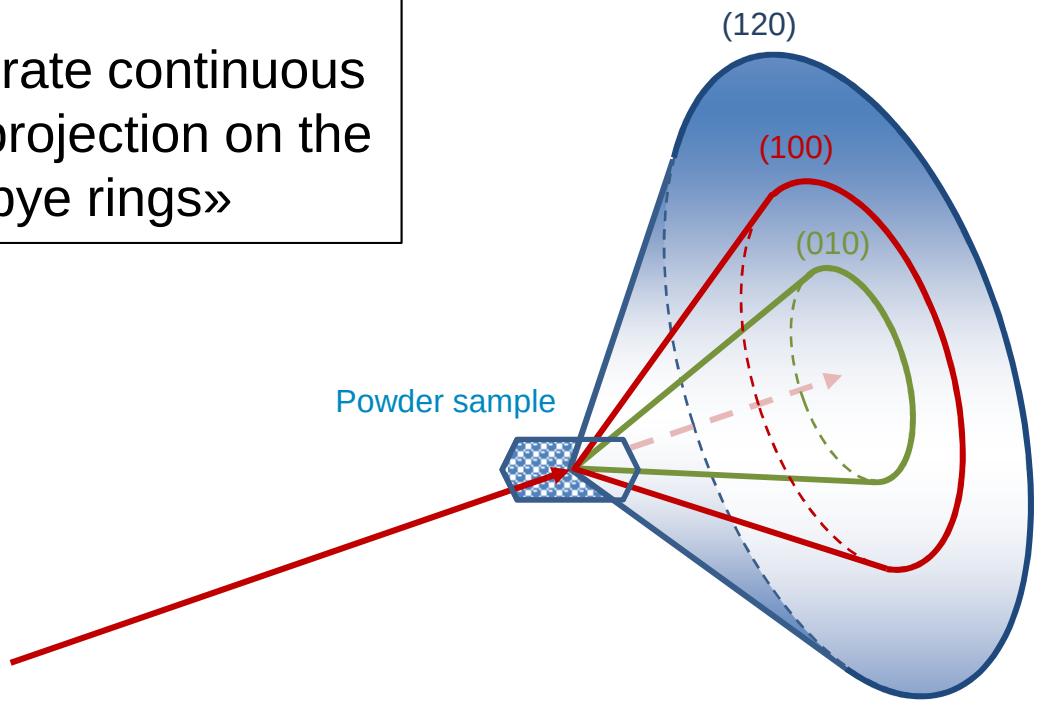
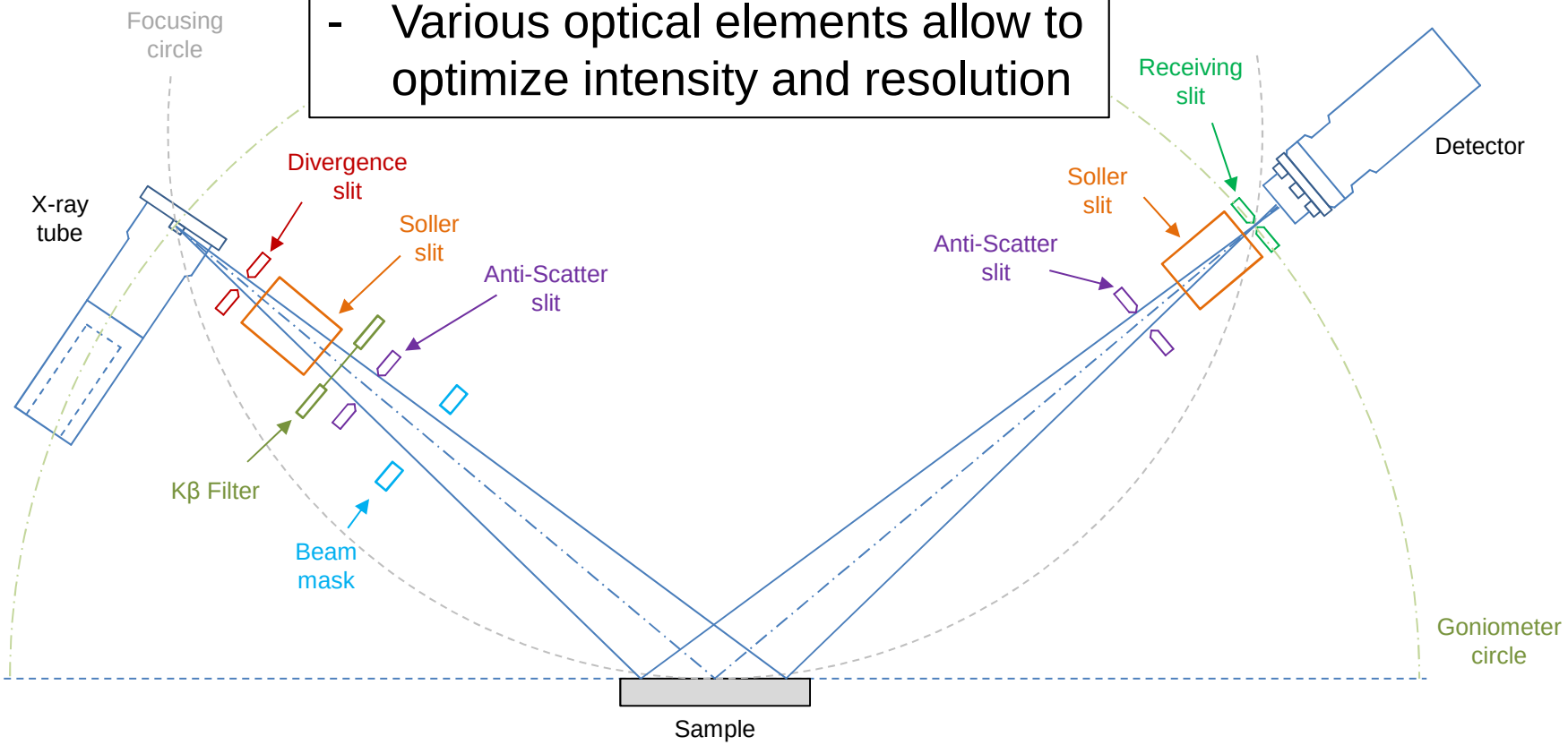
Repetition: Powder XRD Samples

- A fine powder contains particles in all possible orientations
- The orientation distribution is random, no orientation is preferred
- Powder samples generate continuous diffraction cones, the projection on the detector is called «Debye rings»



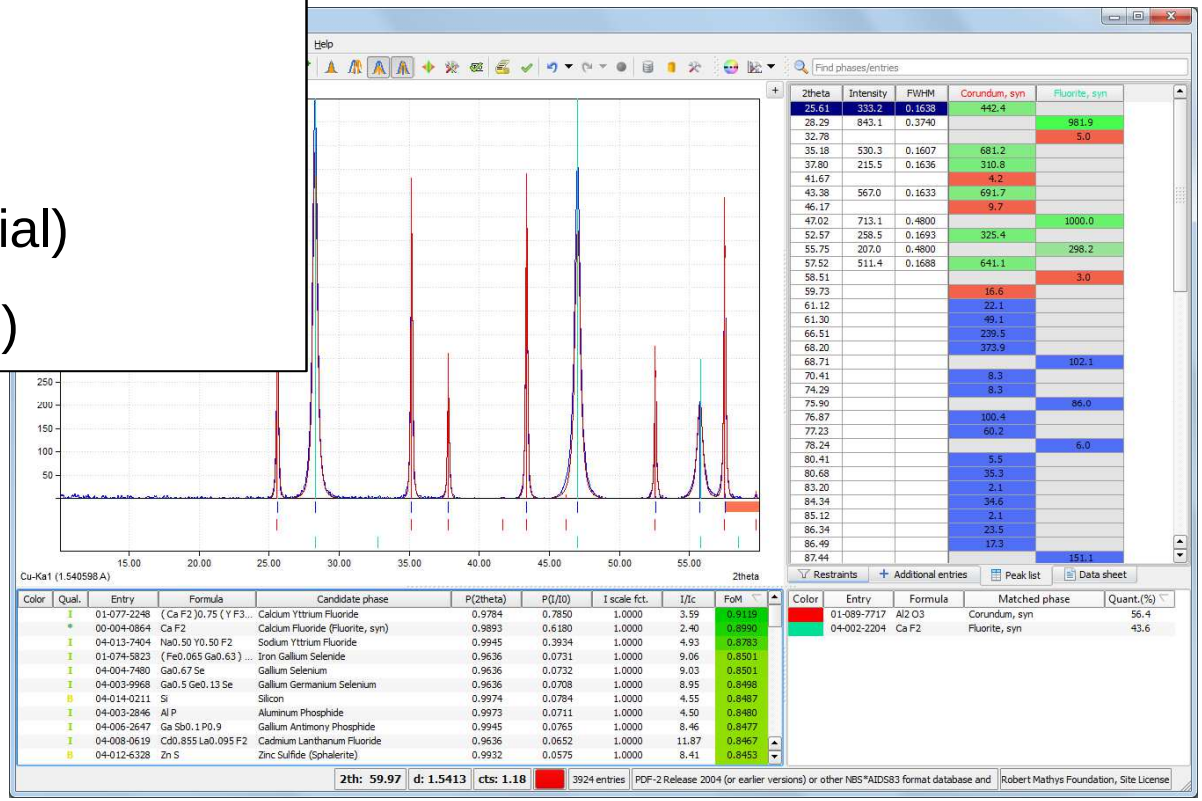
Repetition: Bragg-Brentano Diffractometer

- Bragg-Brentano diffractometer (Reflective / θ-θ geometry)
- Various optical elements allow to optimize intensity and resolution



Repetition: Phase Identification

- Crystalline phases are identified by comparing peak positions with a database (Search/Match)
- Qualitative (sometimes semi-quantitative) results
- Databases:
  - PDF-2/4 (commercial)
  - COD (open-access)



Sample Preparation

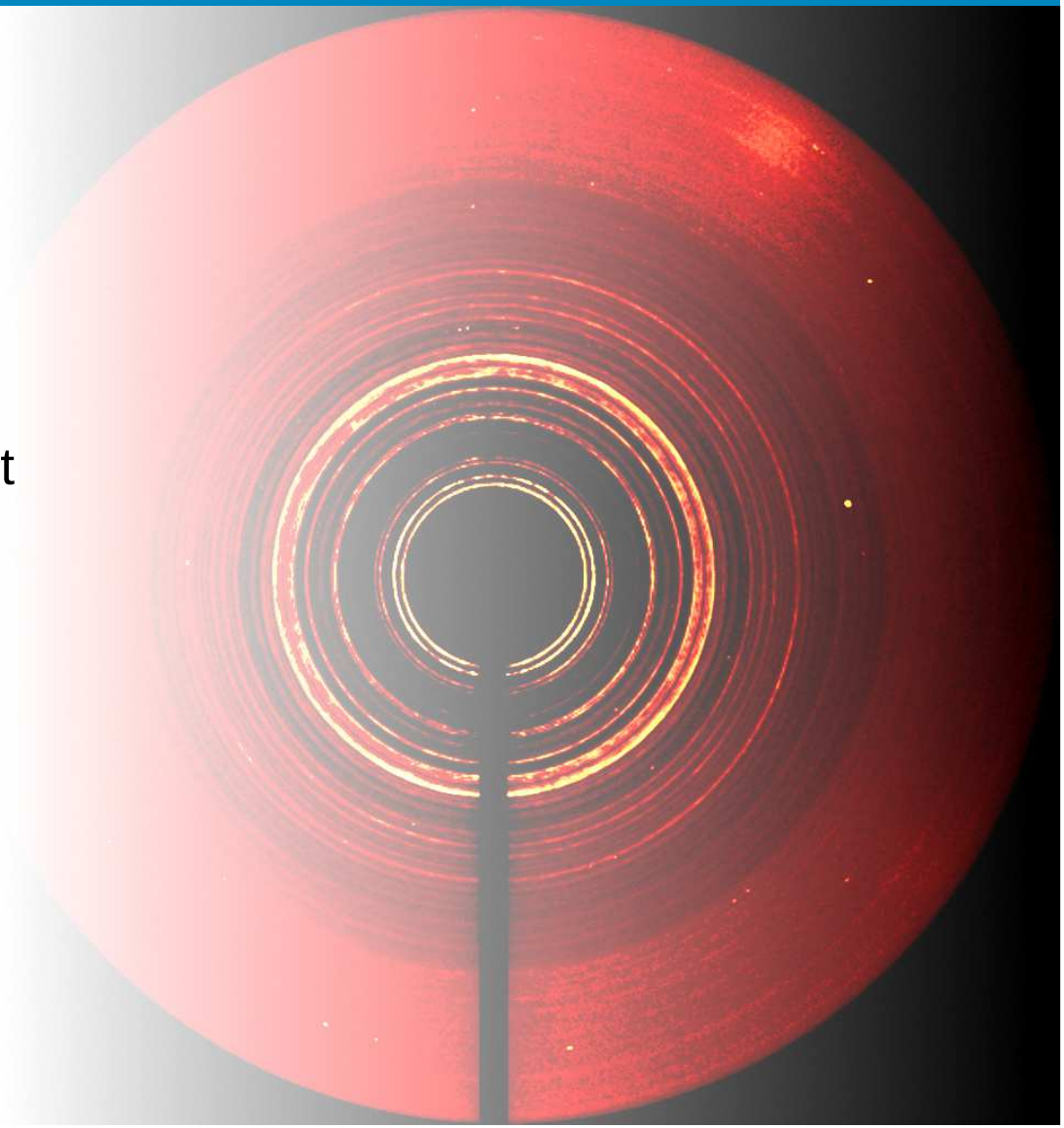
Sample preparation is **ABSOLUTELY CRUCIAL**
for a good diffraction pattern!

Some problems encountered during Rietveld refinement are inherent to the sample.

Some others are related to sample preparation errors.

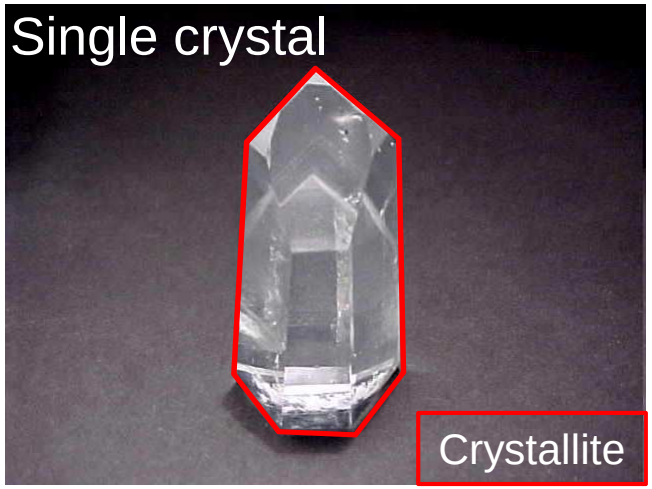
Problems

- Graininess
- Micro-absorption
- Texture
- Crystallite size
- Sample height displacement
- Surface roughness
- Sample transparency



Particles & Crystallites

Crystallite = Domain of coherent crystal structure



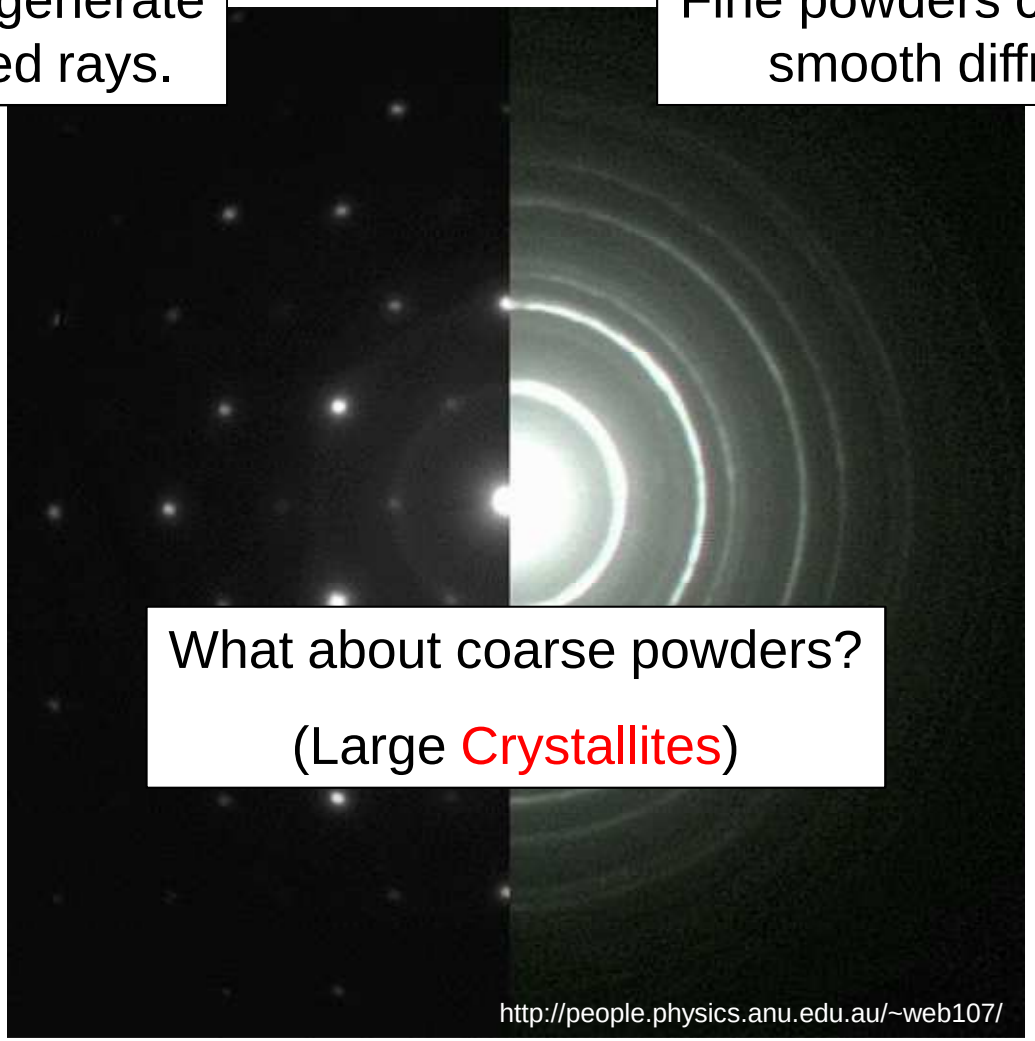
Particle size = Crystallite size

Particle size > Crystallite size

Graininess

Single crystals generate spotty diffracted rays.

Fine powders crystals generate smooth diffraction rings.



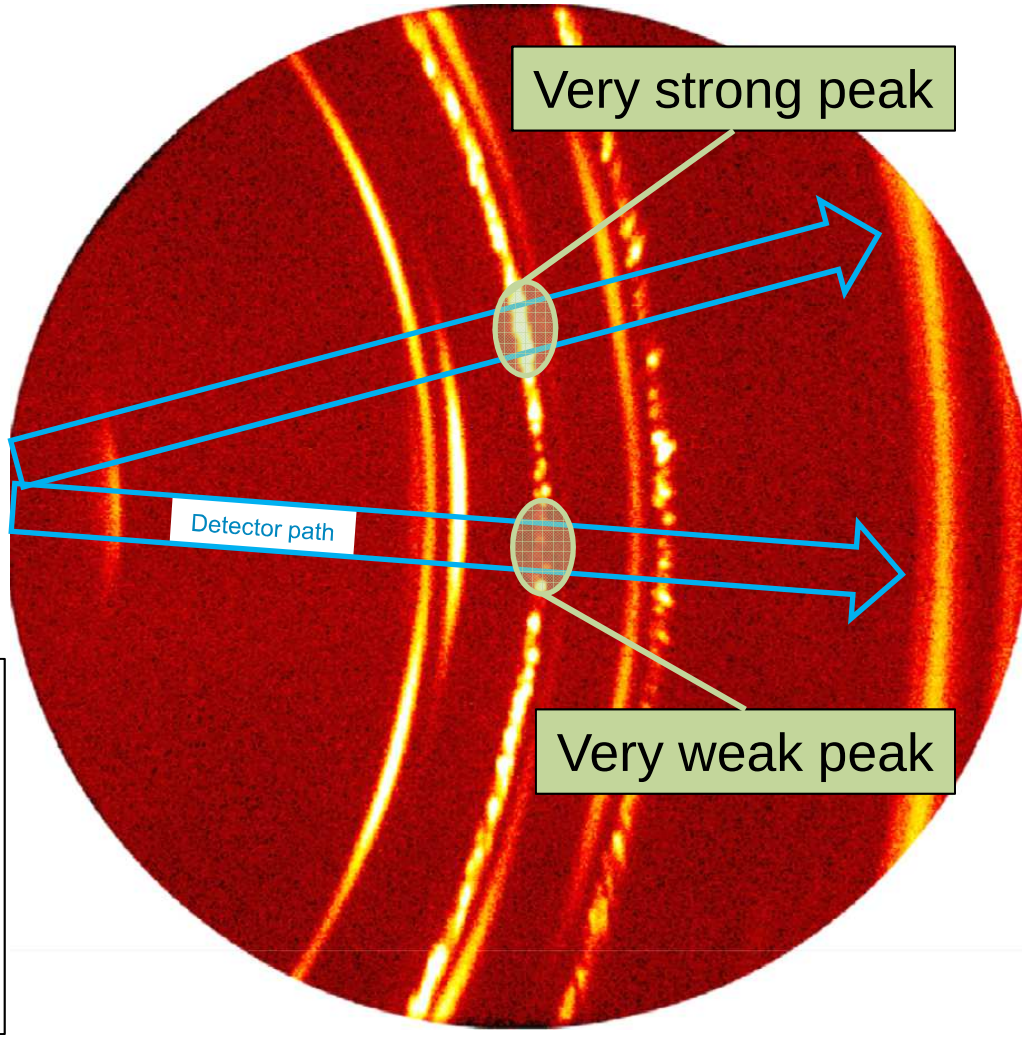
What about coarse powders?

(Large Crystallites)

Graininess

Spotty diffraction rings

The same sample, at
the same 2θ position,
but different intensities!



Grainy samples:

- non-reproducible intensities
- «phantom» peaks
- «missing» peaks

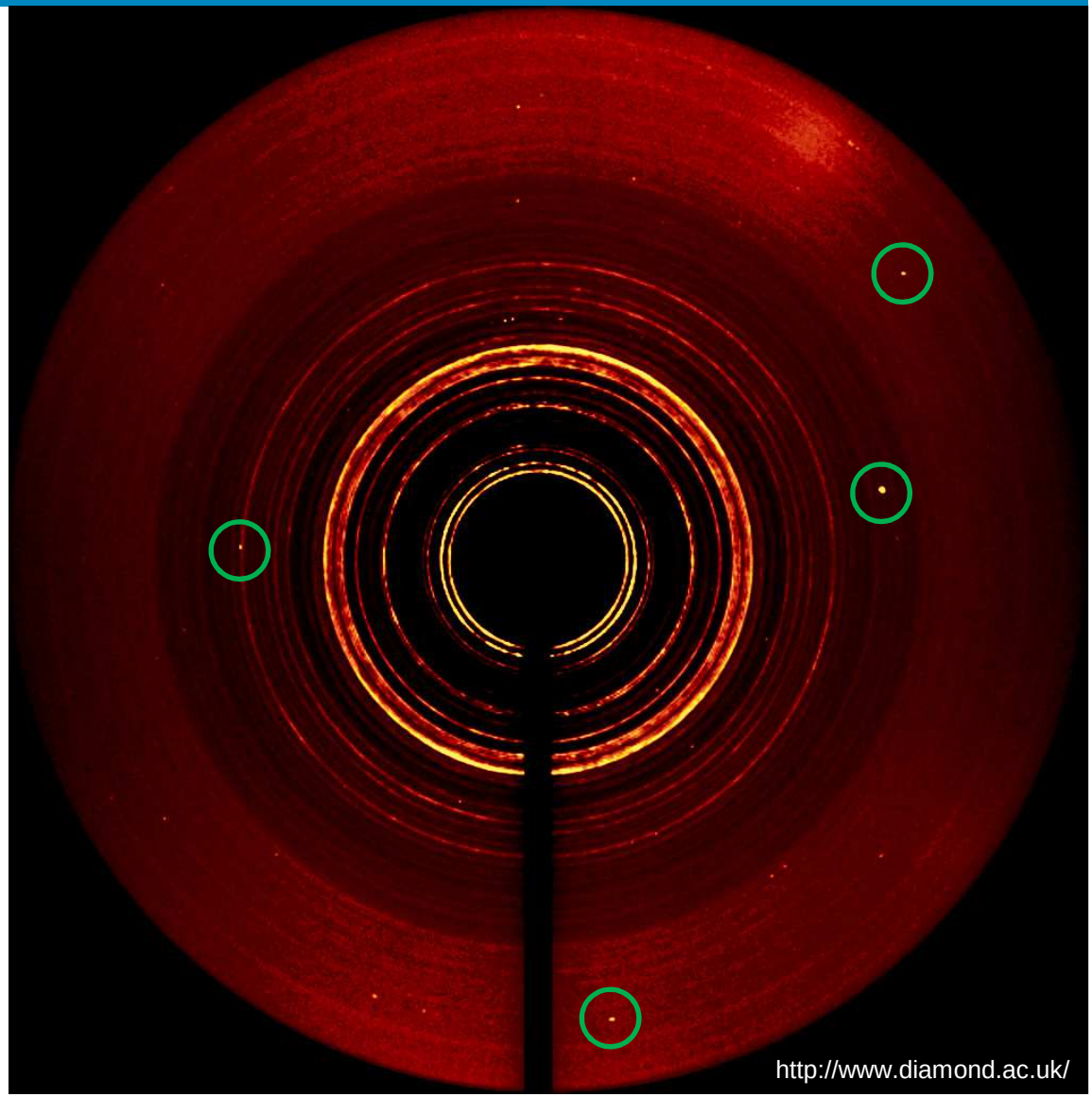
Bruker AXS

Graininess: Rocks in Dust

«Rocks in Dust»:

A few large crystals in a fine matrix

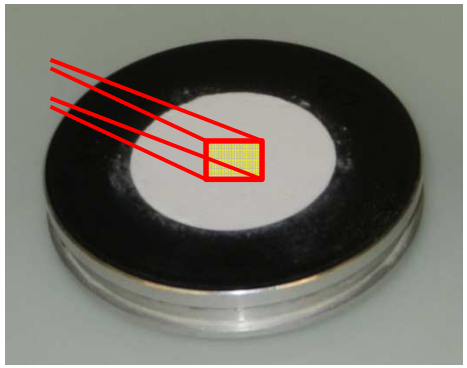
Usually invisible, but if scanned: Strong peaks out of nowhere!



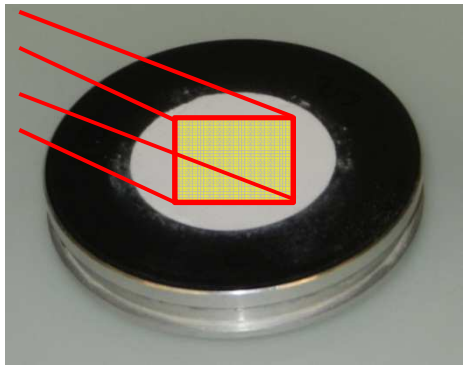
Graininess

Reducing graininess:

- Grinding / milling
- Adjust divergence slit and beam mask for largest possible irradiated area (= more particles contribute to diffraction pattern)
- Use spinning sample stage (= better randomisation)

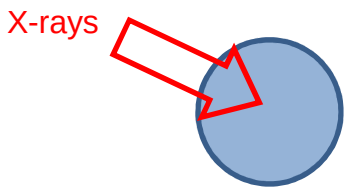


Few diffracting crystallites

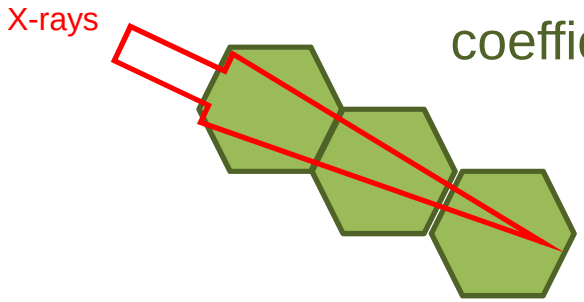


Many diffracting crystallites

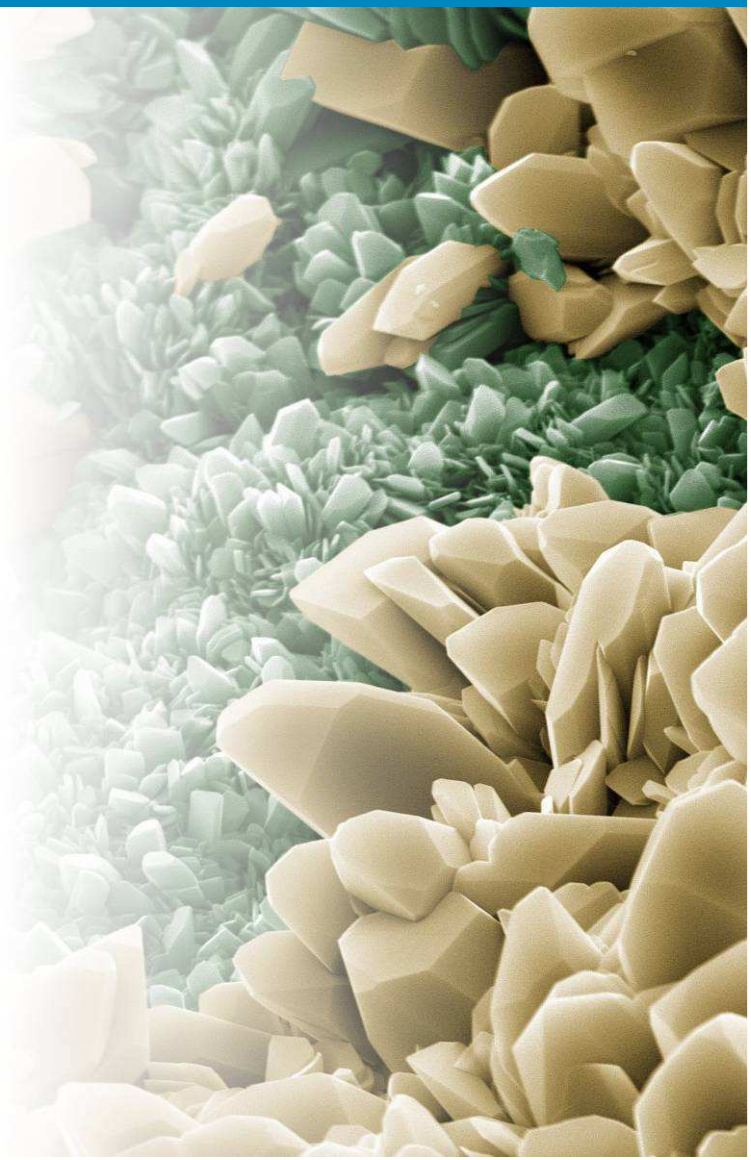
Micro-absorption



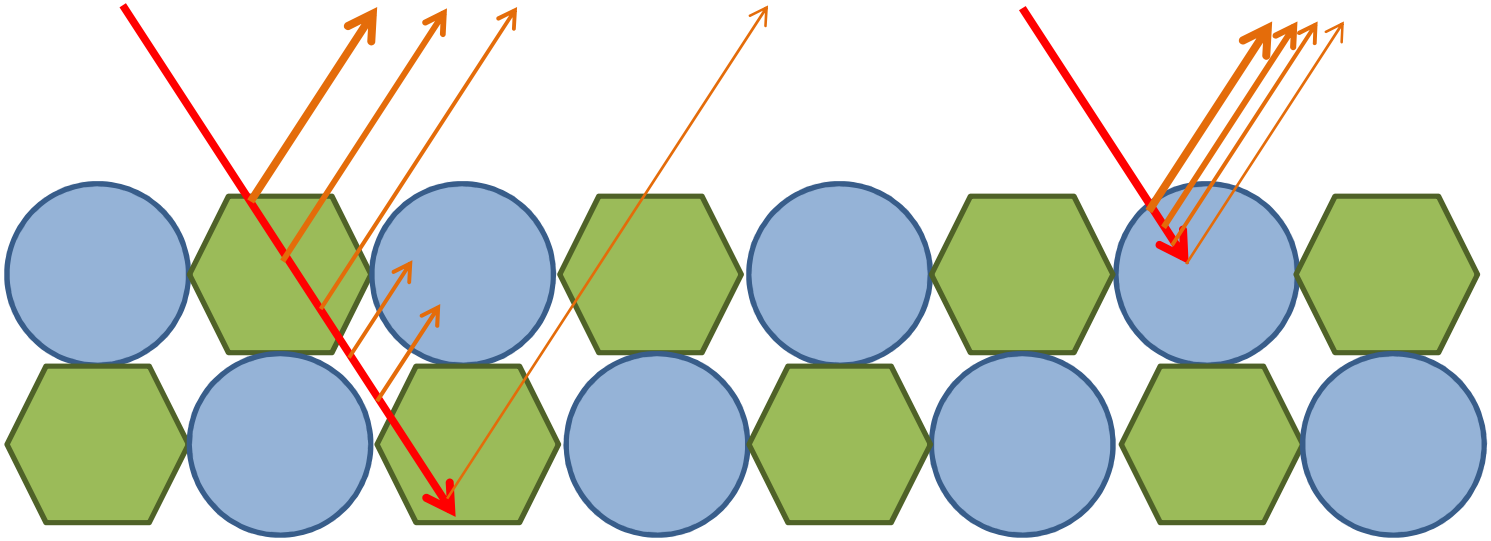
Phase 1: High absorption coefficient for X-radiation



Phase 2: Low absorption coefficient for X-radiation



Micro-absorption



Weak attenuation by phase 2

→ Large volume of interaction

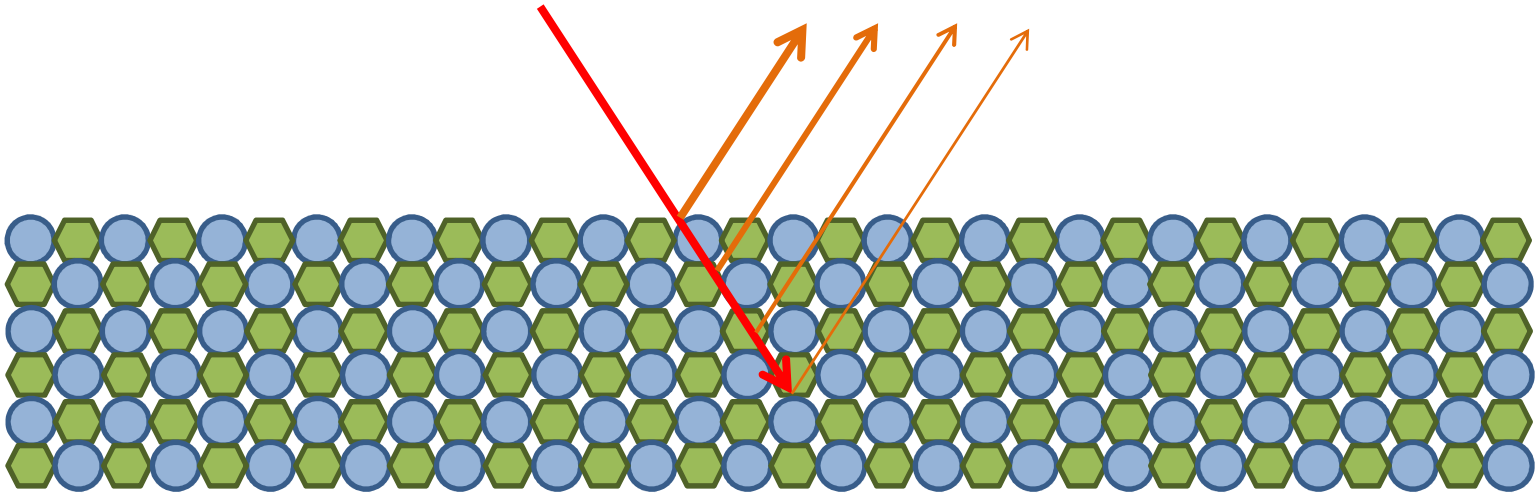
Strong attenuation by phase 1

Large particles absorb significant part of the radiation.

→ Small volume of interaction

Phase quantification biased for phase 2!

Micro-absorption



Small particles absorb insignificant part of the radiation.

→ Similar volumes of interaction with phases 1 & 2

→ Correct phase quantification

Micro-absorption

Micro-absorption occurs in samples with…

- … large **particles (not crystallites!)**
- … phases with large differences in absorption coefficients

Reducing micro-absorption:

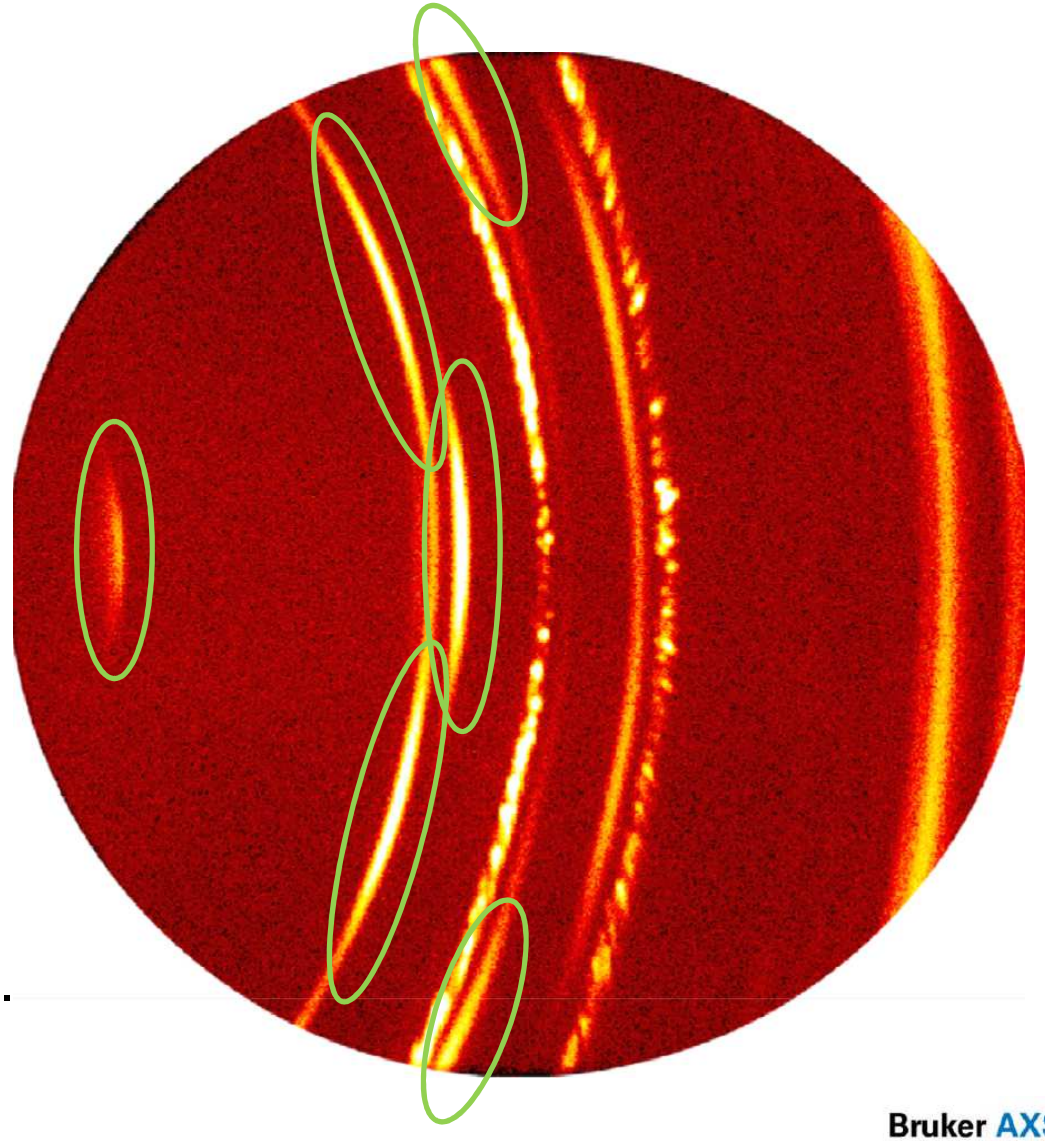
- Grinding / milling to reduce particle size

Mathematical correction:

- Difficult, but possible to a certain degree
  (more about «Brindley correction» in the lesson on «Rietveld refinement»)

Texture, Preferred Orientation

Smooth, but non-continuous diffraction rings

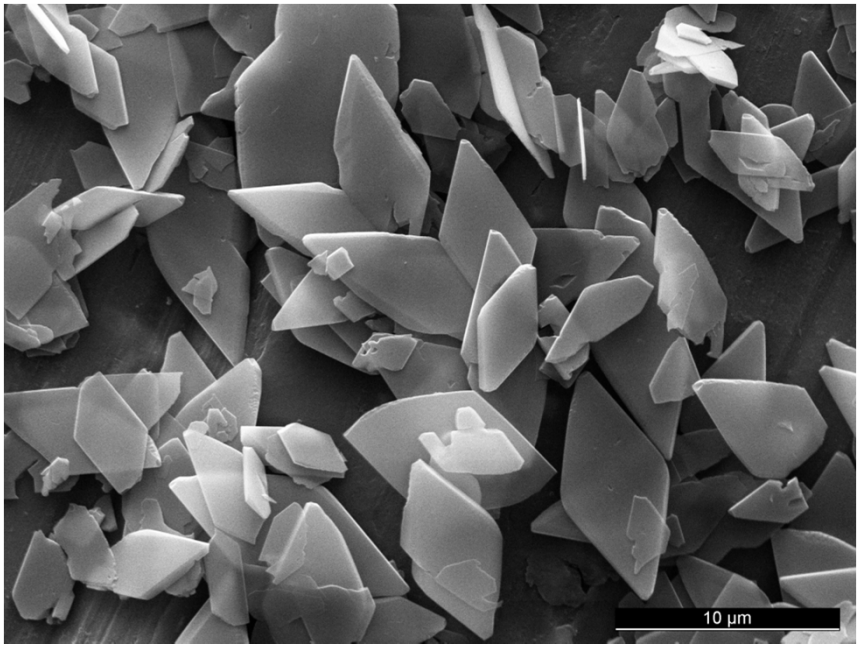


Reason:

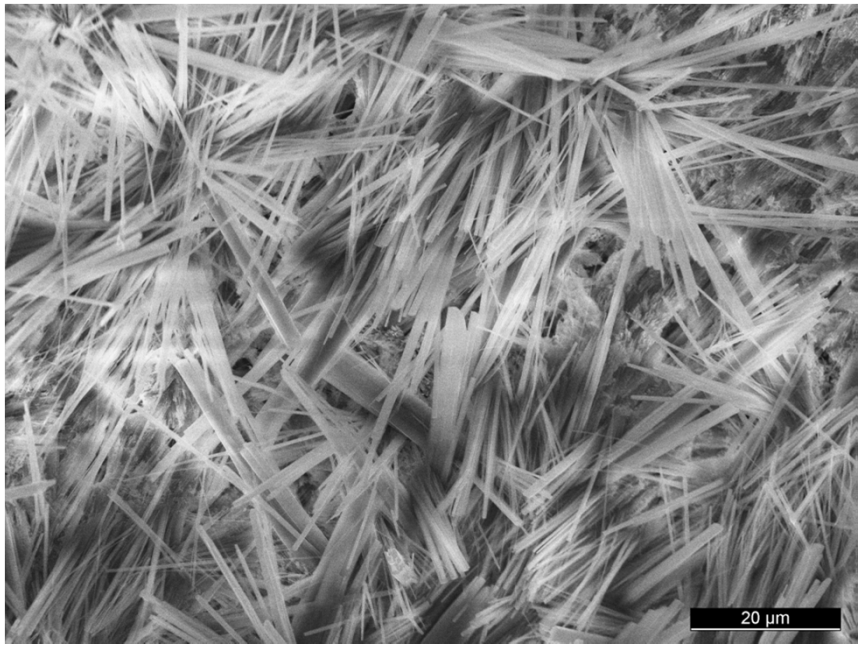
- Orientation of crystallites is not random.
- Some orientations are over-represented, others are under-represented.

Bruker AXS

Texture, Preferred Orientation



Platelets



Needles, Fibers, Whiskers

Random orientation

Preferred orientation

Images: L. Galea, RMS Foundation

Texture, Preferred Orientation

Try to avoid orientation at the surface of the sample:

- Press powder without «rubbing» the surface
- Use back-loading sample holder
- Disorder surface with textured stamp

- Various creative solutions can be found on the internet (involving Vaseline, hair spray, …)

PO can be corrected mathematically, but phase quantification will be biased.
(more on this in the lesson on «Rietveld refinement»)

Crystallite Size

More sources in ordered arrangement
=
More distinct interference pattern

Larger domains of coherent crystal structure
=
More distinct diffraction pattern

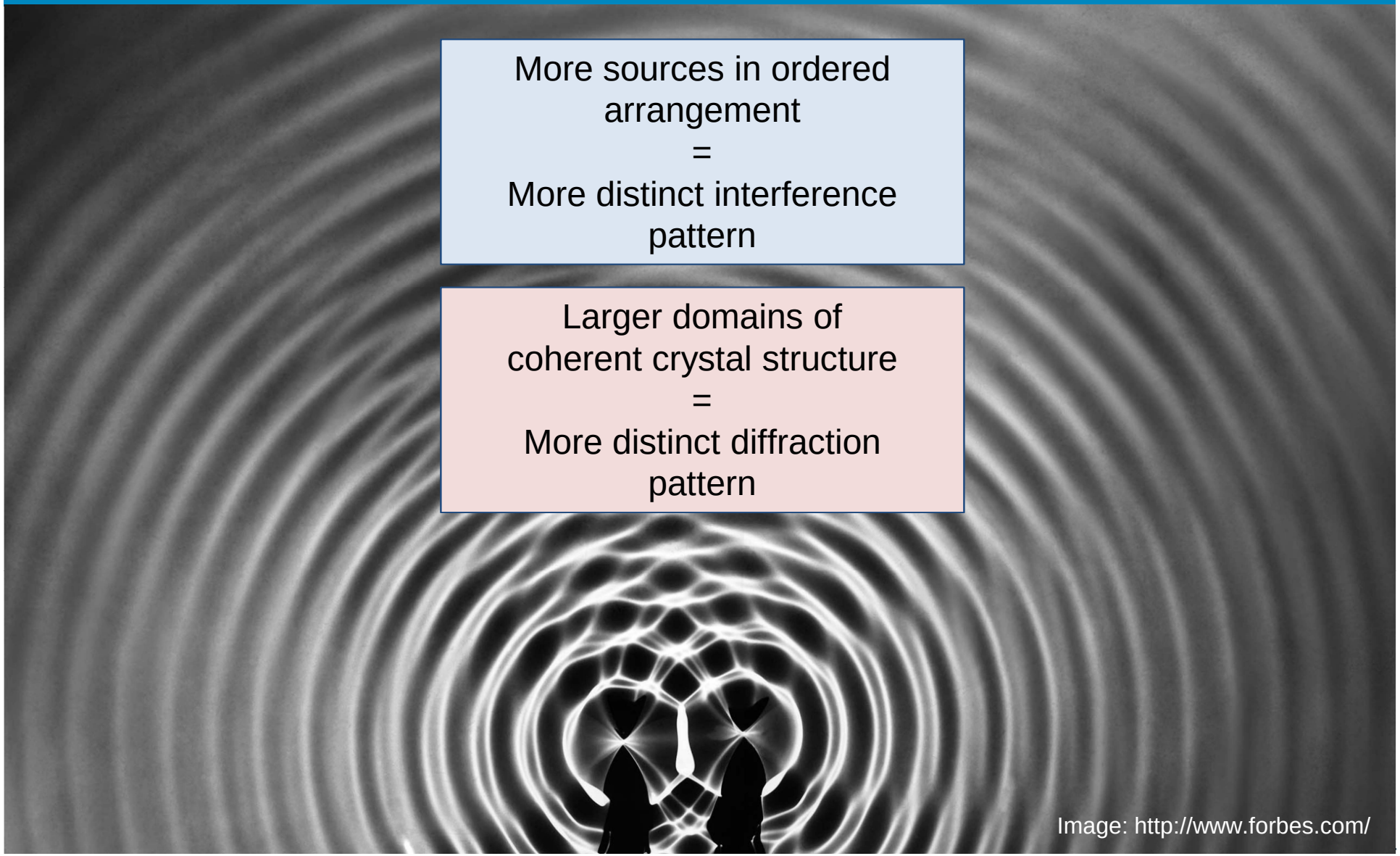
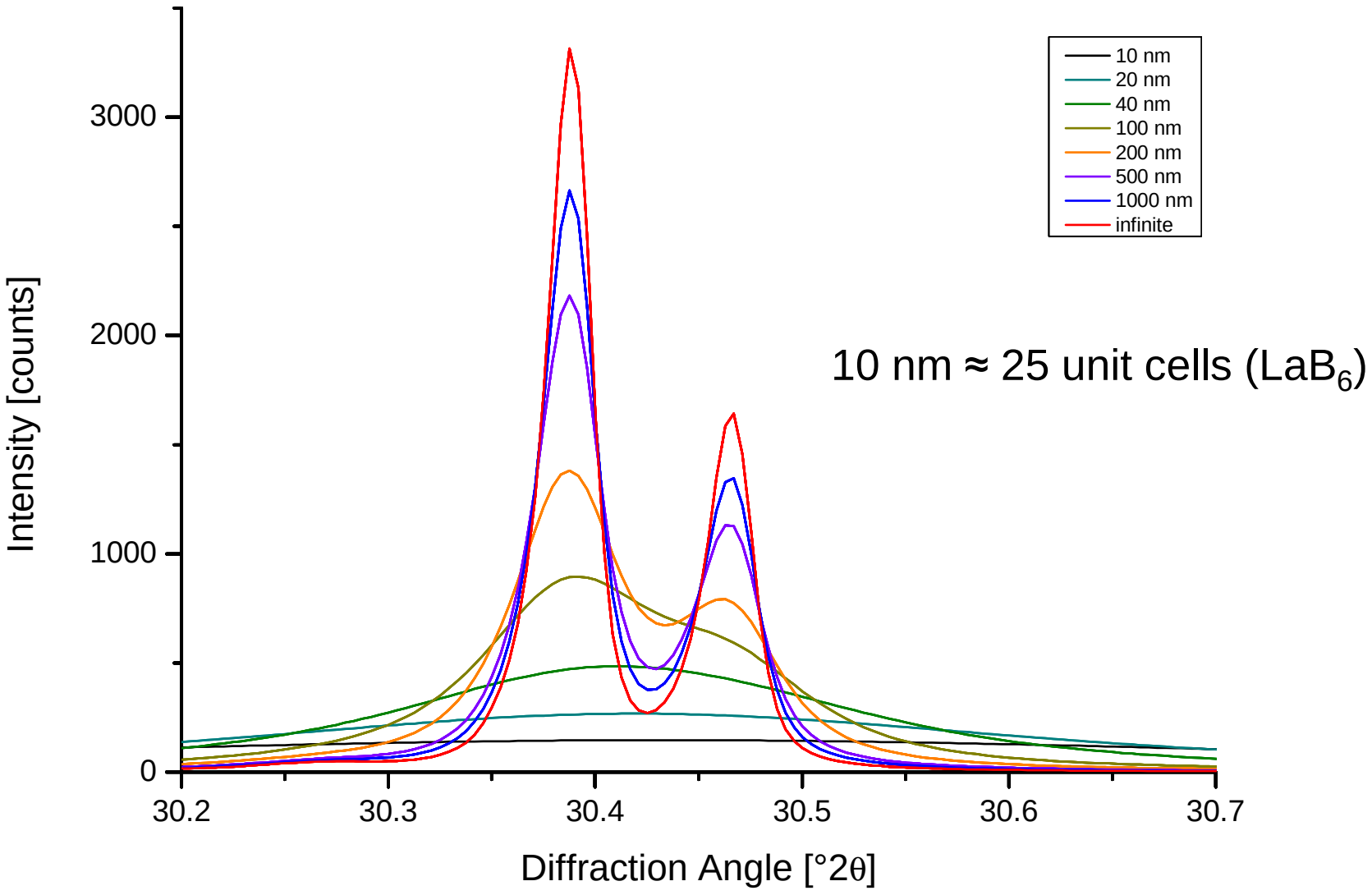


Image: http://www.forbes.com/

Crystallite Size



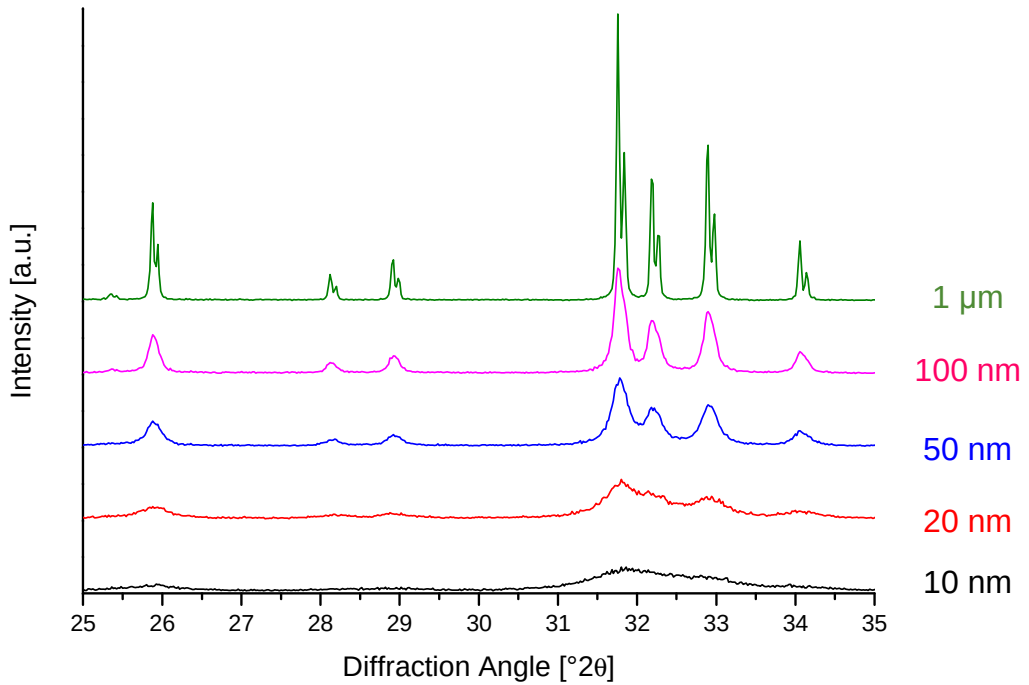
Crystallite Size

Small crystallites generate broad peaks

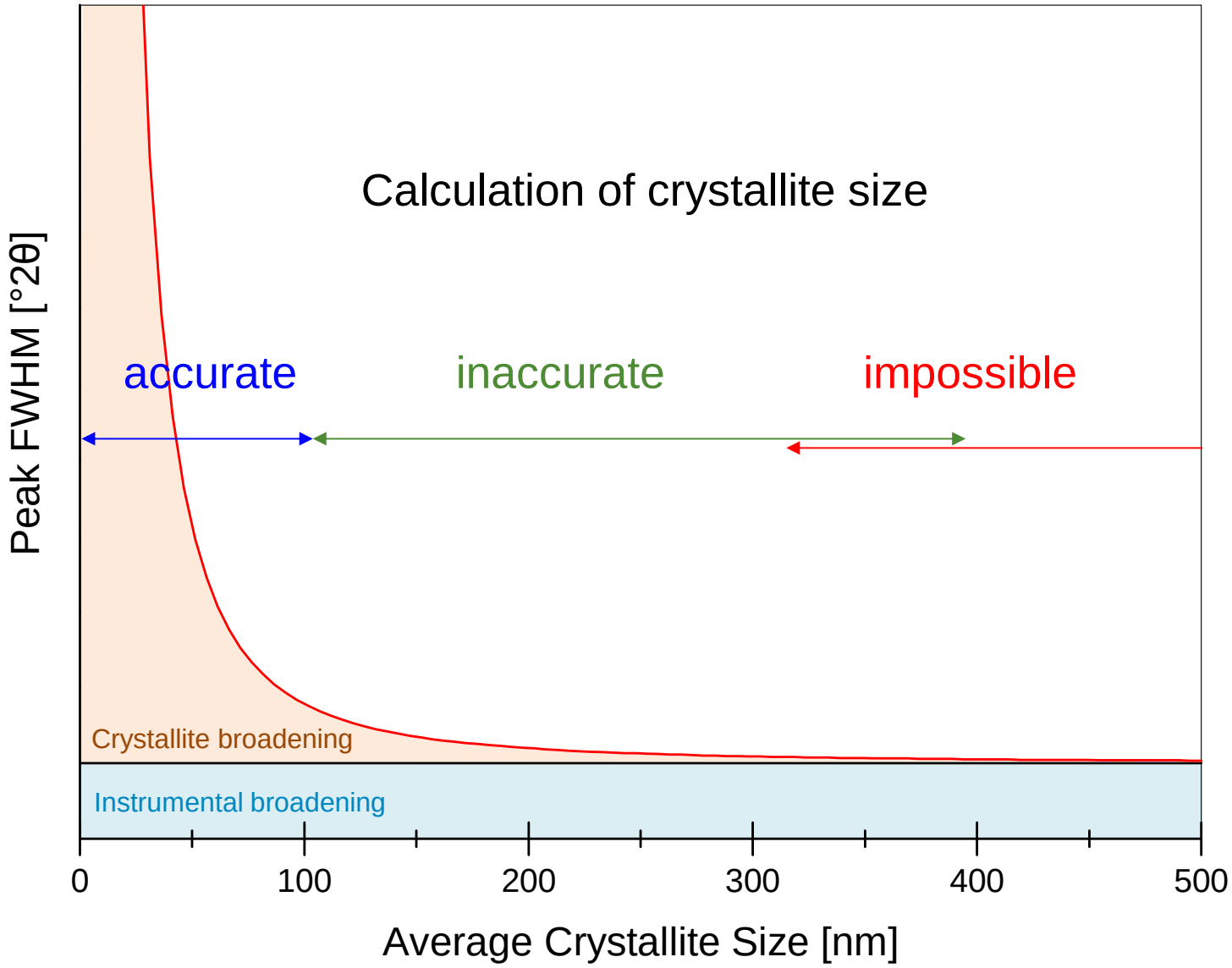
Crystallite size can be calculated from peak broadening

Severe peak broadening:

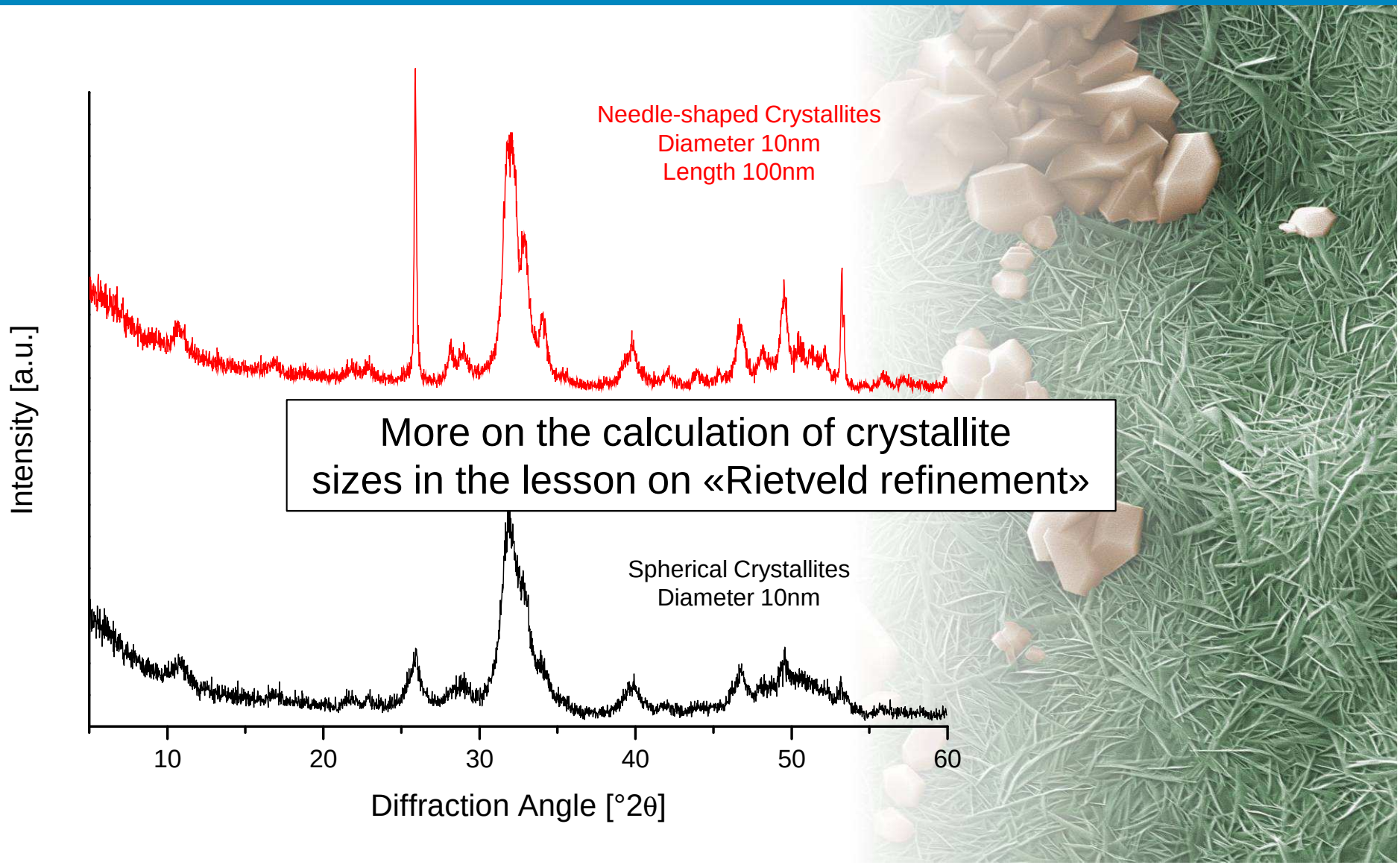
- Excessive peak overlap
- Unusable diffraction pattern



Crystallite Size



Anisotropic Crystallites



Summary: Ideal Particle Size

- Ideal particle and crystallite size: 1–5 µm
- Larger particles: Micro-absorption
- Larger crystallites: Grainy sample

- Caution: High-energy milling (e.g. planetary mill) generates:
  - Lattice defects and strain in the crystal structure
  - Peak broadening due to reduction of crystallite size
  - Amorphous fraction (invisible to XRD)

- Manual milling in agate mortar is usually recommended

Automatic mill for XRD

«Industry standard» for automatic XRD sample milling:

McCrone Micronizing Mill

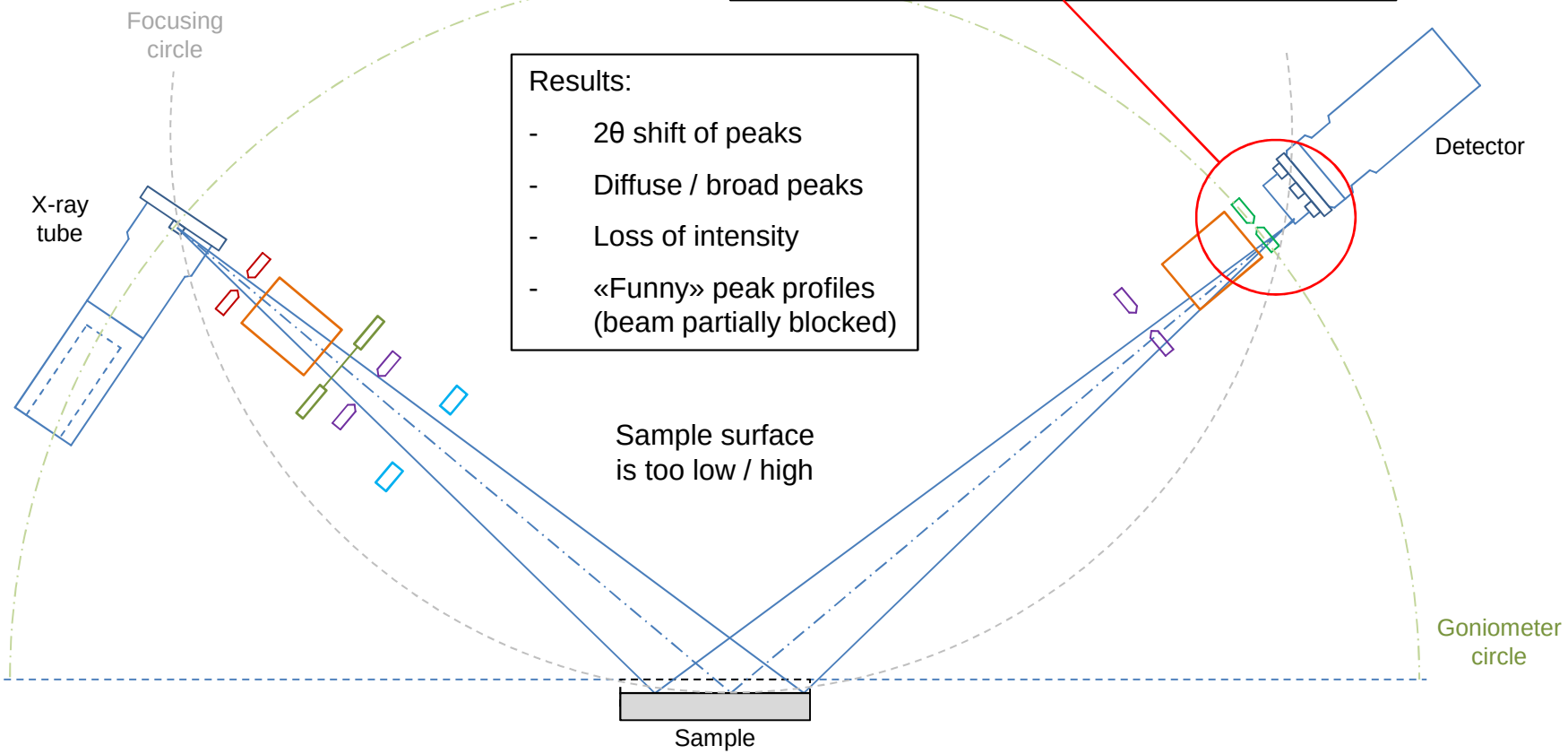
http://www.powderbulksolids.com

Sample Height Displacement

- Focus of diffracted beam is displaced
- Receiving slit / 1D / 2D detector out of focus
- Diffracted beam blocked by optical elements

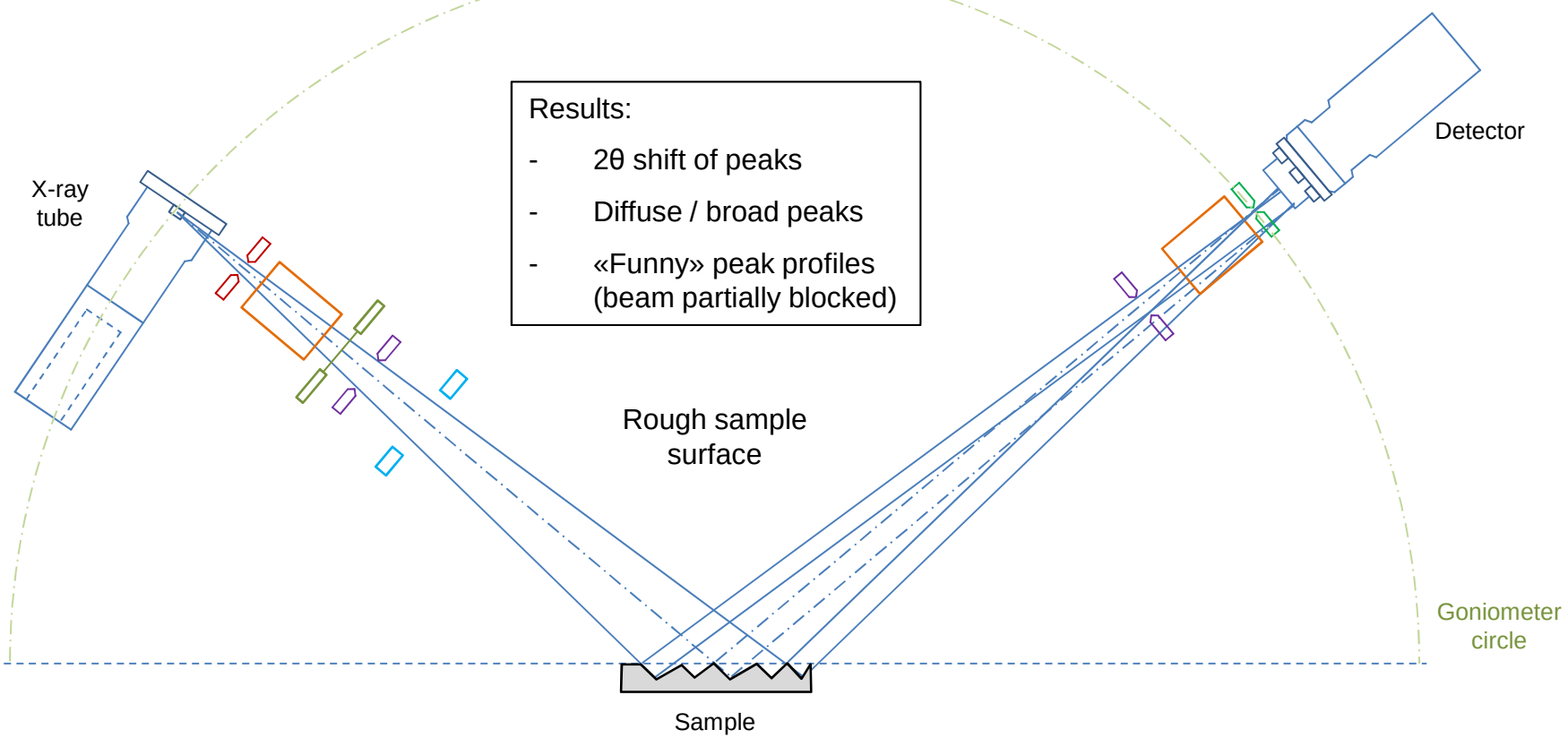
Results:

- 2θ shift of peaks
- Diffuse / broad peaks
- Loss of intensity
- «Funny» peak profiles (beam partially blocked)



Rough Sample Surface

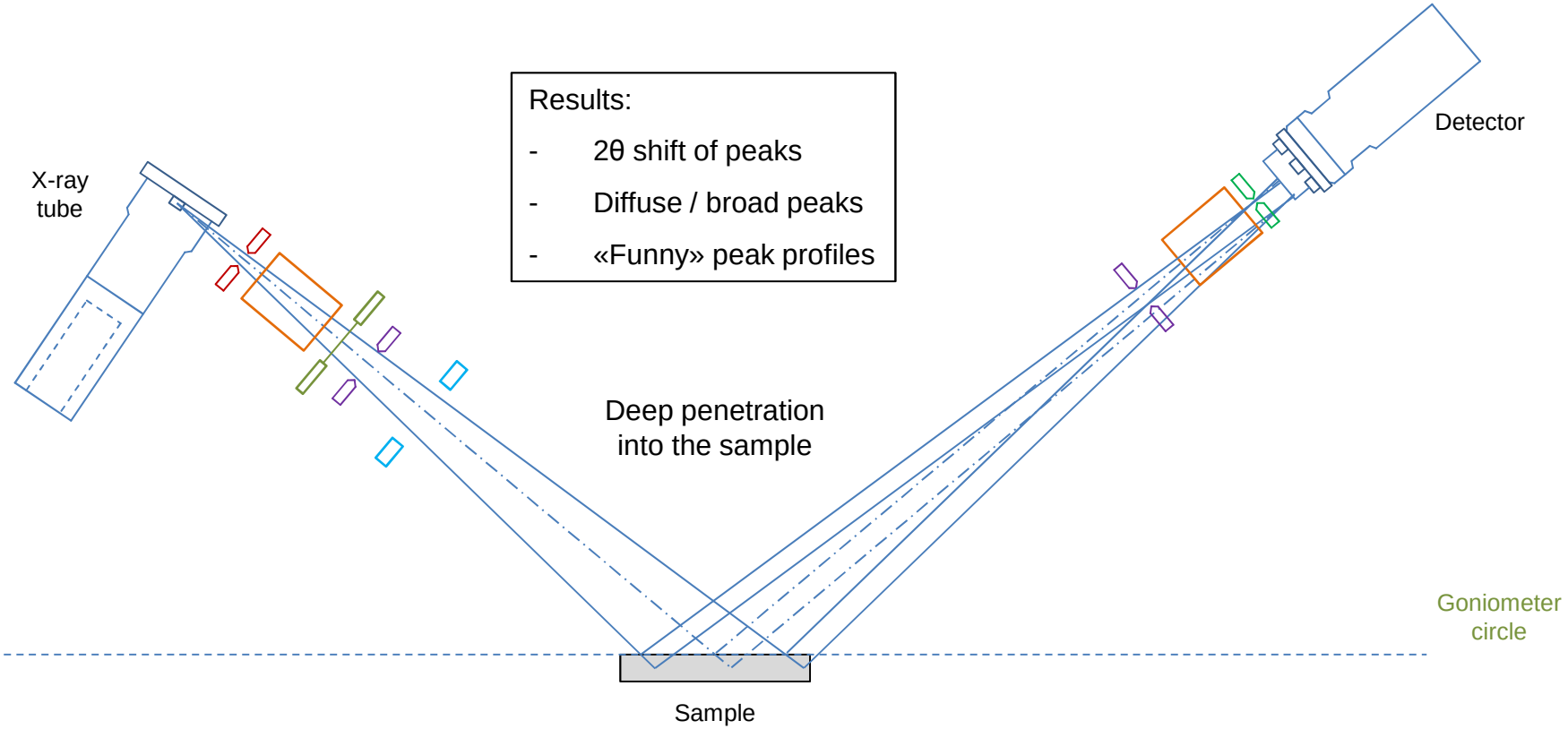
- Diffraction signals from different surface levels
- Focus of diffracted beam is partially displaced
- Receiving slit / 1D / 2D detector out of focus



Sample Transparency

- Diffraction signals from different surface levels
- Focus of diffracted beam is partially displaced
- Receiving slit / 1D / 2D detector out of focus

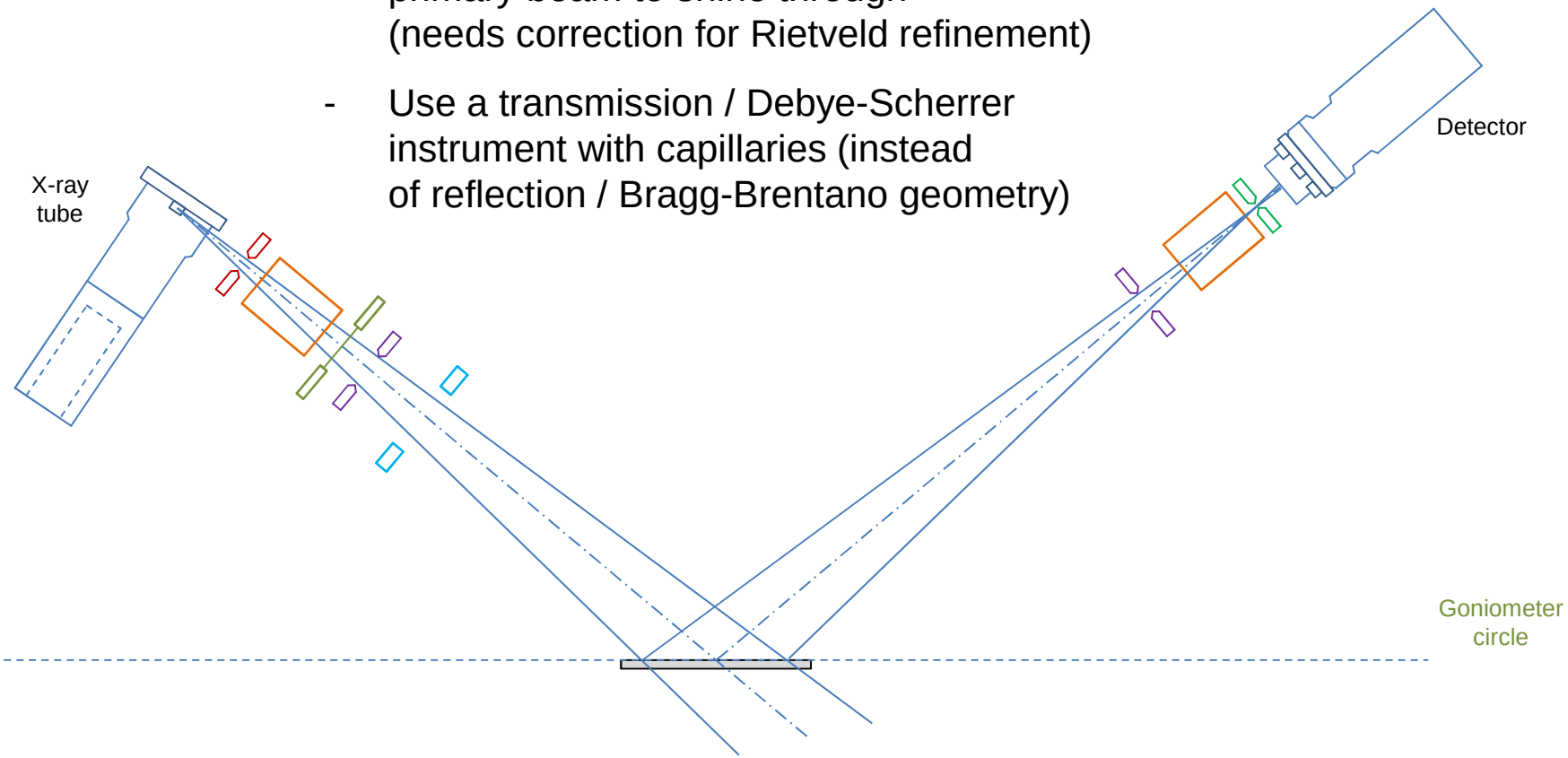
Results:
- 2θ shift of peaks
- Diffuse / broad peaks
- «Funny» peak profiles



Sample Transparency

Possible solutions:

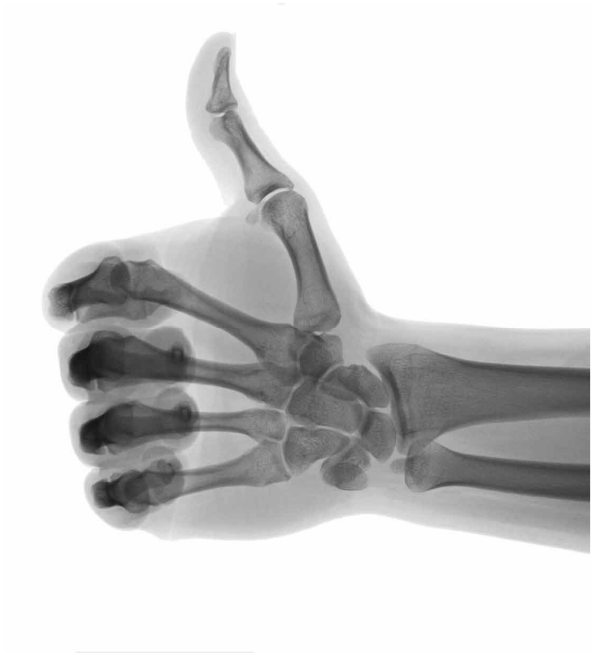
- Use very thin sample, allow the primary beam to shine through (needs correction for Rietveld refinement)
- Use a transmission / Debye-Scherrer instrument with capillaries (instead of reflection / Bragg-Brentano geometry)



Summary: The Perfect Sample

The perfect sample for Bragg-Brentano diffractometers:

- Crystallites and particles of 1-5 µm size
- Perfectly random orientation
- Perfectly flat surface
- Surface precisely centered in the goniometer
- Short penetration depth



Software Download

For tomorrow:

Download software and examples from:

http://www.doebelin.org/nic/xrd

Login name: Riga2013

Password: Rietveld

Software installation sessions:

- Today, 12:00-12:30
- Tomorrow, 08:45-09:15