MSE-238
Structure of Materials

Week 8 - Diffraction

Spring 2025

Marianne Liebi (MX/PSI)

Ecole Polytechnique Fédérale de Lausanne

Overview

Diffraction:

- The scattering vector
- Ewald sphere
- sample types and measurement methods
- influence of imperfect microstructure

mixed with repetition of crystallography on examples

- hard sphere model
- interstitial sites
- crystal symmetry
- crystal planes, family of planes
- quasi-crystal

→(Hammond Chapter 8-10)
→ Phil Willmott, “Introduction to Synchrotron Radiation” Chapter 6

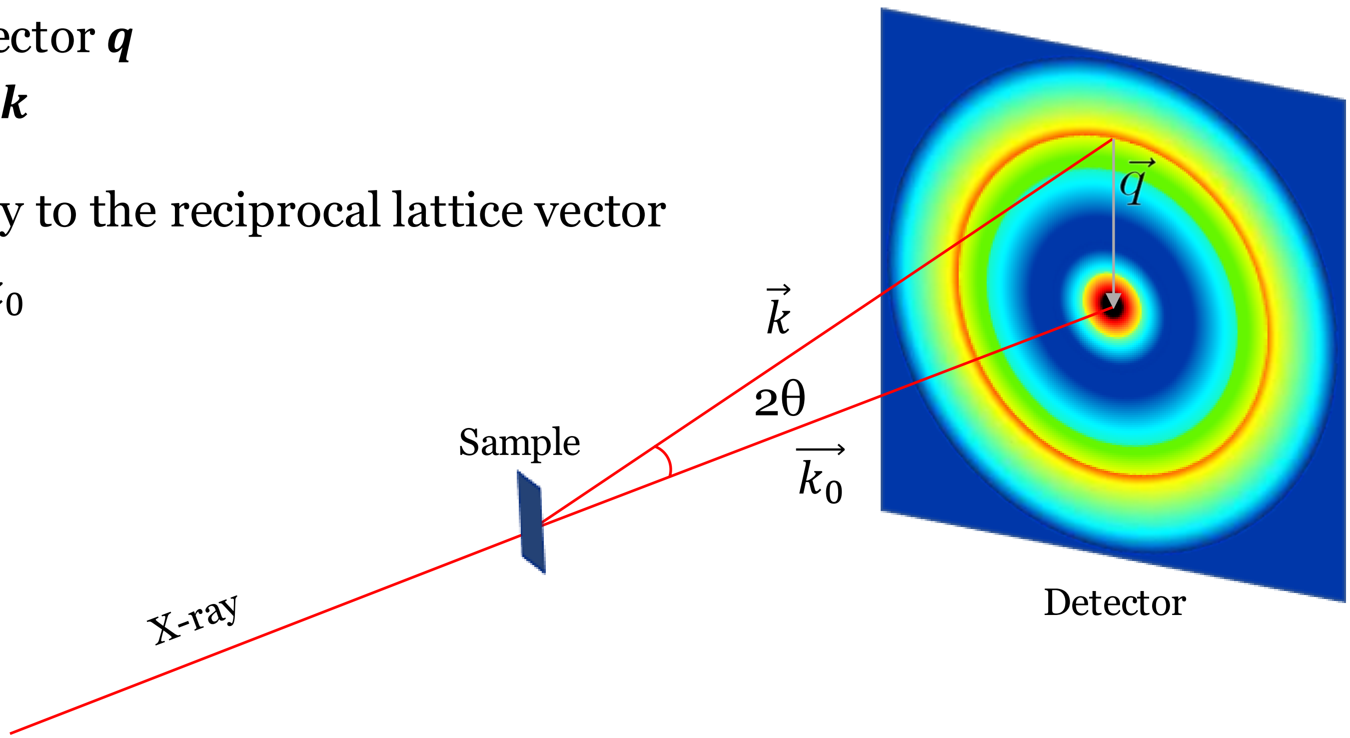
Scattering/Diffraction: the scattering vector

scattering vector $\boldsymbol{q}$

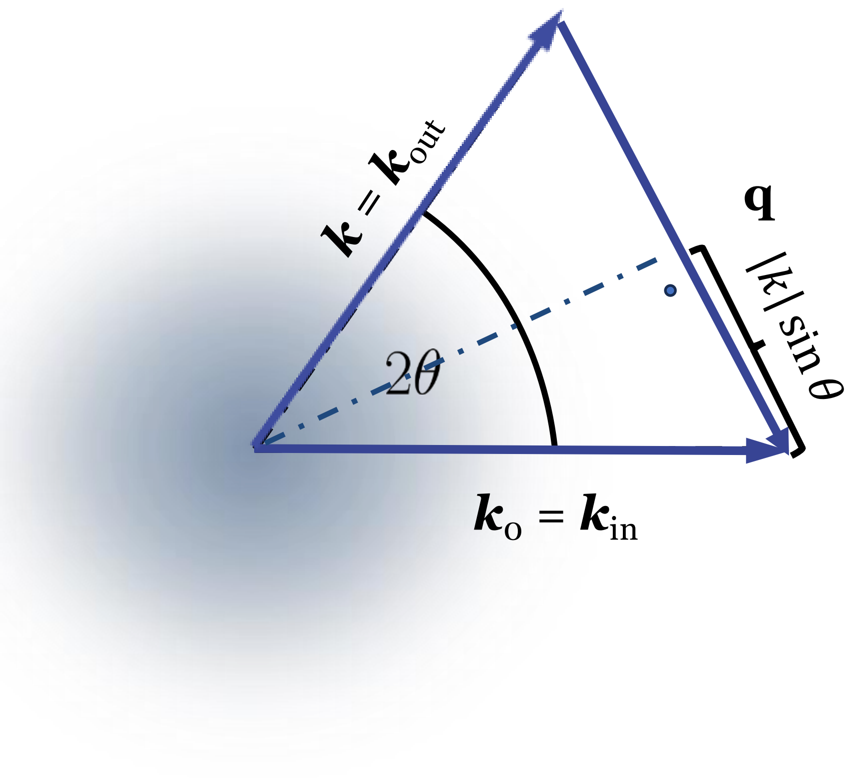
$$\boldsymbol{q} = \boldsymbol{k}_0 - \boldsymbol{k}$$

see similarity to the reciprocal lattice vector

$$\boldsymbol{K} = \boldsymbol{k} - \boldsymbol{k}_0$$



Elastic scattering



wave vector $\boldsymbol{k} = \frac{2\pi}{\lambda}$

elastic scattering: no loss in photon energy but direction of the photon can change with a scattering angle 2θ

$$|\boldsymbol{k}_{in}| = |\boldsymbol{k}_{out}|$$

scattering vector $\boldsymbol{q} = \boldsymbol{k}_0 - \boldsymbol{k}$

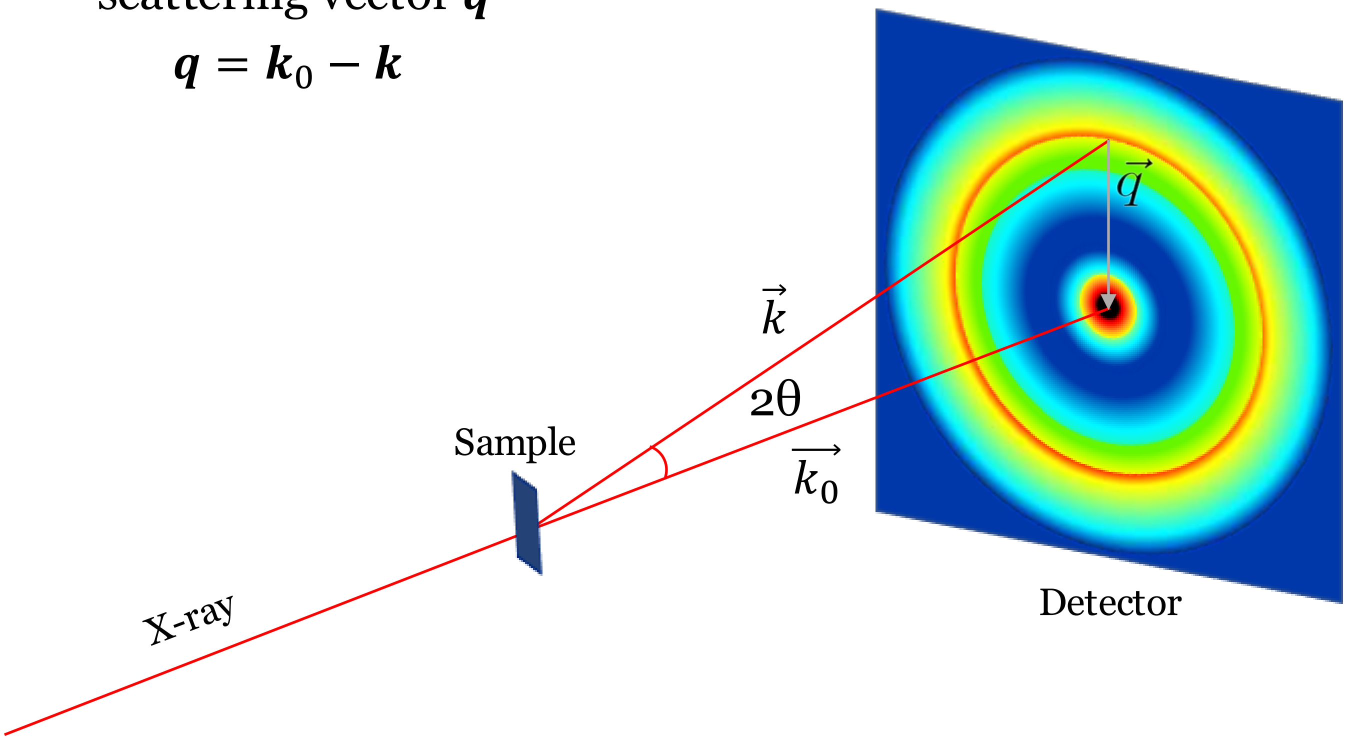
$$q = 2|k| \sin\theta = \frac{4\pi \sin\theta}{\lambda}$$

Scattering/Diffraction

scattering vector $\boldsymbol{q}$

$$\boldsymbol{q} = \boldsymbol{k}_0 - \boldsymbol{k}$$

$$|\vec{q}| = q = \frac{4\pi\sin(\theta)}{\lambda}$$



light λ = 400 to 600 nm
X-ray tube λ = 1 to 2 Å
Cu Kα = 1.5406 Å
synchrotron λ = 0.1 to 5 Å
thermal neutrons λ = 1 to 10 Å
electrons λ = 0.025 Å

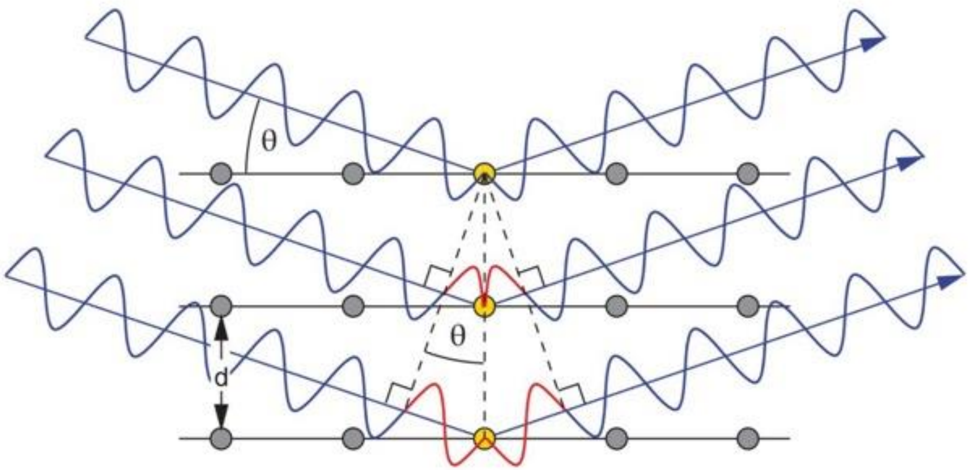
X-ray energy mostly given in keV

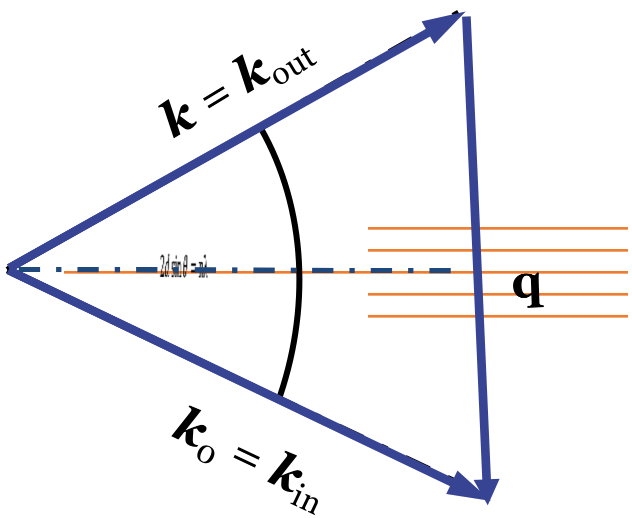
Electronvolt = eV
Energy of an electron after being accelerated from rest in a potential of 1 V
1 eV = 1.6022×10^{-19} J

$E = hc / \lambda$
h is Planck's constant (6.6261×10^{-34} Js)
c is the speed of light (2.9979×10^{8} m/s).

λ [Å] = 12.3984/E [keV]

Bragg law





The scattering vector $\boldsymbol{q}$ always lies perpendicular to the scattering planes if the Bragg condition is fullfilled

the angle subtended by $\mathbf{k}_{in} = 2\pi/\lambda$ (or $\mathbf{k}_{out}$) and the scattering planes is θ.

The scattering angle is 2θ

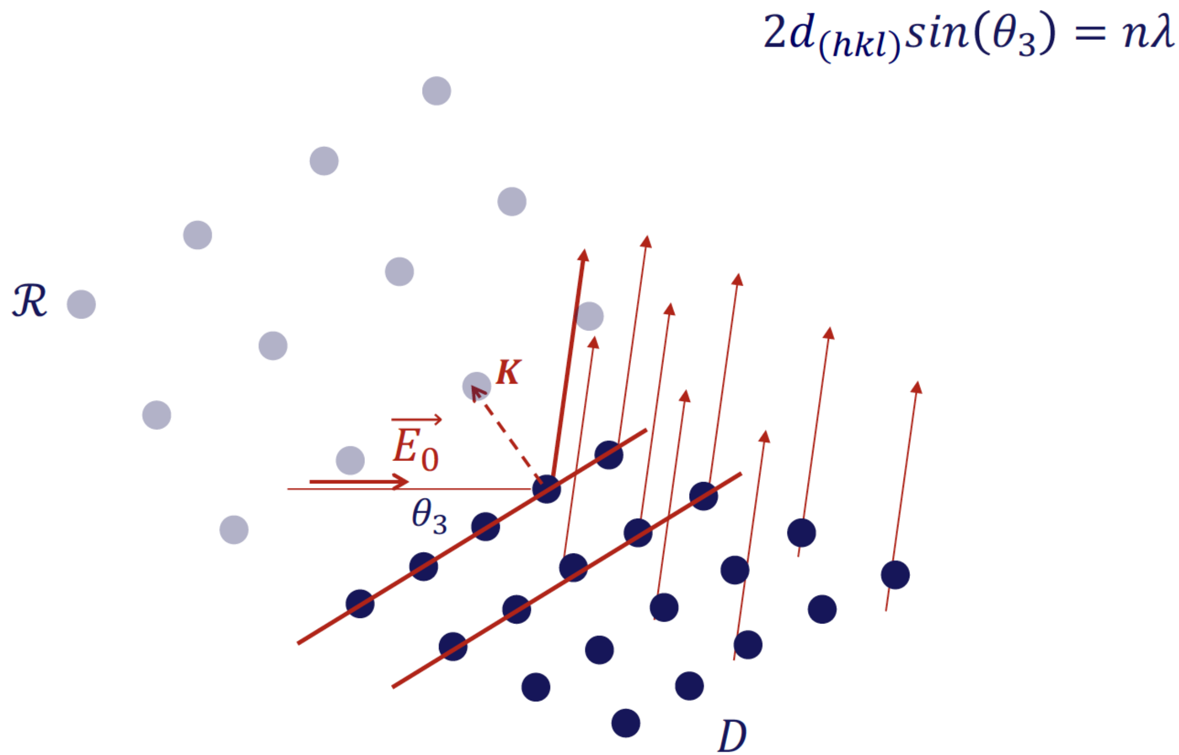
Bragg law: $2d \sin\theta = n\lambda$

$$|\boldsymbol{q}| = q = \frac{4\pi \sin(\theta)}{\lambda}$$

$$d = n\frac{2\pi}{q}$$

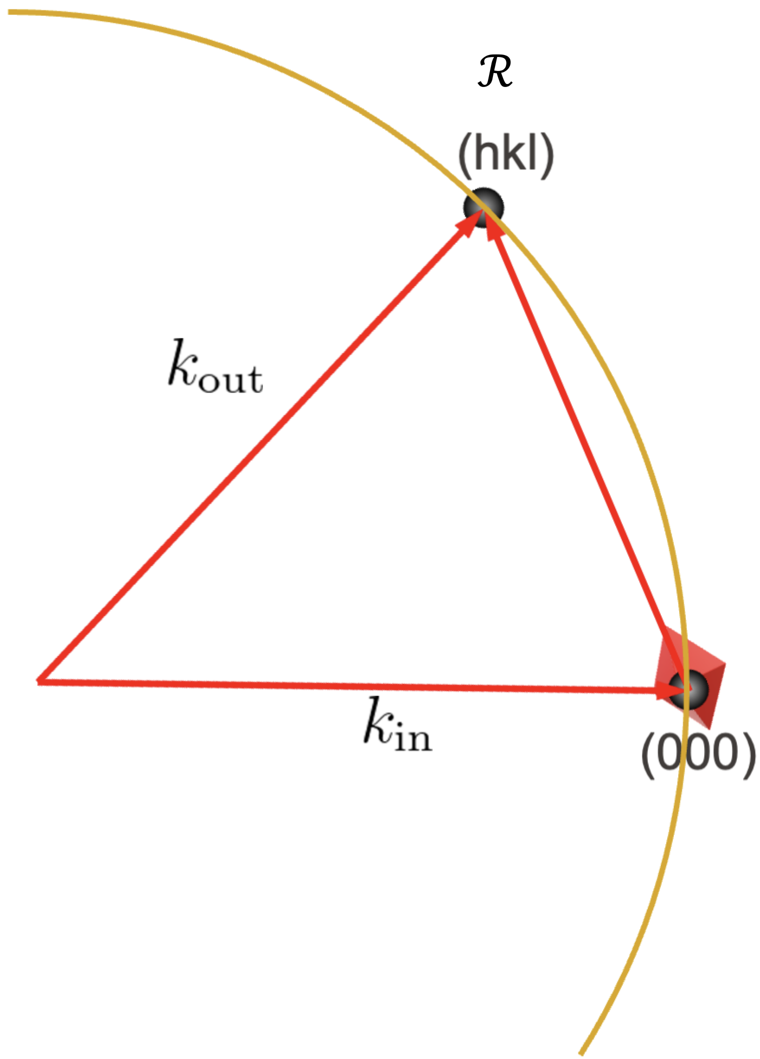
independent of wave length (experimental condition)

Repetition: The reciprocal space lattice



reciprocal lattice vector $\boldsymbol{K} = \boldsymbol{k} - \boldsymbol{k}_0$

Bragg condition and the Ewald sphere



elastic scattering: $|\boldsymbol{k}_{in}| = |\boldsymbol{k}_{out}| = 2\pi/\lambda$

To see a diffraction peak @ (hkl) :

the Bragg points (000), which is at the position of the direct incoming beam

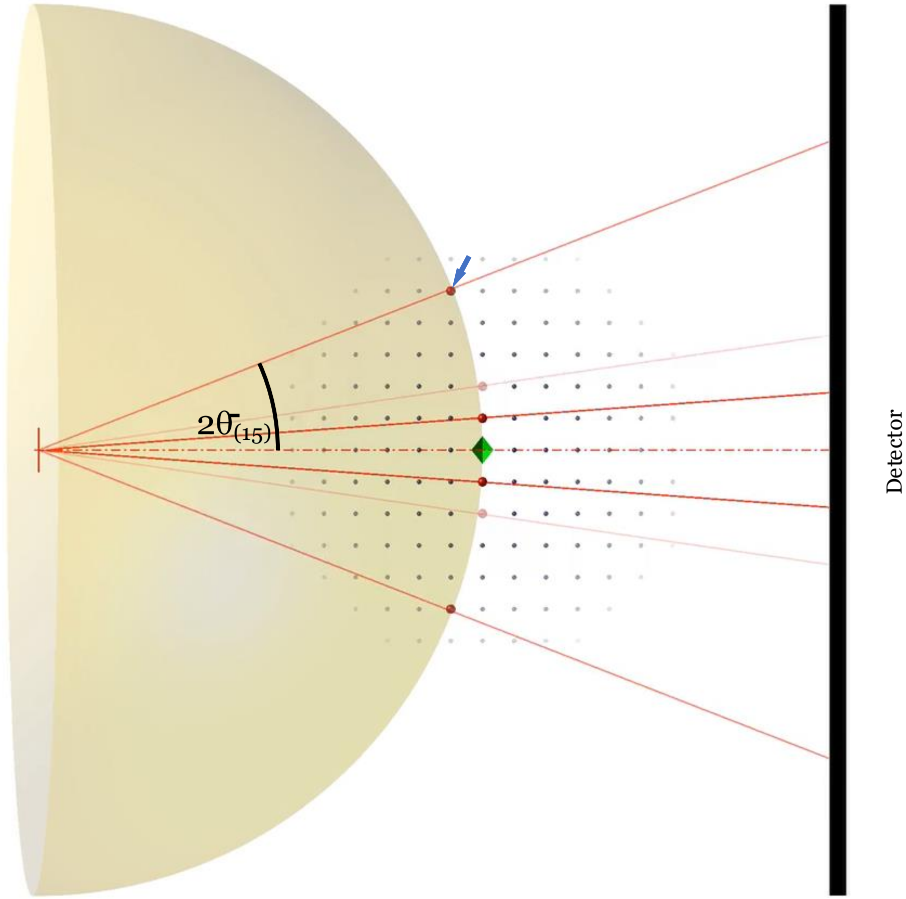
and the Bragg point (hkl) from the reciprocal space lattice

must lie on a sphere of radius equal |k| (the wave vector of the experiment) in reciprocal space $\mathcal{R}$, the so called Ewald sphere

Radius of Ewald sphere: X-rays vs. electrons?

The Ewald sphere

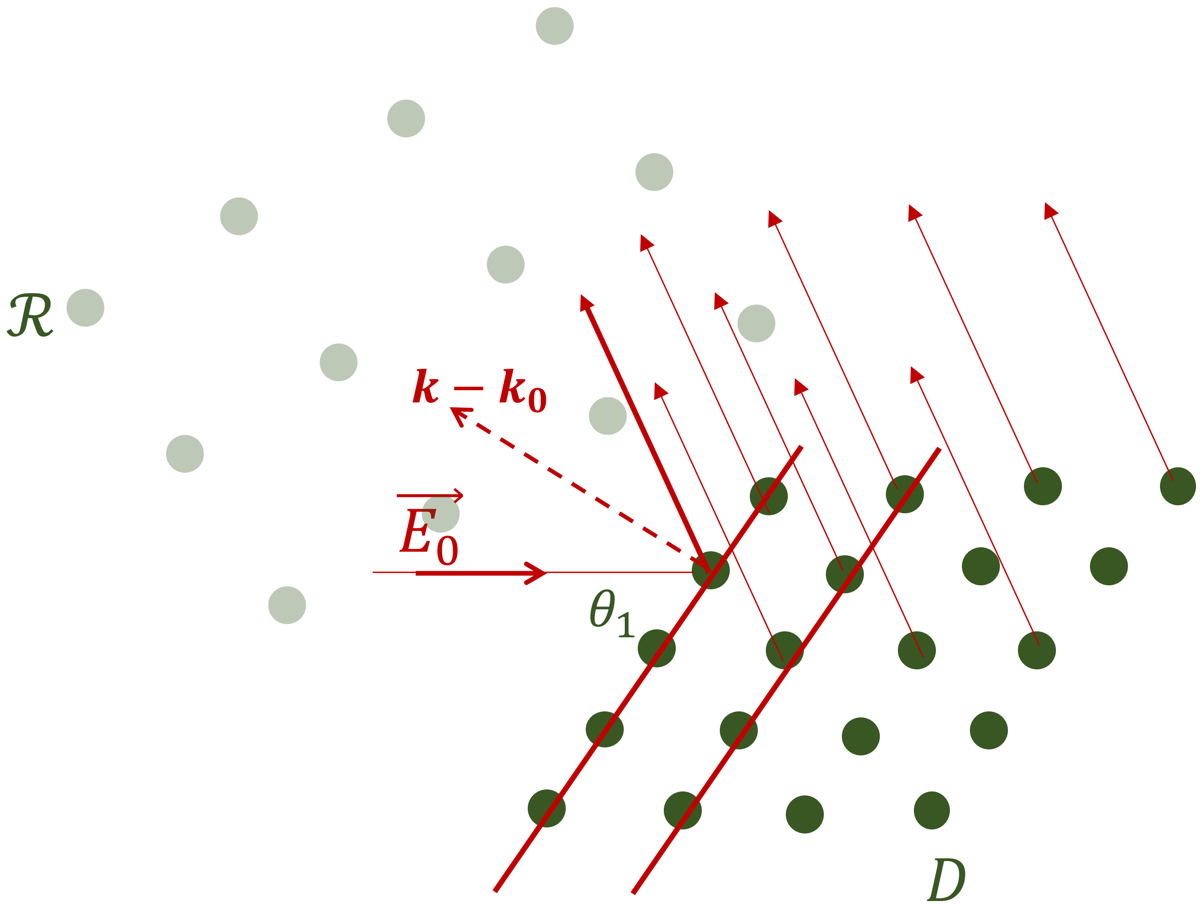
Bragg law defines on a purely geometrical basis for which angles constructive interference **can** occur



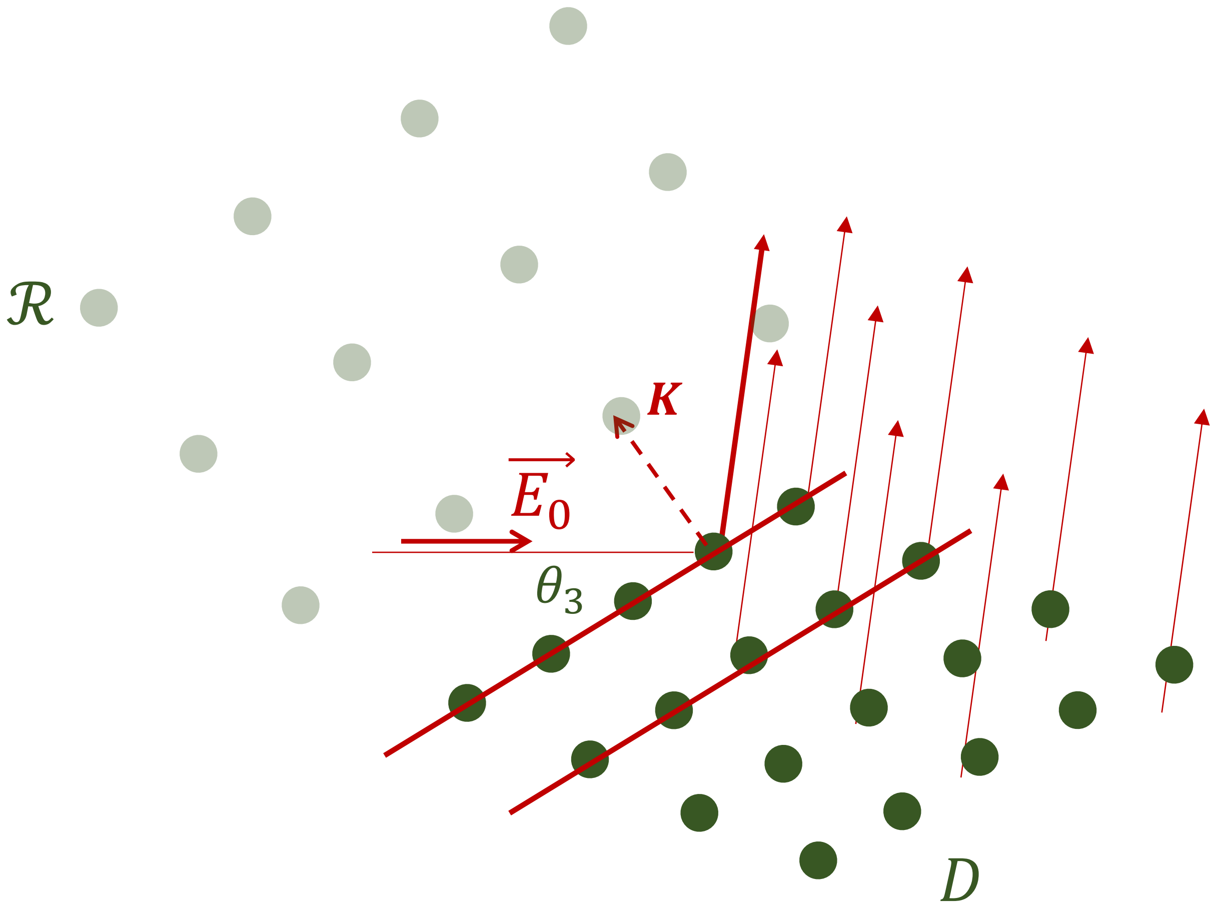
Philip Willmott: Synchrotron and X-ray Free Electron Laser (Part 2)

Sample types

$$2d_{(hkl)} sin(\theta_1) \neq n\lambda$$

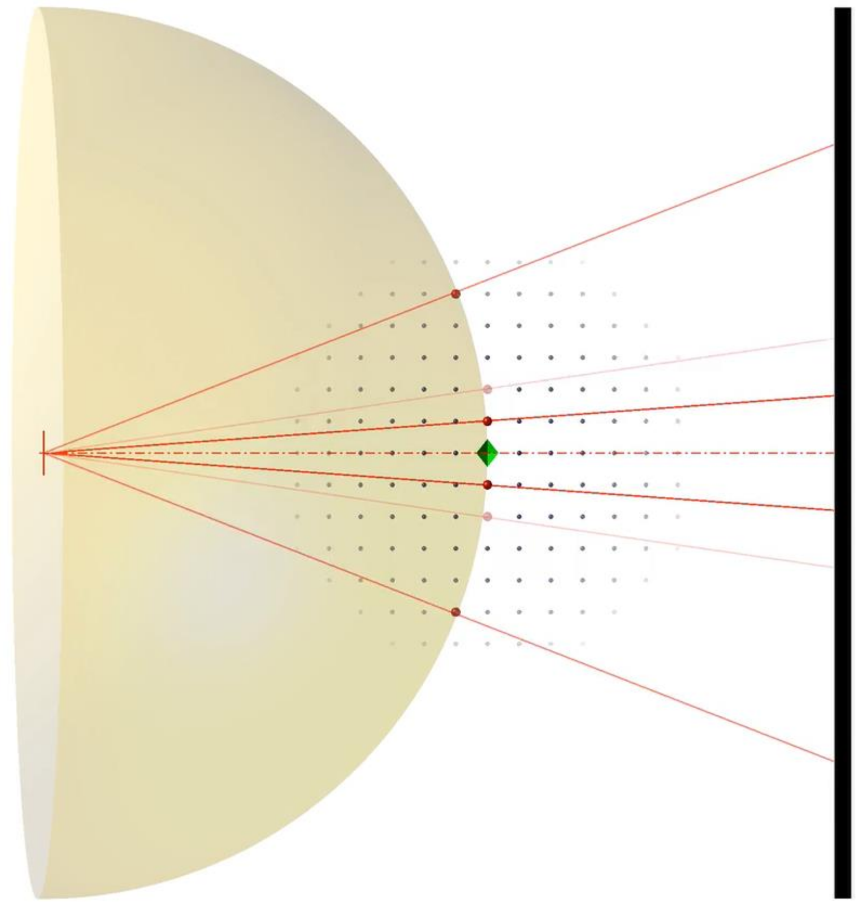


$$2d_{(hkl)}sin(\theta_3) = n\lambda$$



Single crystal diffraction – rotation method

- monochromatic radiation is used
- By rotating the crystal around an axis perpendicular to the incident beam (ϕ), diffraction maxima pass through the surface of the Ewald sphere and are registered on a 2D x-ray detector

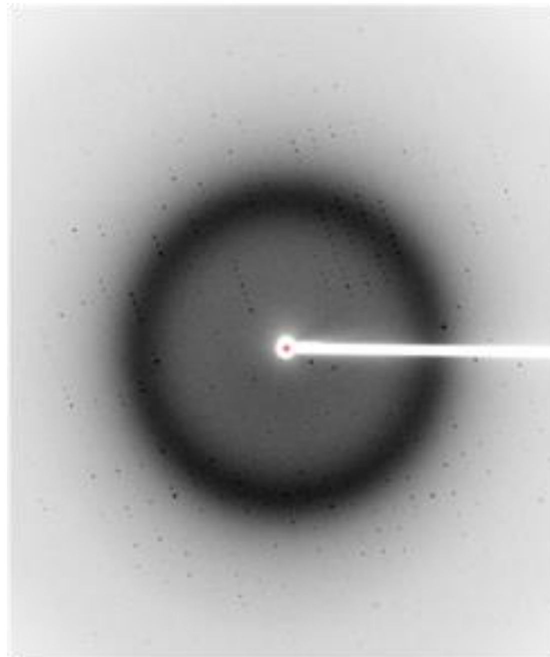


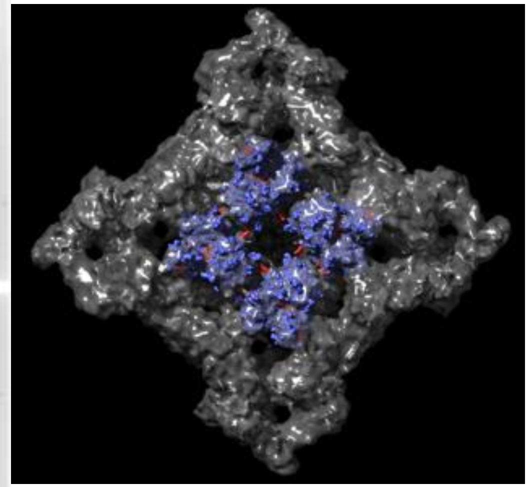
by Phil Willmott

Application: protein crystallography

study the three-dimensional structure of biological macromolecules.

Data collection: wave length = 0.097nm, Canadian Light Source - 1 second per frame,
total of ~360 frames,
step size 0.5 degrees

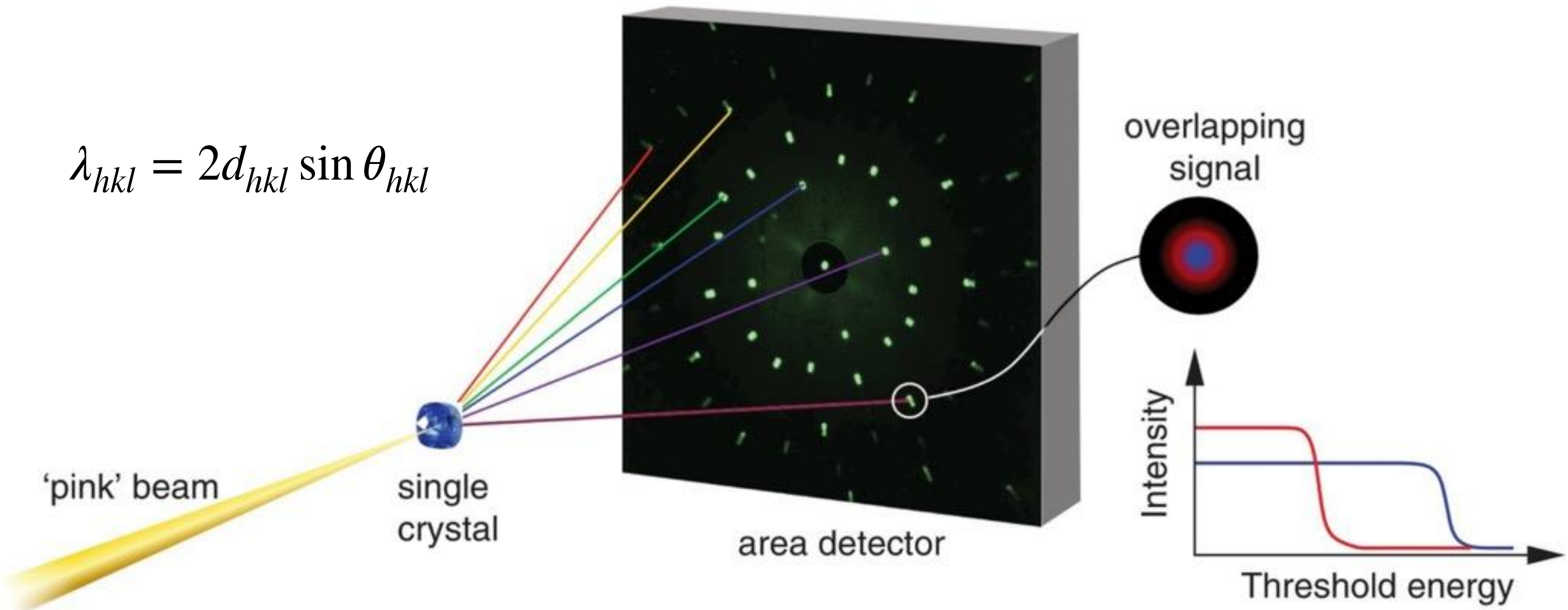




Courtesy: F. Van Petegem, UBC, Canada

to reach higher resolution in the structure determination one needs....

Single crystal diffraction – Laue diffraction



- Pink beam: many wavelengths
- Bragg equation fulfilled for multiple combinations of d and θ

by Phil Willmott

Single crystal diffraction – Laue diffraction

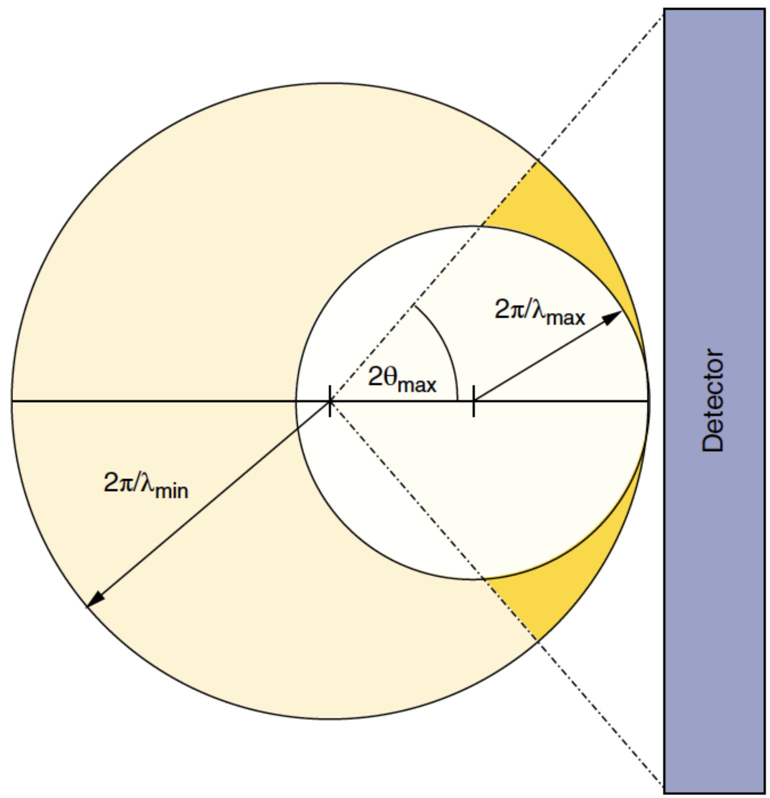
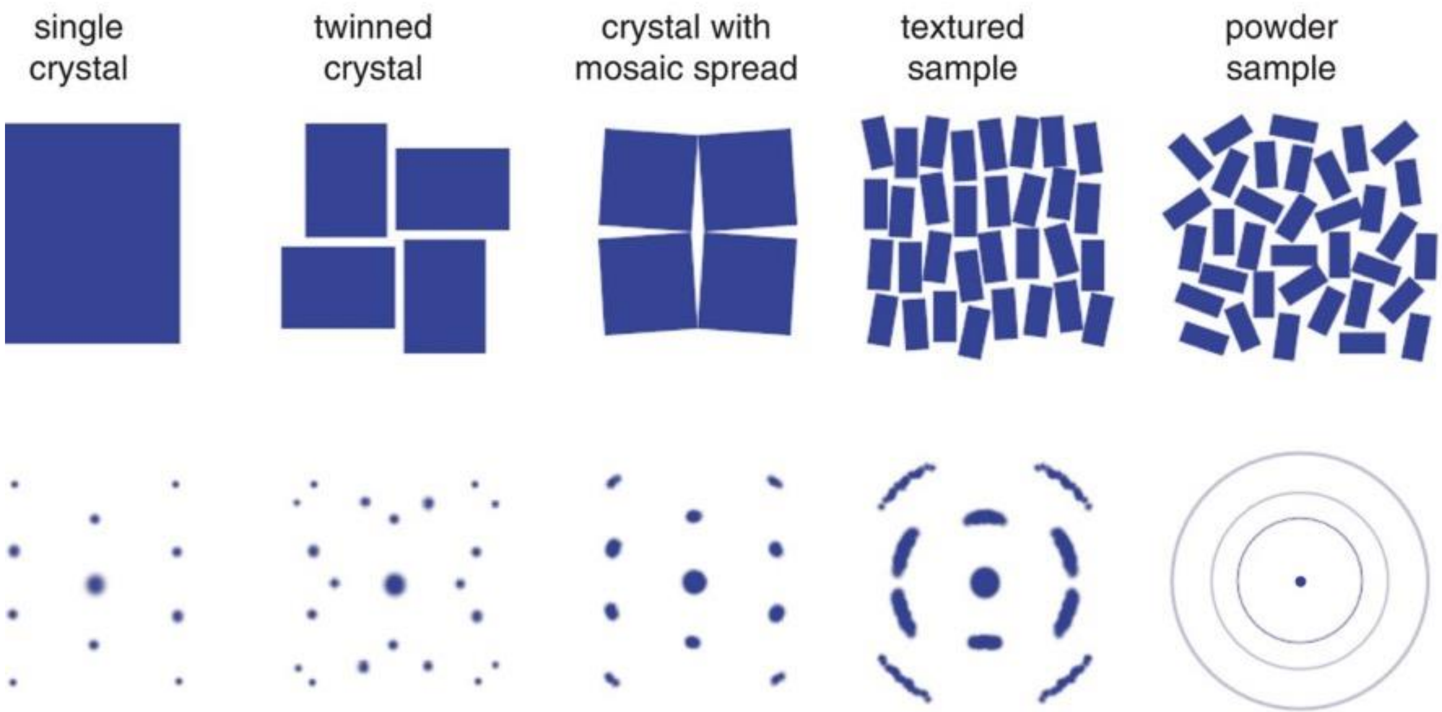


Figure 6.31 The volume of reciprocal space that can be simultaneously accessed in Laue diffraction, shown here in bright yellow, depends on the range of photon energies of the polychromatic beam and the maximum angle that can be subtended by the area detector.

Sample types



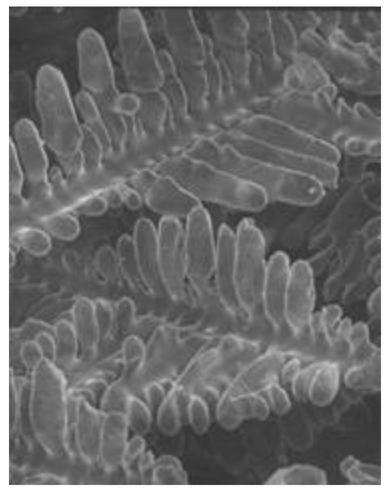
Material structure?

- Atomic structure
    - crystalline vs. amorphous
- Solid materials: Structures at different length scales

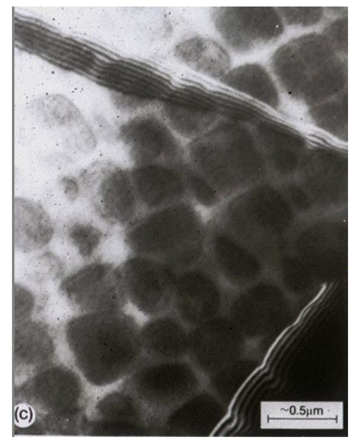
Example: metal

Part of a turbine - Ni
(10 cm)

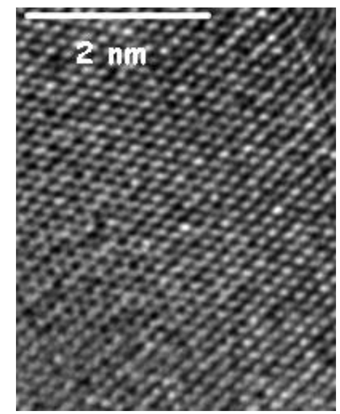
Grains
(mm)



Dendrites
(10-100 mm)



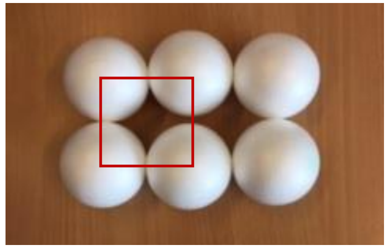
Alloys Ni_3Al
(10-100 nm)

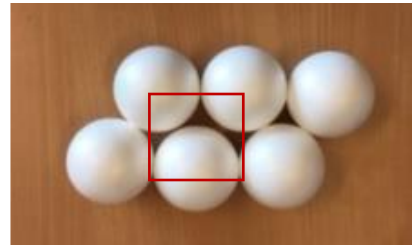


Atoms
(0.1 nm)

The hard sphere model

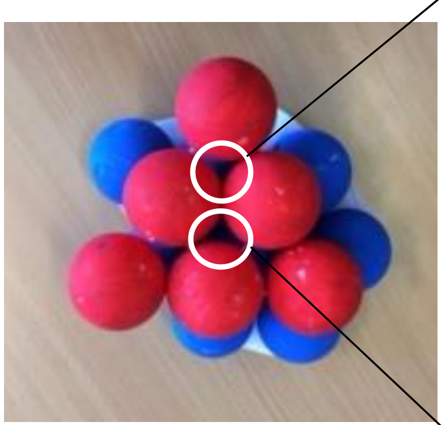
- 2D configuration:

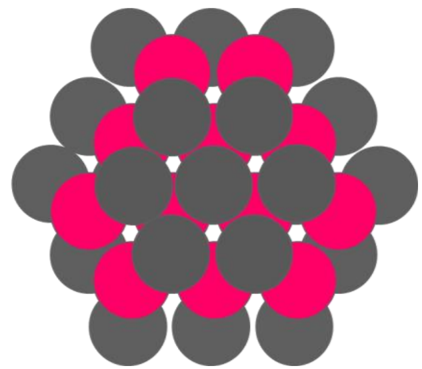




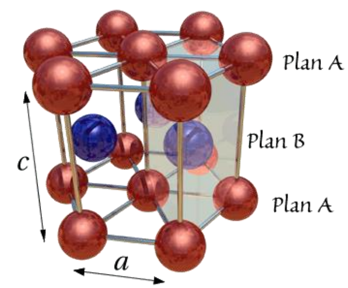
- 3D configuration:

2 possibilities:

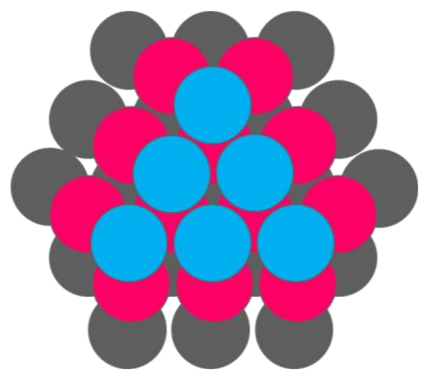




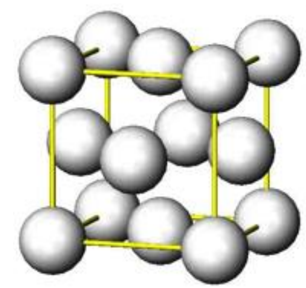
A-B-A



Hexagonal Compact



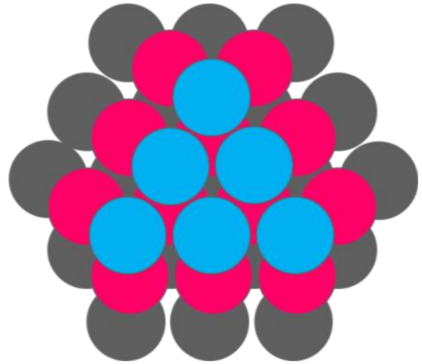
A-B-C



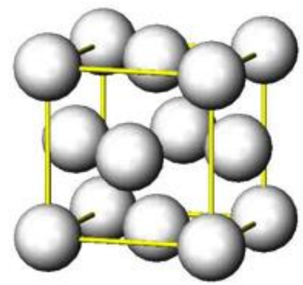
Face-centered Cubic

(= cubic-closed packed)

FCC structure as hard sphere model

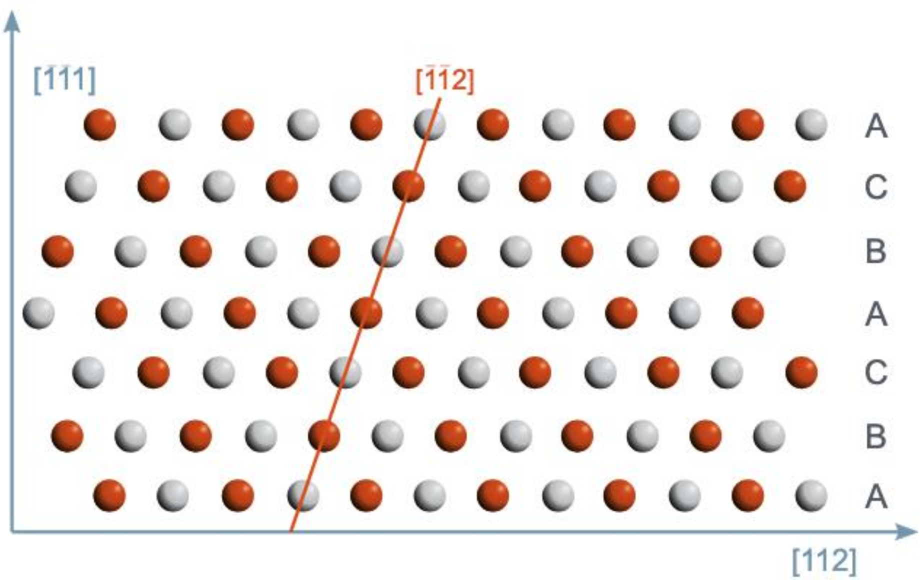


A-B-C

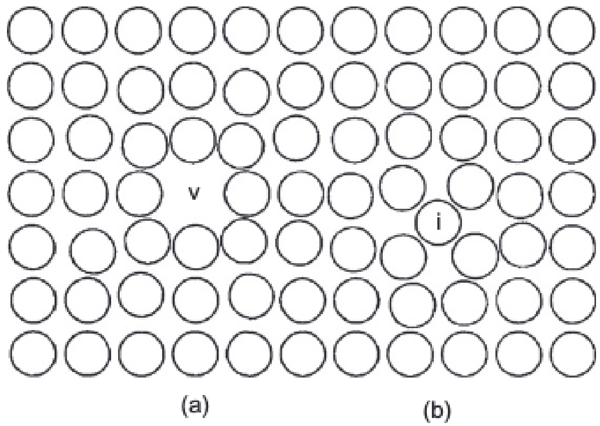


Face-centered Cubic

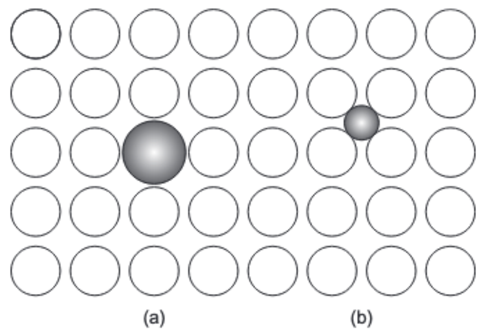
(= cubic-closed packed)



Single crystals: defects!

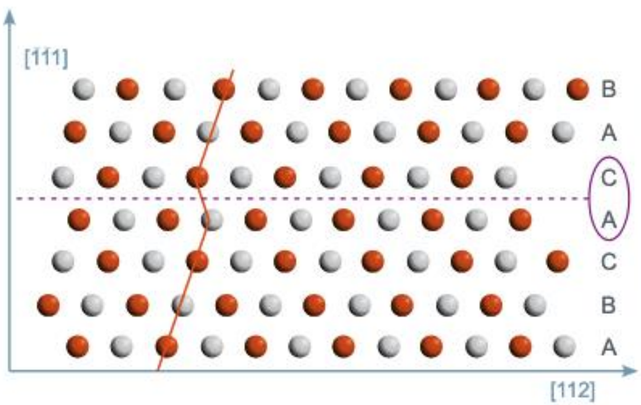


point defects in a simple cubic crystal

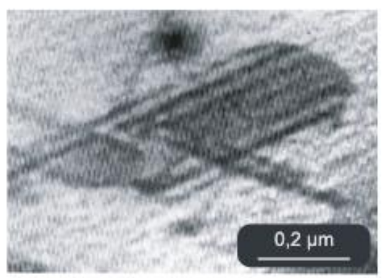


impurities

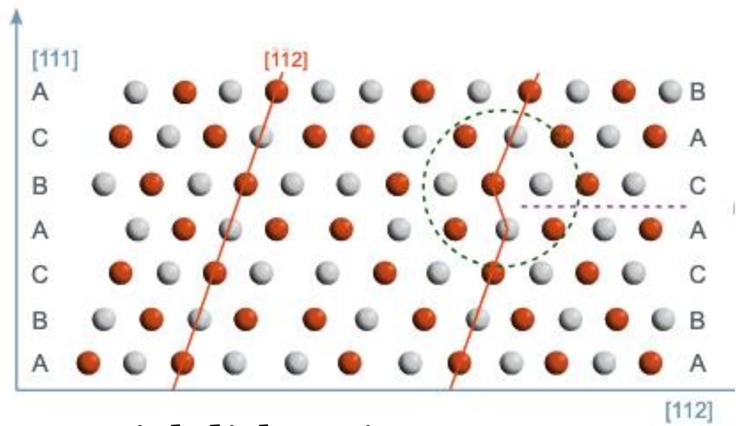
Hull, D. & Bacon, D. J. Defects in Crystals. *Introd. to Dislocations* (2011)



planar defect: stacking fault



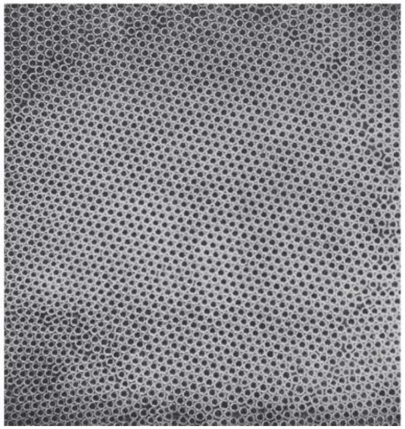
https://nte.mines-albi.fr/



partial dislocation

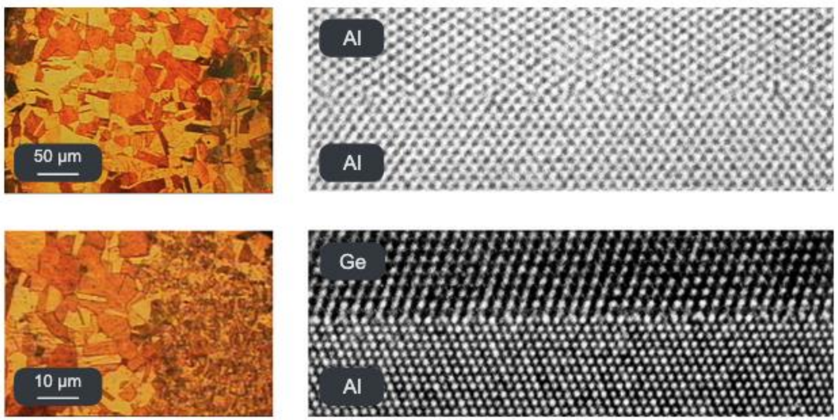
Polycrystalline material grain boundaries

grain boundaries



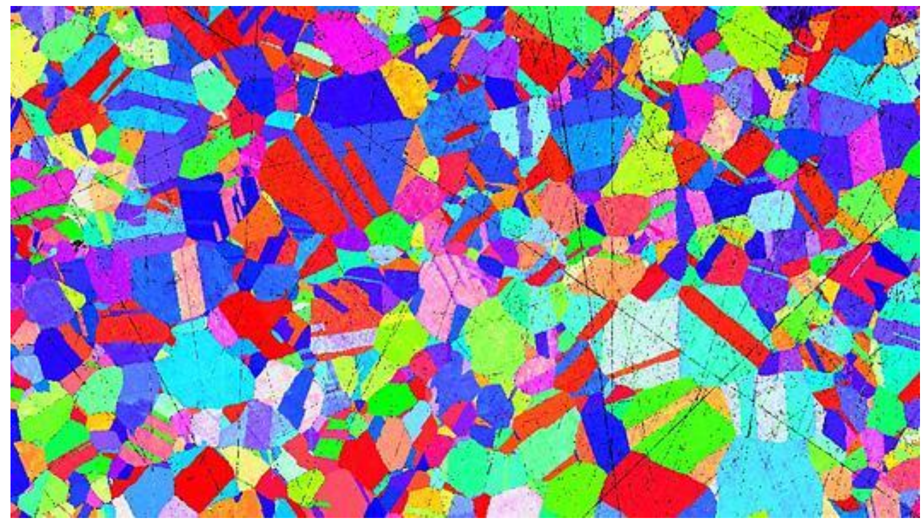
grain boundaries are both sources and traps for point defects and dislocations. Grain boundaries also play an important role in plastic deformation as they can induce dislocations under the action of a stress and constitute as well obstacles to the movement of dislocations.

Hull, D. & Bacon, D. J. Defects in Crystals. *Introd. to Dislocations* (2011)



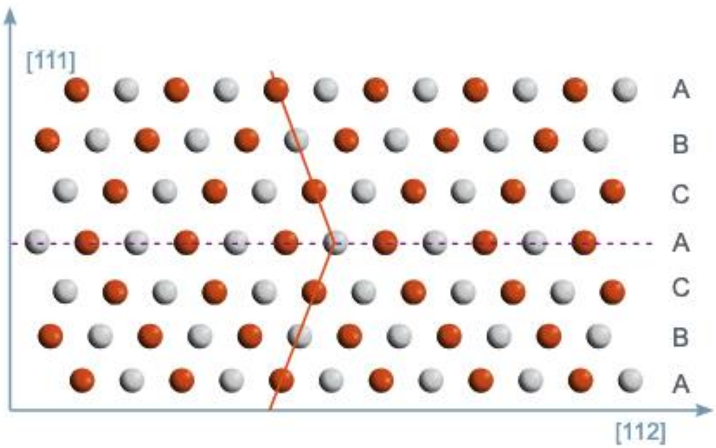
Optical micrographic views of a stainless steel showing grains and grain boundaries constituting (left) and grain boundaries (right) viewed using a TEM (interface between aluminium and -aluminium at top; and aluminium and-germanium at bottom).

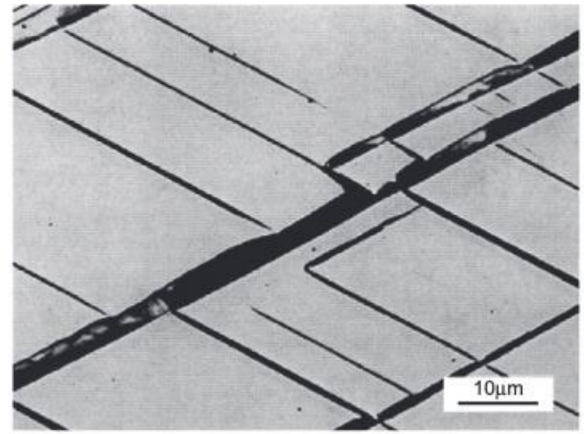
https://nte.mines-albi.fr/



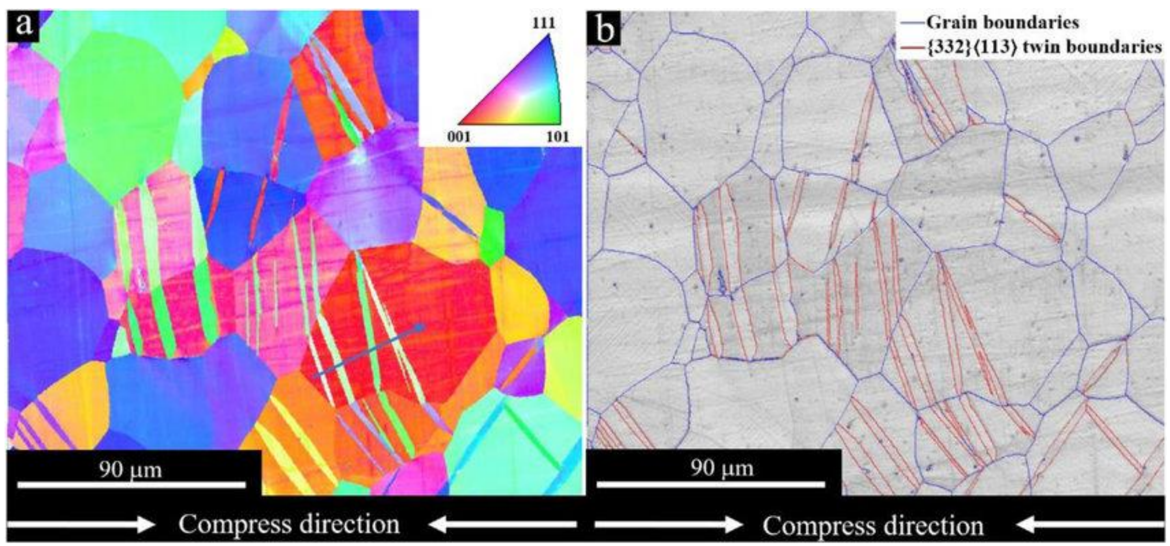
electron back scatter diffraction (EBSD) shows different orientations of grains

Twins





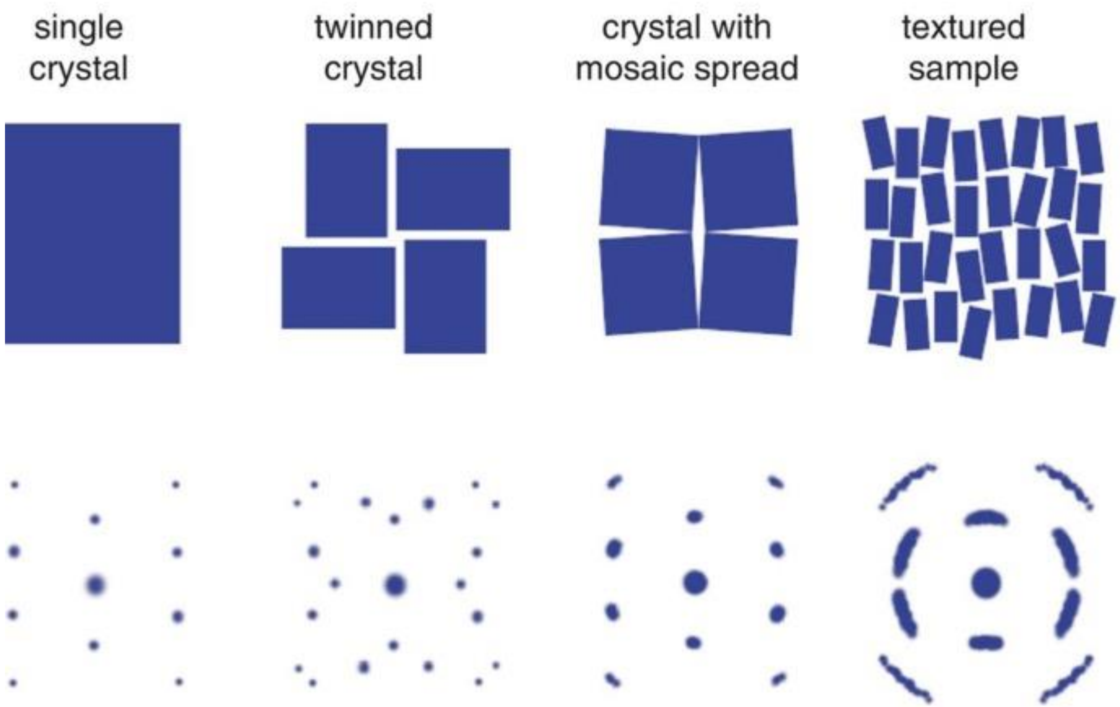
deformation twins in silicon iron



Yang et al. J. of Materials Science & Technology 73 (2021) 52-60

electron back scatter diffraction (EBSD)

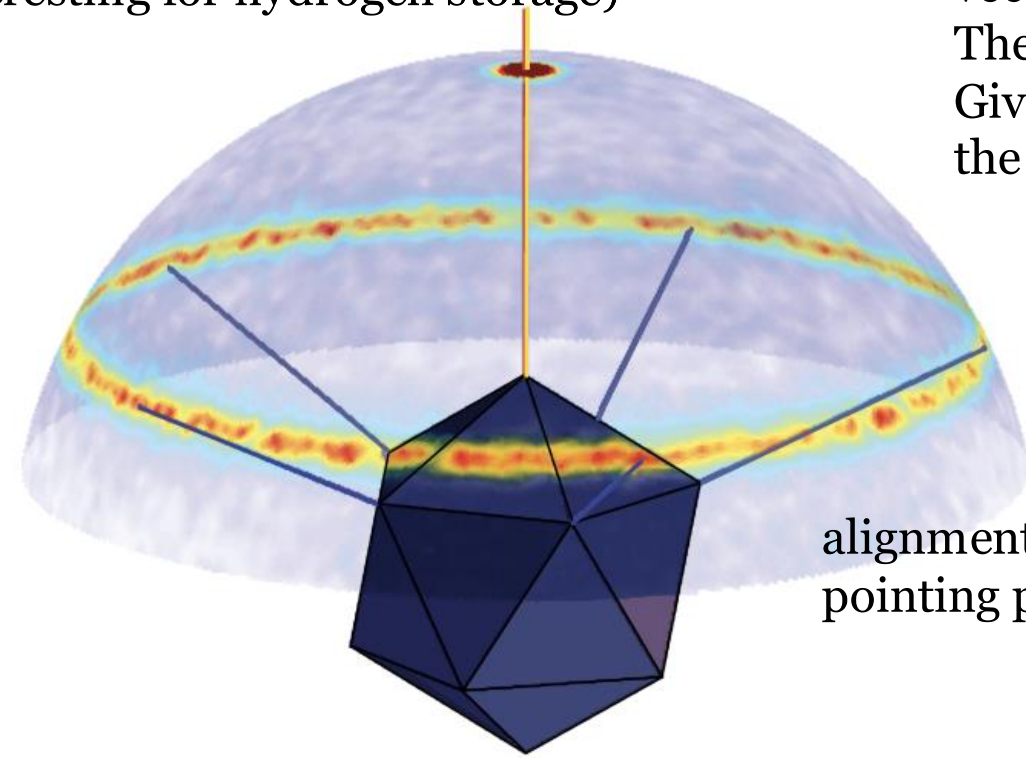
Sample types



Textured sample and pole figure

Ti-Ni-Zr alloy thin films
(interesting for hydrogen storage)

Given a specific set of reciprocal lattice vectors, *{hkl}*
The pole figure $P_{hkl}(q)$
Gives the probablity of finding that plane in the direction, q

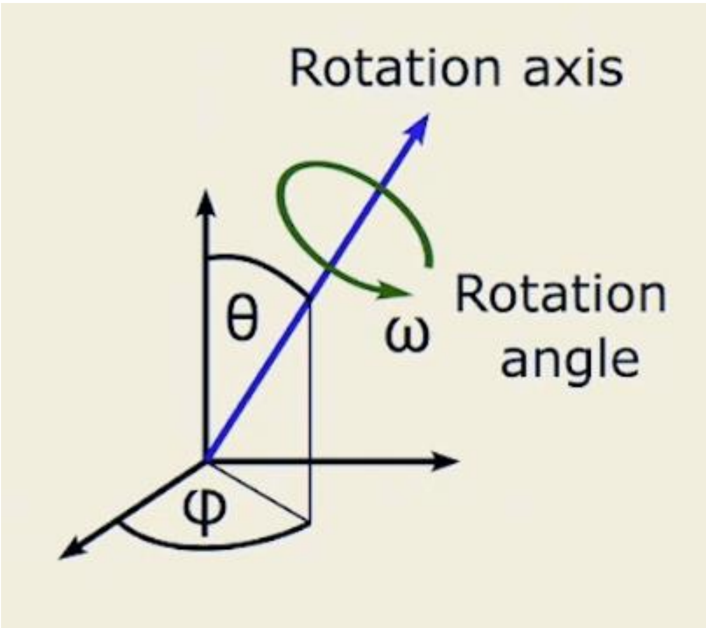


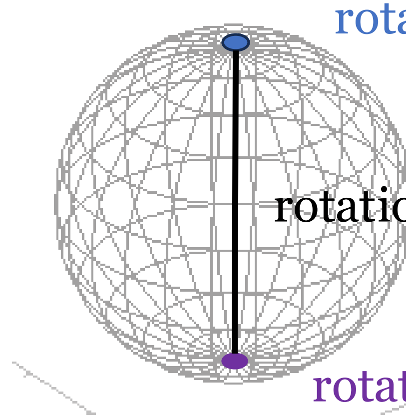
alignment of one of the symmetry axis pointing perpendicular out of the thin film

illustrated here is the structure of a icosahedron which has a five-fold symmetry

→ is this a crystal system?

Textured samples: orientation information



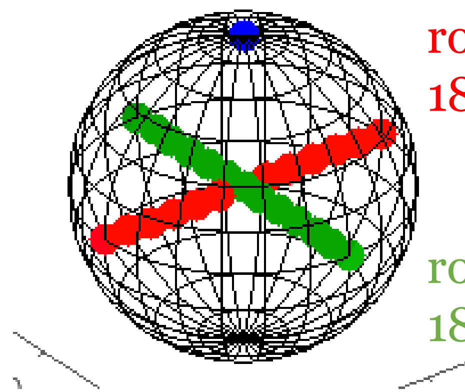


rotation around z-axis by 180°

rotation axis = z-axis

rotation around z-axis by -180°

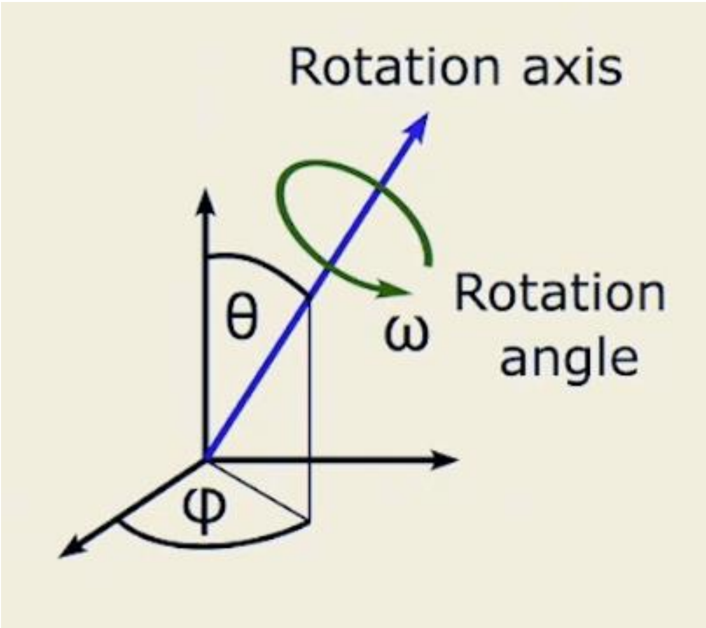
axis-angle representation of 3D orientation
one vector defining the axis, and an angle defining the rotation around it

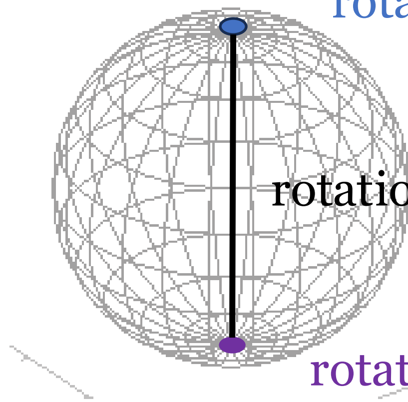


rotation around x-axis from -180° till 180° in steps of 30°

rotation around y-axis from -180° till 180° in steps of 30°

Textured samples: orientation information

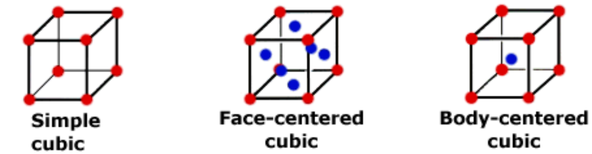
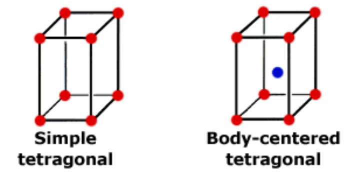
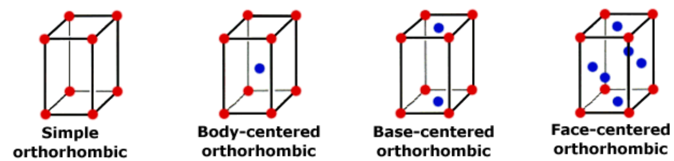
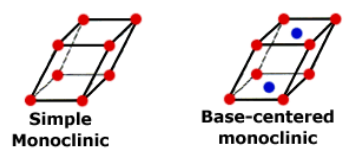




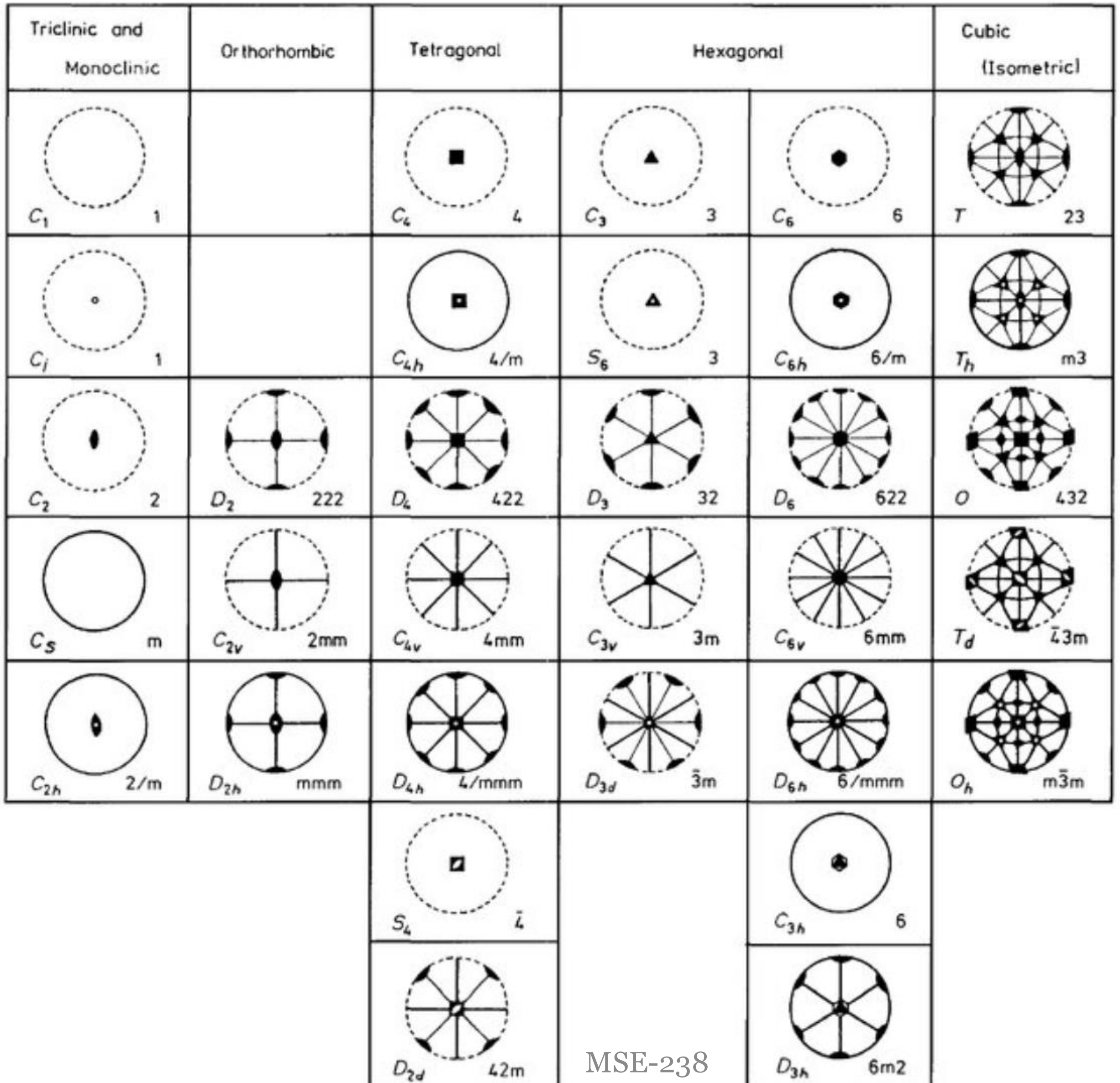
axis-angle representation of 3D orientation
one vector defining the axis, and an angle defining the rotation around it

if there is a two-fold **symmetry** around that axis, rotation of 0° and 180° and -180° are equivalent!

what defines if certain orientations are equivalent?

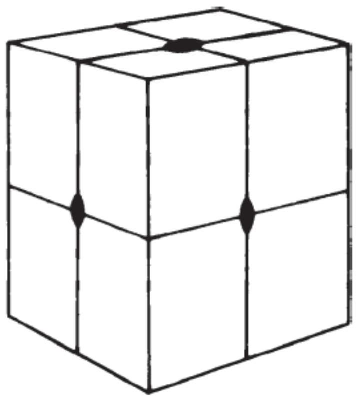
crystal system		Bravais lattices	defining symmetry
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^o$		4x 3-fold axis 3x 4-fold axis
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^o$		4-fold axis
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^o$		3x 2-fold axis
Trigonal or rhombohedric	$a = b = c$ $\alpha = \beta = \gamma \neq 90^o$		3-fold axis
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^o;\ \gamma = 120^o$		6-fold axis
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^o \neq \beta$		2-fold axis
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$		1-fold axis

32 Point groups in 3D



Point symmetry elements examples

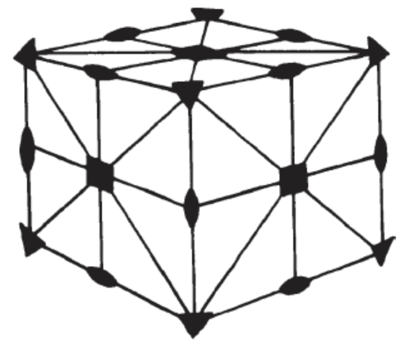
orthorhombic



→ 3 times 2-fold axis, perpendicular to the faces

→ three mirror planes parallel to faces planes

cubic



→ highest symmetry, makes it hard to see!

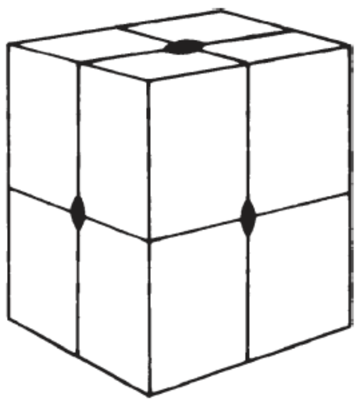
→ 3 times 4-fold axis perpendicular to the faces
→ 4 times 3-fold axis between opposite cube corners
→ 6 times 2-fold axis between opposite center of edges

9 mirror planes
→ 3 parallel to faces planes
→ 6 parallel to the face diagonals

plus center of inversion and rotoinversions!

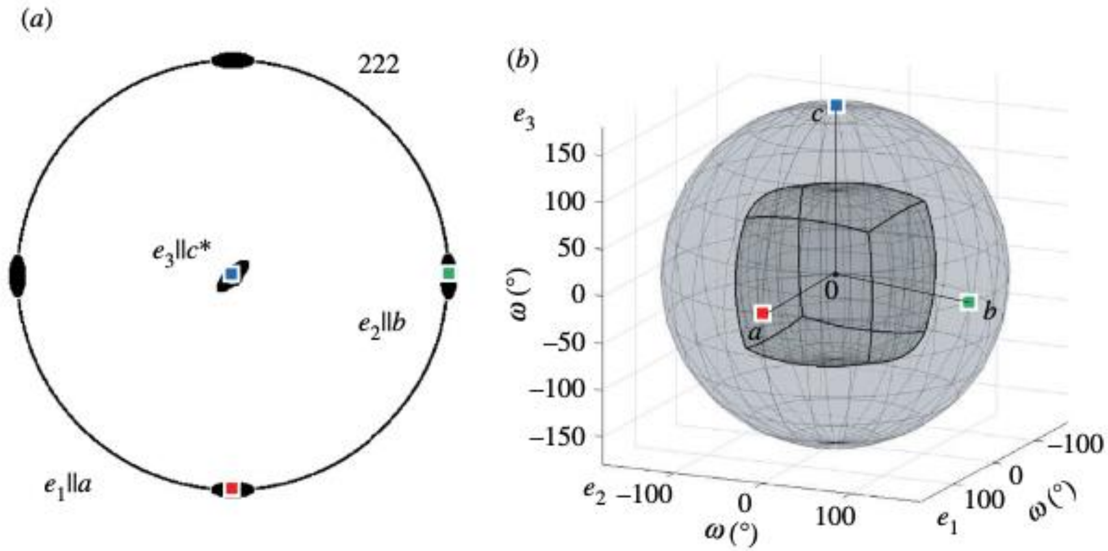
Orientation of a crystal and crystal symmetry

orthorhombic



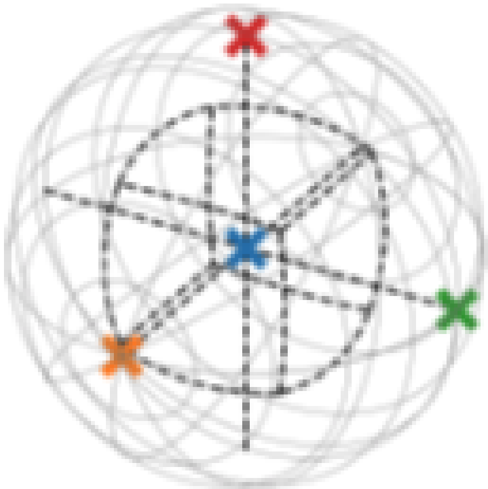
→ 3 times 2-fold axis, perpendicular to the faces
222

→ three mirror planes parallel to faces planes



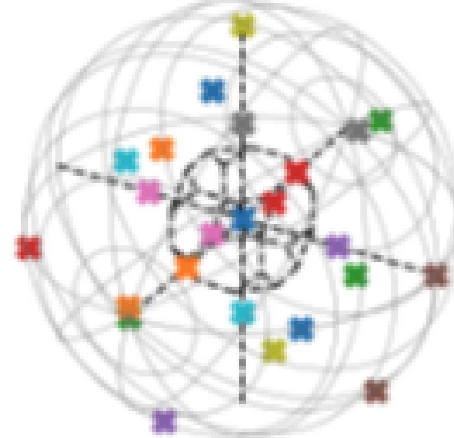
for plotting all possible orientation, only a subset of the sphere is needed → called the fundamental zone

Orientation of a crystal and crystal symmetry



point group 222

622



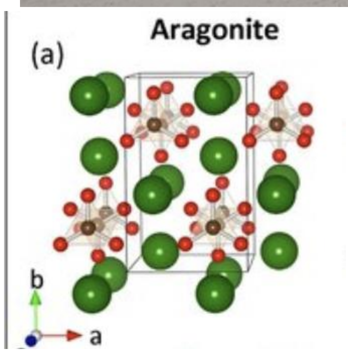
432

crystal system

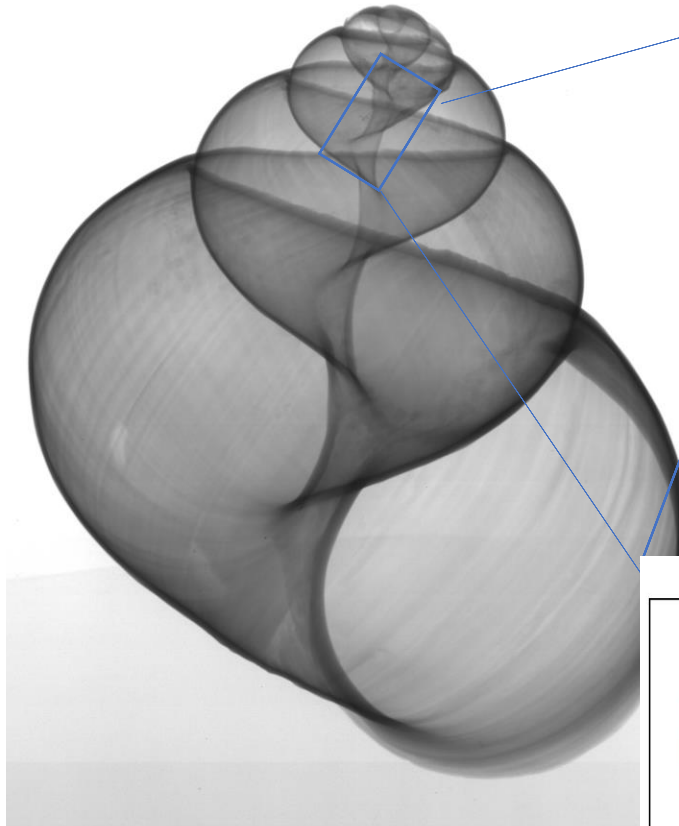
the more symmetry elements a point group has, the smaller is the fundamental zone since more and more orientation become equivalent

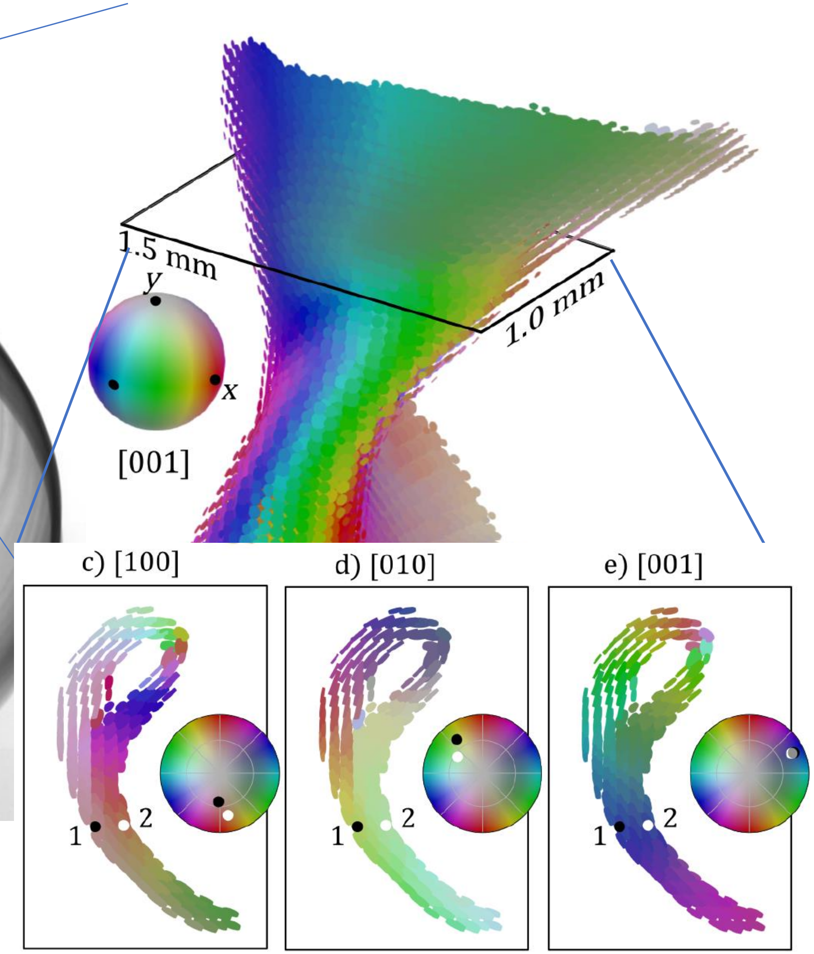
Outer shape and symmetry:Biomineral

Roman snail shell



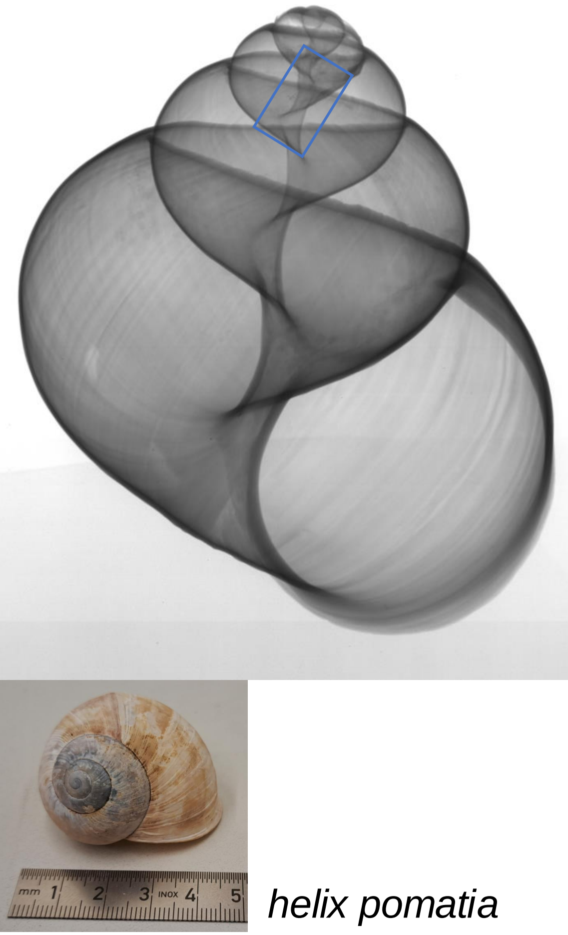
aragonite orthorombic



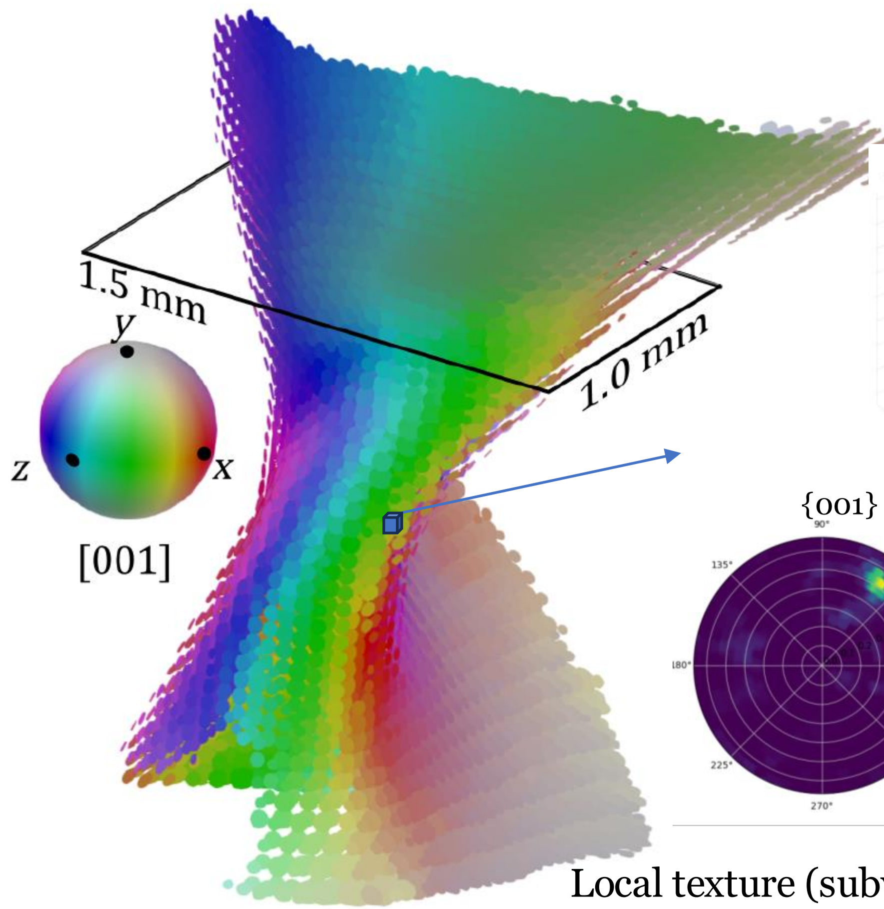


M. Carlsen *et al*. Applied Crystallography 2025

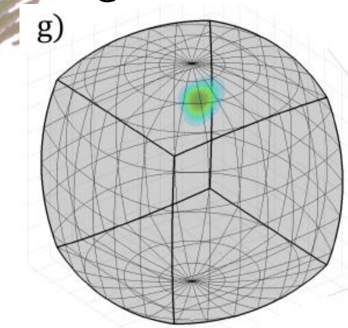
Roman snail shell: local texture as mosaic single crystal



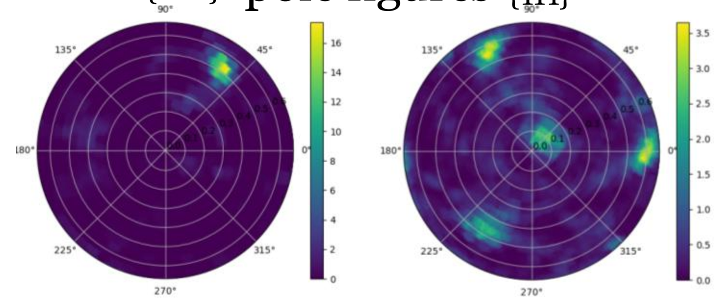
helix pomatia



3D ODF



{001} pole figures {111}



Local texture (subvolume 50µm x 50µm x 50µm)
mosaic single-crystal like
with ~10° spread

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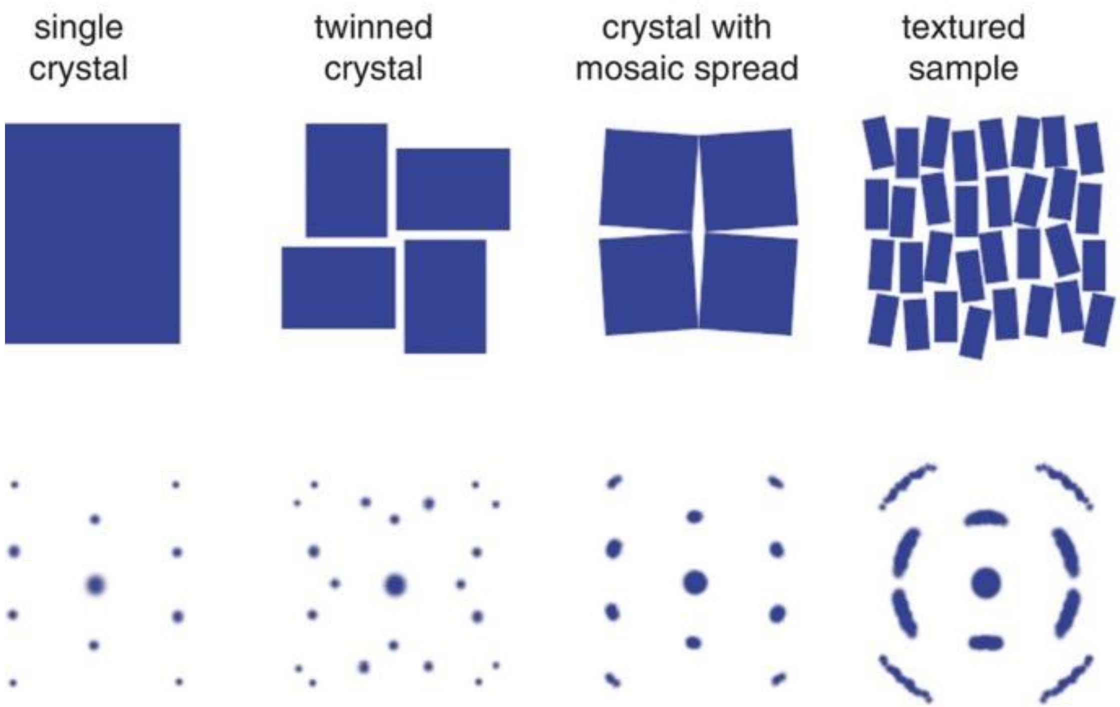
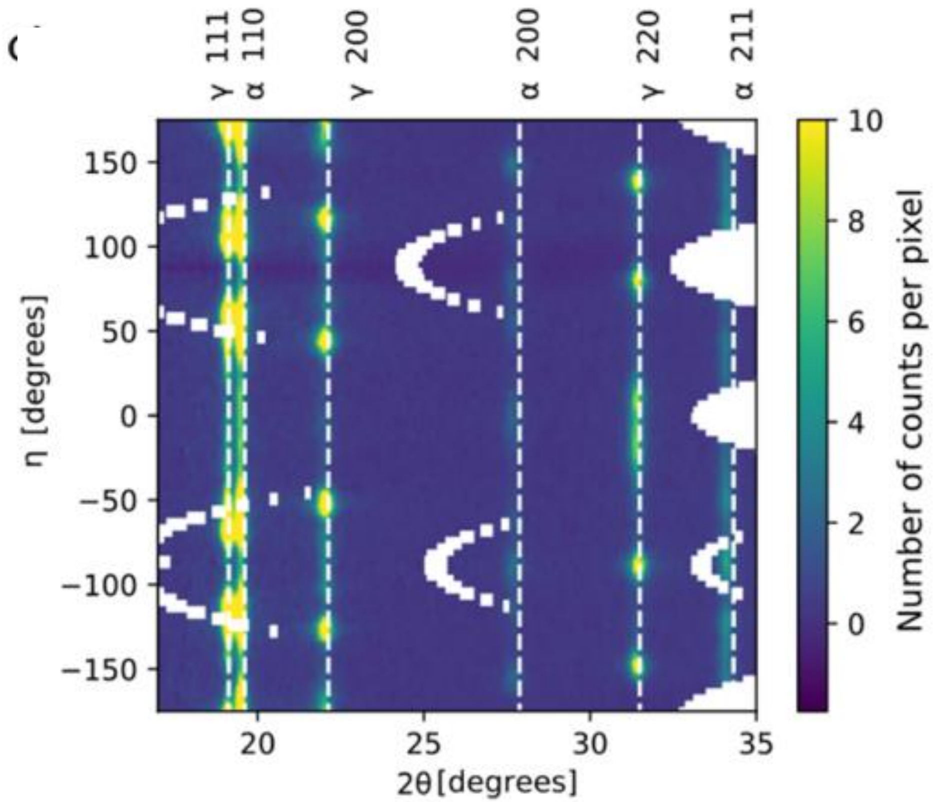
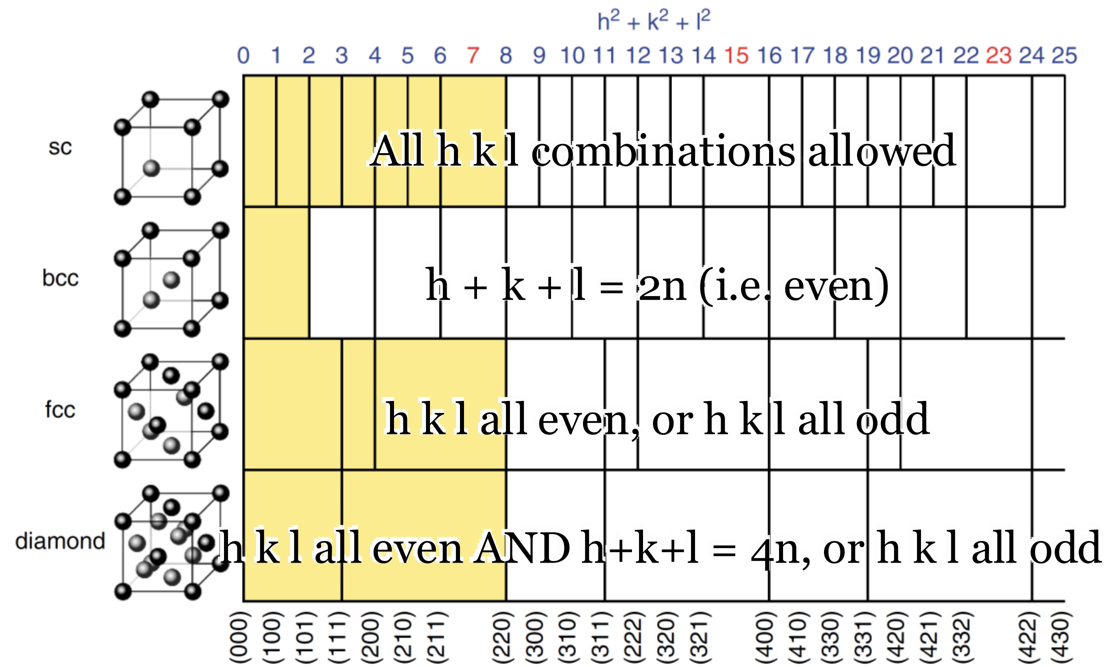
Sample types



Fibre texture: drawn metal wire

drawn metal wire made of stainless steel





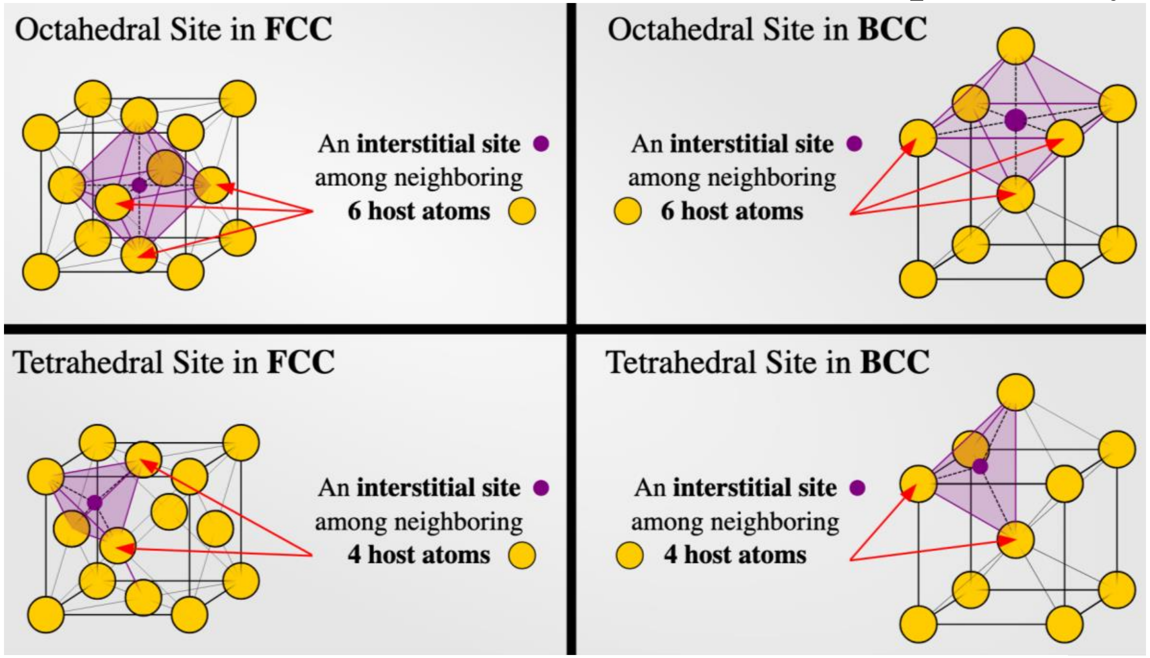
what is the crystal system of the α phase?
what is the crystal system of the γ phase?

Carbon: 0.12% maximum
Manganese: 2.00% maximum
Phosphorus: 0.045% maximum
Sulfur: 0.030% maximum
Silicon: 1.00% maximum
Chromium: 17.0–19.0%
Nickel: 8.0–10.0%
Nitrogen: 0.10% maximum
Iron: Balance

Fibre texture: drawn metal wire

drawn metal wire made of stainless steel

there is 0.12% carbon inside that material, in which phase do you expect it to be?

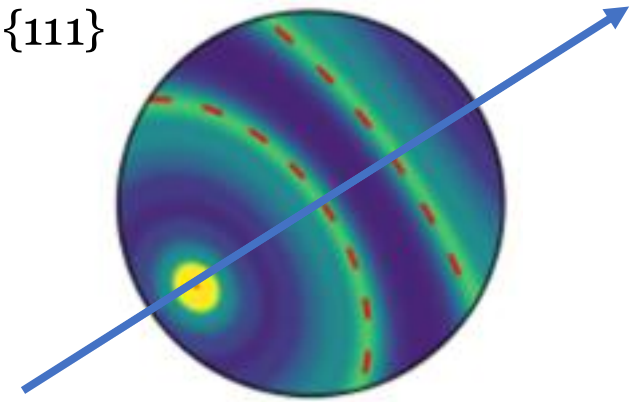


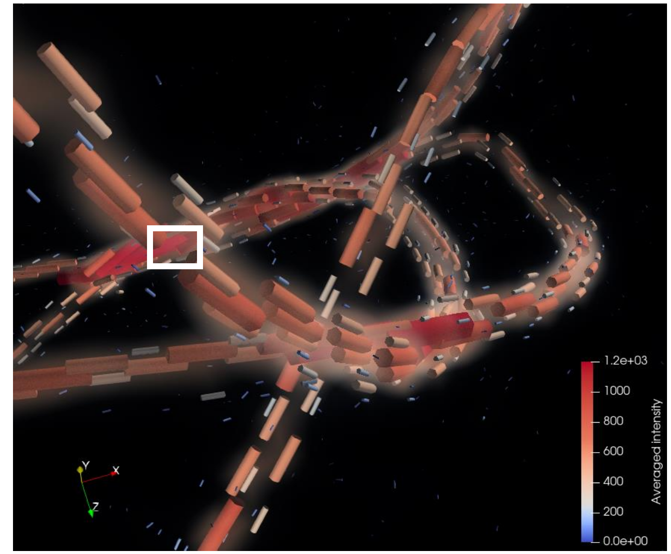
Crystal Structure	FCC	BCC
Number and Size of Octahedral Voids	4 voids, r = 0.414 R	6 voids, r = 0.155 R
Number and Size of Tetrahedral Voids	8 voids, r = 0.225 R	12 voids, r = 0.291 R

Carbon: 0.12% maximum
Manganese: 2.00% maximum
Phosphorus: 0.045% maximum
Sulfur: 0.030% maximum
Silicon: 1.00% maximum
Chromium: 17.0–19.0%
Nickel: 8.0–10.0%
Nitrogen: 0.10% maximum
Iron: Balance

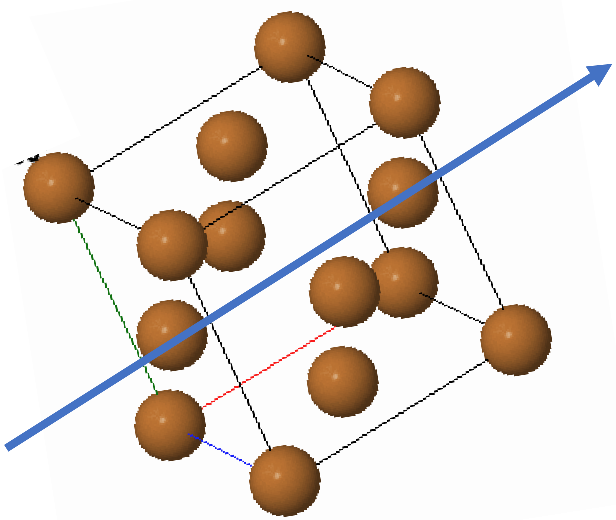
Fibre texture: drawn metal wire

pole figure for {111}

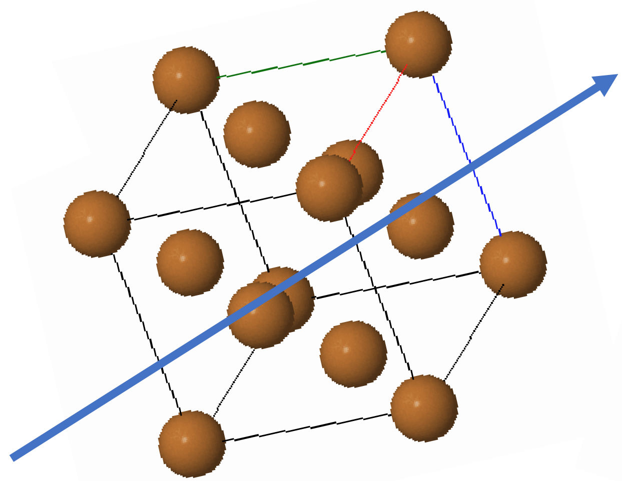




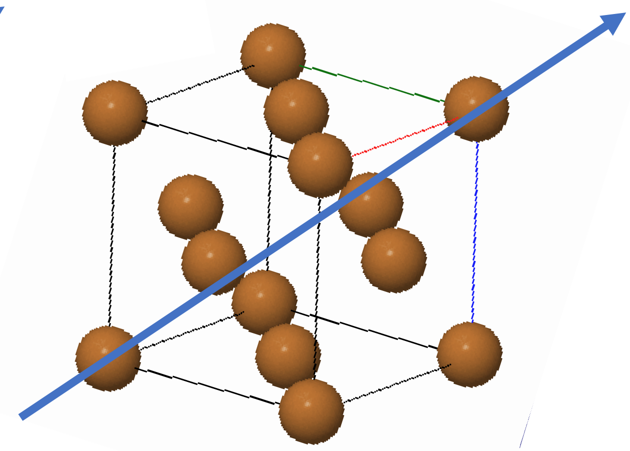
"face-on"



"edge-on"



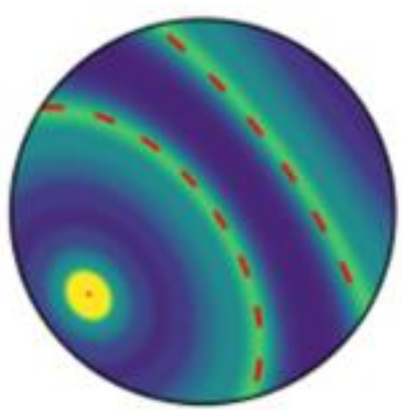
"corner-on"

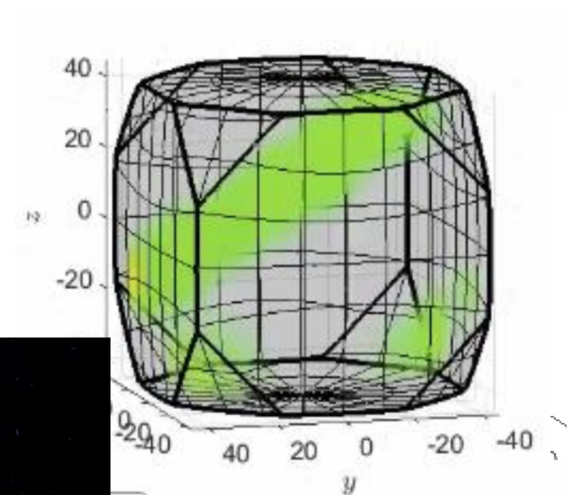


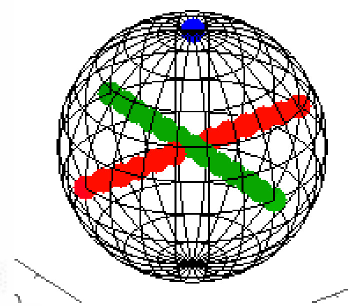
Texture analysis

- The pole figure
  - Given a specific set of reciprocal lattice vectors, *{hkl}*
  - The pole figure gives the probablity of finding that plane in the direction, q

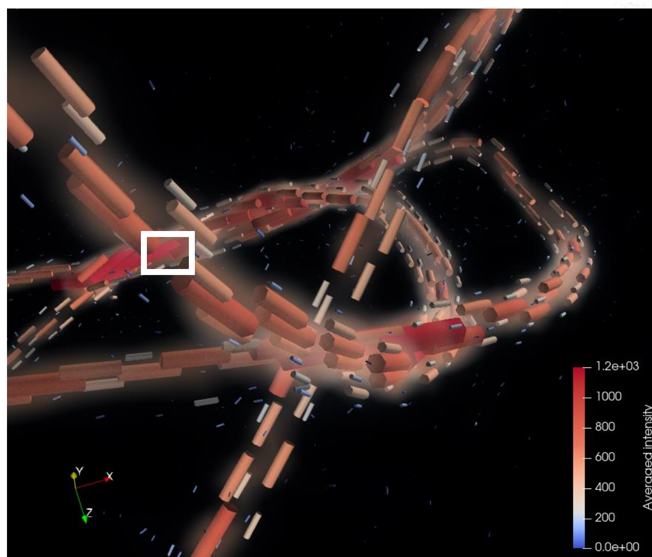
3D orientation distribution function (ODF) how is the crystal lattice oriented with respect to the actual sample







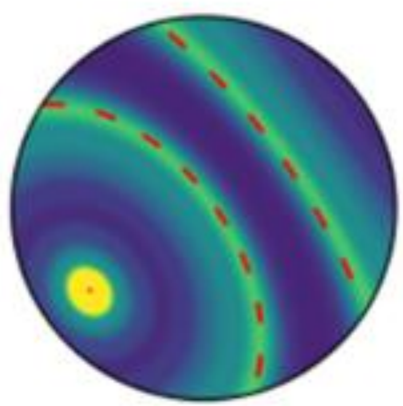
fiber texture: peaks smear into a ring



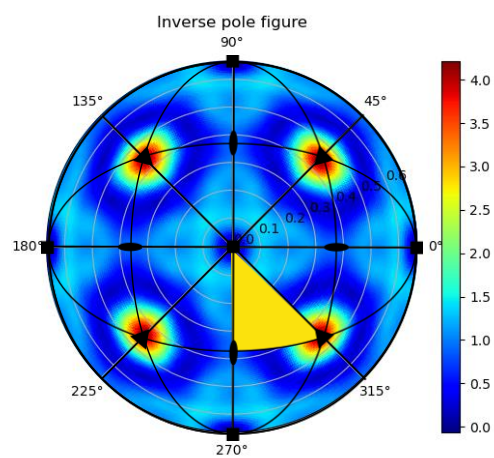
fiber texture: fixed symmetry axis, but free rotation around
→ a line

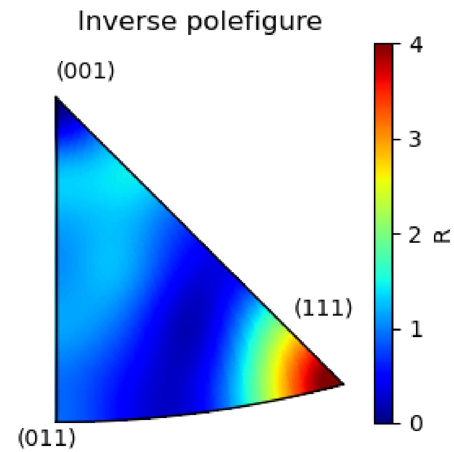
Texture analysis

- The pole figure
  - Given a specific set of reciprocal lattice vectors, *{hkl}*
  - The pole figure gives the probablity of finding that plane in the direction, q



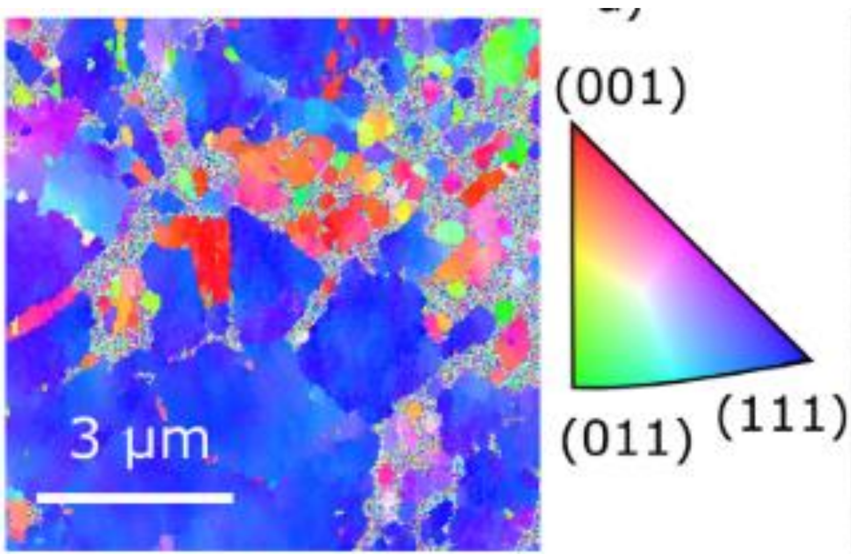
- The inverse pole figure
  - Given a specific direction *y* in the sample (here: the wire direction = draw direction)
  - The inverse pole figure gives the probability that *y* falls in a certain lattice orientation.

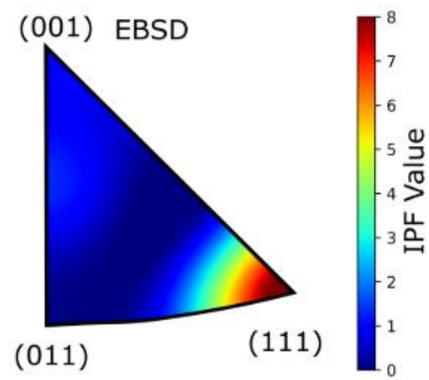




Inverse pole figures

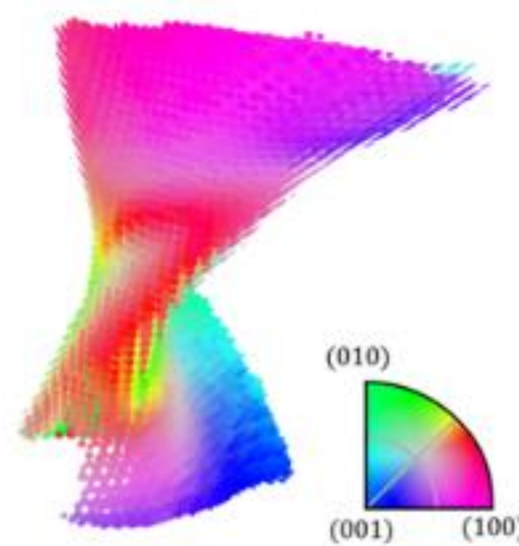
electron back-scattered diffraction (EBSD)
on a cut with the surface normal to the wire direction
inverse pole figure map





fcc

inverse pole figure map of the snail shell

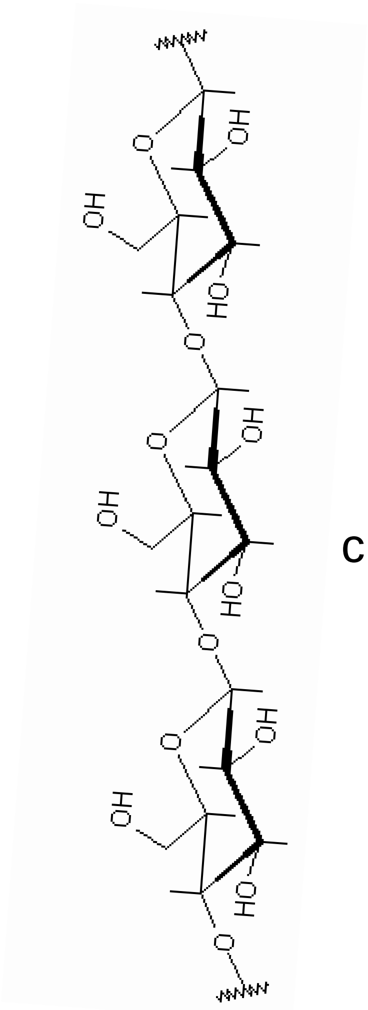


orthorhombic

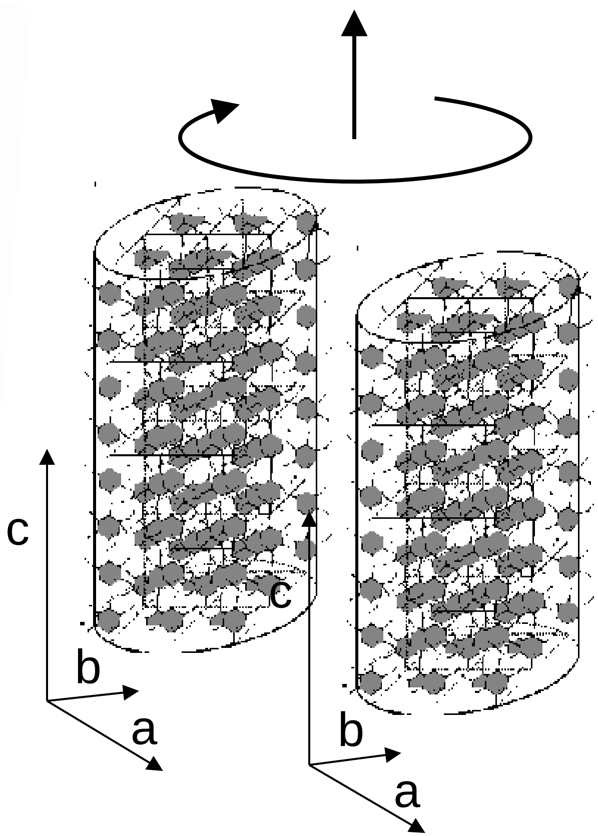
note that the portion from the circle depends on crystal symmetry!

Fibre texture are very common

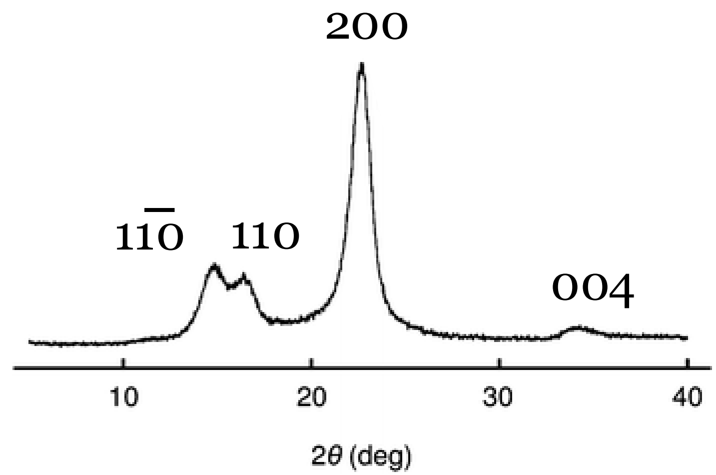
cellulose fiber



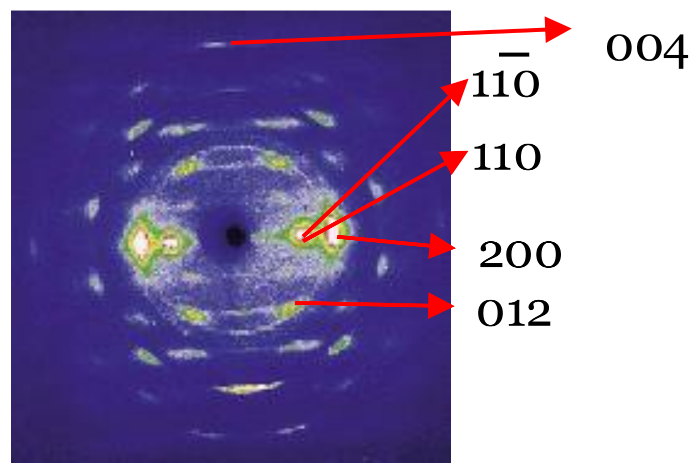
Cellulose molecule



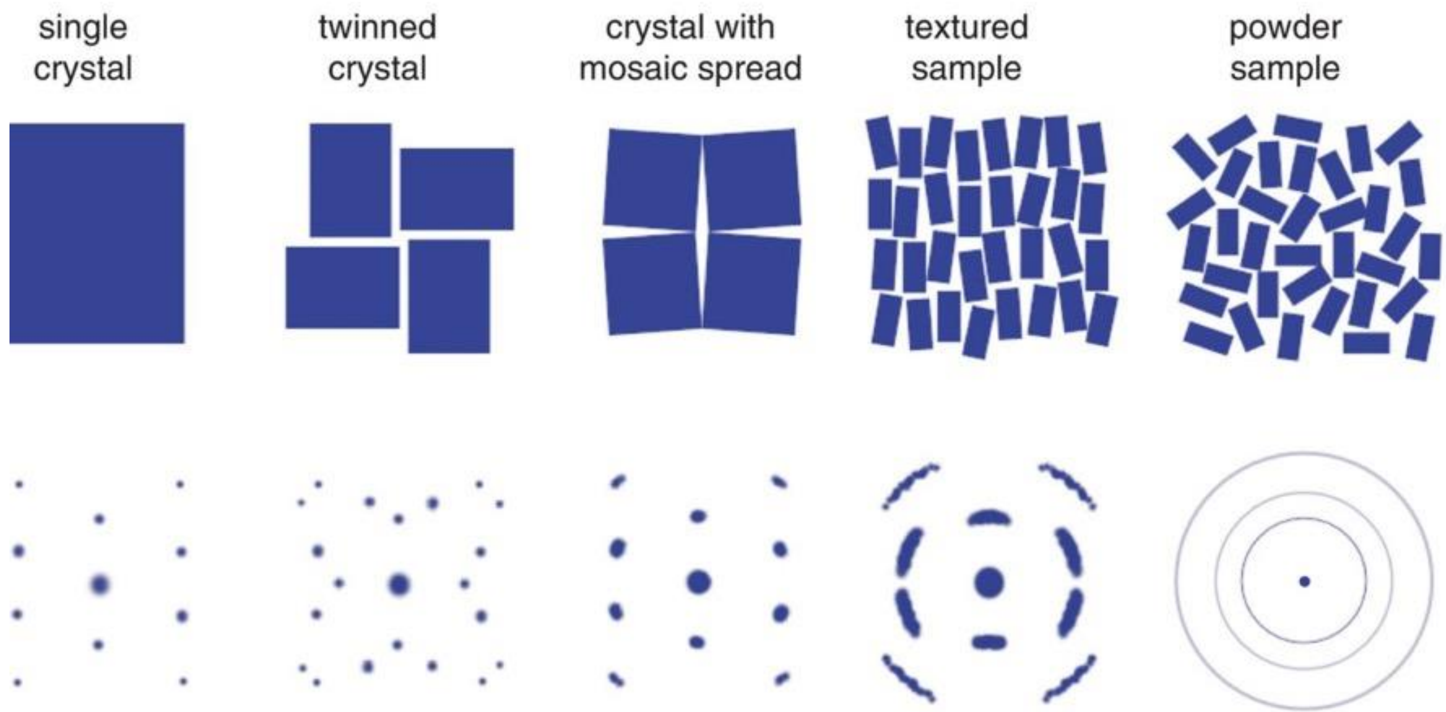
Crystalline cellulose fibers



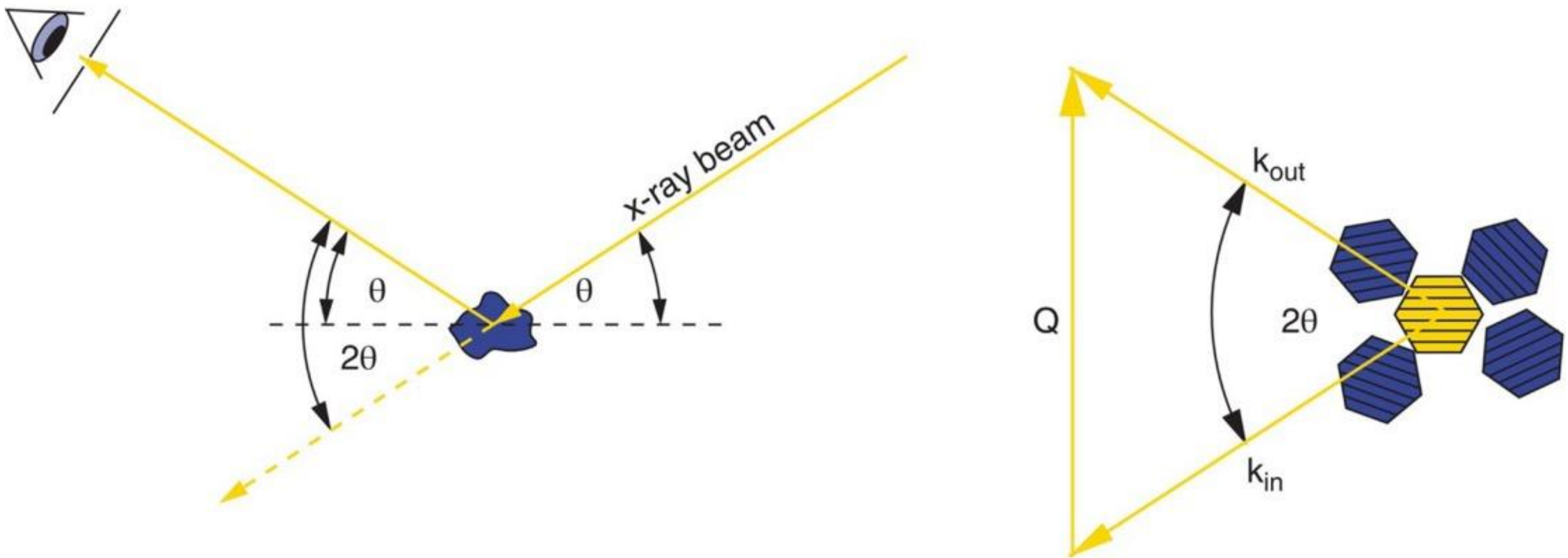
2D diffraction pattern
→ information of crystallin orientation



Sample types



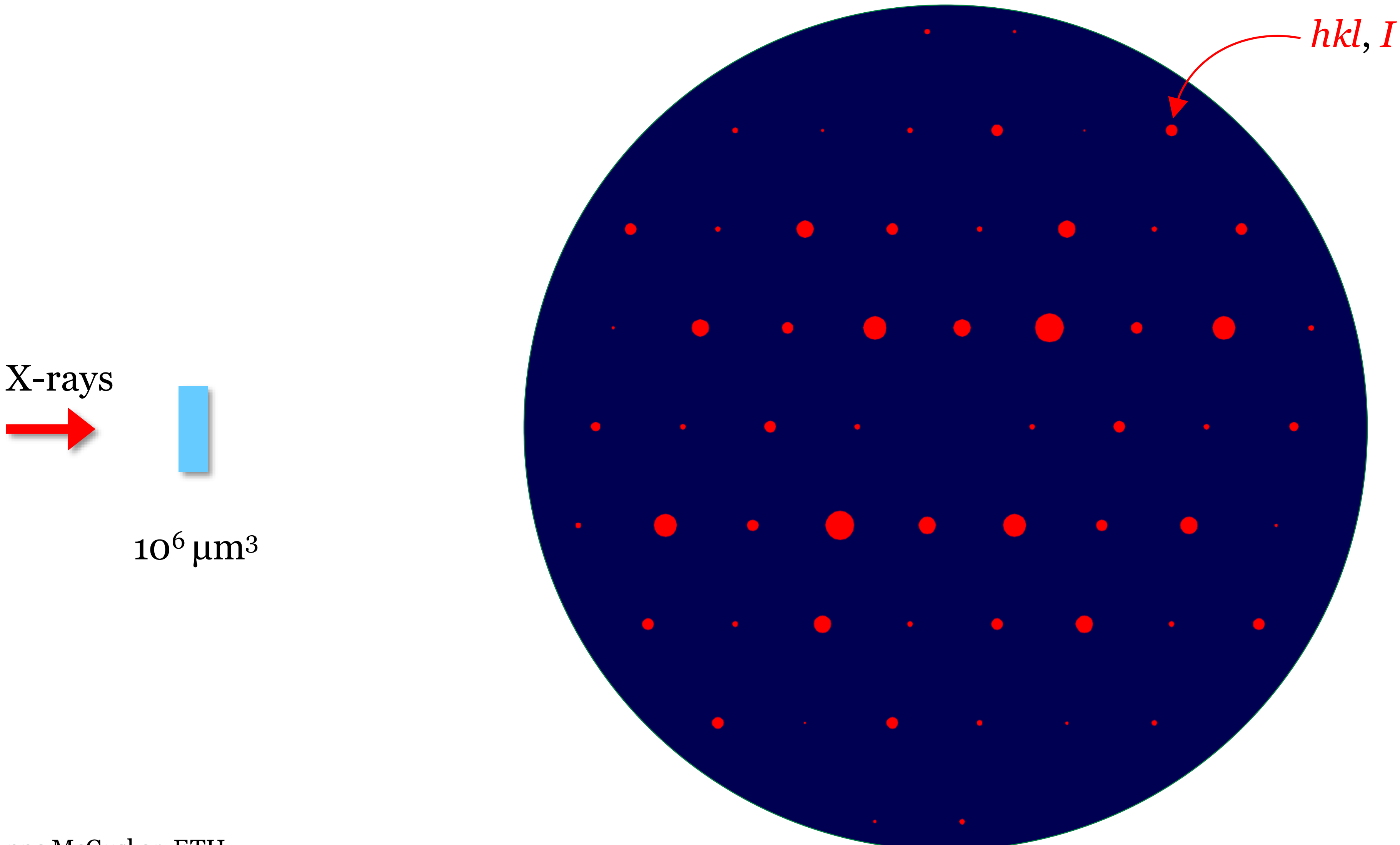
Powder diffraction



Conditions for diffraction in a powder sample. A detector will only see a diffracted signal if the d_{hkl} spacing, the orientation of the crystallite, and the angle of the detector 2θ to the incident x-ray beam lead to the diffraction condition being satisfied. This is fulfilled by the yellow-highlighted crystallite.

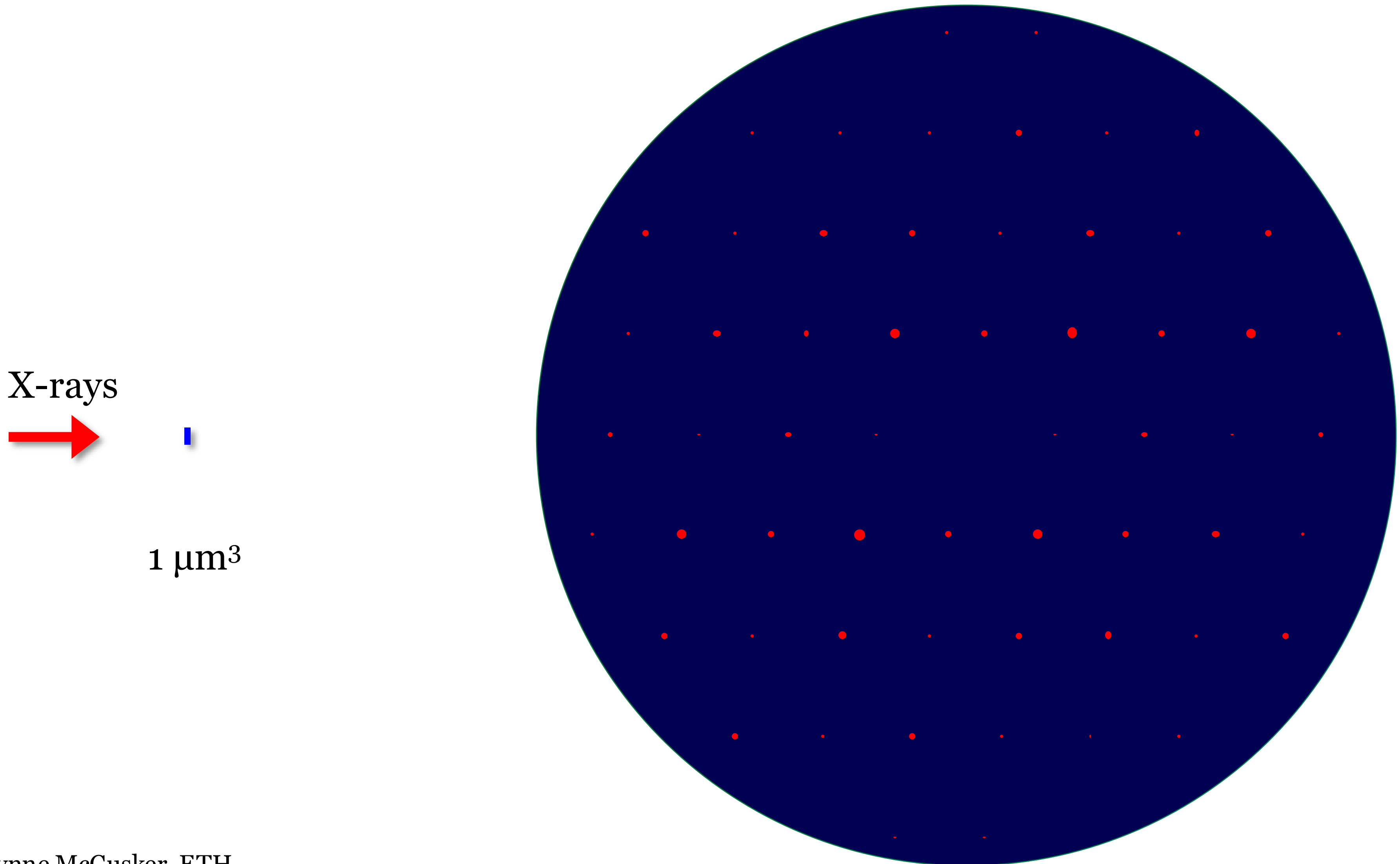
by Phil Willmott

Single Crystal Diffraction



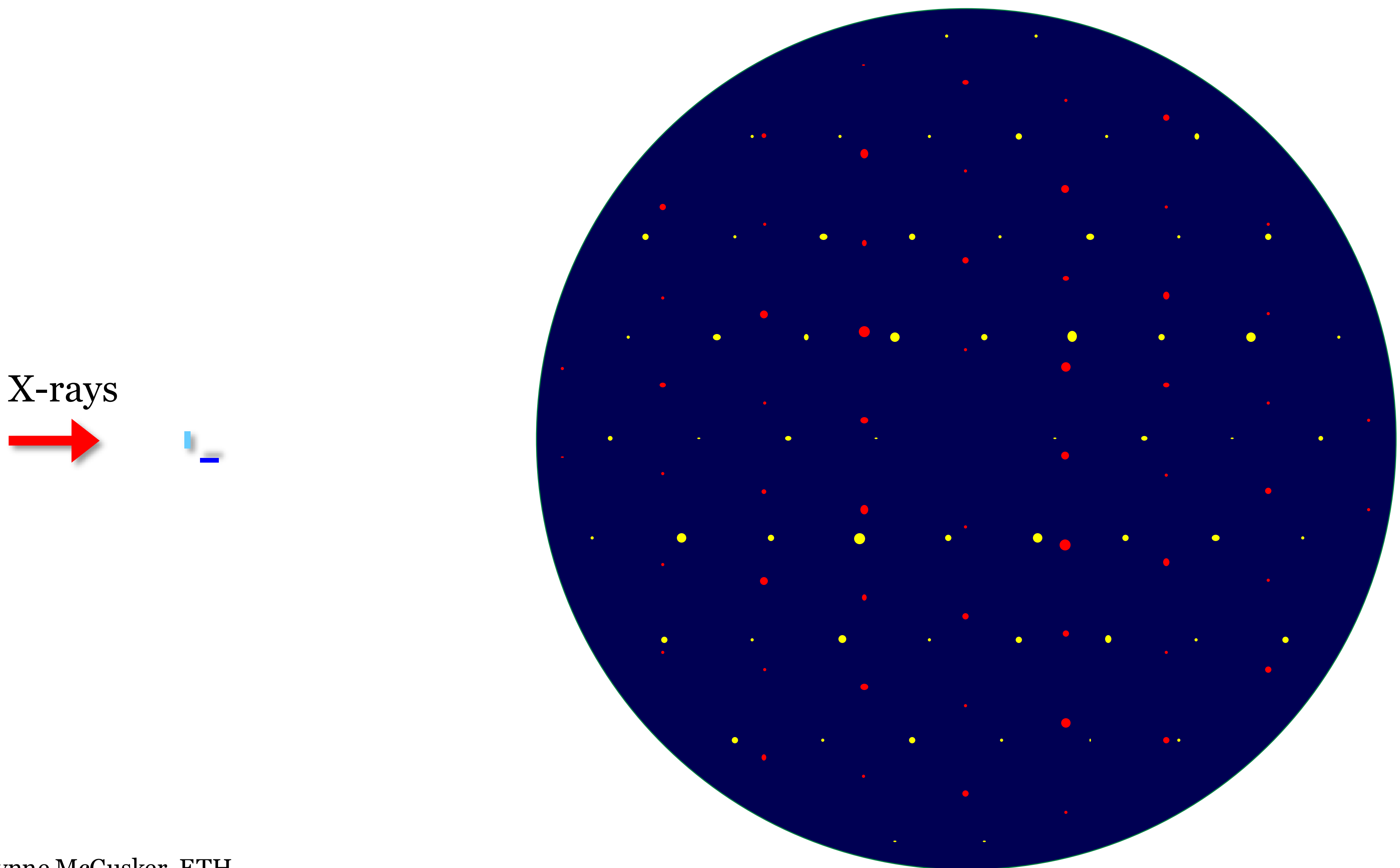
Lynne McCusker, ETH

Powder Diffraction



Lynne McCusker, ETH

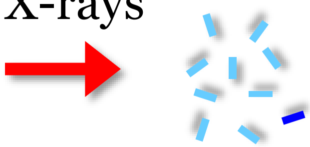
Powder Diffraction

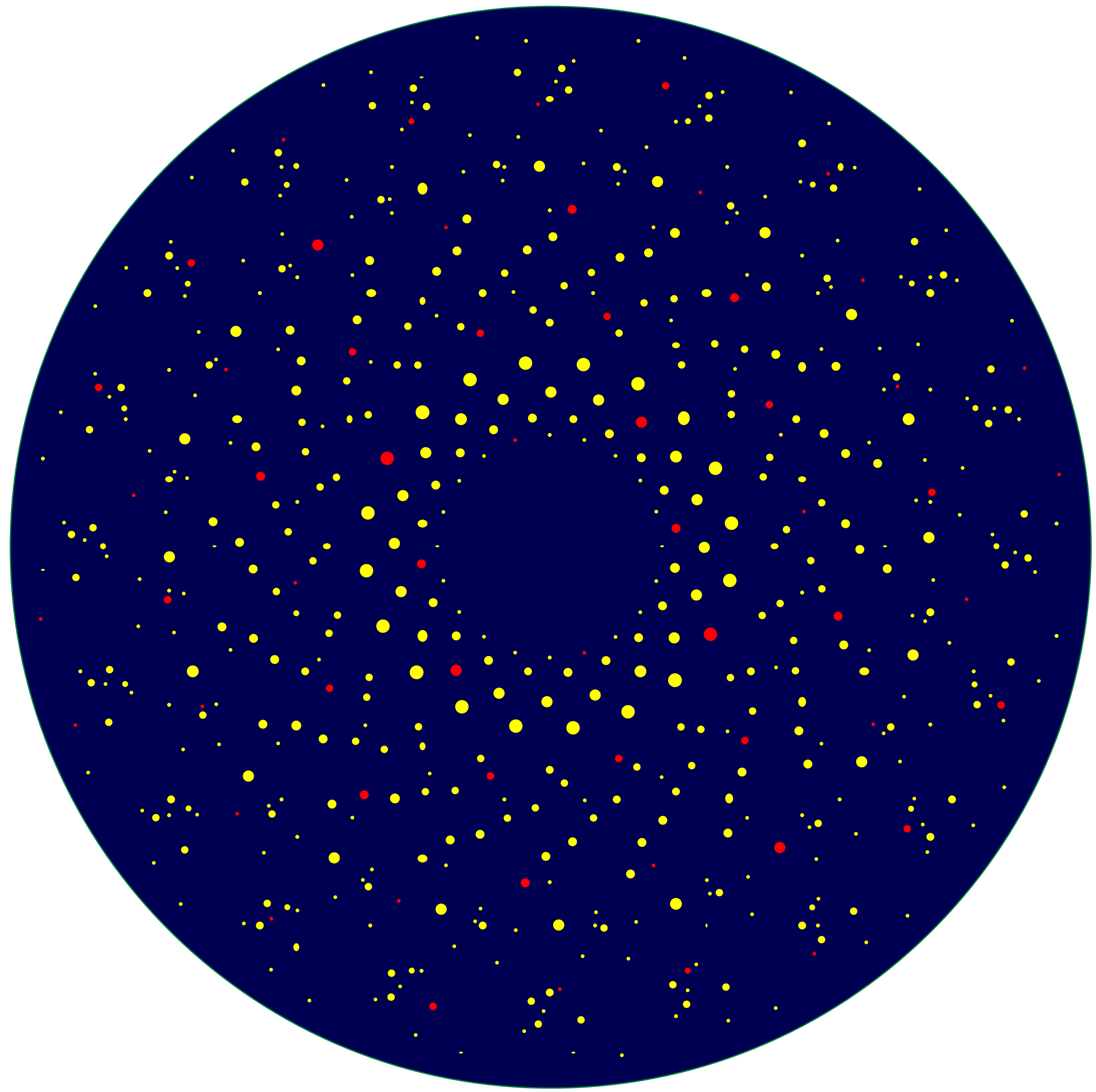


Lynne McCusker, ETH

Powder Diffraction

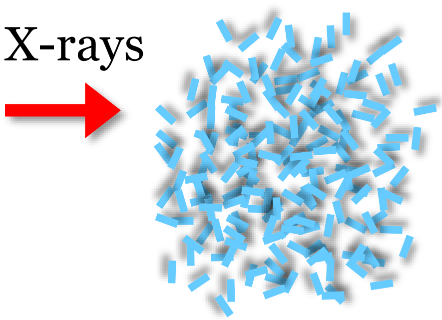
X-rays

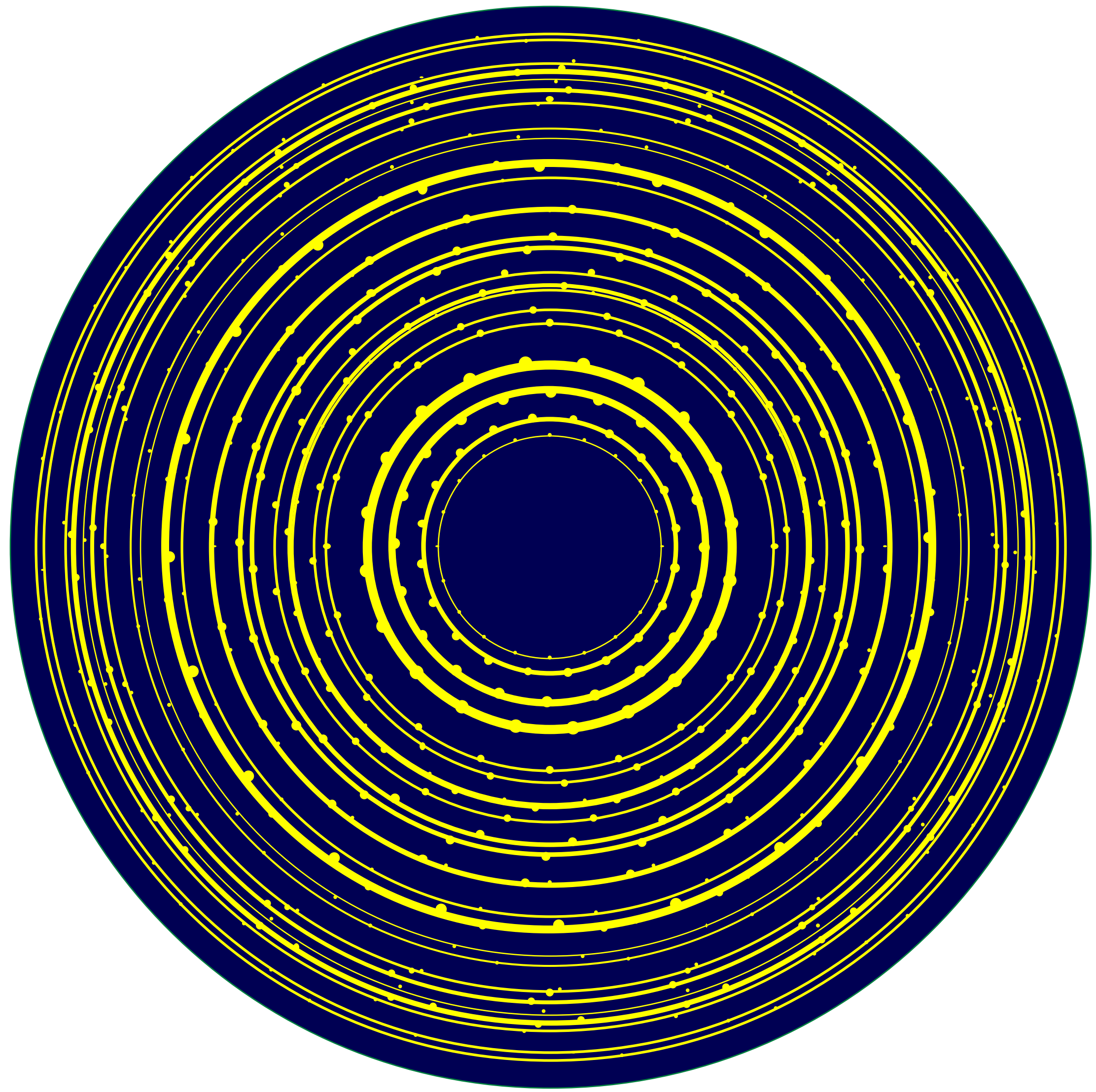




Lynne McCusker, ETH

Powder Diffraction

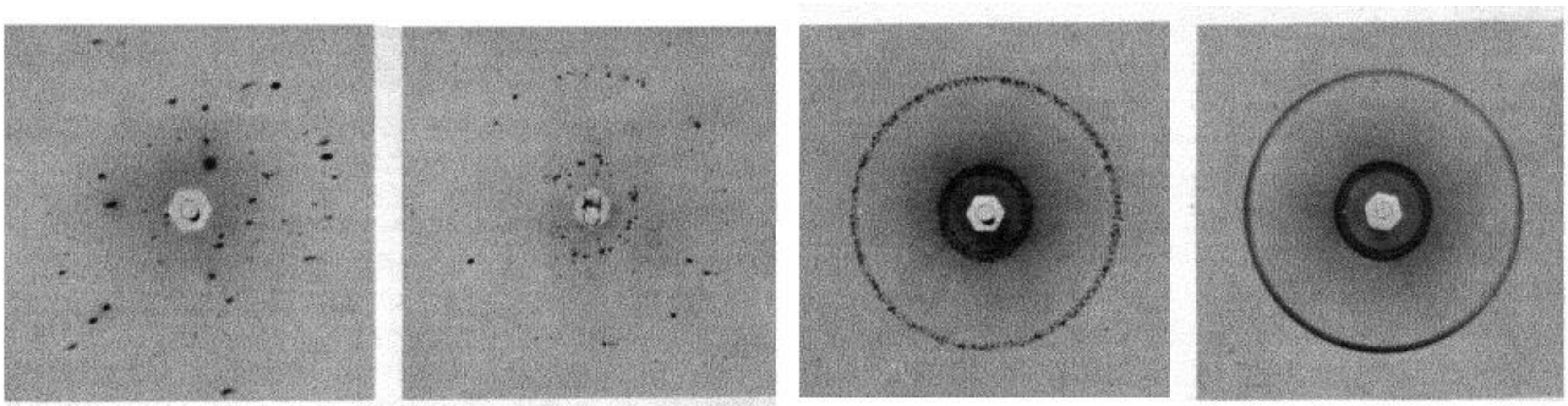




Lynne McCusker, ETH

Polycrystallinity

Example: XRD of recrystallized aluminium

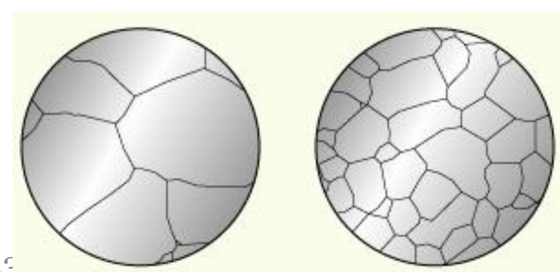


Decrasing grain size

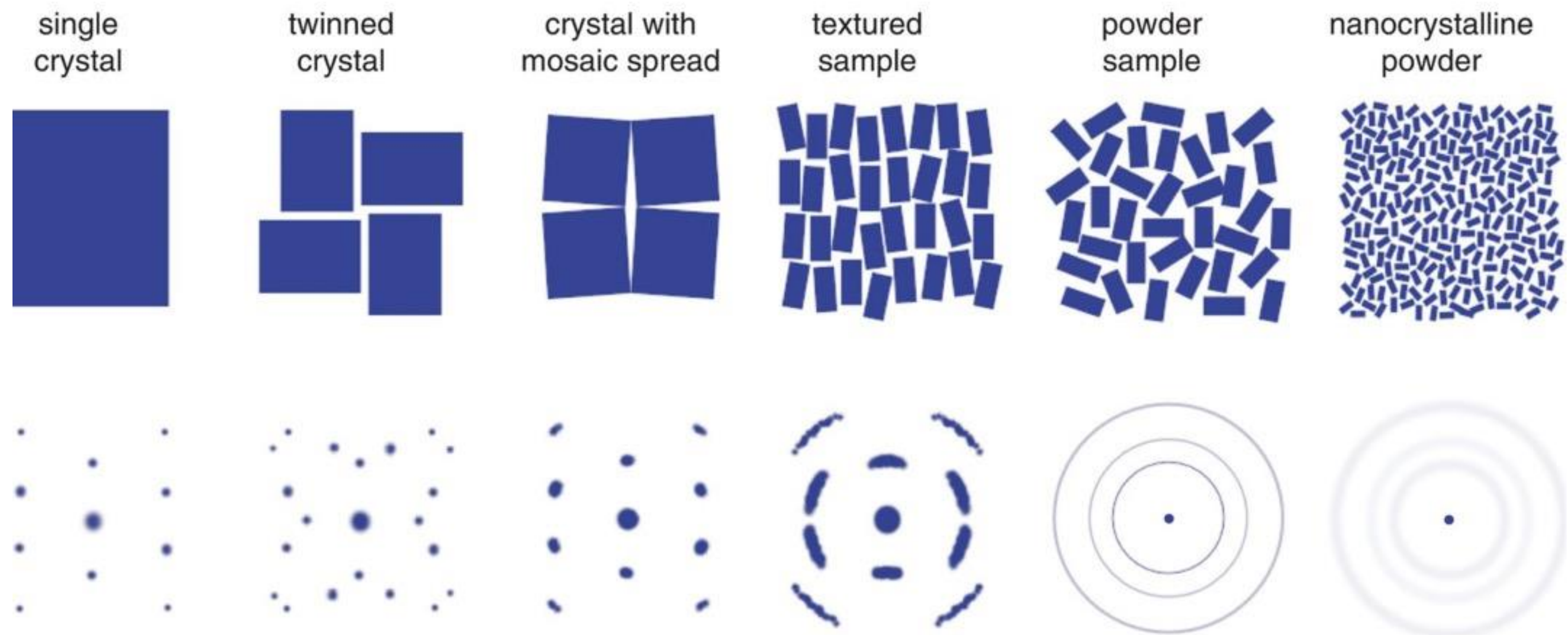
Grain size be determined by comparing XRD-patterns recorded under **identical conditions** (in particular beam size!)

Schematic: number of grains in beam:

(smaller beams „see“ fewer crystallites)

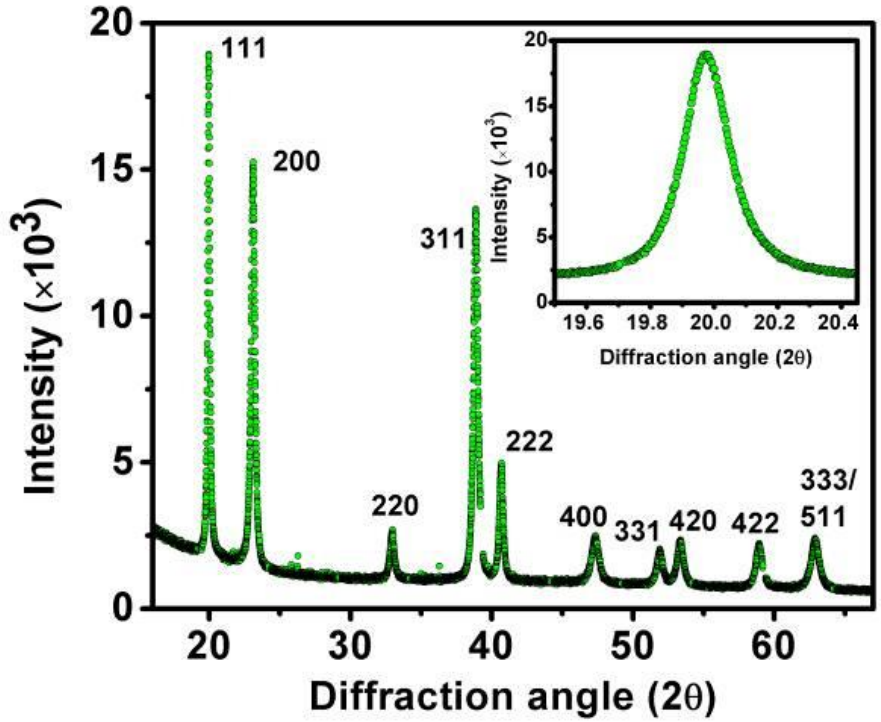


Sample types



Nanocrystalline powder

- Example: nanocrystalline Ni

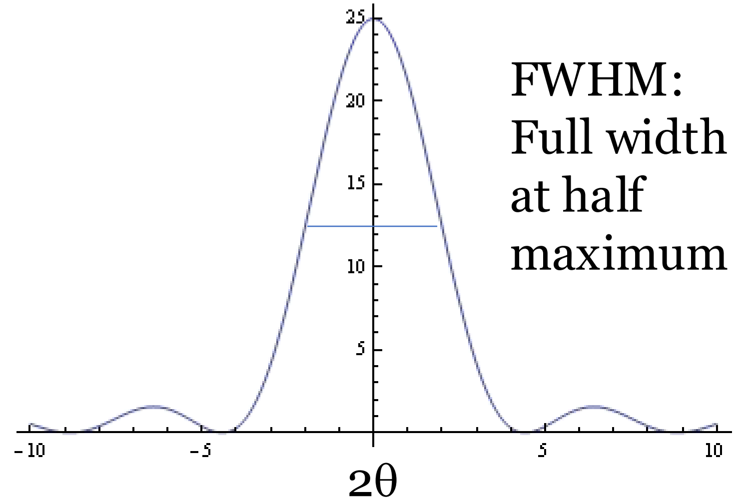


XRD
Imperfect microstructure

- large crystal with perfect atomic arrangement give rise to perfectly sharp peak (except of instrumental broadening)
- imperfections such as grain boundaries, defects at dislocations, stacking faults, stresses → peak broadening, as well as possibly peak position shifts
- small crystal size: “defect” as the long-range atomic arrangement is disrupted at the interface → peak broadening

XRD: Crystal size

Scherrer width
$$B = \frac{K \cdot \lambda}{D \cdot \cos\theta}$$



FWHM: Full width at half maximum

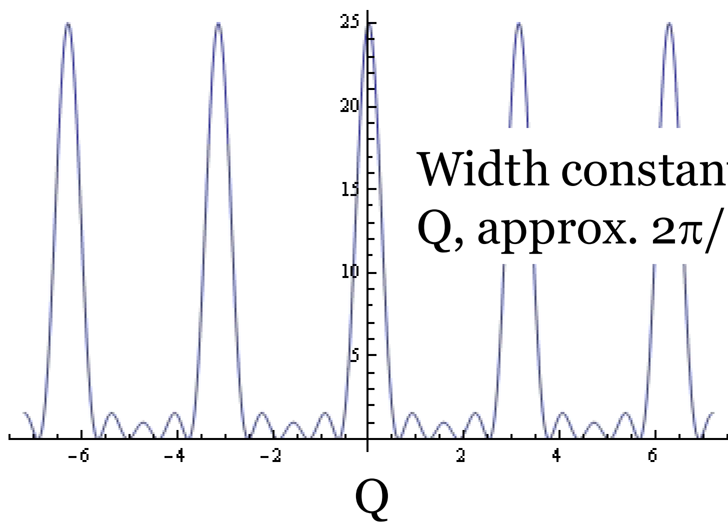
B: broadening of diffraction line at half maximum, in 2θ measured in radians

D: diameter of crystallite

K: constant, ≈ 1, depends on crystal structure

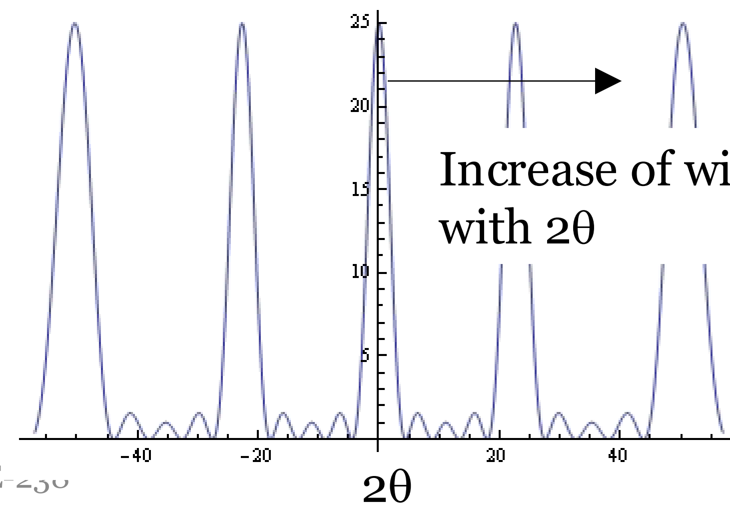
small crystal –> broad peak

Plot versus Q



Width constant in Q, approx. $2\pi/D$

Plot versus 2θ

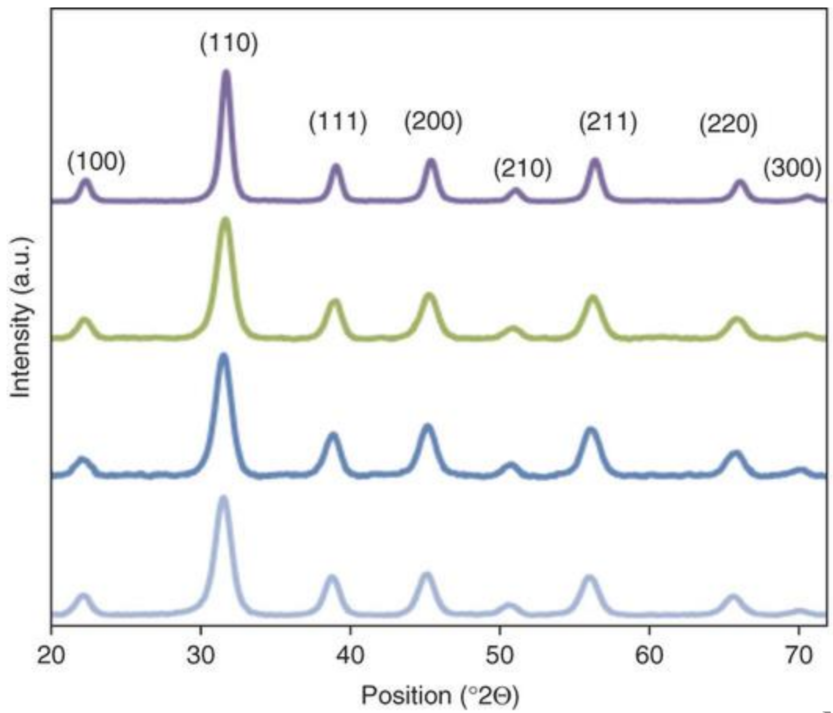


Increase of width with 2θ

XRD: Crystal size

BaTiO3 nanoparticles

Large-scale synthesis of $BaTiO_3$ nanopowders using a bioinspired process at nearly room temperature (25 °C). Size changes during sintering:

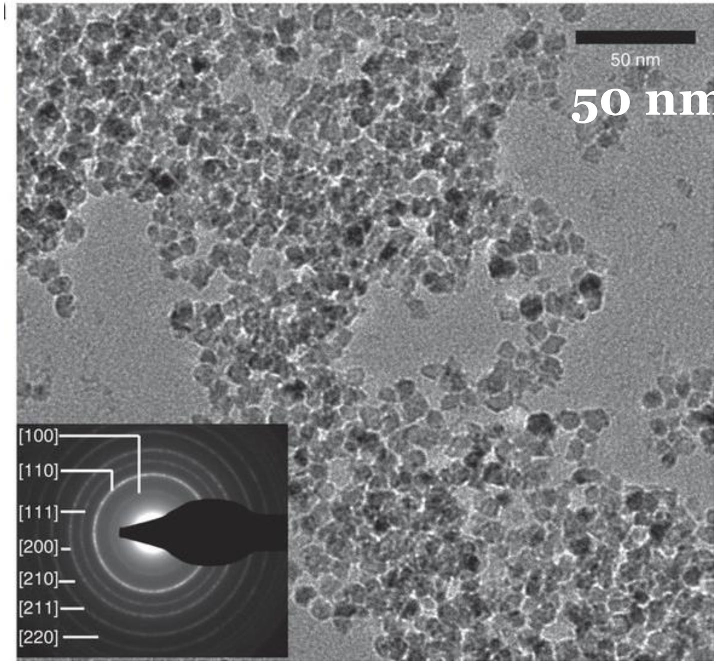


700°C, 10 nm

500°C, 7 nm

300°C, 6 nm

30°C, 6 nm



Ould-Ely et al., *Nature Protocols* 6, 97–104 (2011)

XRD: Strain broadening

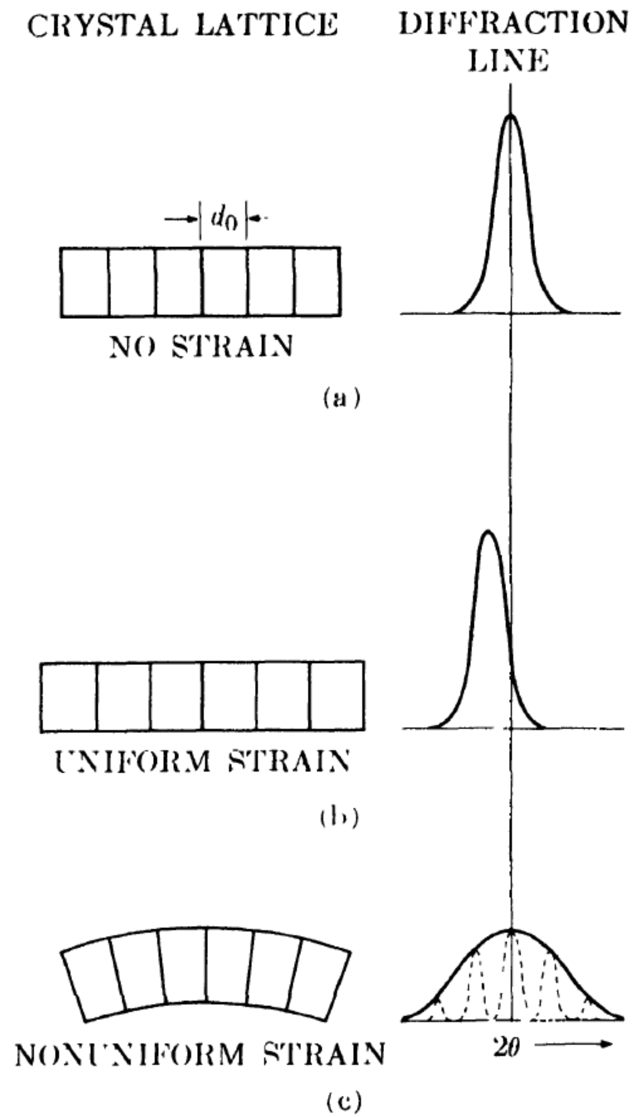
Line broadening due to non-uniform lattice distortions.

Broadening related to strain:

$$b = \Delta 2\theta = -2\frac{\Delta d}{d}\tan\theta = -2\varepsilon\tan\theta$$

Often occurs with size broadening, difficult to separate.

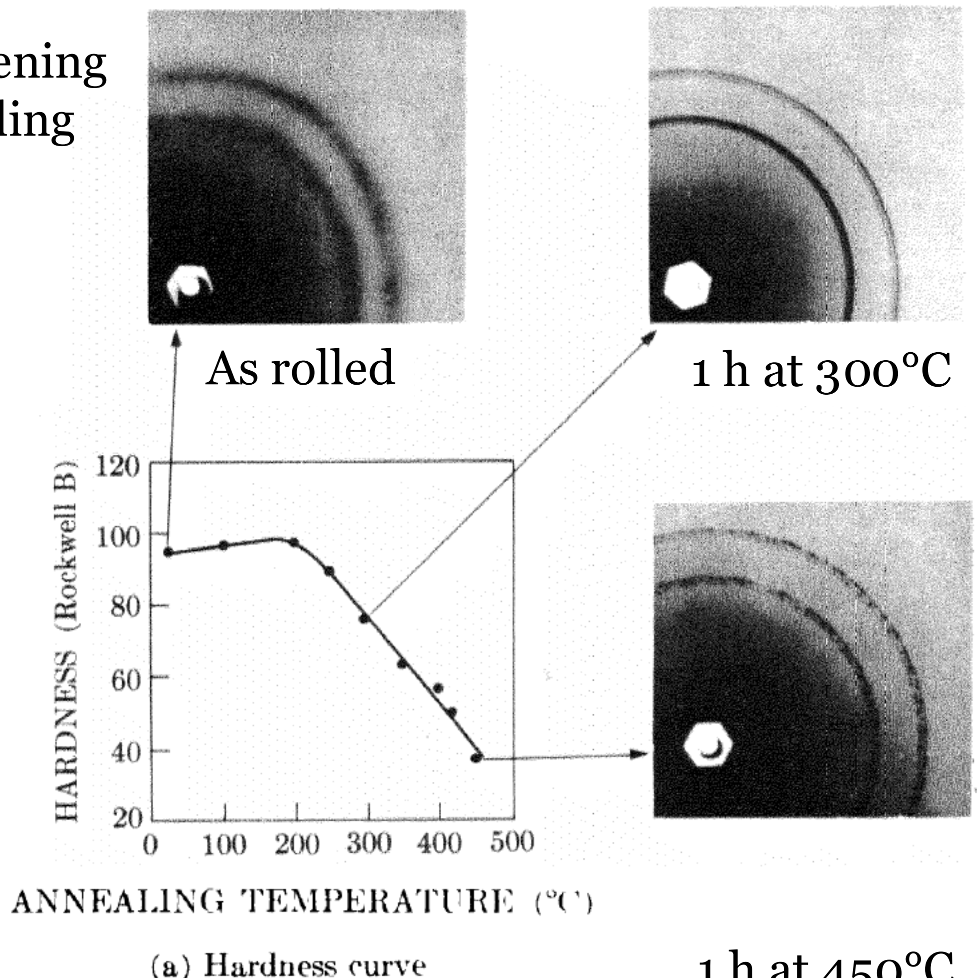
Stronger dependence on θ (width increases for higher order reflections). Also different line shape.



XRD: Strain broadening

Strain broadening after cold rolling

Recovery



As rolled

1 h at 300°C

Recrystallization

1 h at 450°C

XRD
Imperfect microstructure

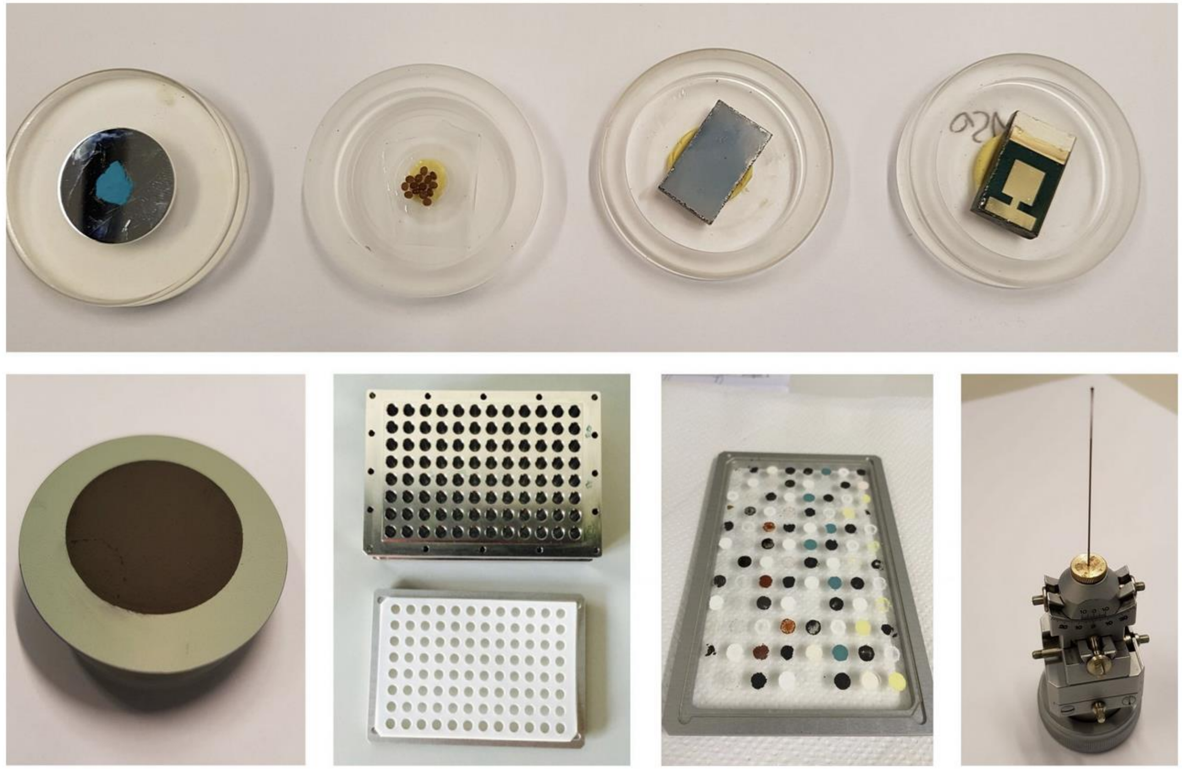
- large crystal with perfect atomic arrangement give rise to perfectly sharp peak (except of instrumental broadening)
- imperfections such as grain boundaries, defects at dislocations, stacking faults, stresses → peak broadening, as well as possibly peak position shifts
- small crystal size: “defect” as the long-range atomic arrangement is disrupted at the interface → peak broadening
- when looking at more than one order of a reflection, the effect of ”size” and “strain” can be separated
- Rietfeld refinement to get all information out of powder diffraction data

Peak profiles

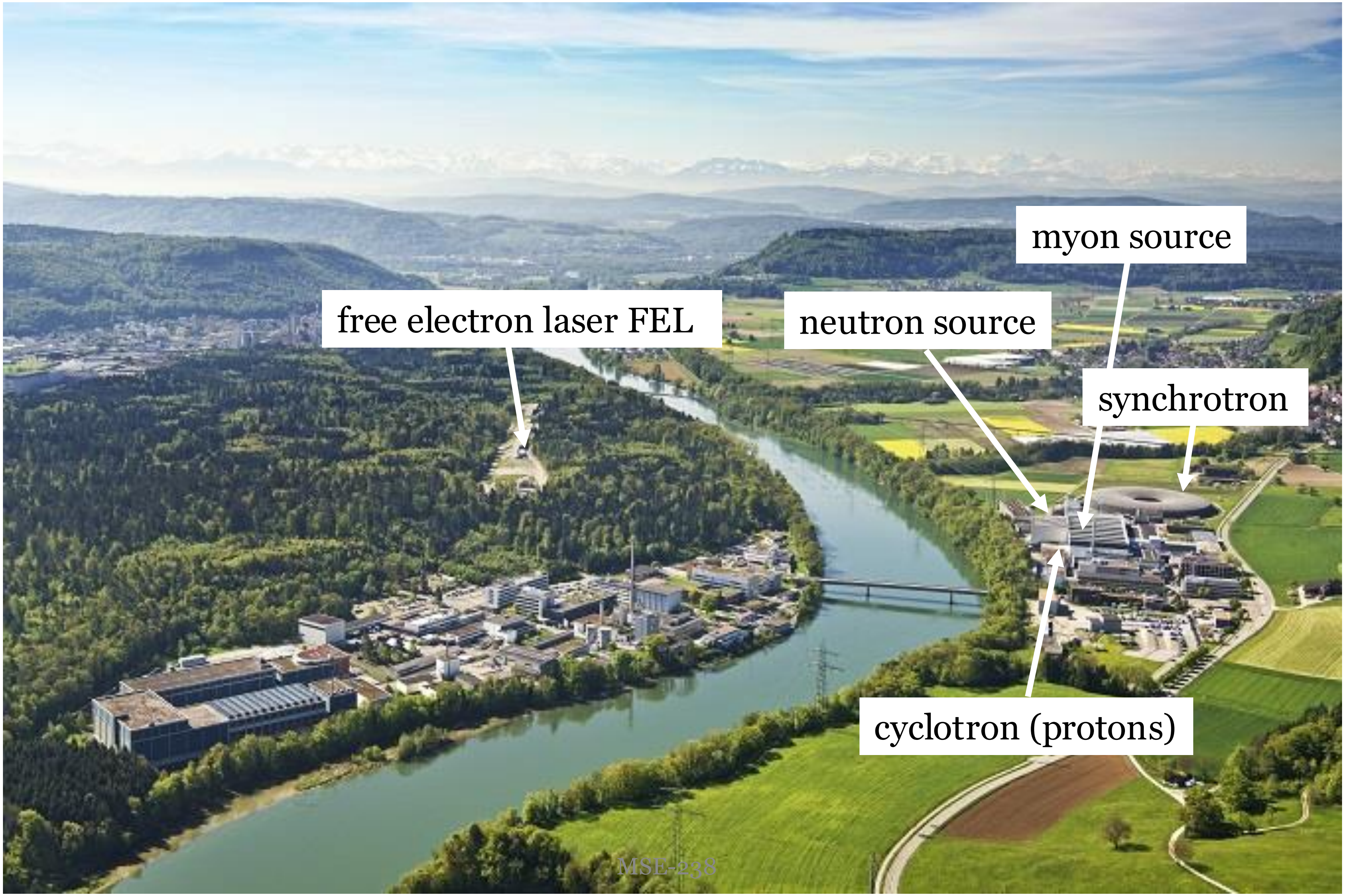
- Peak profiles are determined by many factors. The most important ones include:
  - Resolution function
  - Coherent scattering length
  - Microstrain
    - Inhomogeneous elastic strain
    - Anti-phase boundaries
    - Faulting
    - Dislocations
    - Grain surface relaxation
  - Solid solution inhomogeneity
  - Temperature factors
- Peak profile is a convolution of the profiles from all of these contributions

Lab-source diffractometers for powder and single-crystal diffraction

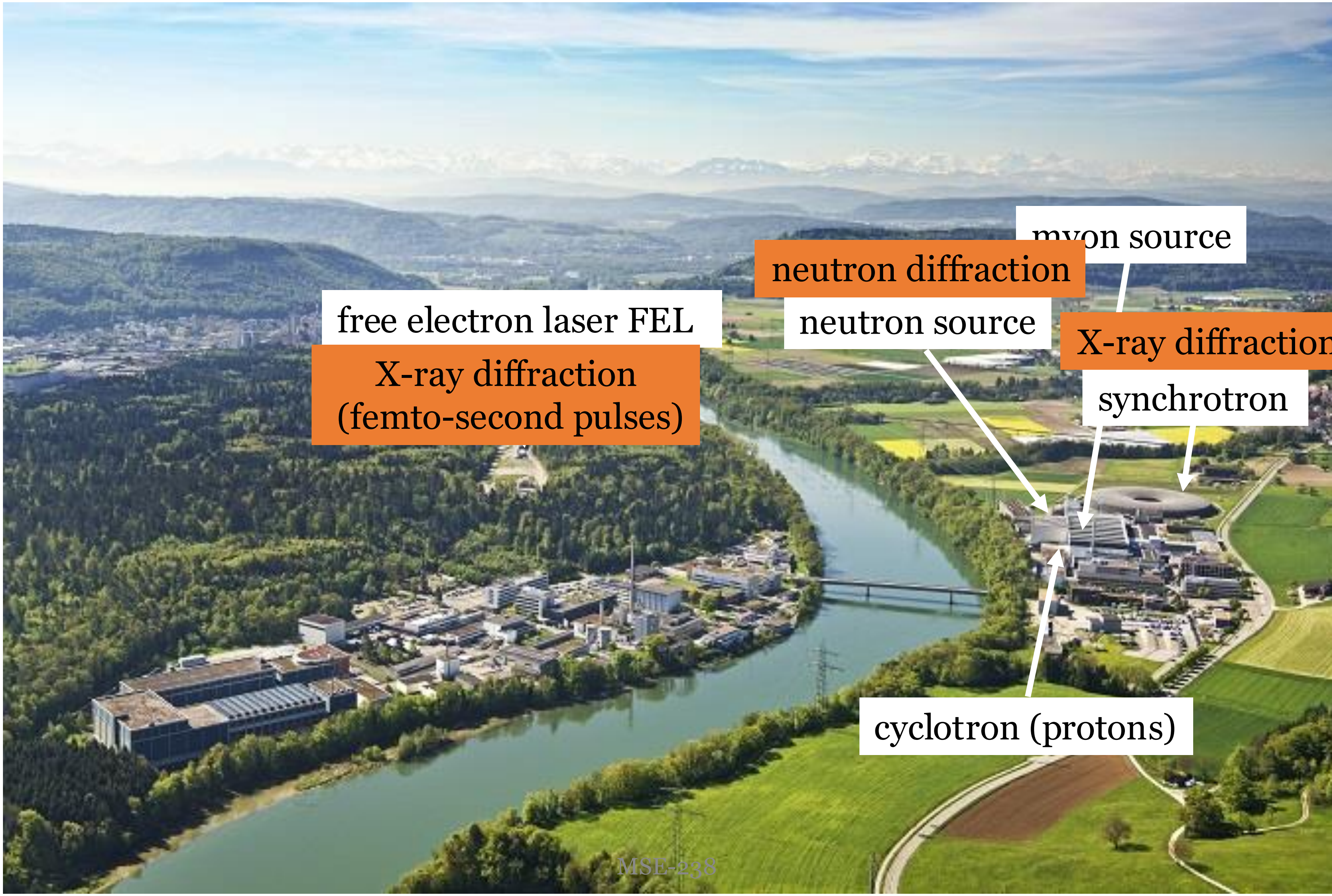
https://www.epfl.ch/schools/sb/research/isic/platforms/x-ray-diffraction-and-surface-analytics/x-ray-instrumentation/x-ray-scattering-instrumentation/



Samples: some examples of commonly measured samples are shown on **top**, from left to right: Metalorganic framework (MOF) powder sample, polymer beads, perovskite thin film, perovskite film with electrode. **bottom**, left to right: Solid Oxide Fuel Cell (SOFC), high throughput sample changer for synthesis robot (before and after loading), powder under Argon atmosphere in glass capillary.


myon source
free electron laser FEL
neutron source
synchrotron
cyclotron (protons)

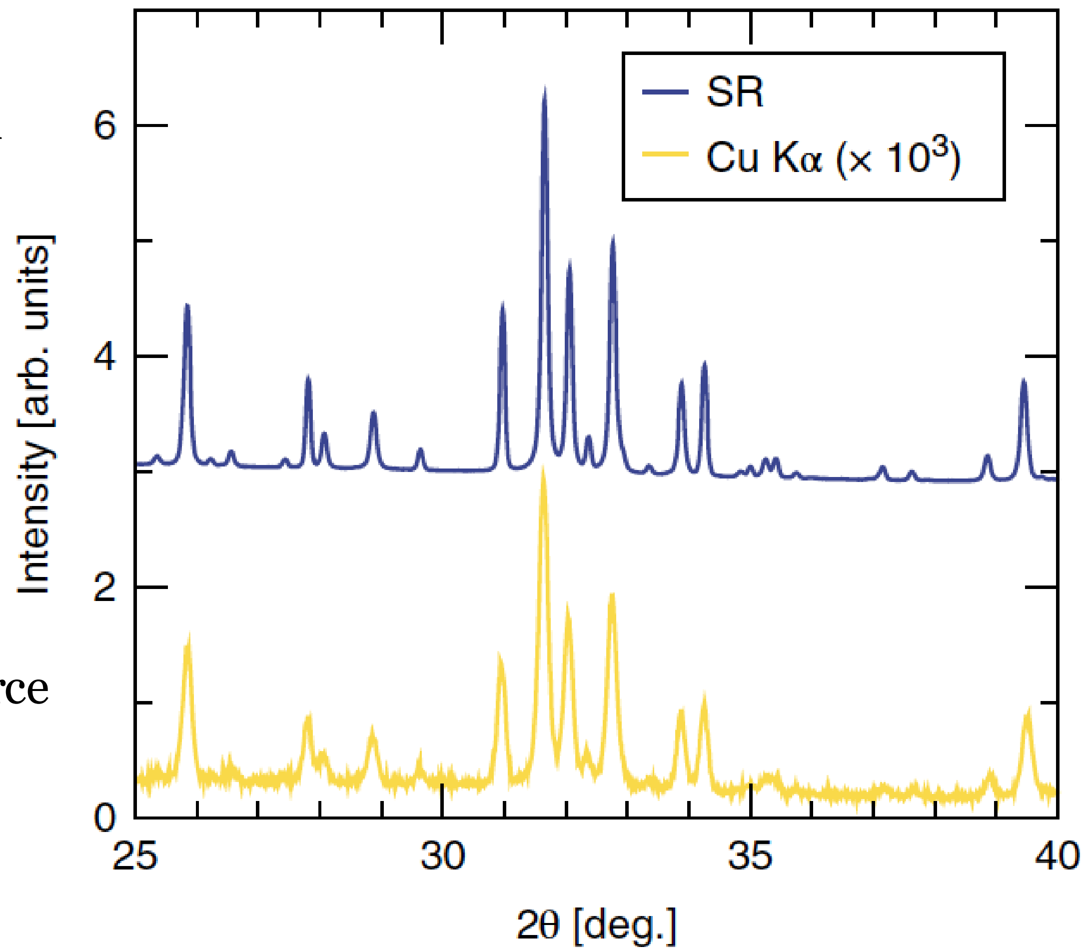
PAUL SCHERRER INSTITUT



Lab source vs. Synchrotron

powder diffraction of Calcium Phosphate

synchrotron



measured in 5s

lab source

measured in 9800s (resulting still in 1000 times less intensity)

N. Casati, PSI

Summary

Diffraction:

- The scattering vector q
- Ewald sphere to determine which reciprocal lattice points are in Bragg condition in a certain geometry
- single crystal diffraction: rotation method or Laue diffraction
- imperfect crystals: defects, grainboundaries, strain: change peak width and/or position
- preferred direction of certain crystallographic directions: textured sample influence of symmetry
- polycrystalline material without preferrd direction: “powder sample”
- X-ray diffraction Lab sources vs. synchrotrons