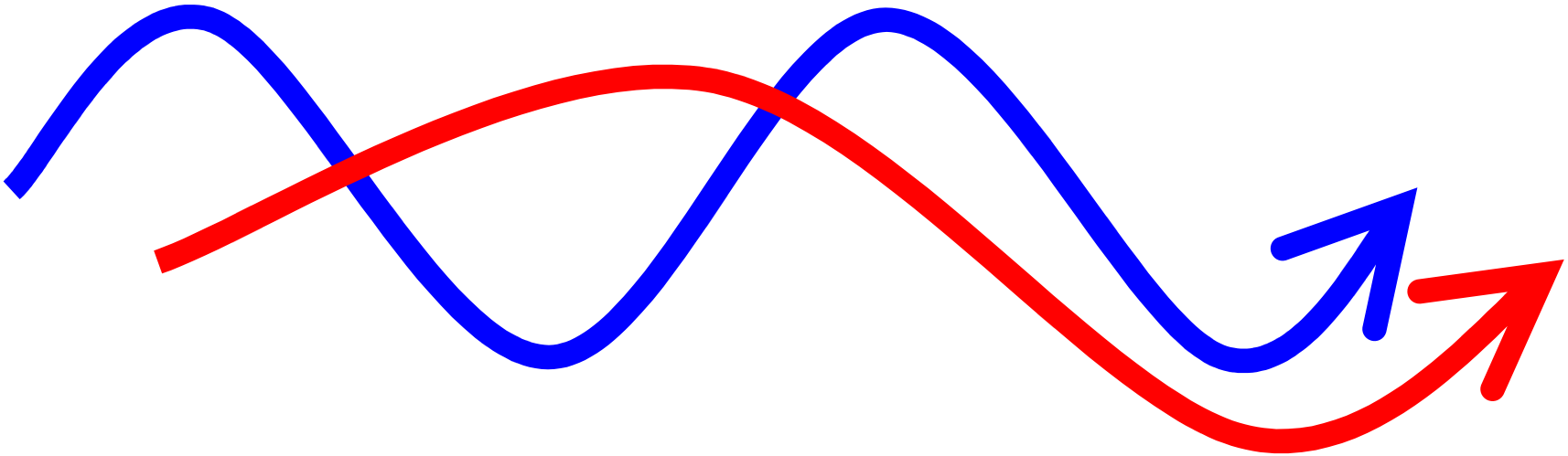
Outline of the day

- Introduction
- Basic X-ray diffraction
  - Powders, thin films, single crystals
- Small-angle X-ray scattering
- X-ray absorption spectroscopy
  - Atomic structure
  - Electronic structure (Ben Ruck)
- Advanced X-ray diffraction
  - Anomalous diffraction
  - Total X-ray scattering
- Designing experiments
  - In situ measurements

Basic X-ray Diffraction

- Peak positions
- Peak intensities
- Experiment setup
- Different types of samples
  - Single crystals
  - Powders
  - Thin films
- Information that can be obtained
  - Phase analysis
  - Crystallite size
  - Full pattern analysis
  - Preferred orientation

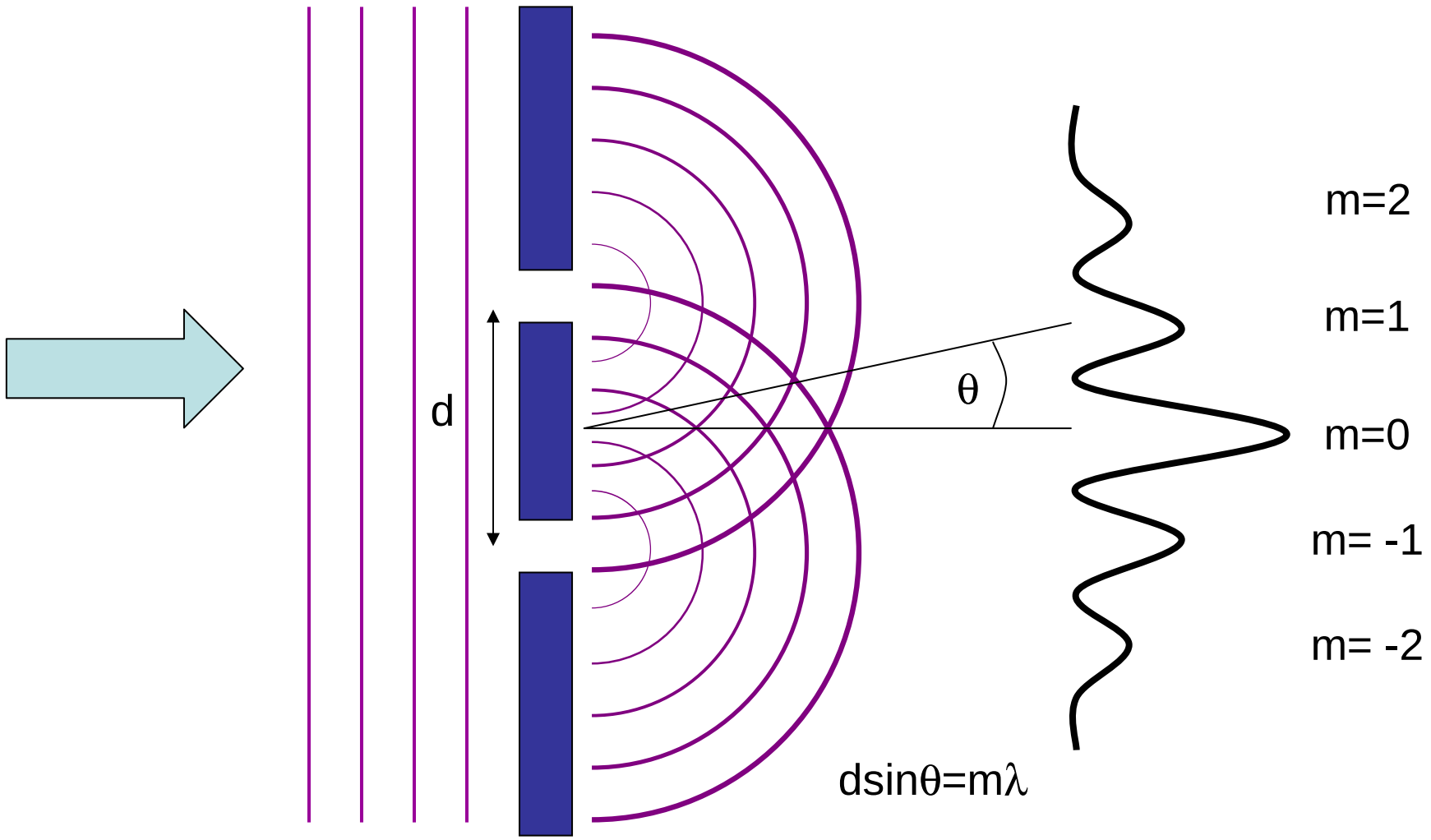
Properties of light



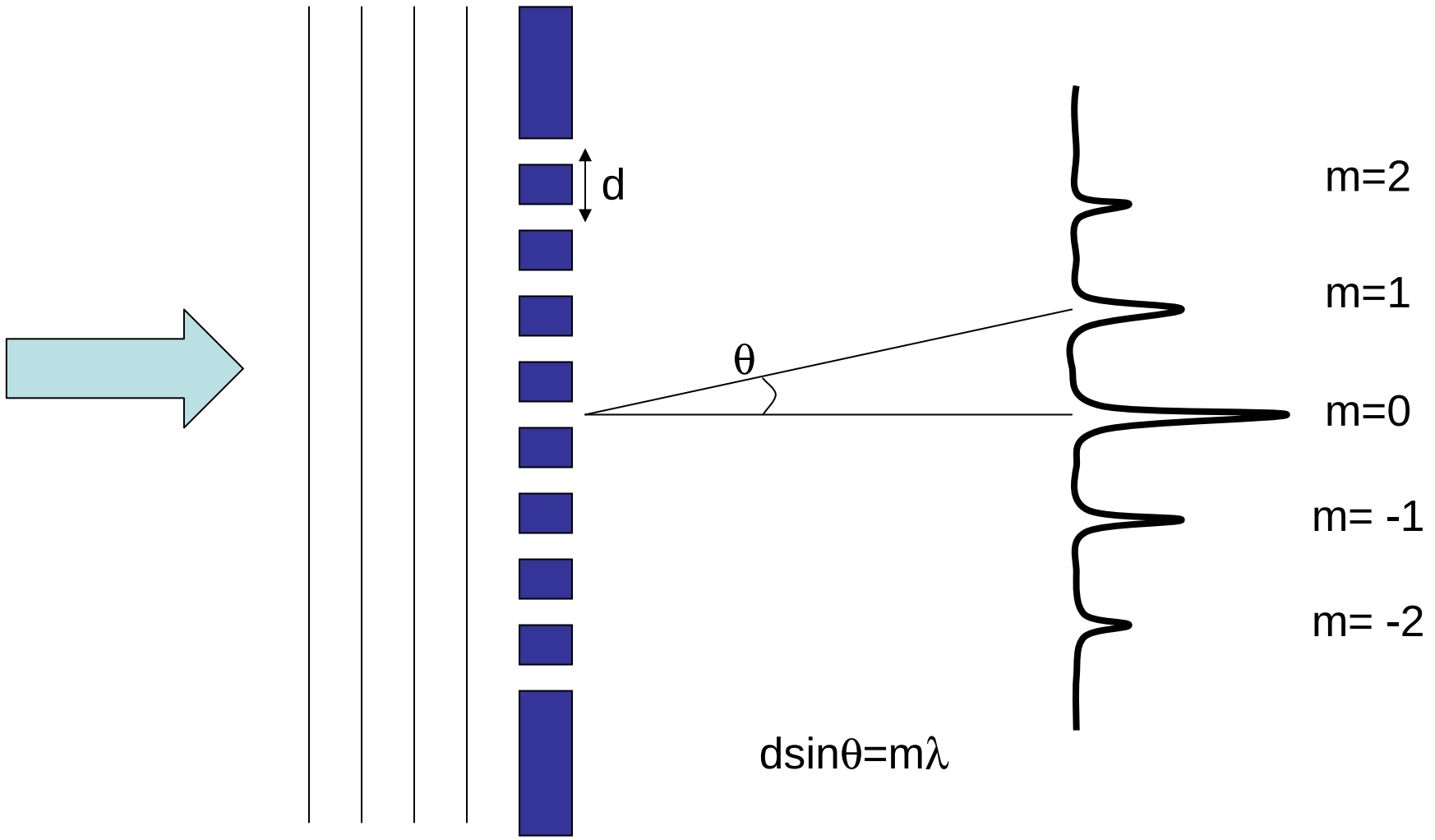
- Wavelength = 1/frequency
- Amplitude = intensity
- Particle nature: photon

Visible	**X-rays**
Colour	Energy

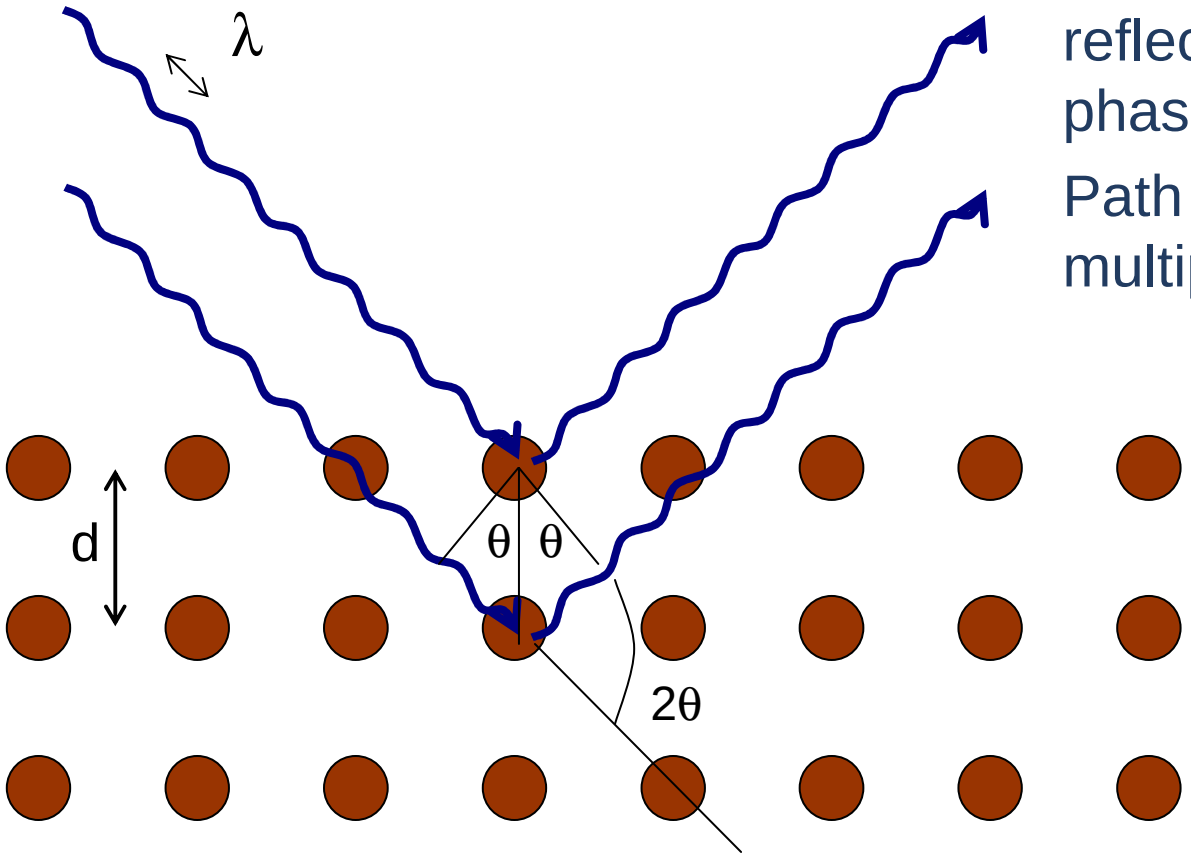
Two slit experiment



Diffraction grating



A ‘grating’ made of atoms



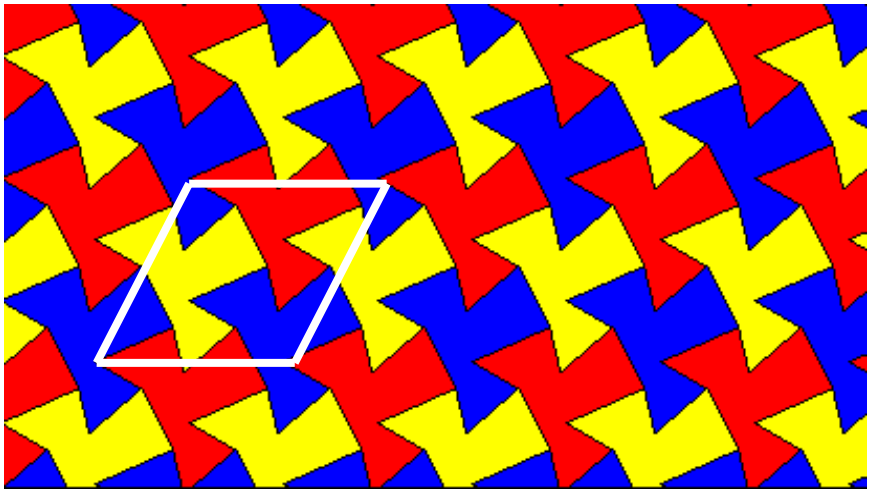
For constructive interference, reflected light must be in phase

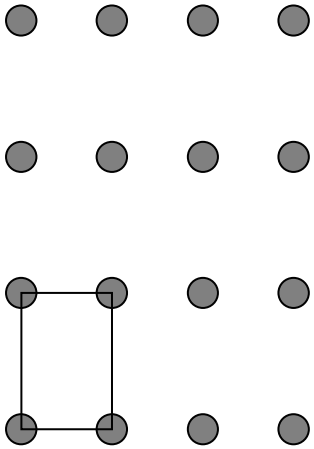
Path difference ($2d\sin\theta$) is a multiple of the wavelength λ

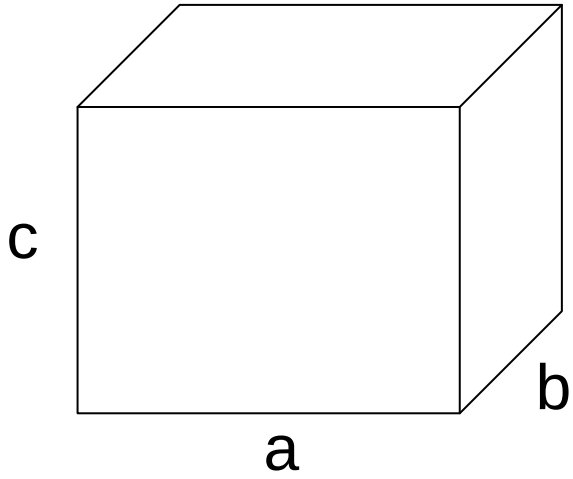
Bragg’s Law:

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

The unit cell





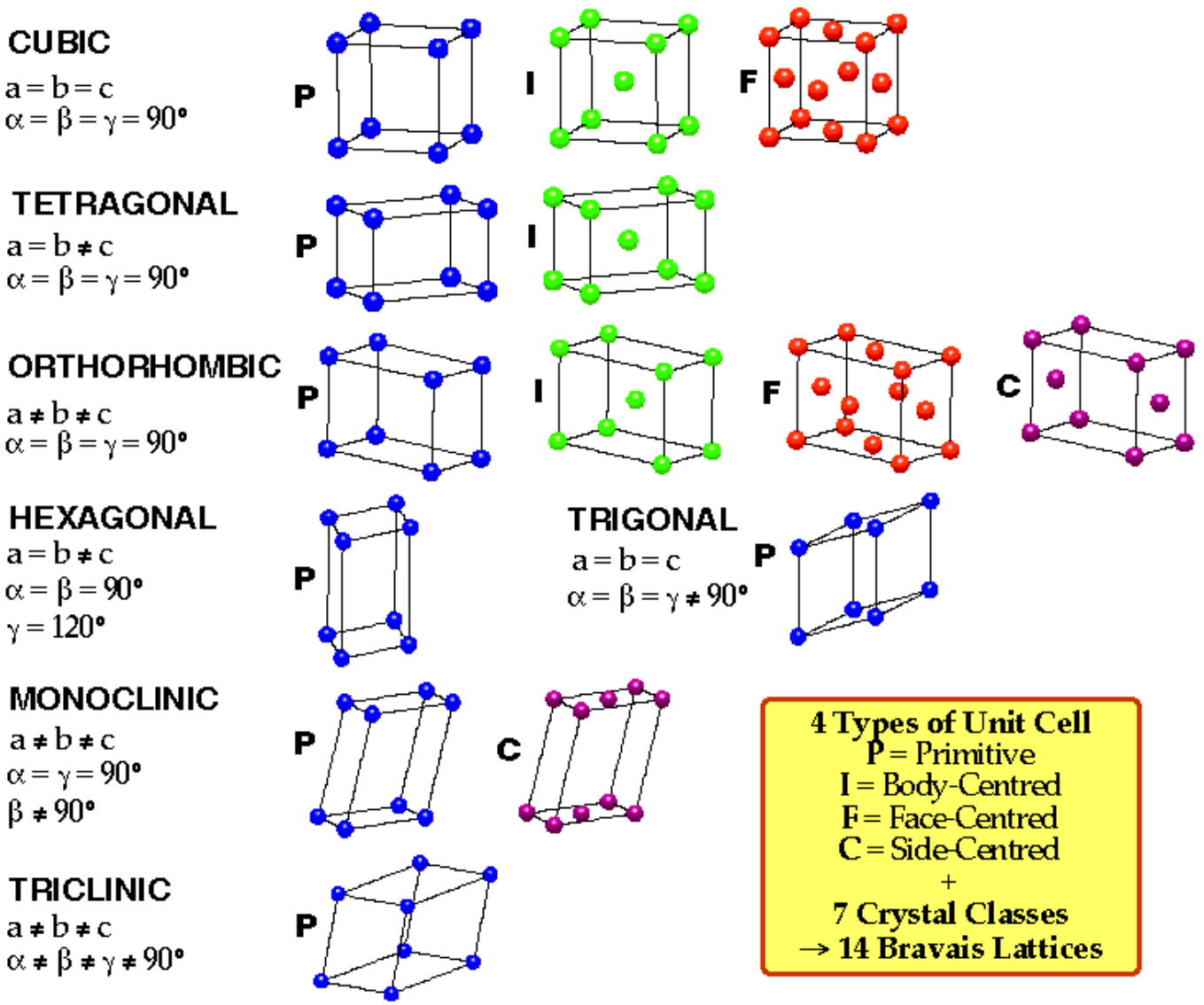


α = angle between b and c

β = angle between a and c

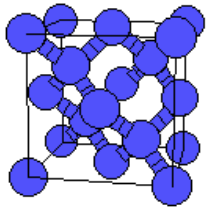
γ = angle between a and b

Bravais lattices

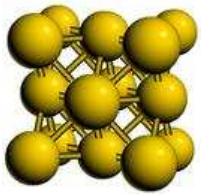


Examples

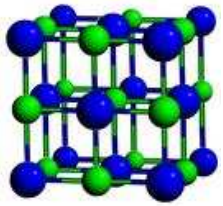
Cubic



Diamond

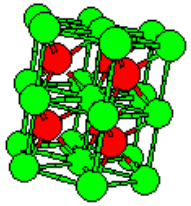


fcc

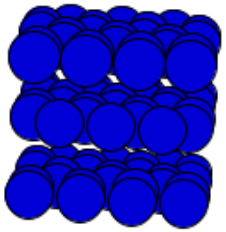


NaCl

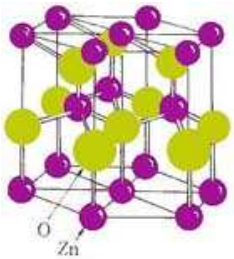
Hexagonal



WC

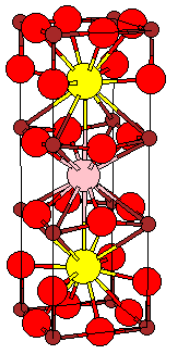


Graphite



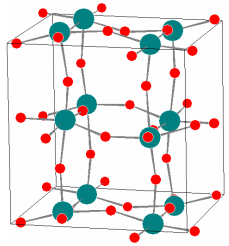
Wurtzite

Orthorhombic



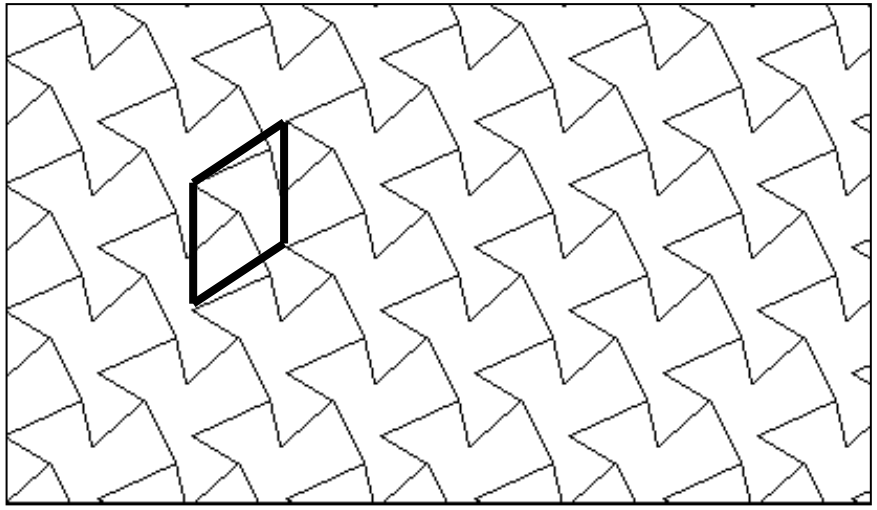
YBCO

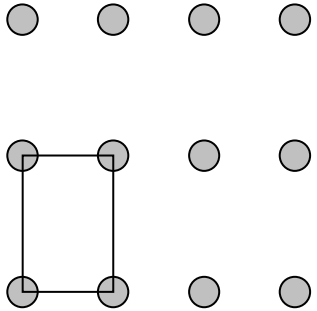
Triclinic



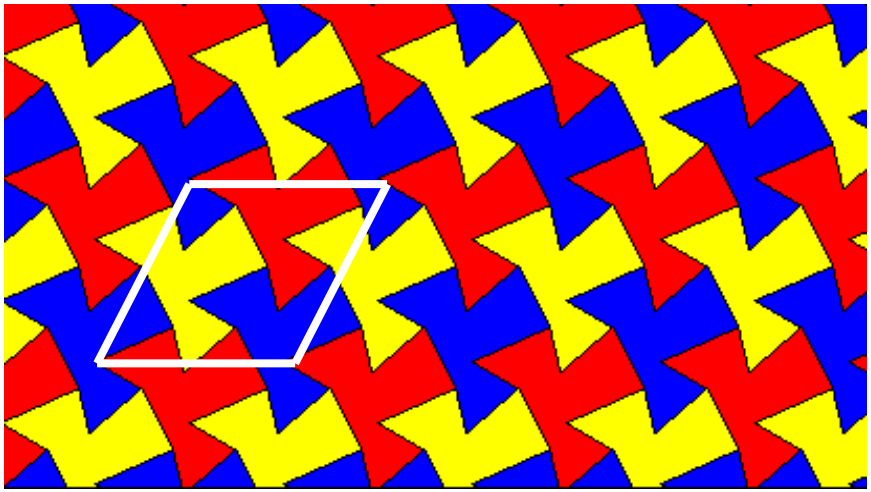
WO_3 (distorted perovskite)

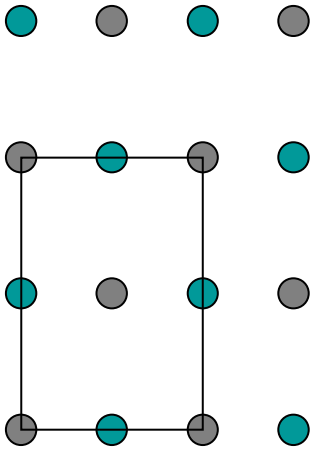
Supercells

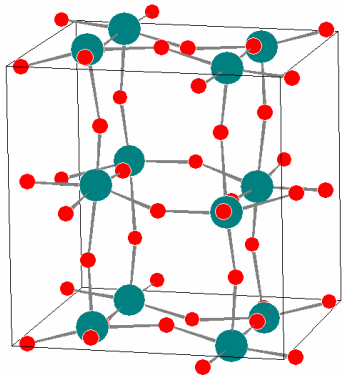




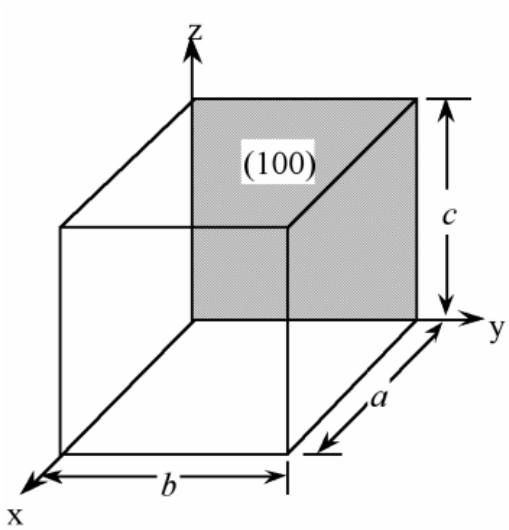
- lattice distortions
- ordering
  - atoms
  - vacancies



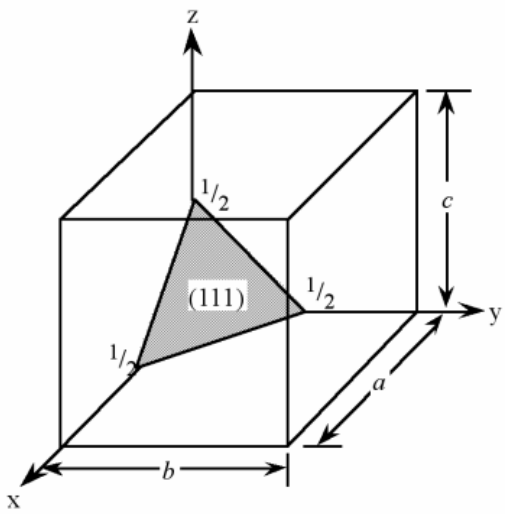




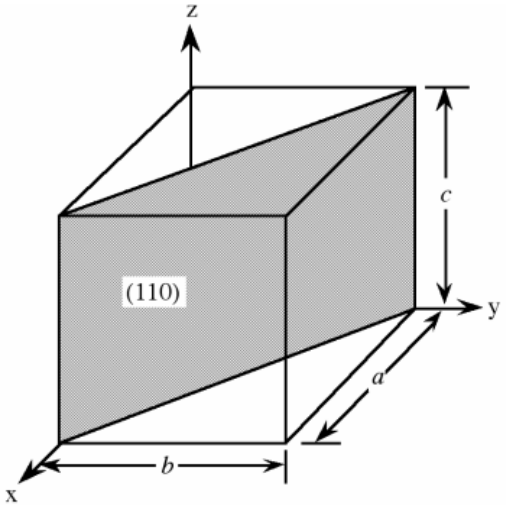
Diffracting planes in a crystal



$$\frac{h}{1}\ \frac{k}{\infty}\ \frac{l}{\infty} = (100)$$

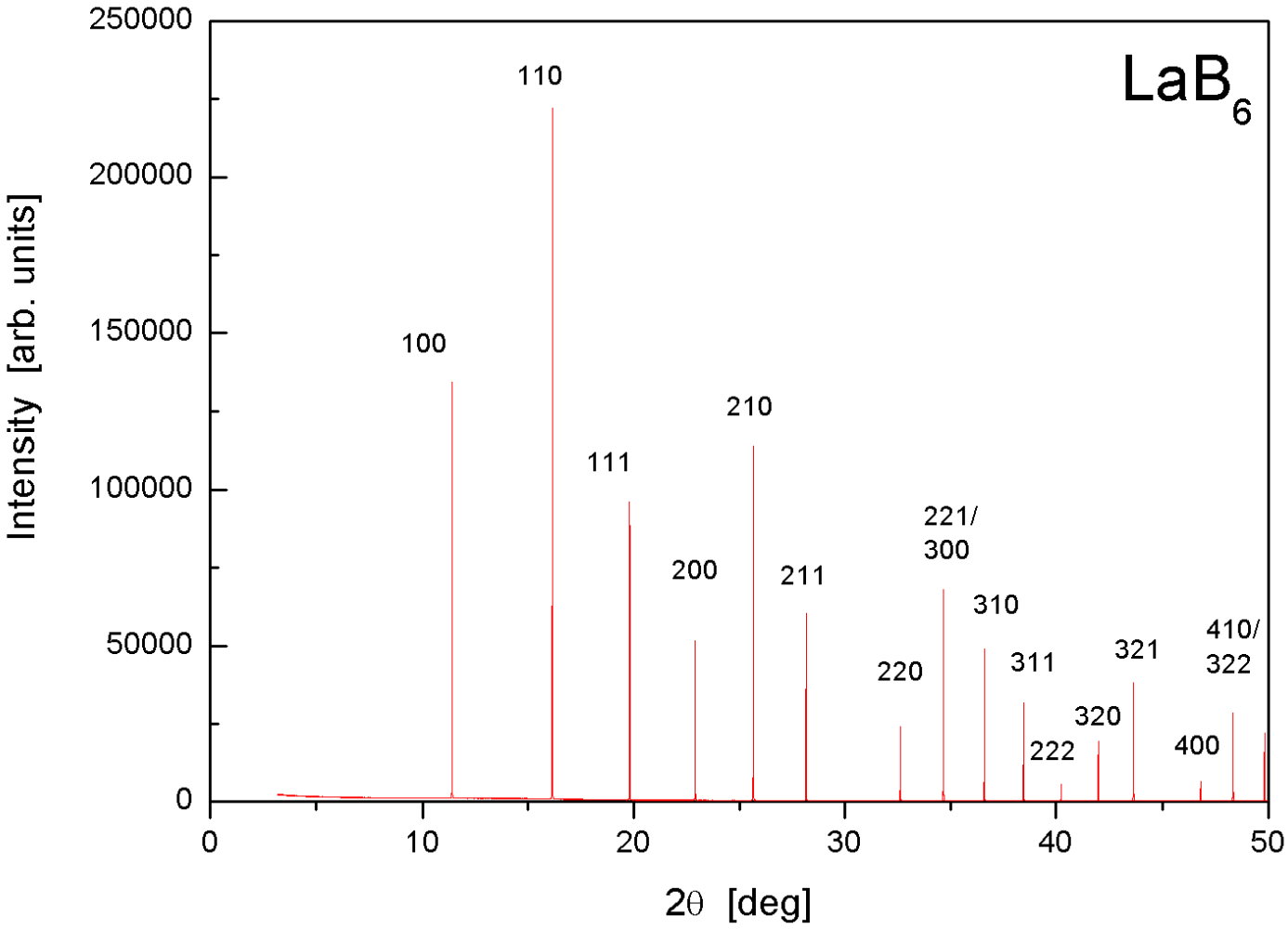


$$\frac{h}{1/2}\ \frac{k}{1/2}\ \frac{l}{1/2} = (222) = (111)$$



$$\frac{h}{1}\ \frac{k}{1}\ \frac{l}{\infty} = (110)$$

Peak positions



Peak position:

$$d^2 = \frac{h^2+k^2+l^2}{a^2}$$

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

Diffraction intensity

$$I_{(hkl)\alpha} = \frac{I_0 \lambda^3}{64\pi r}\left(\frac{e^2}{m_e c^2}\right)^2 \frac{M_{(hkl)}}{V_\alpha^2}\left|F_{(hkl)\alpha}\right|^2\left(\frac{1+\cos^2(2\theta)\cos^2(2\theta_m)}{\sin^2\theta\cos\theta}\right)_{hkl}\frac{v_\alpha}{\mu_s}$$

Geometrical

Electron scattering power

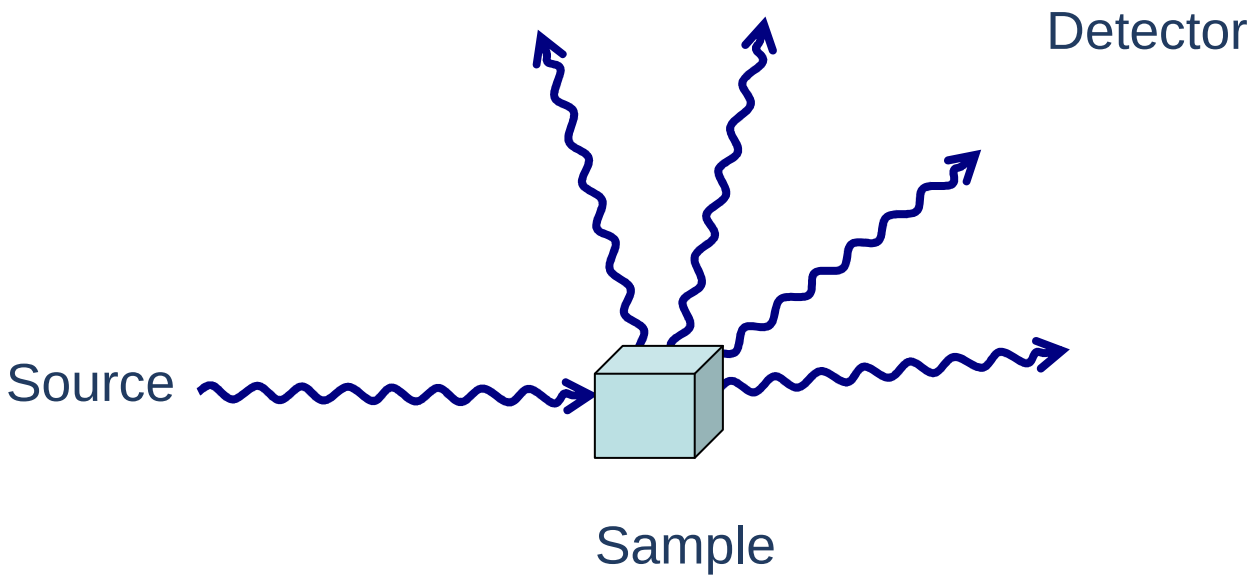
Symmetry

Structure factor

X-ray polarisation factor

Sample absorbance

X-ray diffraction experiment setup



Different sources

IRL laboratory instrument

Australian Synchrotron

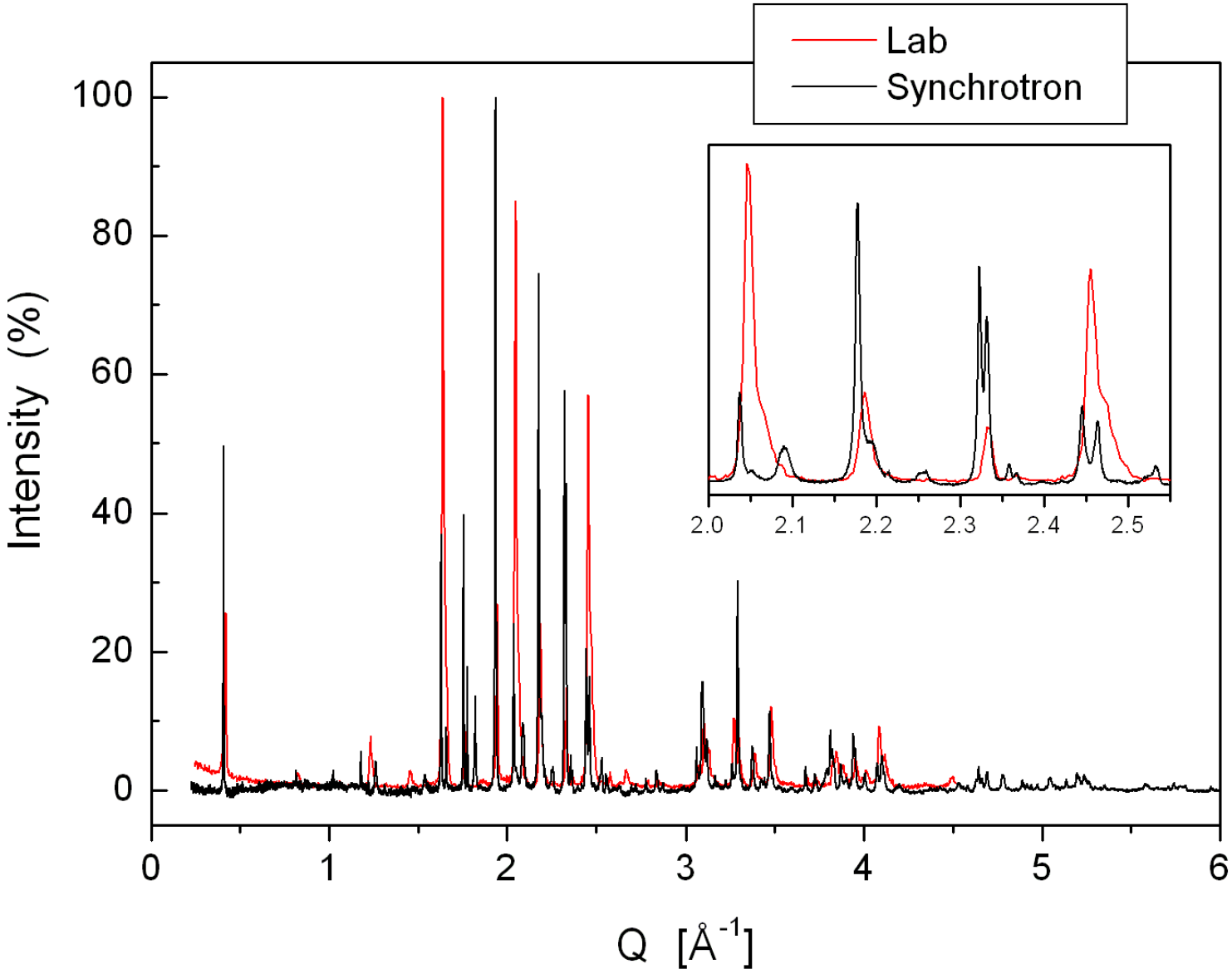
Photon flux ratio 1:1,000,000

Advantages of using a synchrotron source for X-ray diffraction

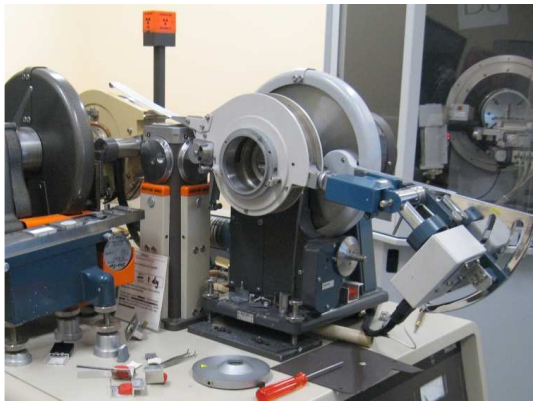
- Increased flux
  - Smaller samples
  - Weakly scattering samples
    - Poorly crystalline, low Z
  - Faster measurement
    - Real-time experiments
    - High throughput
- Lower divergence
  - Better resolution

Question: Which would be suitable for X-ray diffraction: bend magnet, wiggler, or undulator?

Instrument resolution

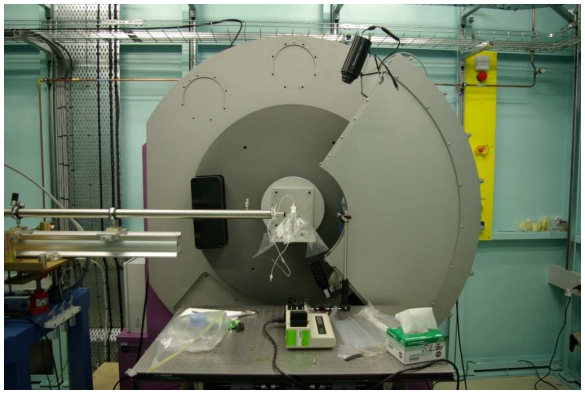


Different detectors



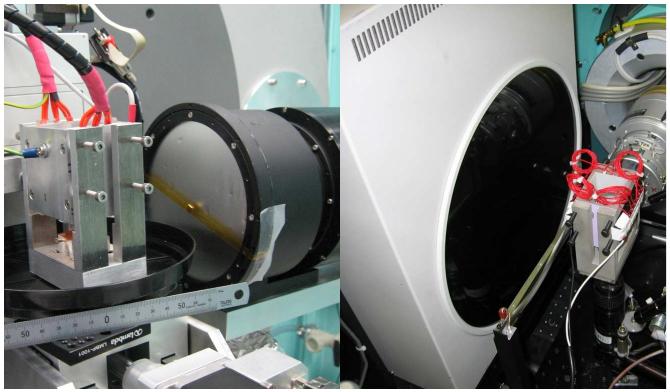
Point detector

- high resolution
- post-sample collimation: grazing incidence
- $
- slow



Strip detector

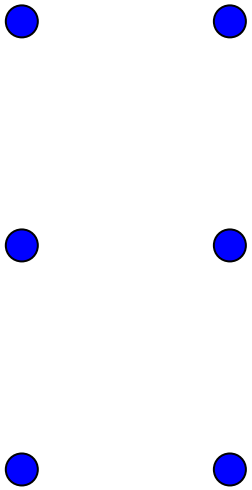
- collect entire pattern at once
- fast readout
- $$
- no post-sample collimation



Area detector

- collect entire pattern at once
- fast, direct observation of texture
- $$$
- limited resolution
- no post-sample collimation

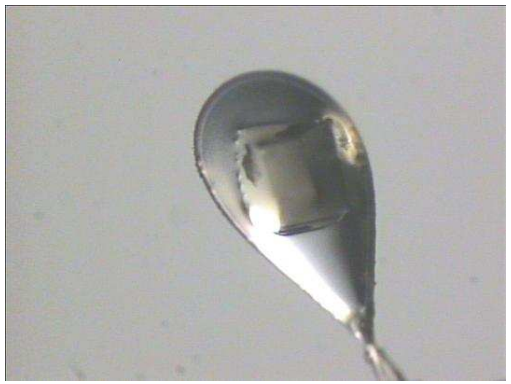
Different types of samples: single crystal

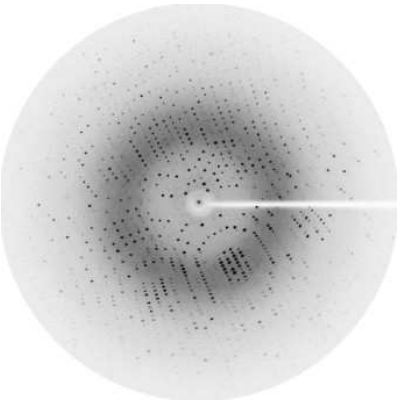


One large crystallite

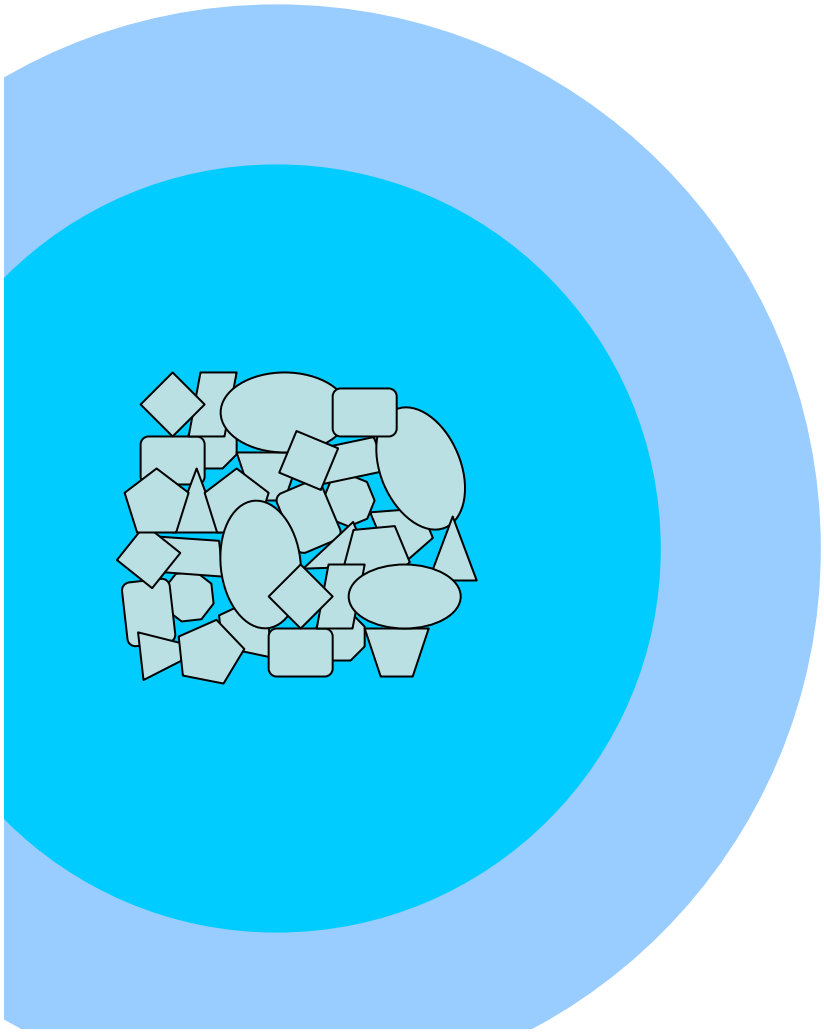
Diffraction condition is met at points in 3D reciprocal space

Measure using 2D detector, rotate sample





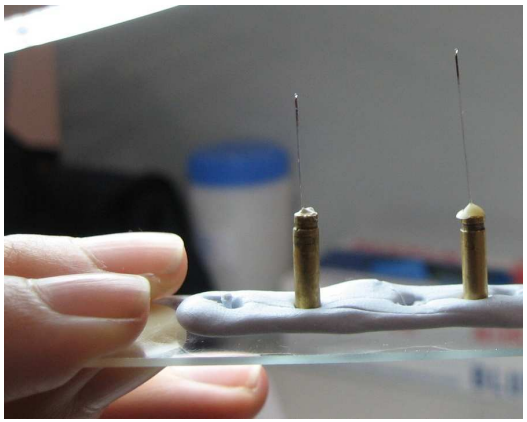
Different types of samples: powder

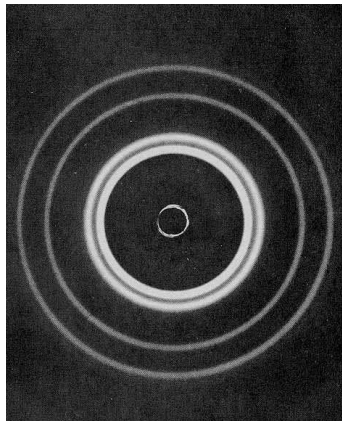


Many small crystallites, randomly oriented

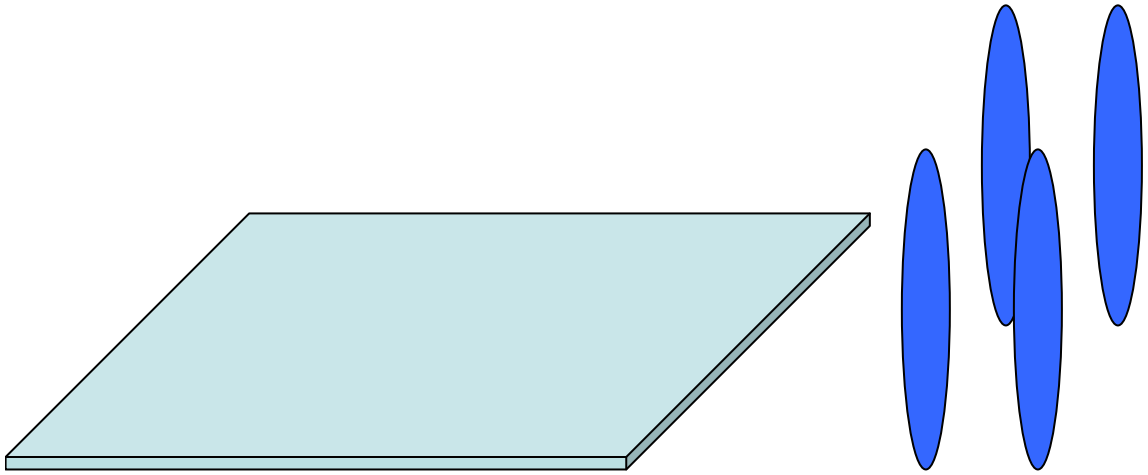
Diffraction condition is met at spheres in 3D reciprocal space - isotropic

Measure in one direction (point or strip detector ok)



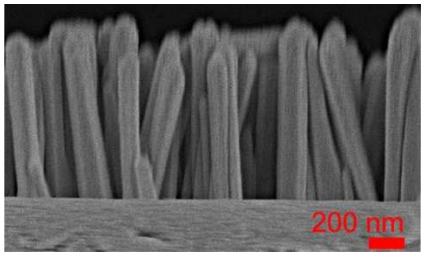


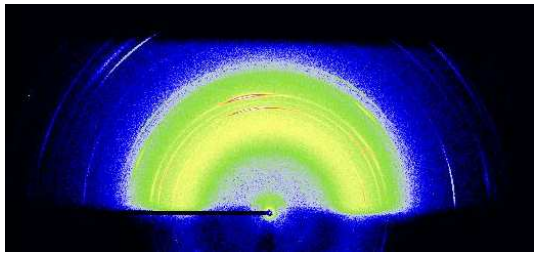
Different types of samples: thin film

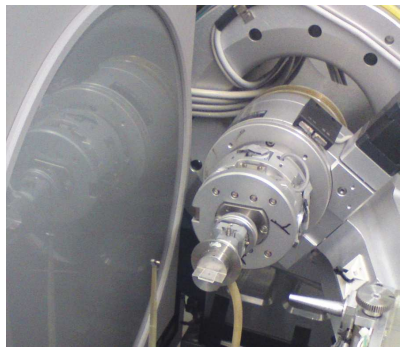


May be oriented out of plane (isotropic in plane) or epitaxial

Normally use grazing incidence to reduce substrate diffraction



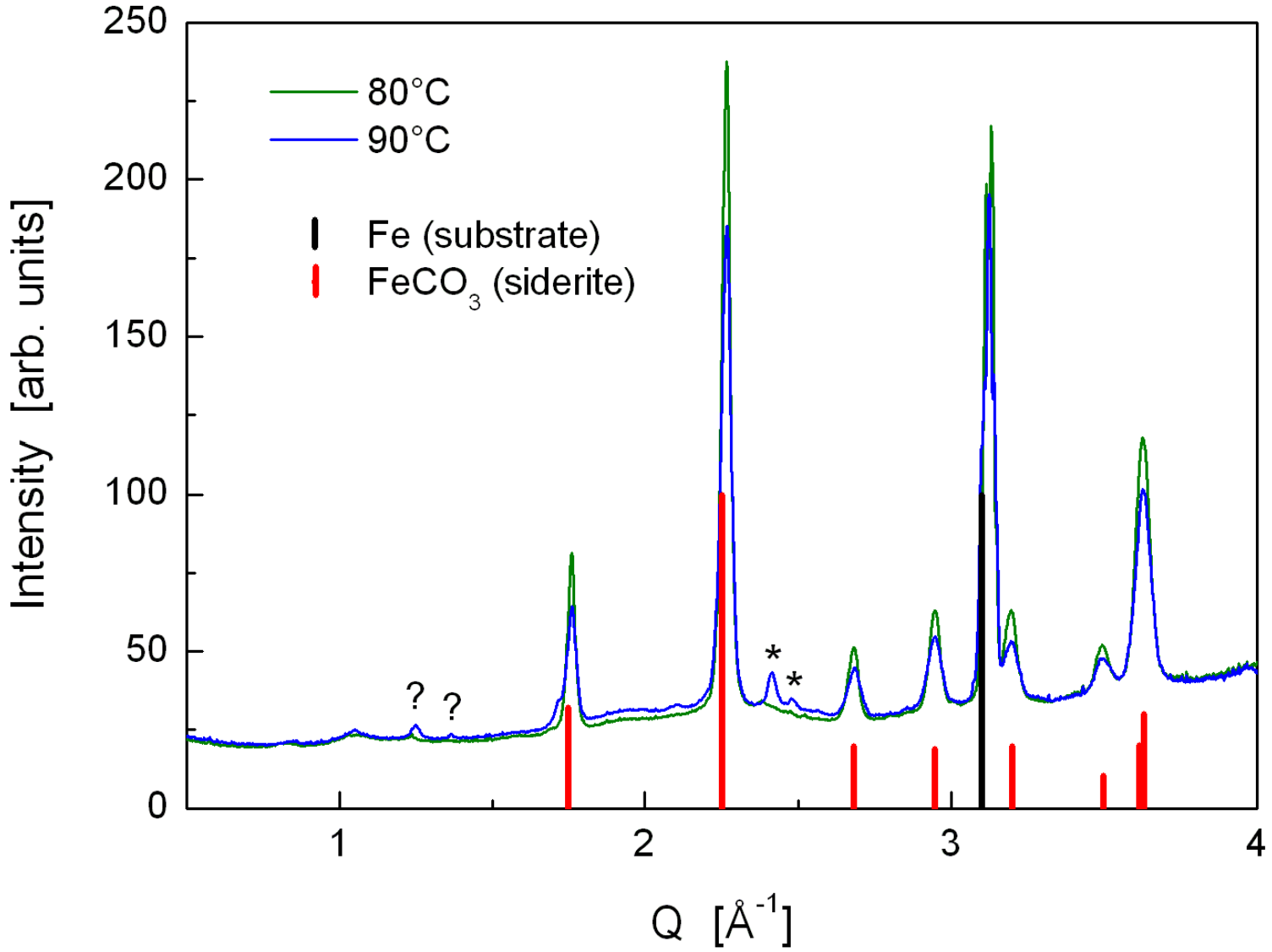


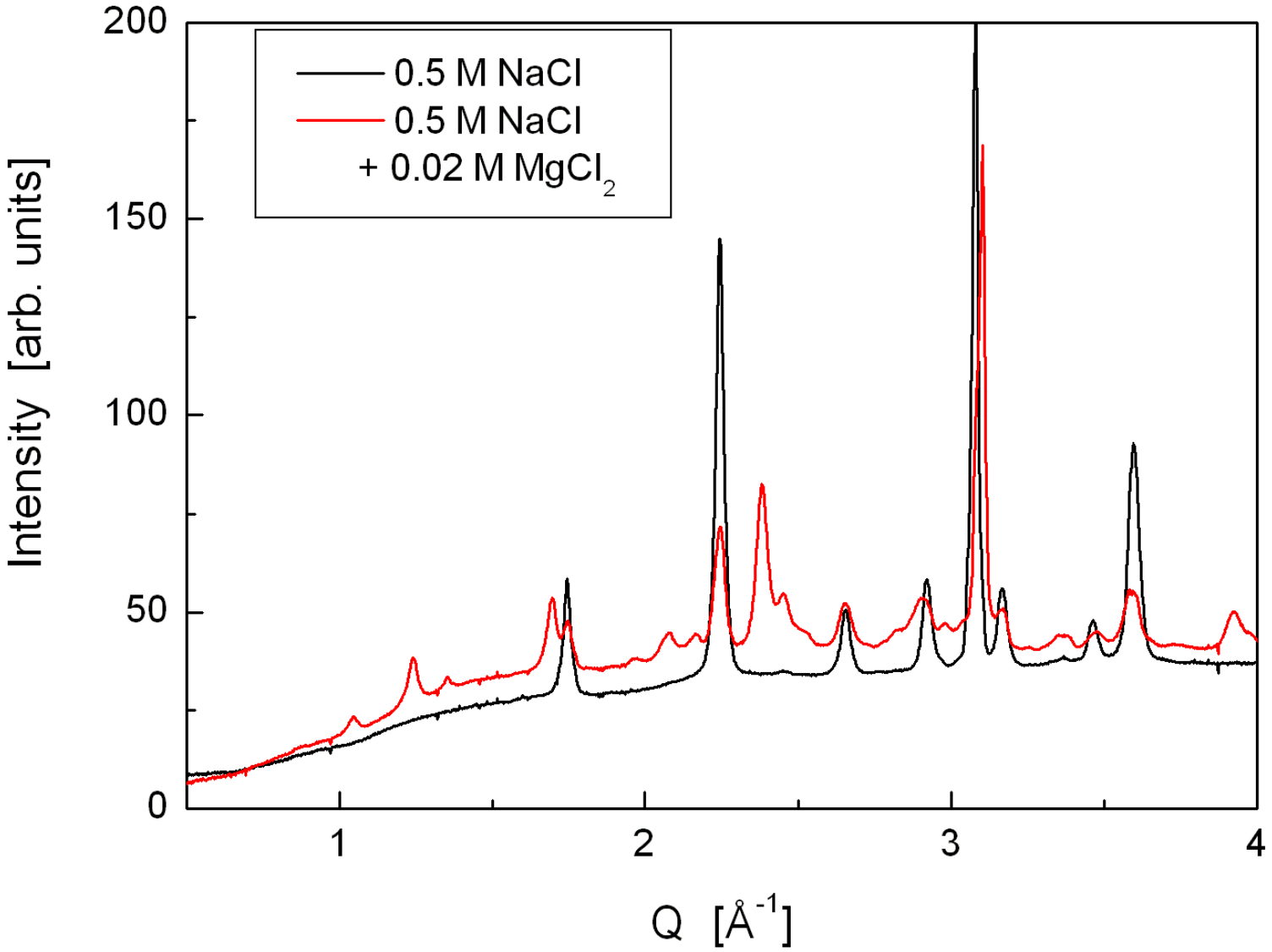


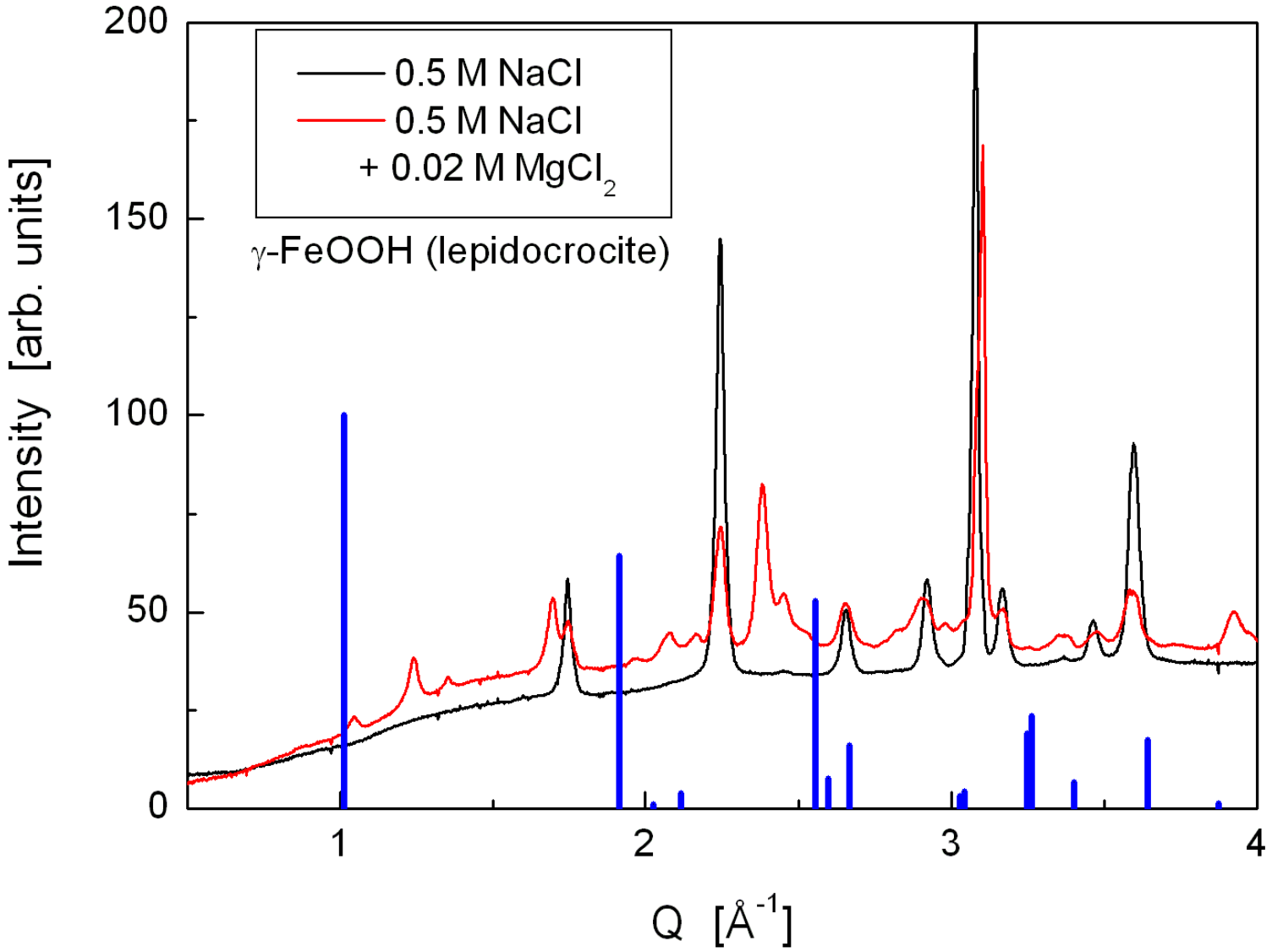
What can we find out?

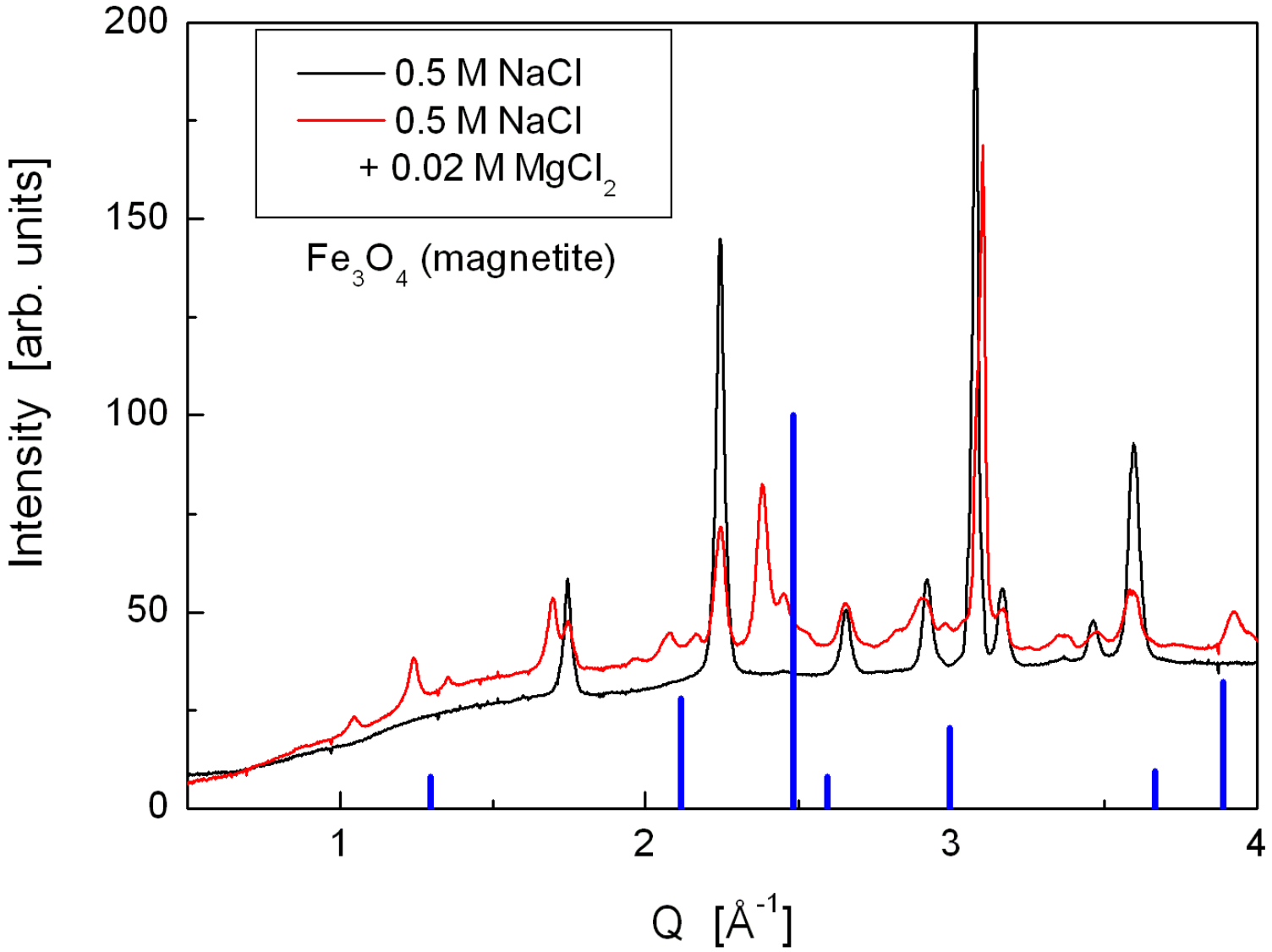
- Phases
  - Composition, ratio
- Peak positions: lattice parameters
- Peak width: crystallite size, strain
- Full pattern analysis
  - Accurate lattice parameters, atomic positions
- Texture (preferential orientation)
  - Direction and degree of texture

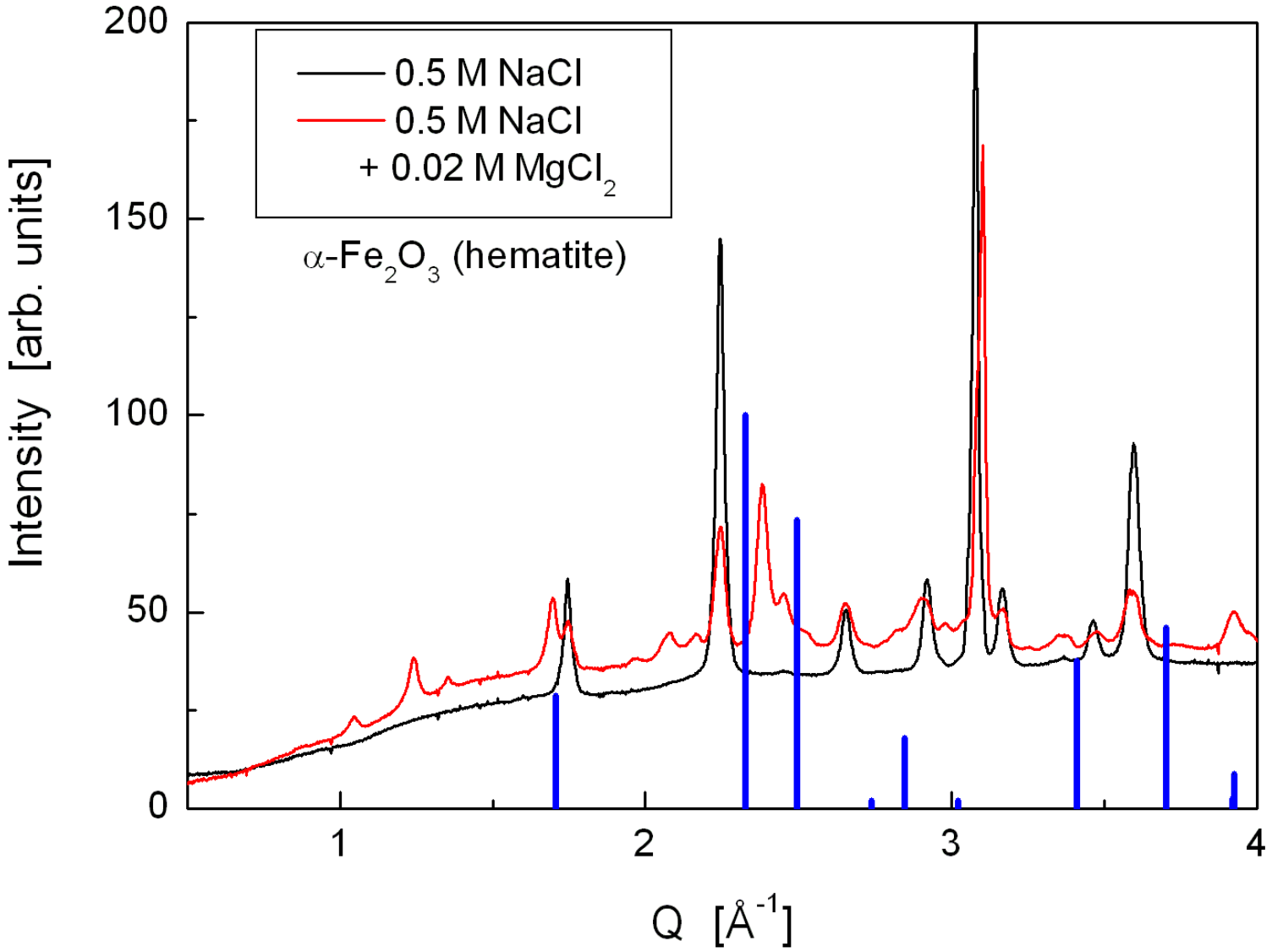
1. Phase analysis

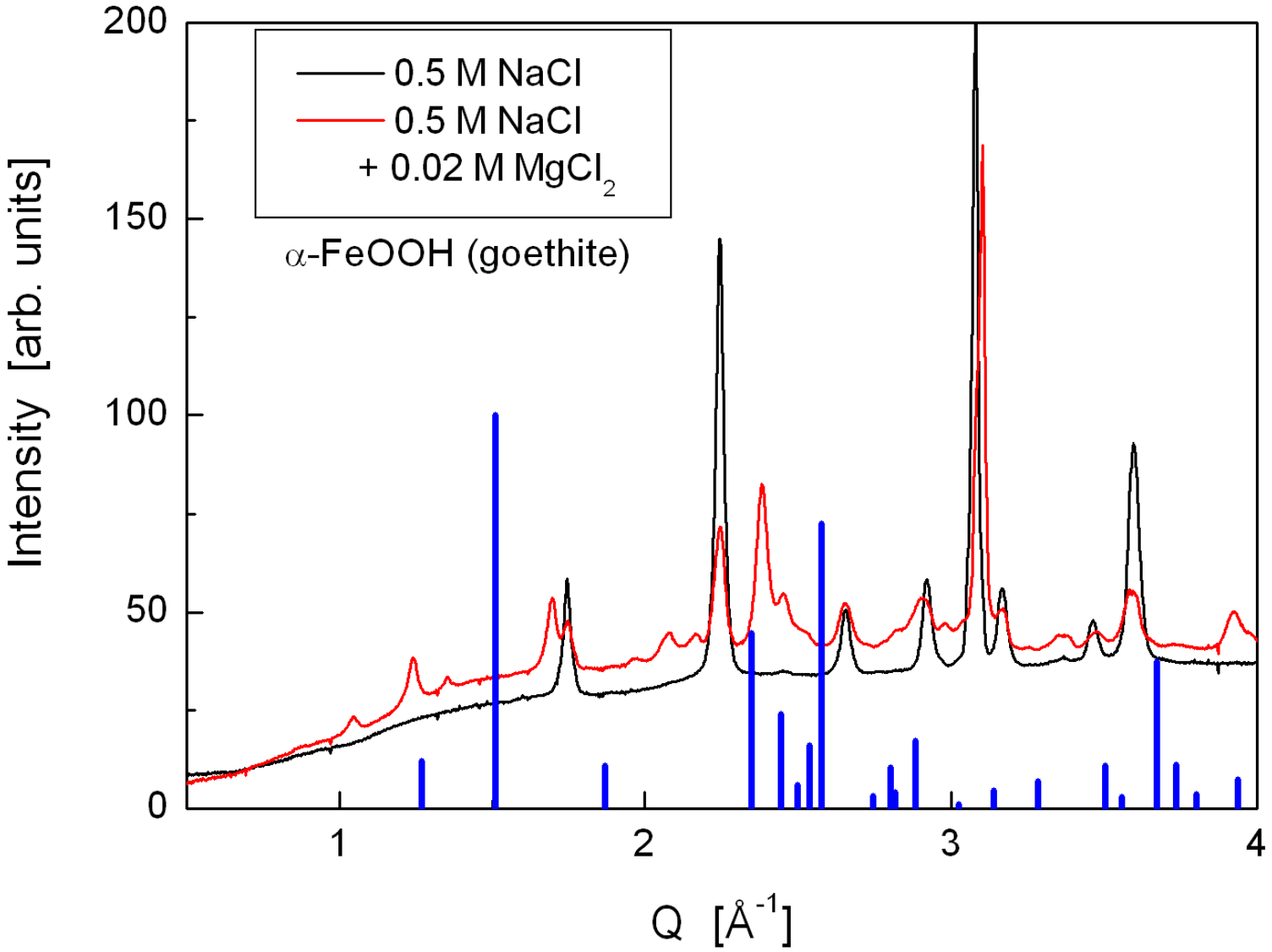


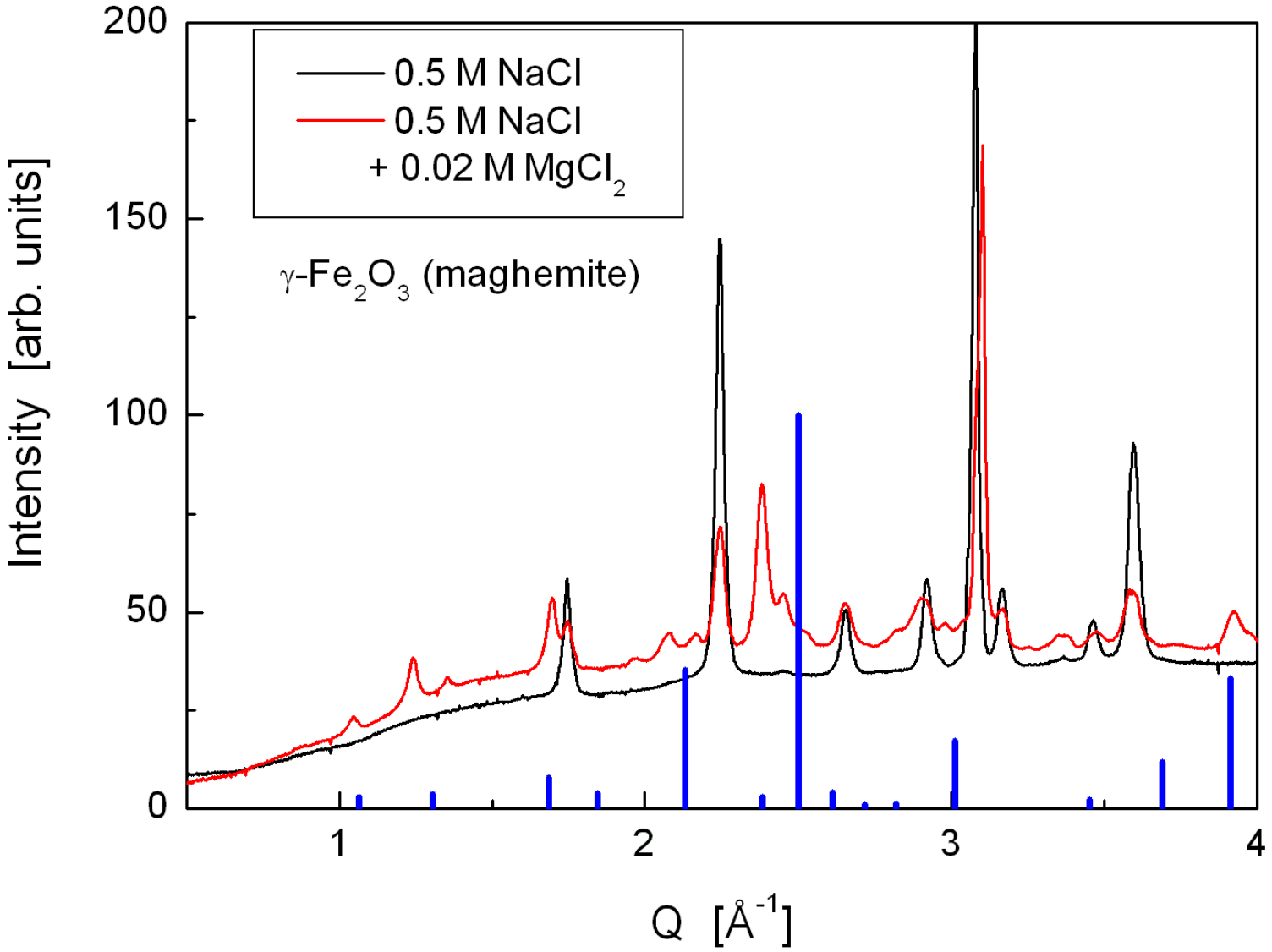

0.5 M NaCl
0.5 M NaCl
+ 0.02 M MgCl2
Intensity [arb. units]
Q [Å-1]
0
50
100
150
200
1
2
3
4

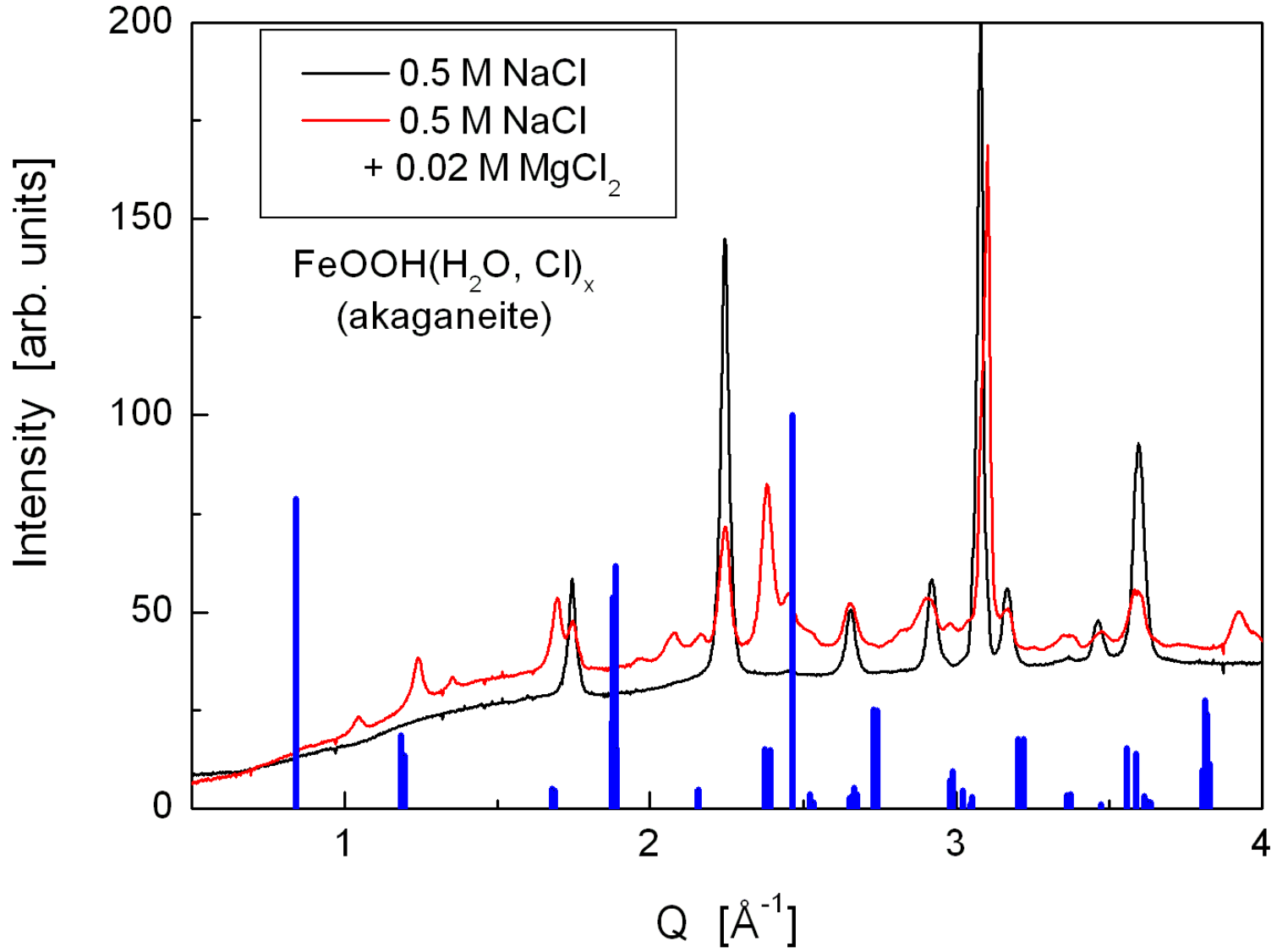

0.5 M NaCl
0.5 M NaCl
+ 0.02 M MgCl2
γ-FeOOH (lepidocrocite)
Intensity [arb. units]
Q [Å-1]
0
50
100
150
200
1
2
3
4

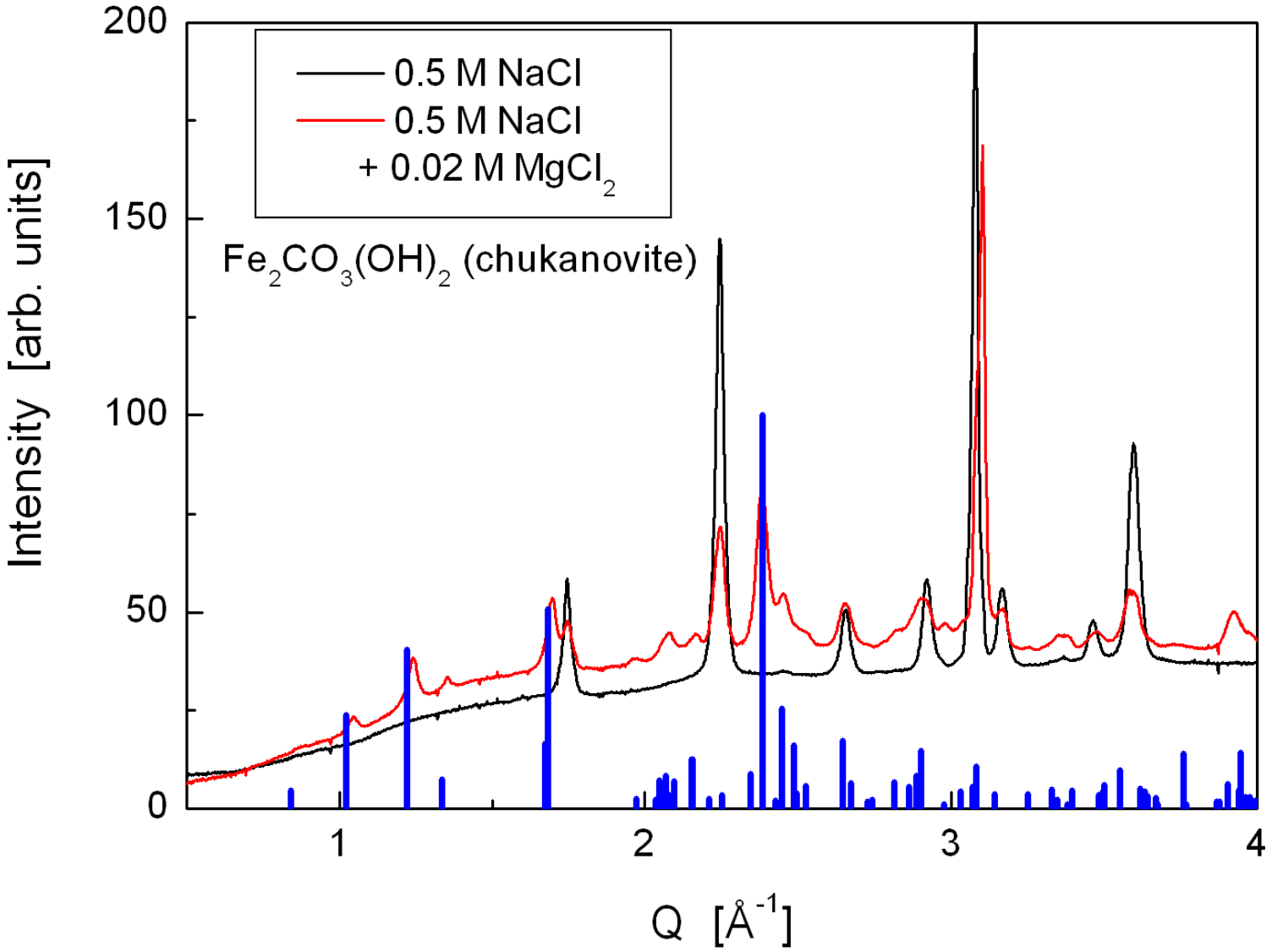

0.5 M NaCl
0.5 M NaCl
+ 0.02 M MgCl2
Fe3O4 (magnetite)
Intensity [arb. units]
Q [Å-1]
0
50
100
150
200
1
2
3
4


0.5 M NaCl
0.5 M NaCl
+ 0.02 M MgCl2
α-Fe2O3 (hematite)
Intensity [arb. units]
Q [Å-1]
0
50
100
150
200
1
2
3
4

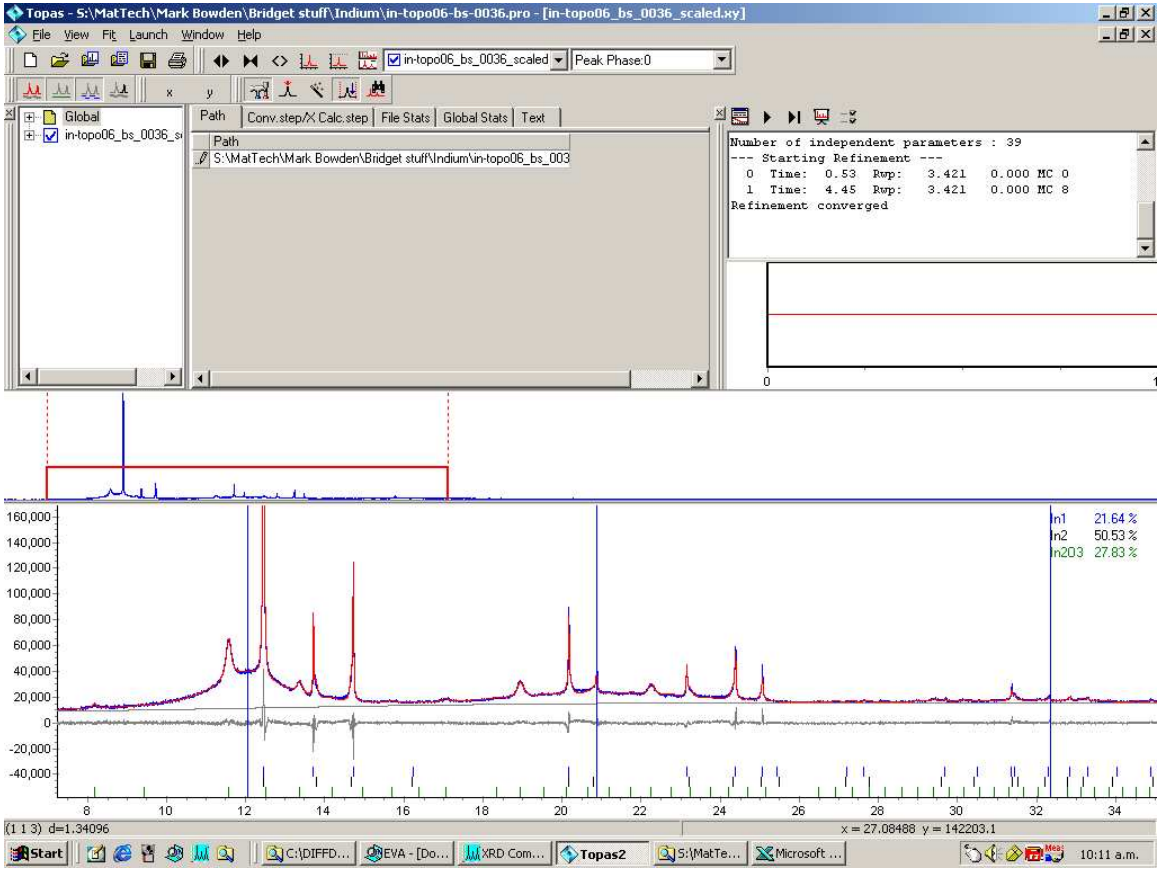

0.5 M NaCl
0.5 M NaCl
+ 0.02 M MgCl2
α-FeOOH (goethite)
Intensity [arb. units]
Q [Å-1]
0
50
100
150
200
1
2
3
4


0.5 M NaCl
0.5 M NaCl
+ 0.02 M MgCl2
γ-Fe2O3 (maghemite)
Intensity [arb. units]
Q [Å-1]
0
50
100
150
200
1
2
3
4


0.5 M NaCl
0.5 M NaCl
+ 0.02 M MgCl2
FeOOH(H2O, Cl)x
(akaganeite)
Intensity [arb. units]
Q [Å-1]
0
50
100
150
200
1
2
3
4


0.5 M NaCl
0.5 M NaCl
+ 0.02 M MgCl2
Fe2CO3(OH)2 (chukanovite)
Intensity [arb. units]
Q [Å-1]
0
50
100
150
200
1
2
3
4

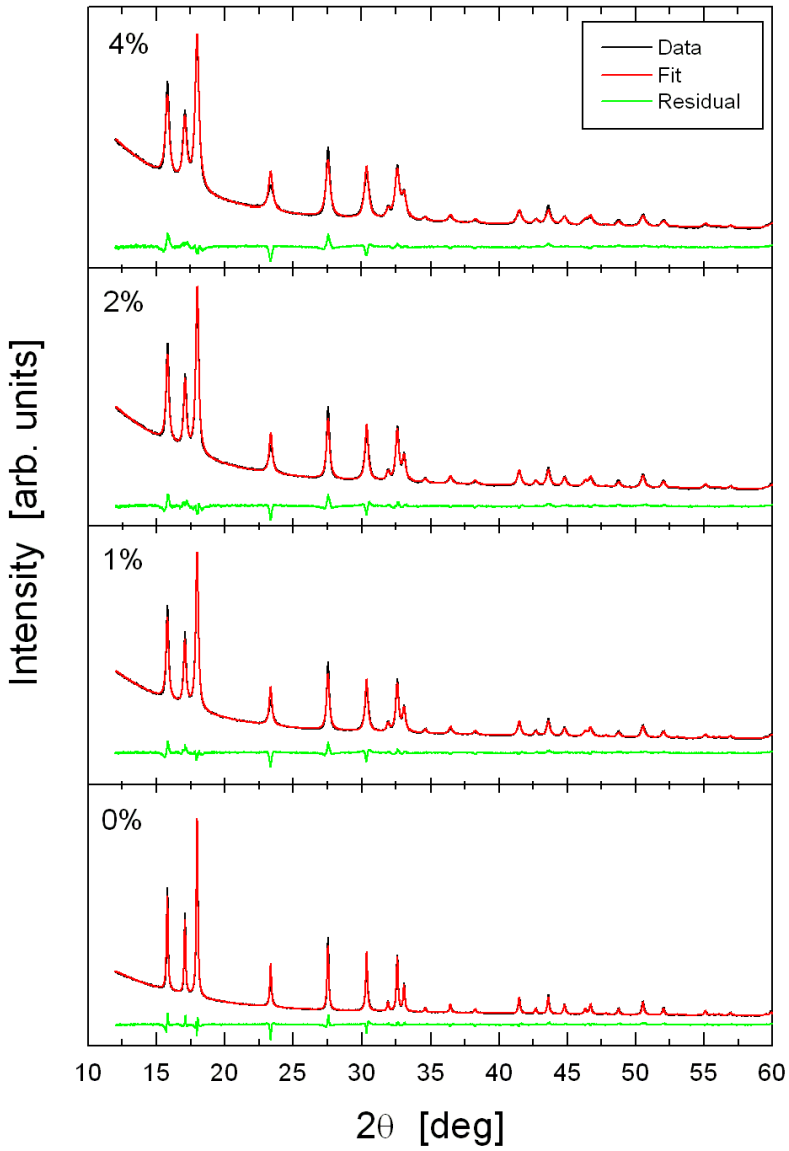
2. Full pattern analysis

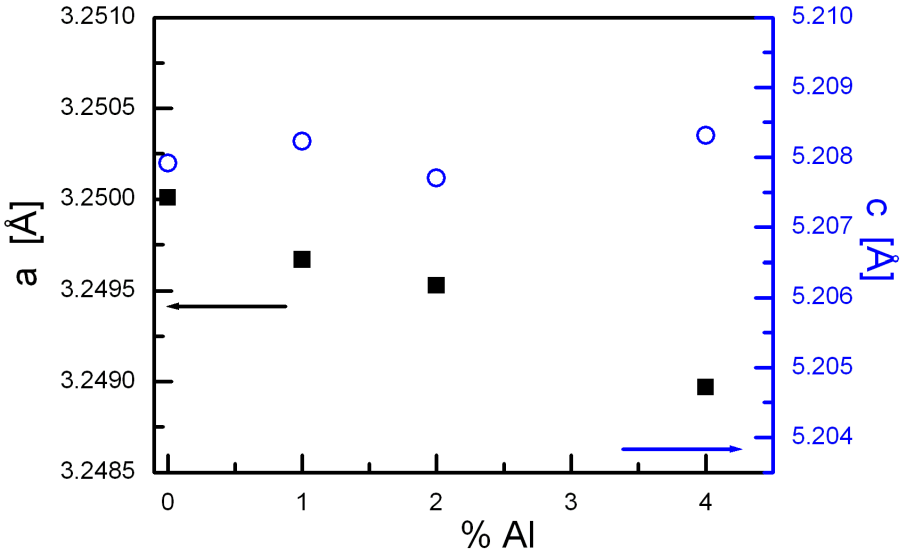


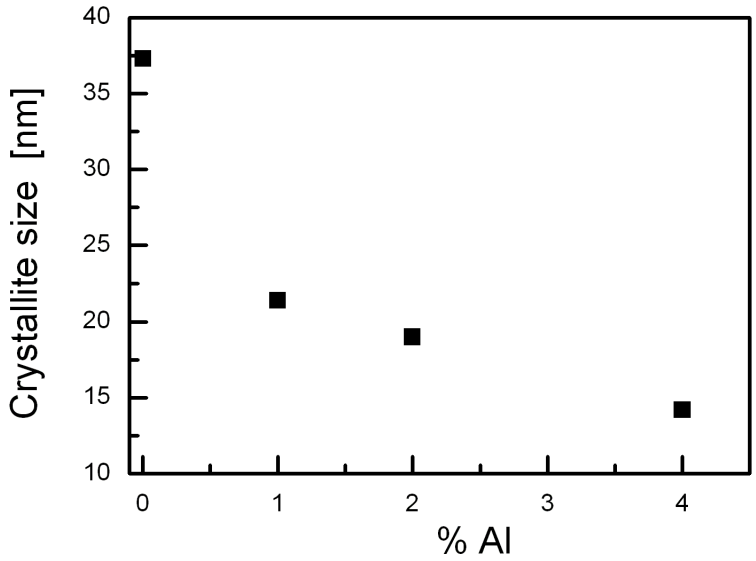
Using standard packages (e.g. GSAS, TOPAS)

Obtain accurate lattice parameters, crystallite size, strain, atomic positions (Rietveld refinement)

Case study: Al-doped ZnO

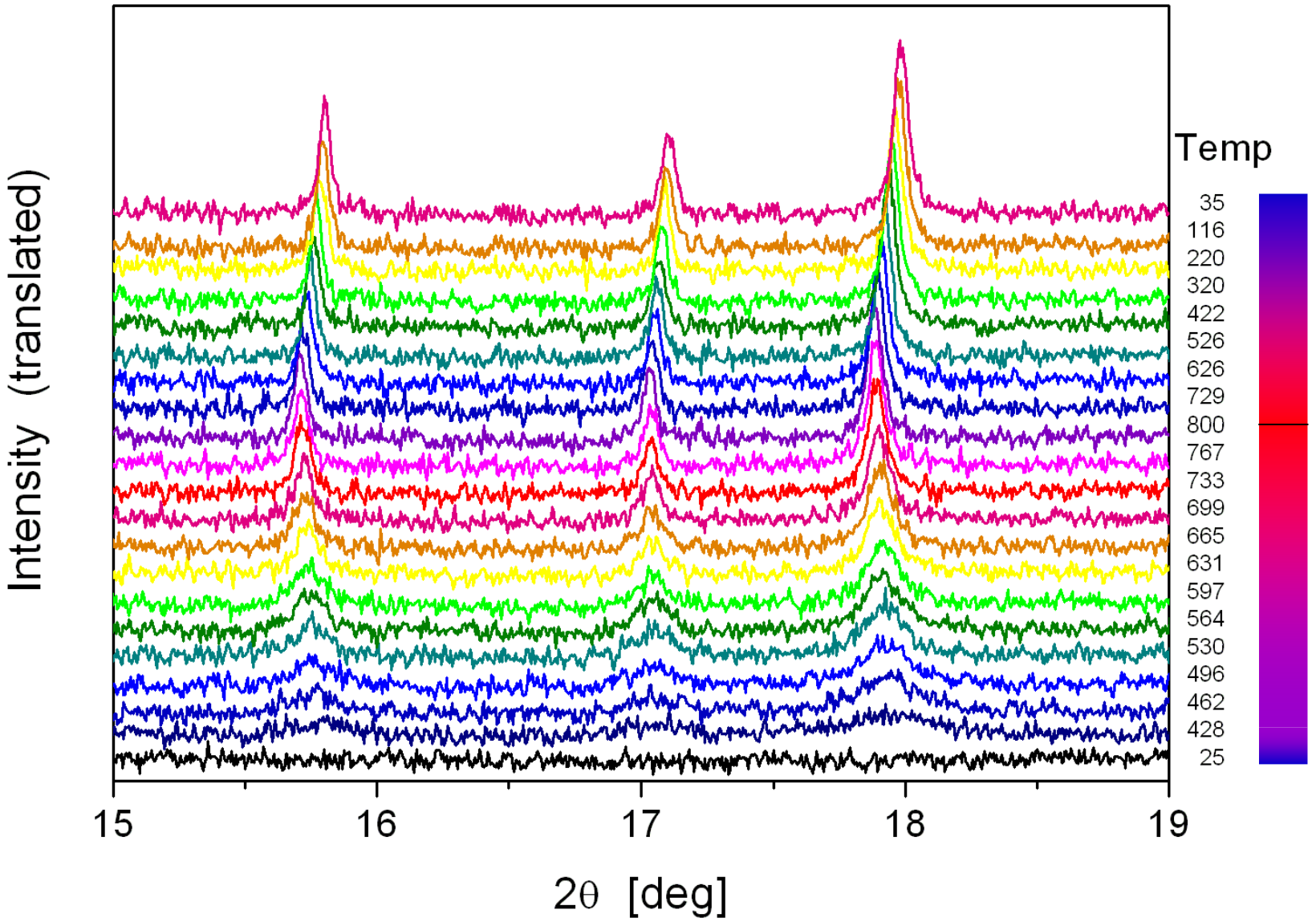




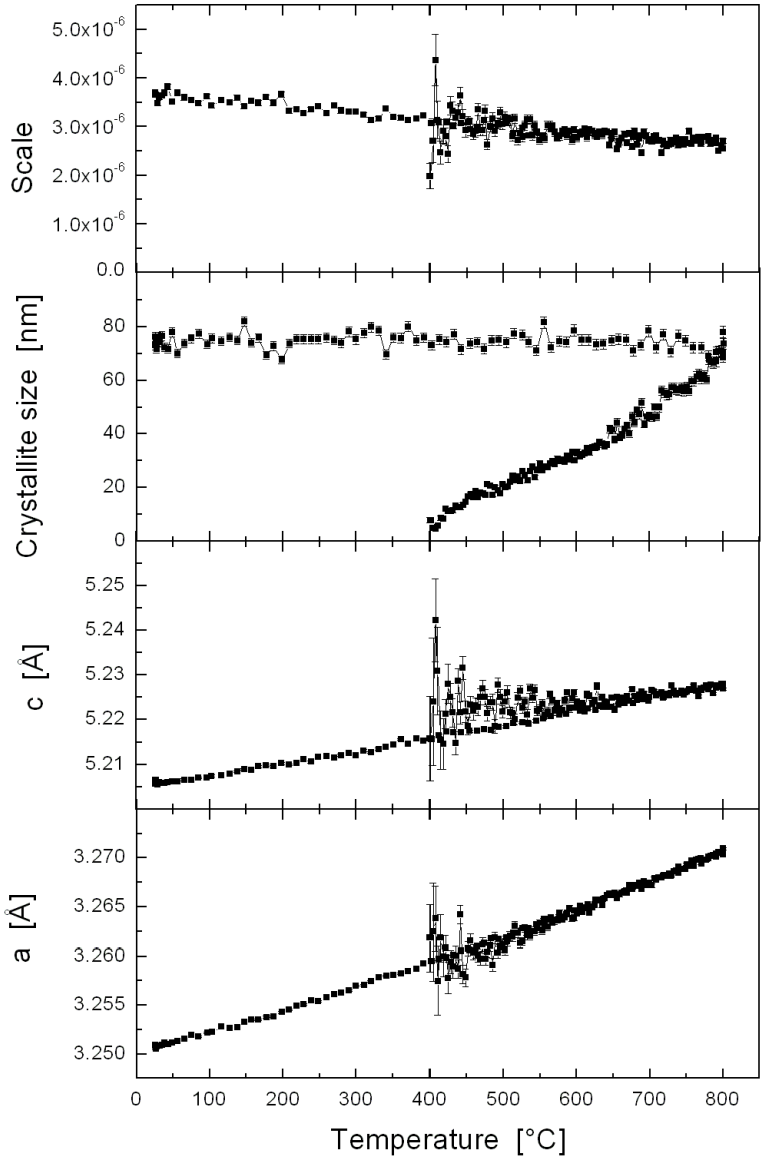


T. Kemmitt et al., *J. Phys. Chem. C* (2011) DOI: 10.1021/jp204283k

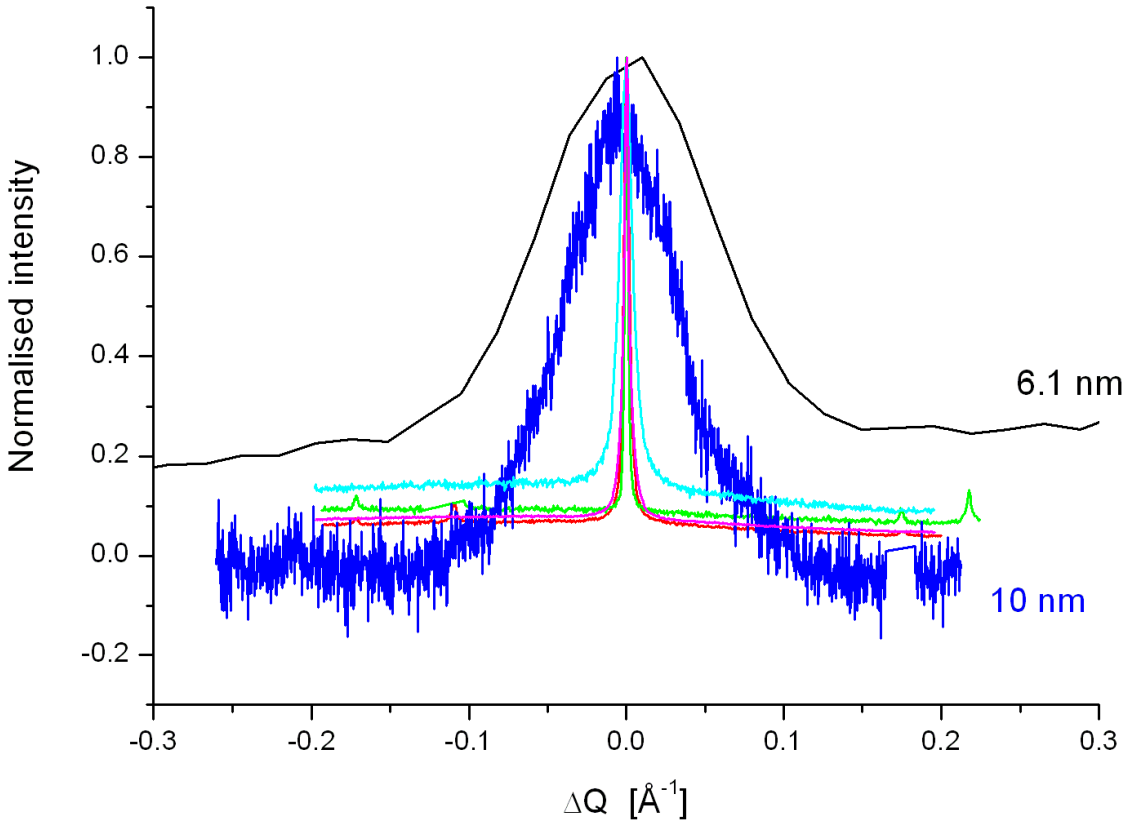
Temperature/time series



Temperature/time series results



3. Peak width: crystallite size, deformations

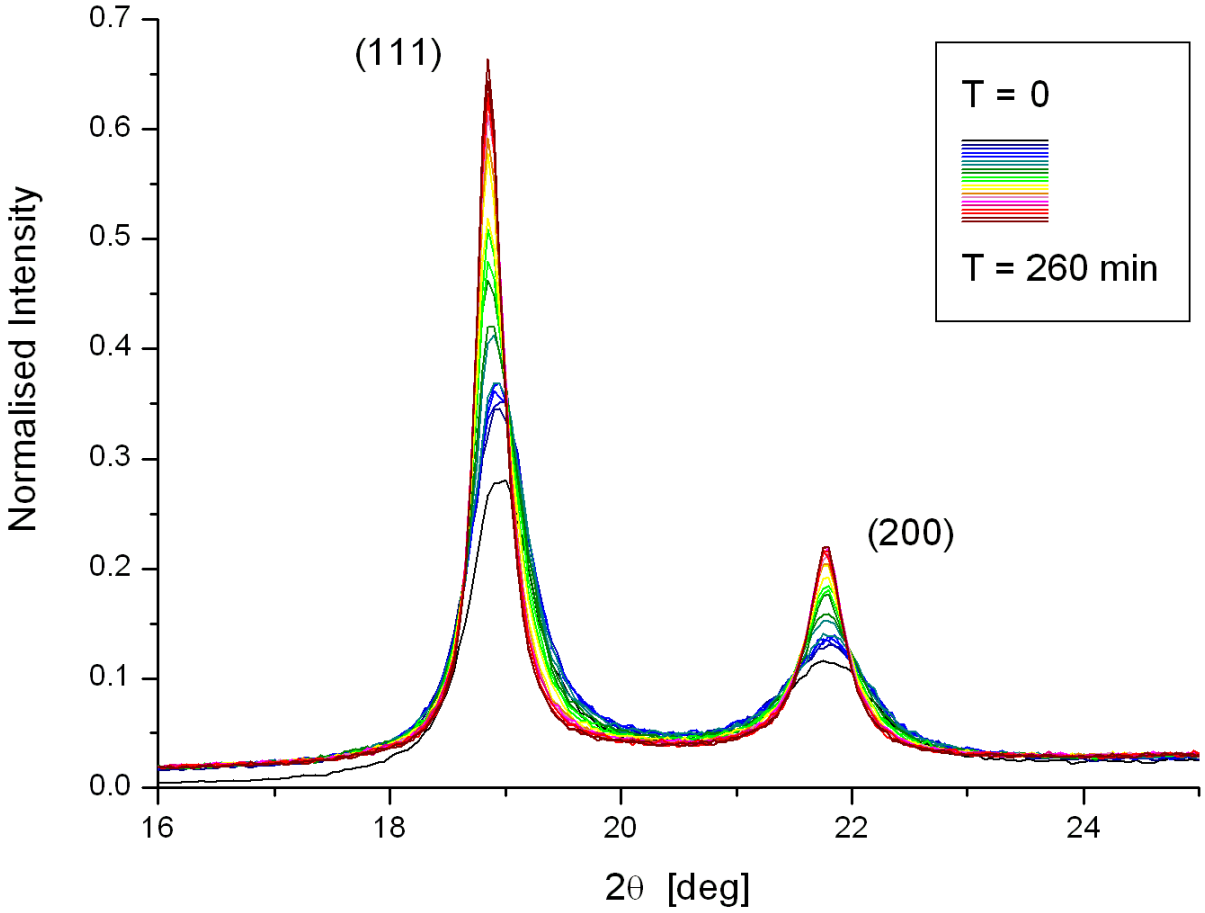


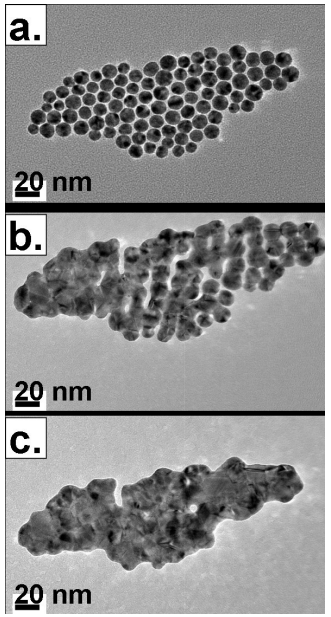
Peaks are broadened by crystal defects: finite size, deformations

Scherrer equation:

$$\text{Crystallite size} = \frac{0.9\lambda}{FW\cos\theta}$$

Case study: Au nanoparticle coalescence





t = 0

t = 15 min

t = 30 min

Observe:

- Peaks become sharper
  - grain growth
- Peaks move apart
  - release of strain (fault density decreases)
- Peak area constant
  - no melting, transformation

B. Ingham et al., *Chem. Mater.* (2011) DOI: 10.1021/cm200354d

Analysis

For *fcc* metals, $$\Delta(2\theta_{200} - 2\theta_{111})^\circ = \frac{-90\sqrt{3}\alpha}{\pi^2}\left(\frac{\tan\theta_{200}}{2} + \frac{\tan\theta_{111}}{4}\right)$$

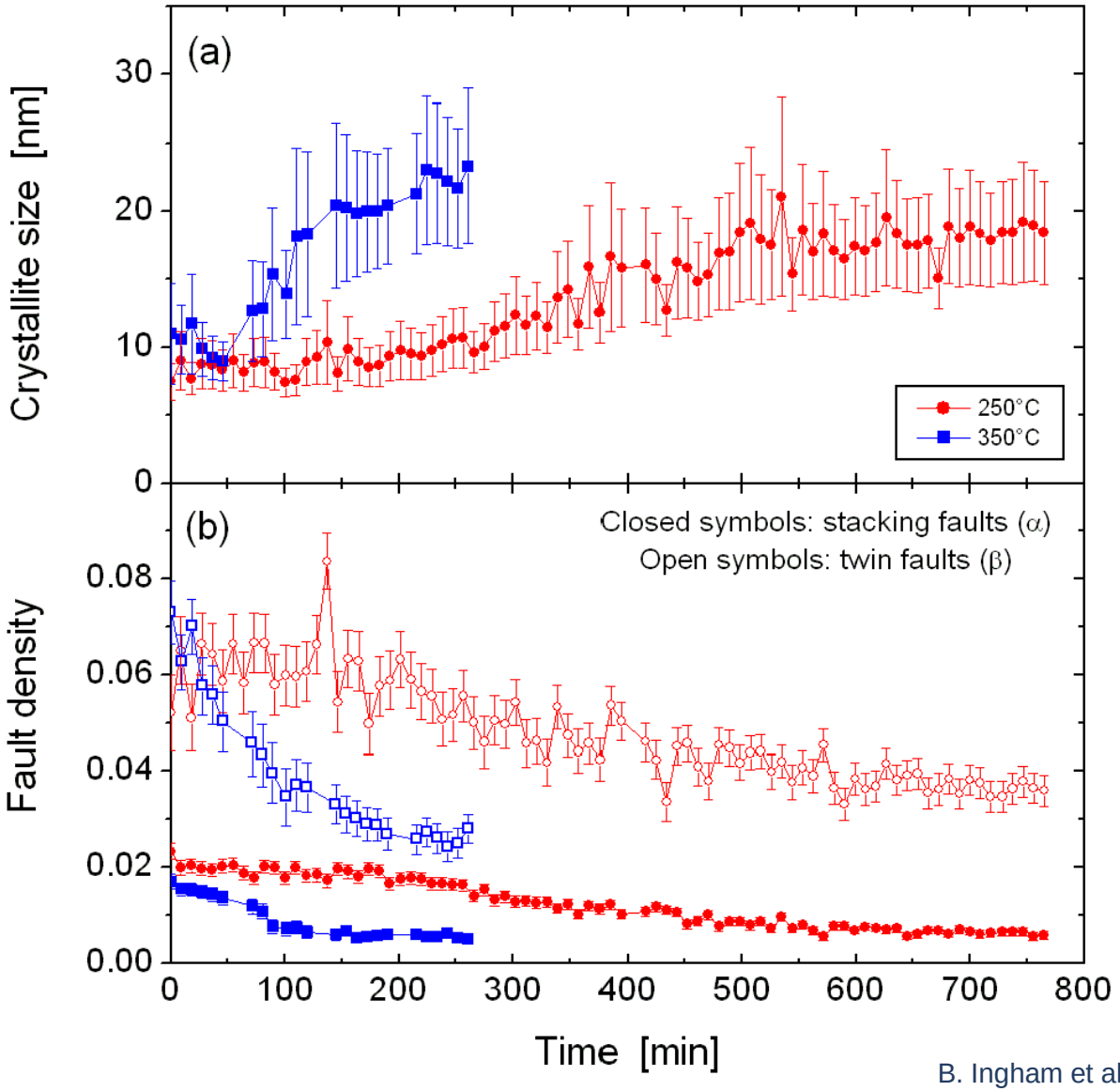
For the (111) peak, $$\frac{1}{D_{eff\,(111)}} = \frac{1}{D} + \frac{3}{16}\frac{(1.5\alpha + \beta)}{a}$$

For the (200) peak, $$\frac{1}{D_{eff\,(200)}} = \frac{1}{D} + \frac{(1.5\alpha + \beta)}{a}$$

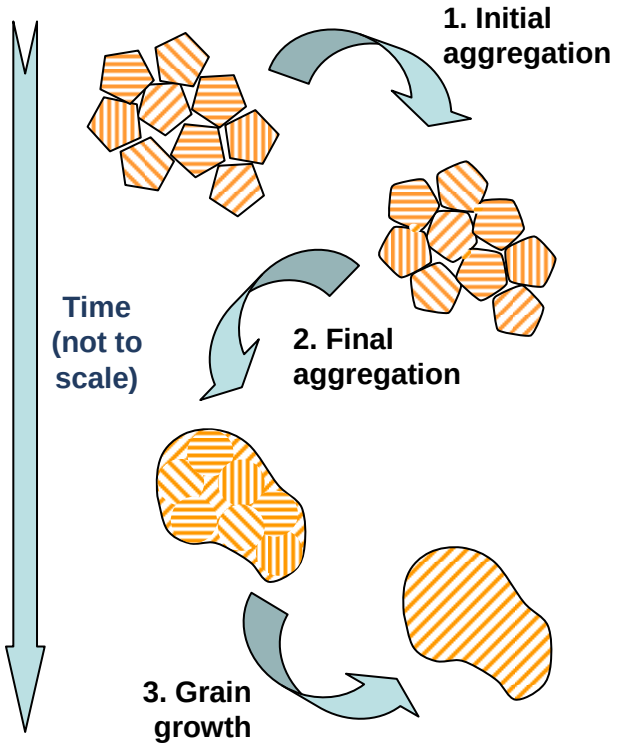
B. E. Warren, *X-ray Diffraction*, Dover Publishers (1969)

Therefore the deformation fault density α, the twin fault density β, and the true crystallite size D can be obtained by comparing the peak separation and peak widths together.

Results



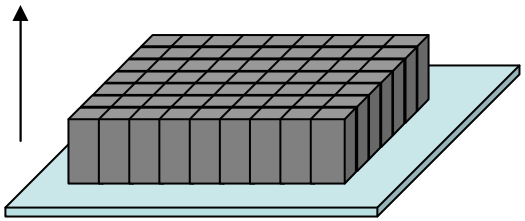
Combine with SAXS to compare the difference between particle size and crystallite size vs. time

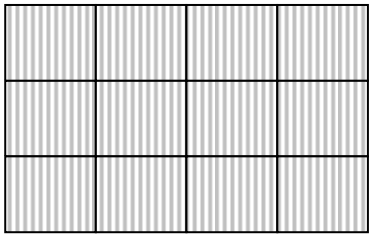


B. Ingham et al., *Chem. Mater.* (2011) DOI: 10.1021/cm200354d

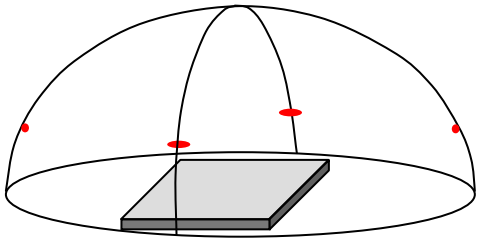
4. Texture (preferential orientation)

Epitaxial



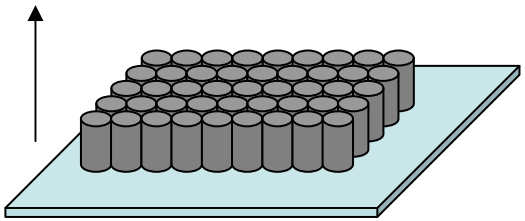


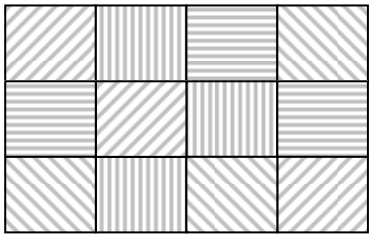
Top view

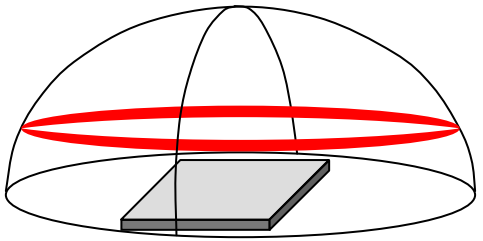


Diffraction

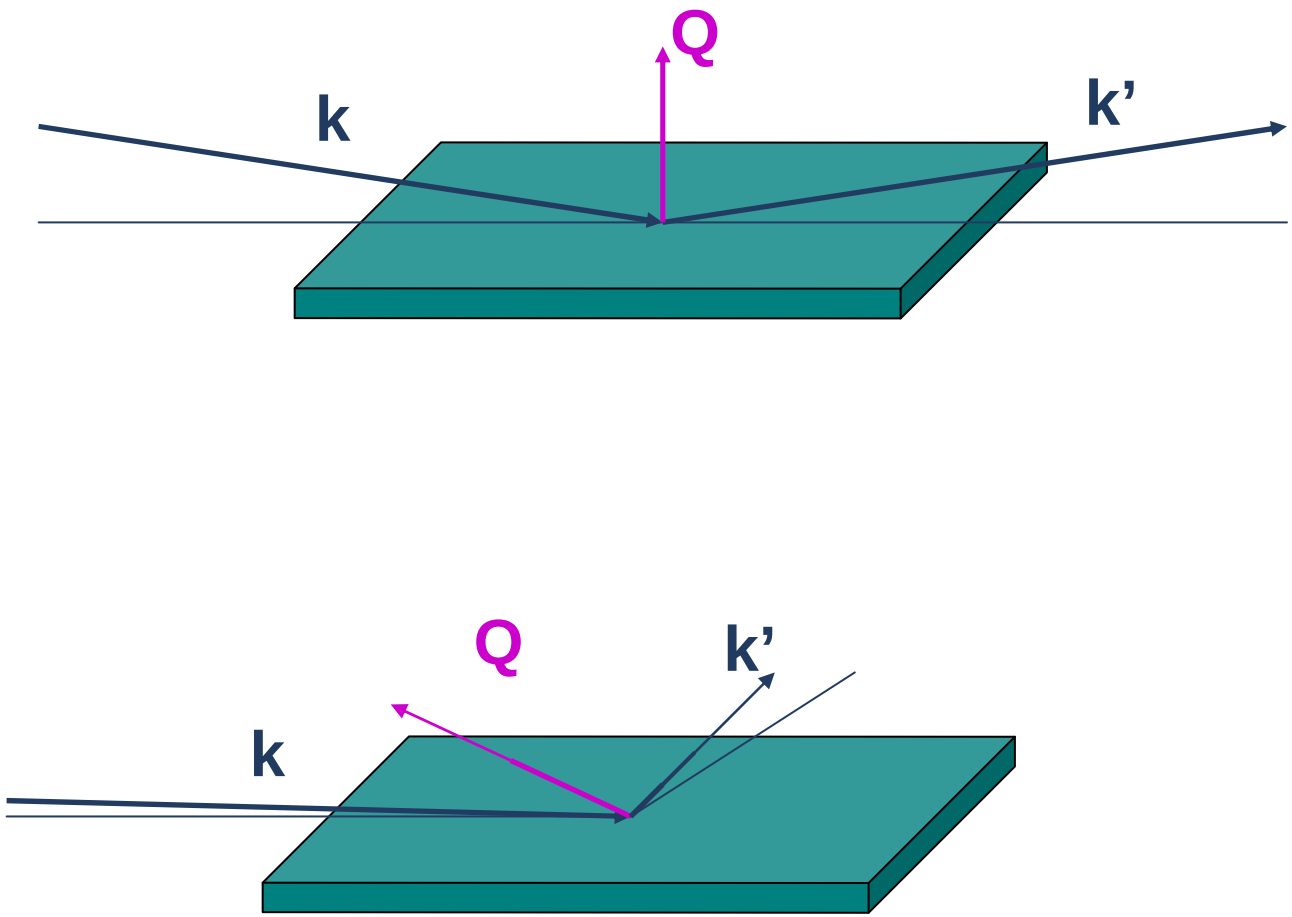
Fibre texture



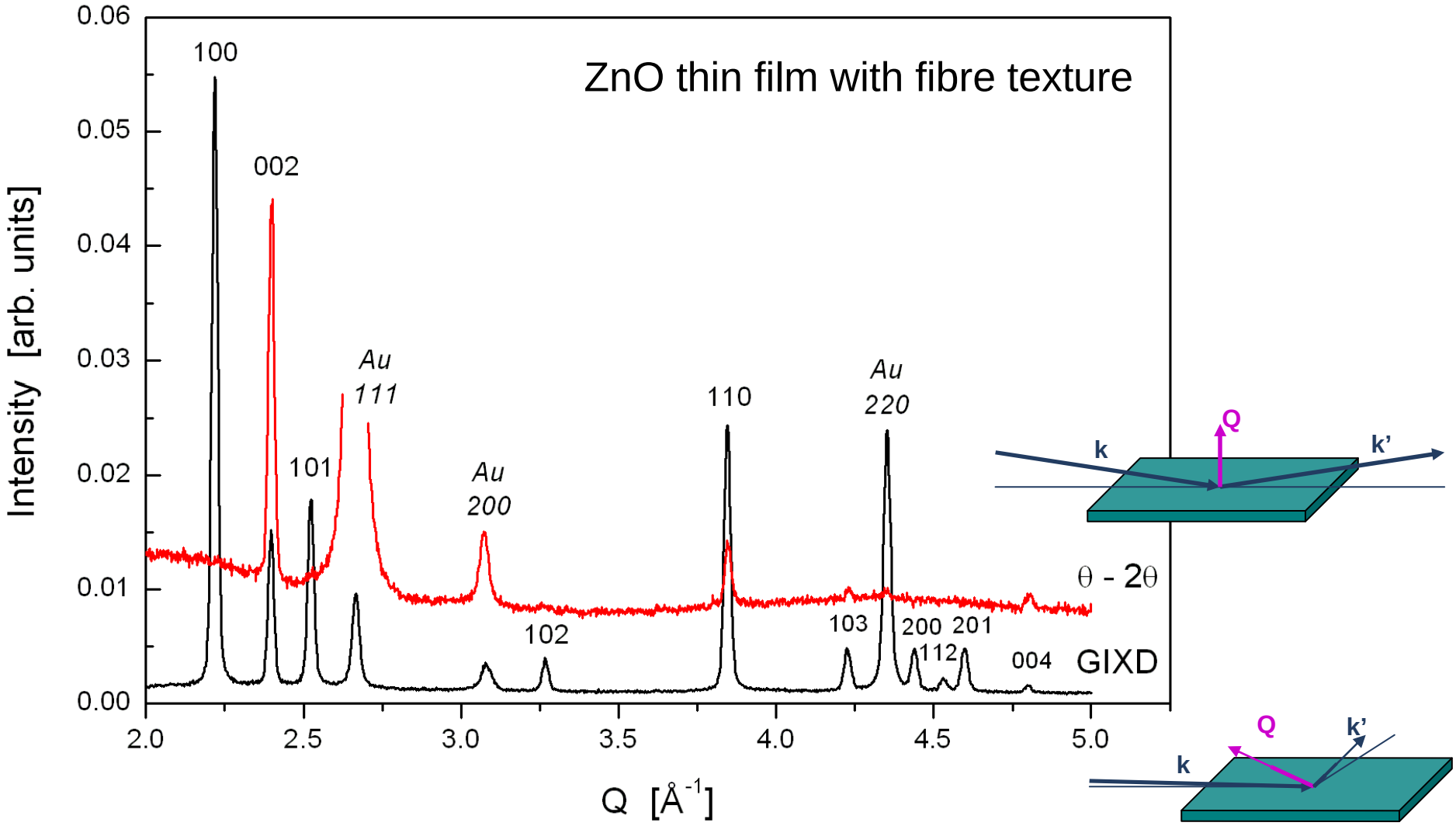




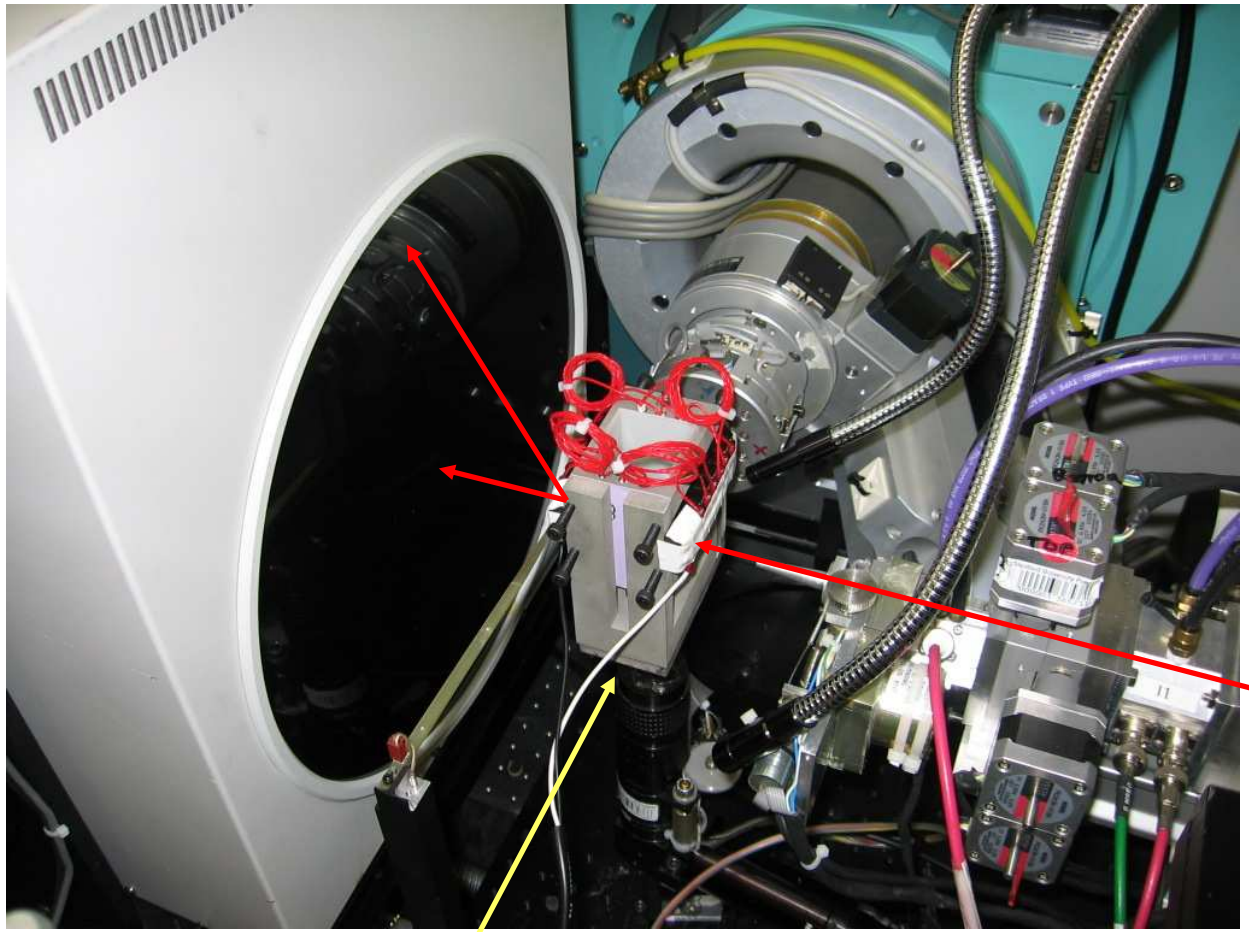
Different XRD geometries



Different XRD geometries

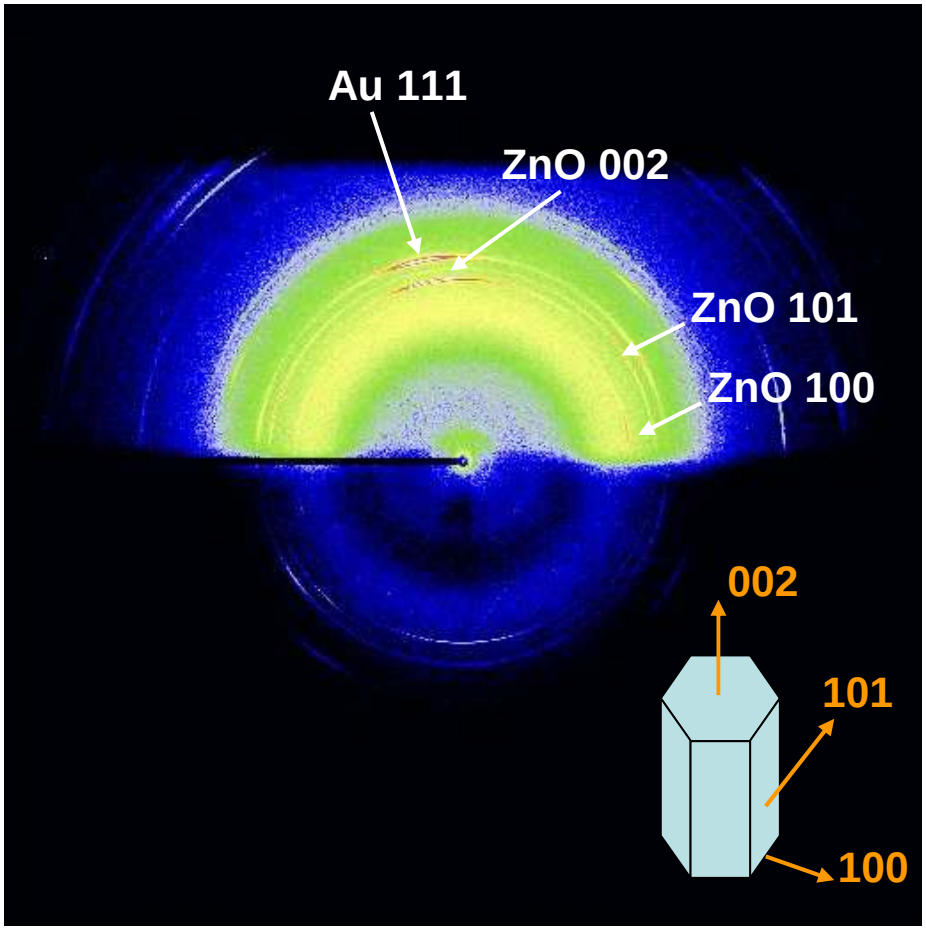


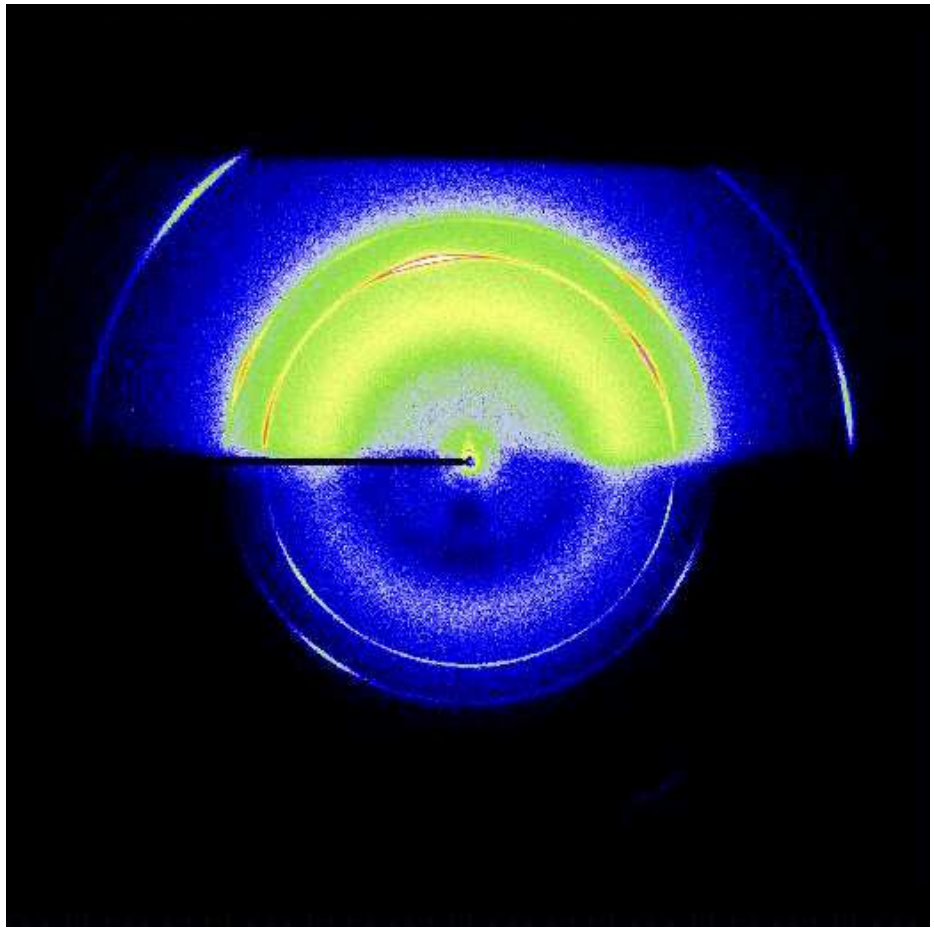
Case study: ZnO electrochemical deposition



Electrochemical cell

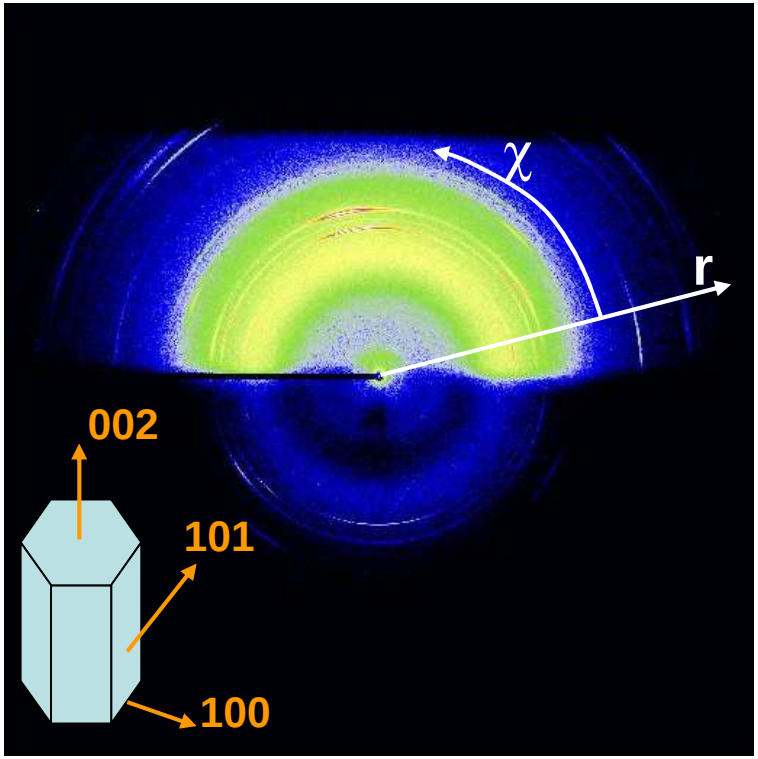
Raw data

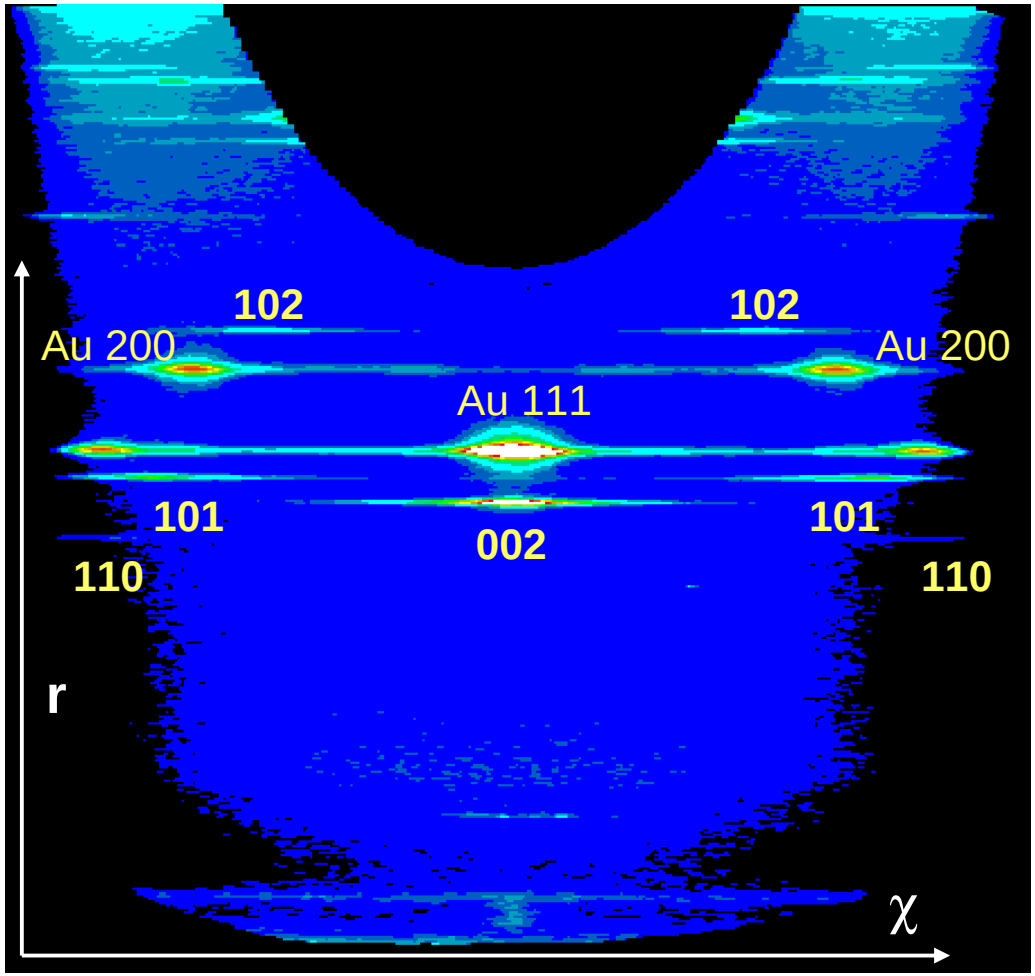




B. Ingham et al., *J. Phys. Chem. C* 112 (2008) 14863

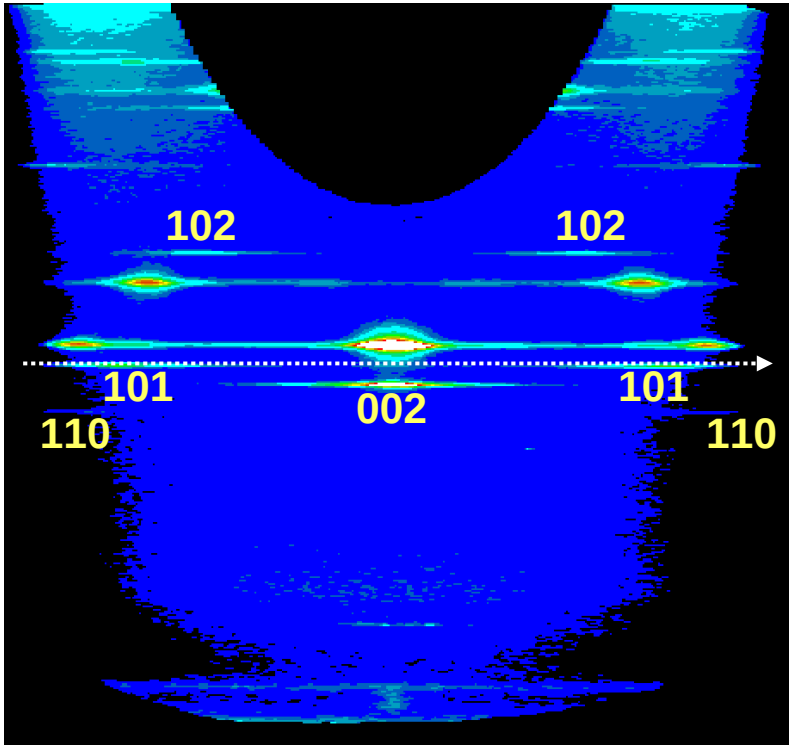
Data reduction

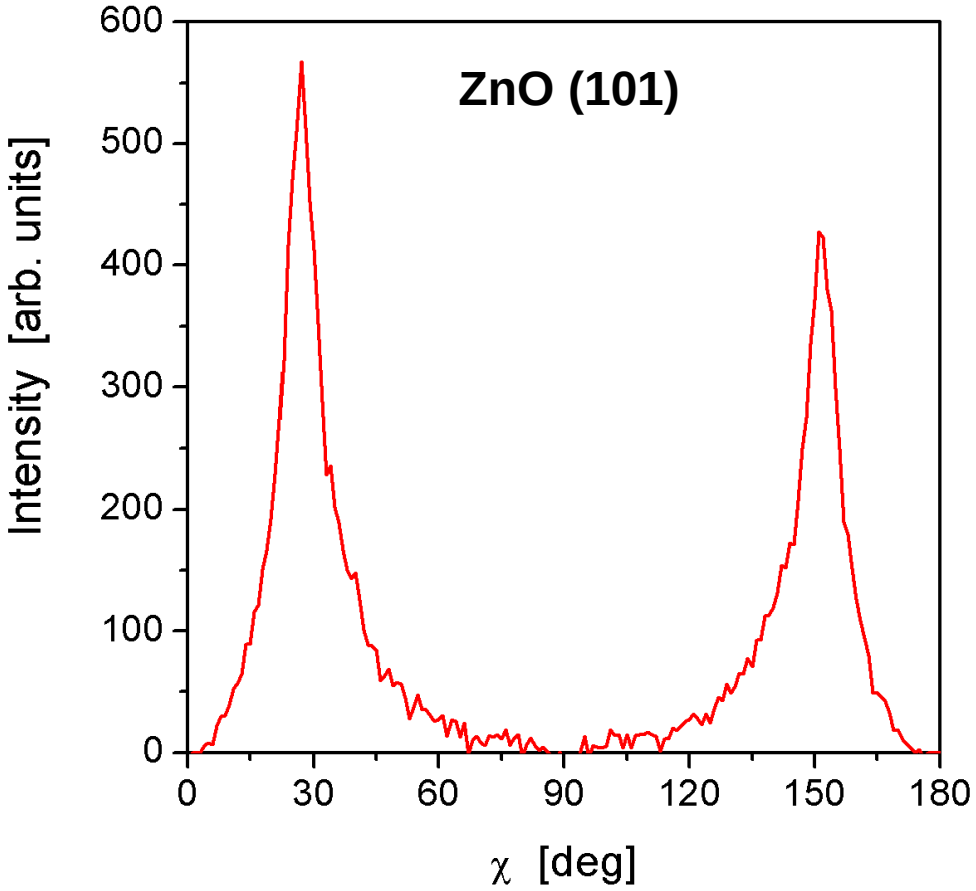




B. Ingham et al., *J. Phys. Chem. C* 112 (2008) 14863

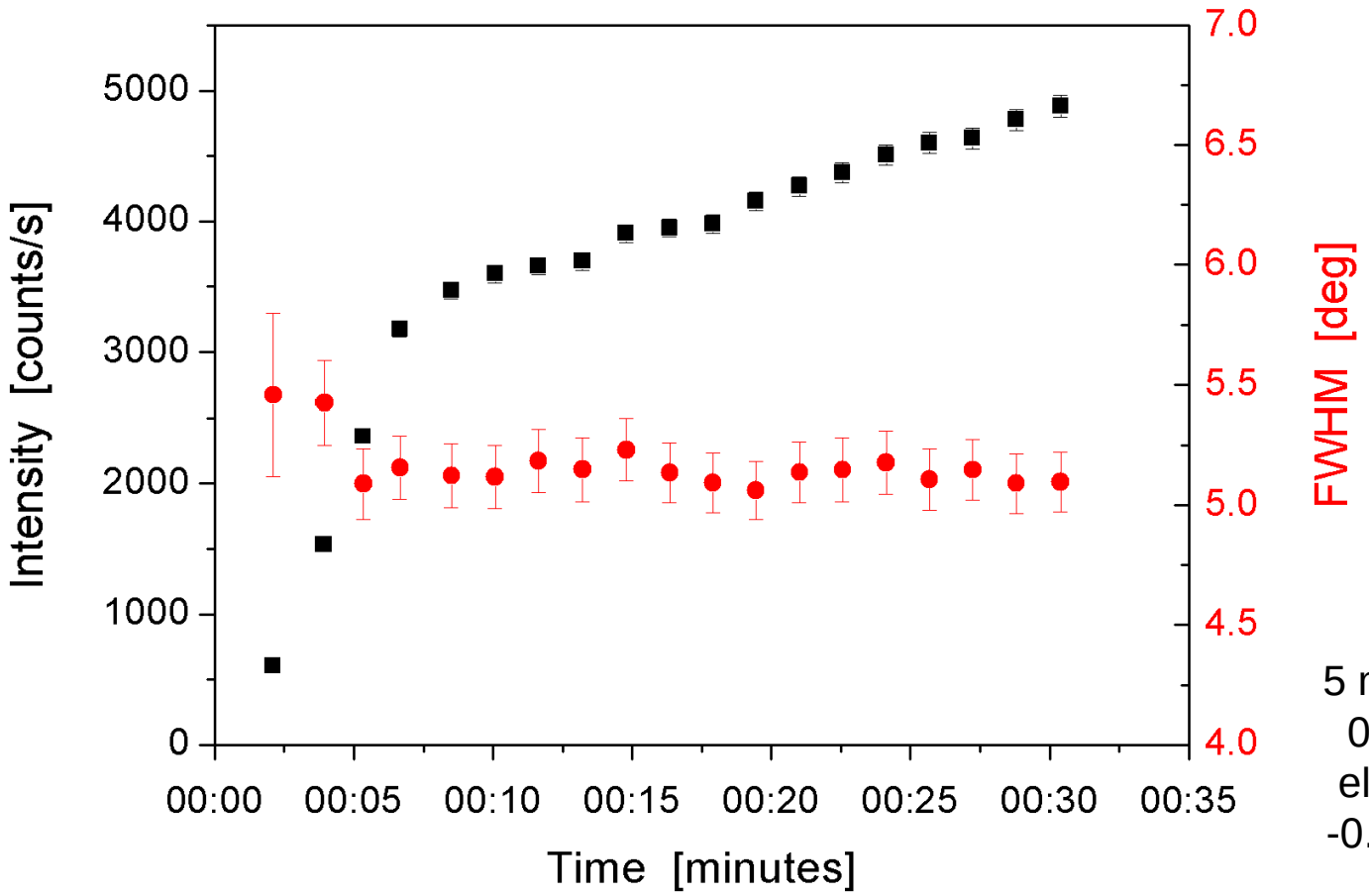
Data analysis





B. Ingham et al., *J. Phys. Chem. C* 112 (2008) 14863

Time series results



5 mM $ZnCl_2$, 0.1 M KCl electrolyte, -0.5V (SHE)

B. Ingham et al., *J. Phys. Chem. C* 112 (2008) 14863

Outline of the day

- Introduction
- Basic X-ray diffraction
  - Powders, thin films, single crystals
- Small-angle X-ray scattering
- X-ray absorption spectroscopy
  - Atomic structure
  - Electronic structure (Ben Ruck)
- Advanced X-ray diffraction
  - Anomalous diffraction
  - Total X-ray scattering
- Designing experiments
  - In situ measurements