# Synchrotron X-ray Powder Diffraction

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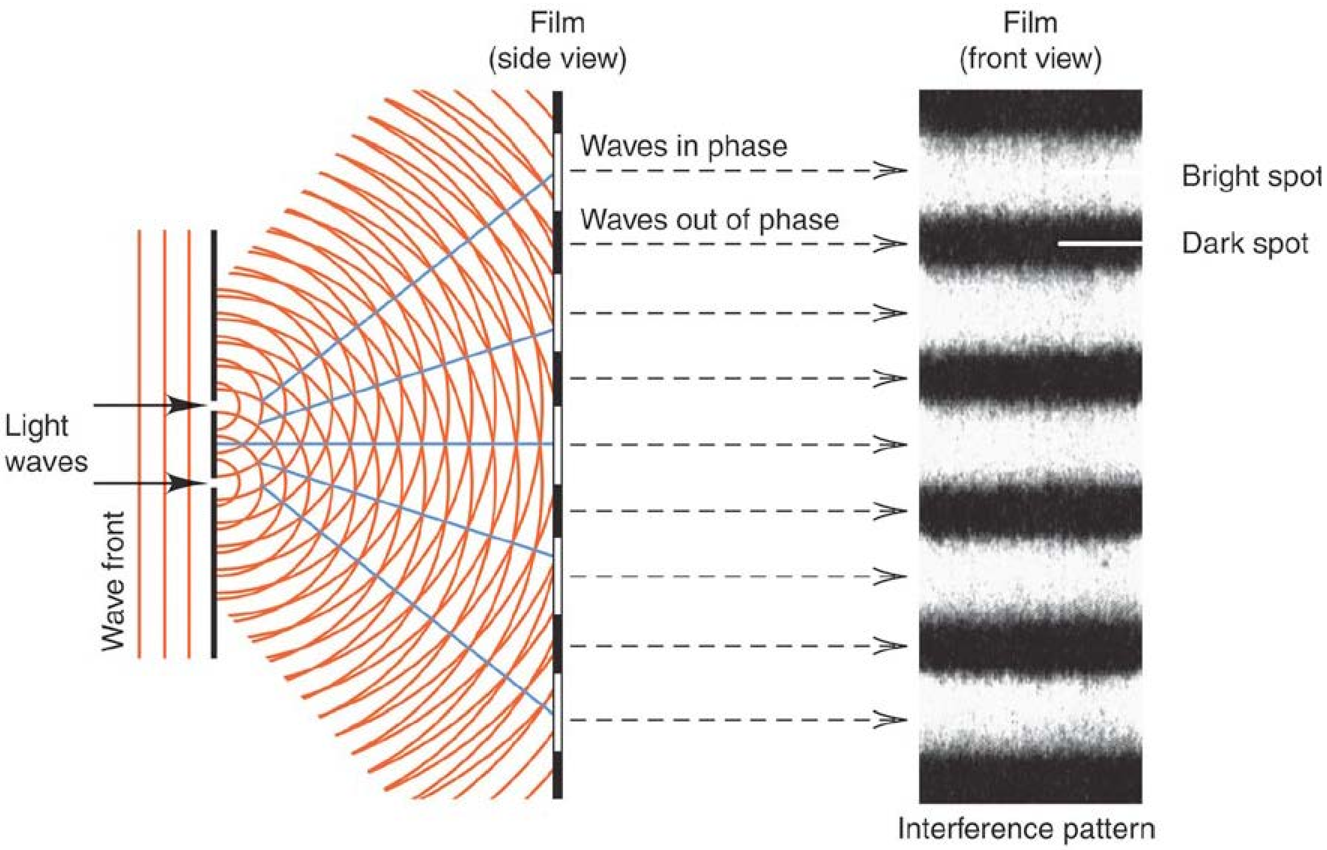
# Outline

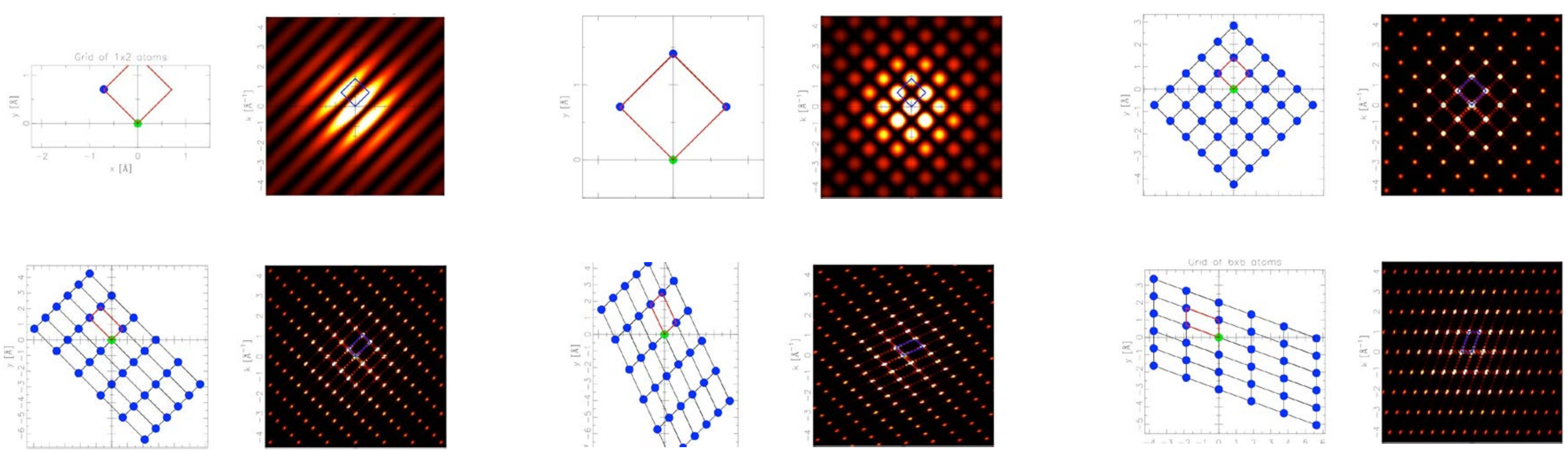
- Diffraction – recap
- X-ray crystallography
  - Single crystal diffraction
  - Powder diffraction
- Conventional X-ray diffraction
  - Sources and limitations
- Synchrotron X-ray diffraction
  - Advantages and bonus features

# Diffraction

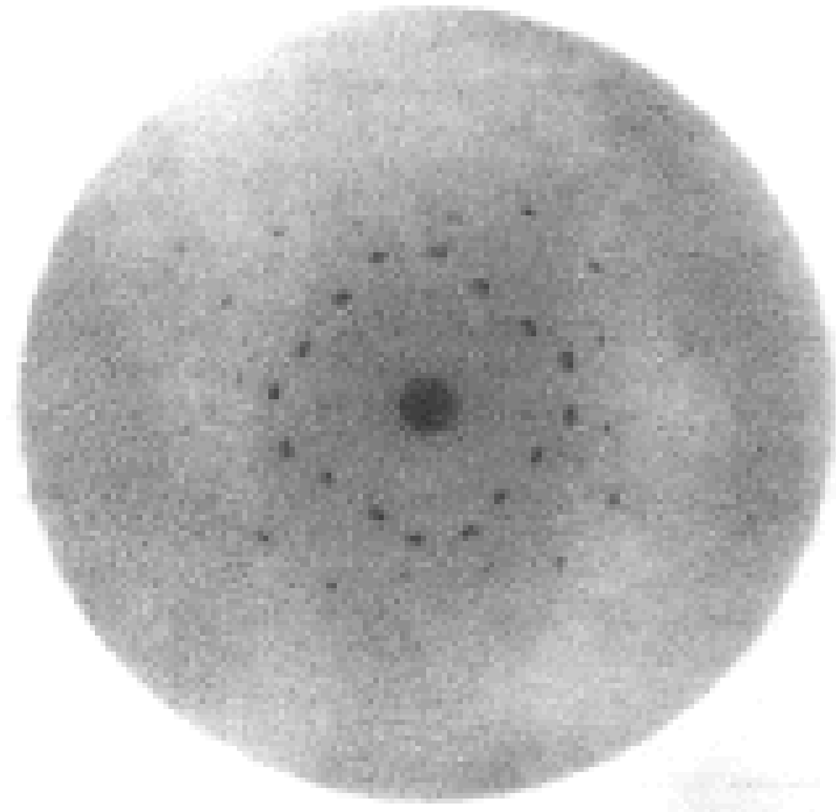
*In three slides*

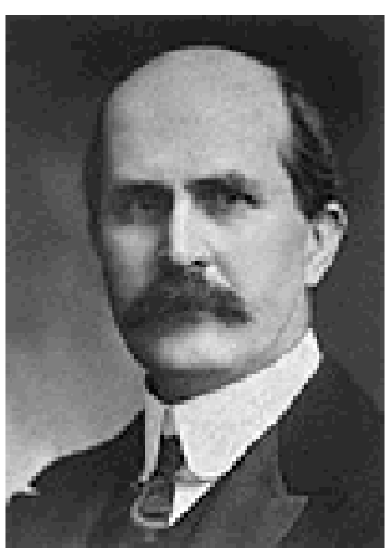
# Wave diffraction

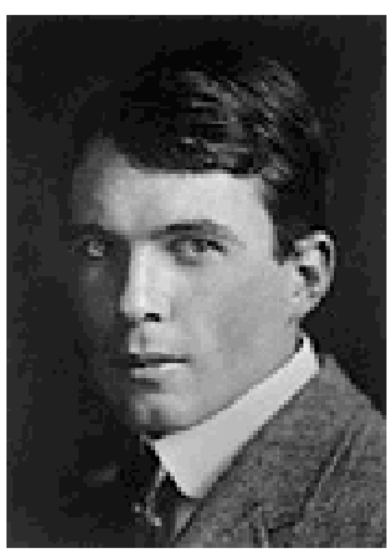


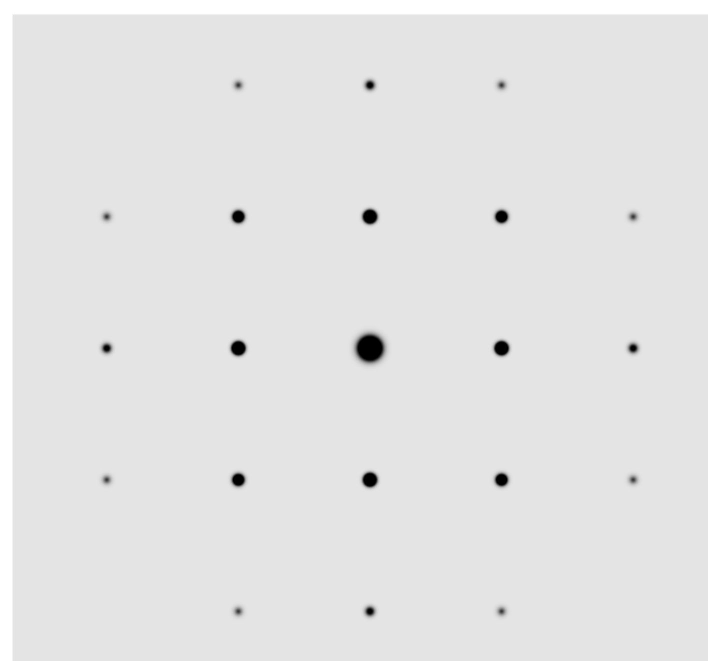



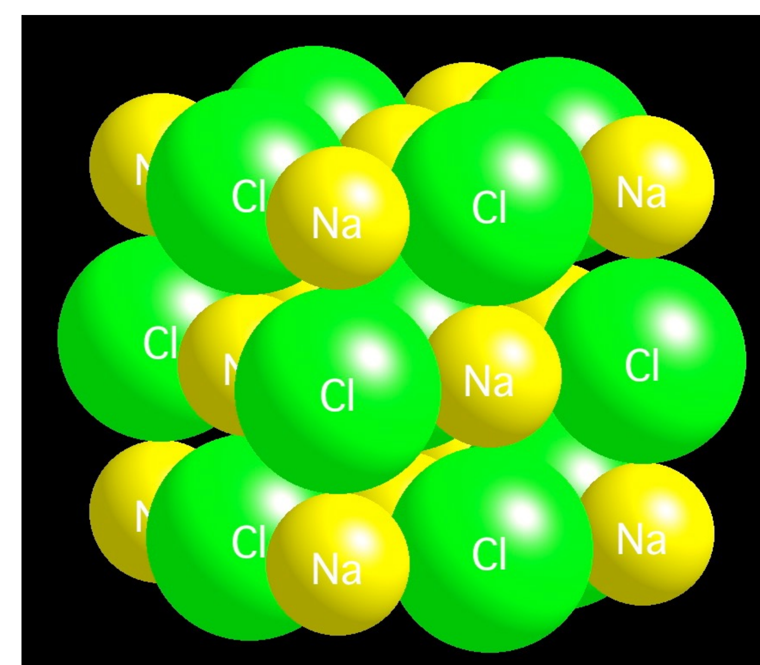
# Crystals, lattice planes and X-rays



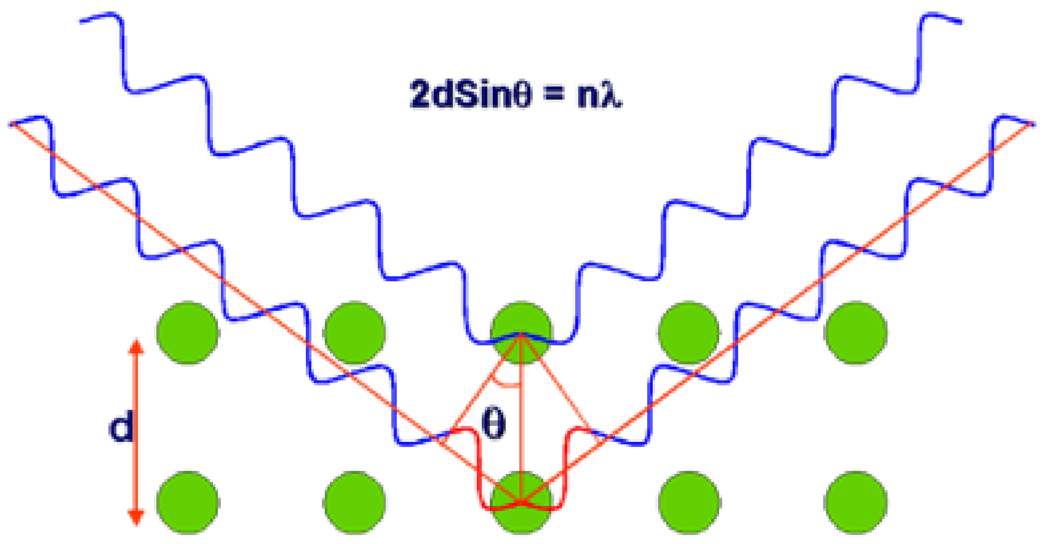


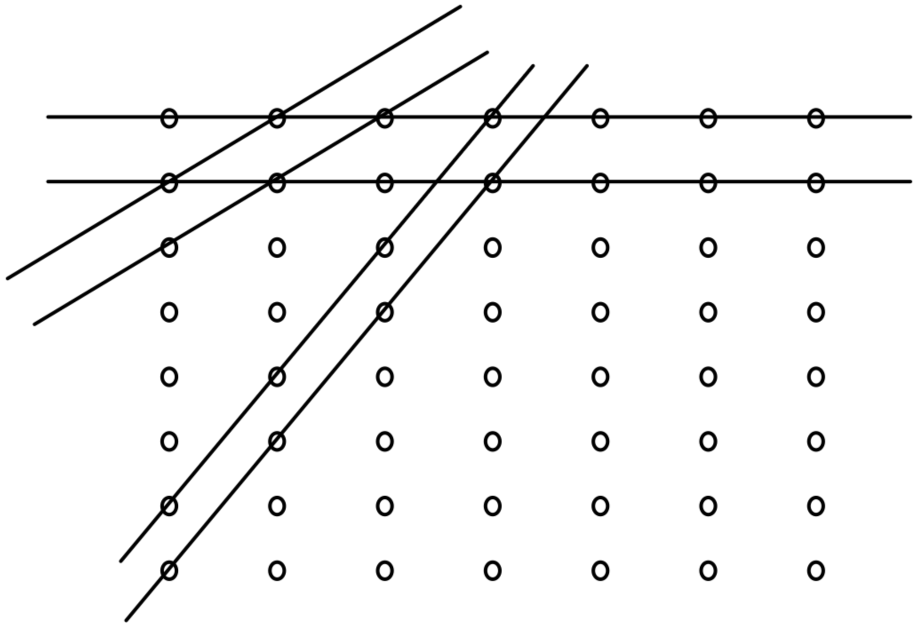






# Bragg's law and crystallography



Note that the sets of lattice planes that are closer together have smaller *d*-spacings and therefore higher 2θ angles.

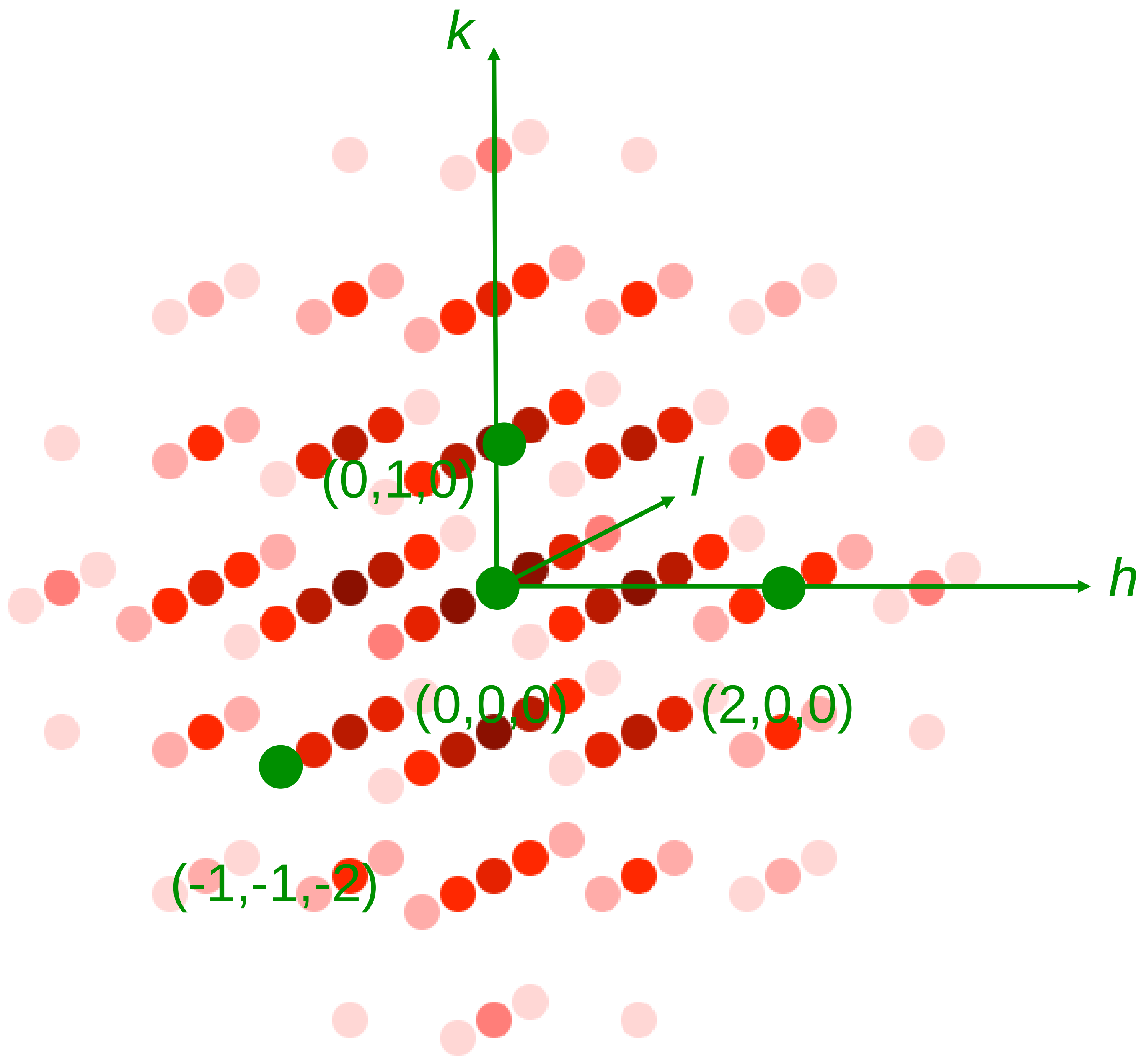
These planes produce less coherent diffraction, because the *size* of the atoms (hence the uncertainty in their positions) becomes more significant relative to the interlayer spacing *d*. Therefore, reflections get weaker as 2θ angle increases.

# X-ray crystallography

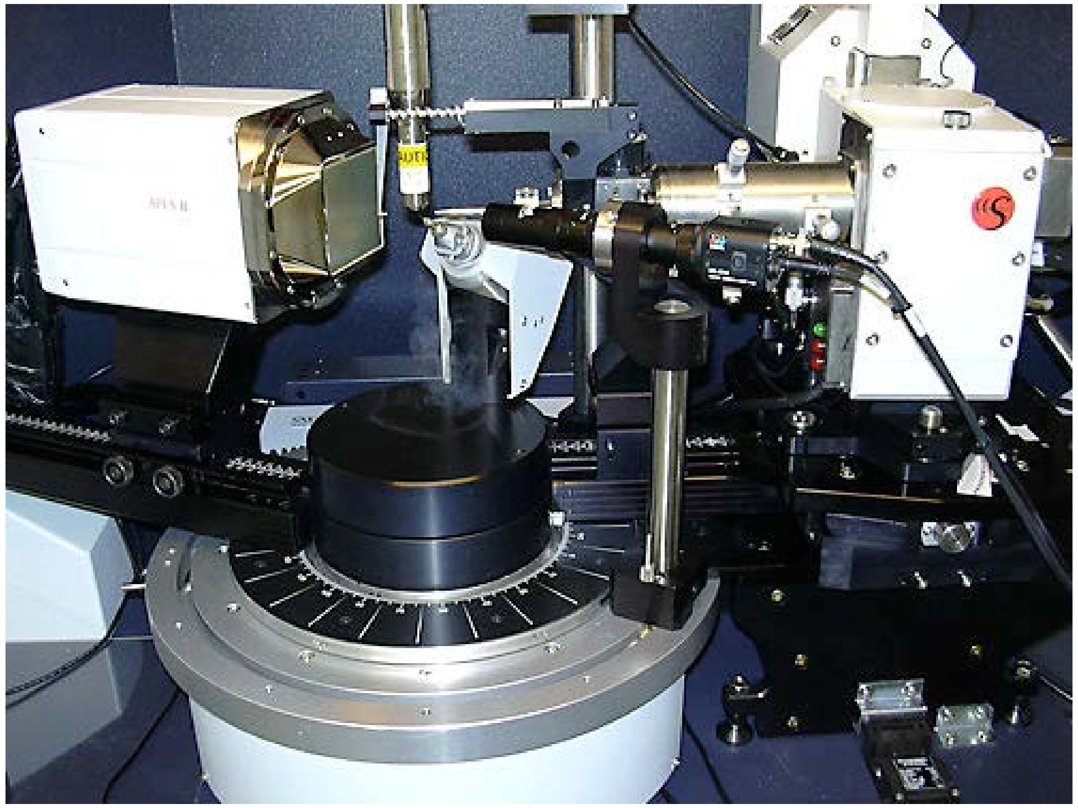
*Modern laboratory instruments and techniques for crystal structure determination*

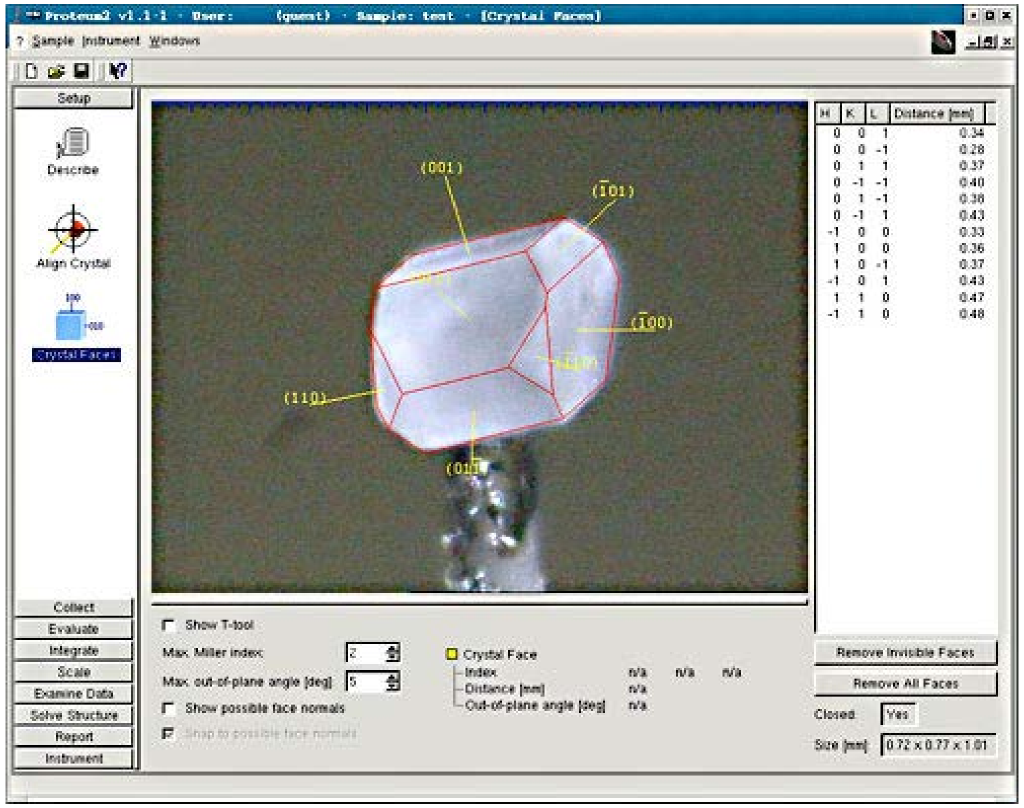
# Single crystal diffraction

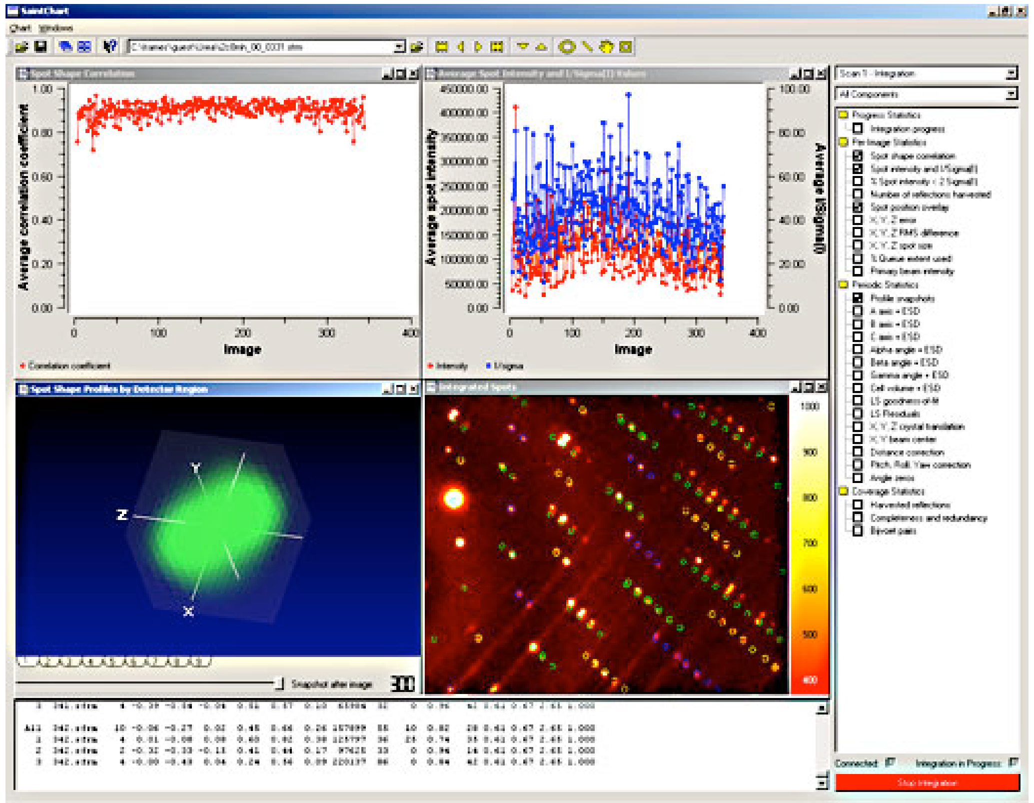
3-D reciprocal lattice

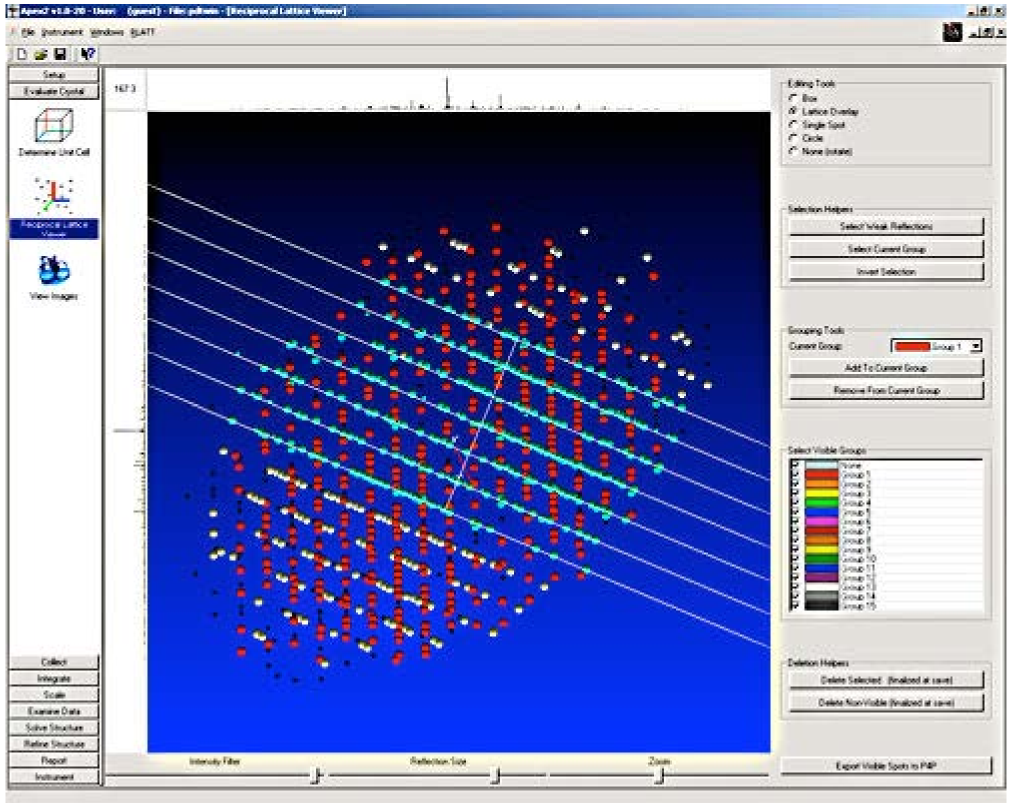


# Single crystal diffraction





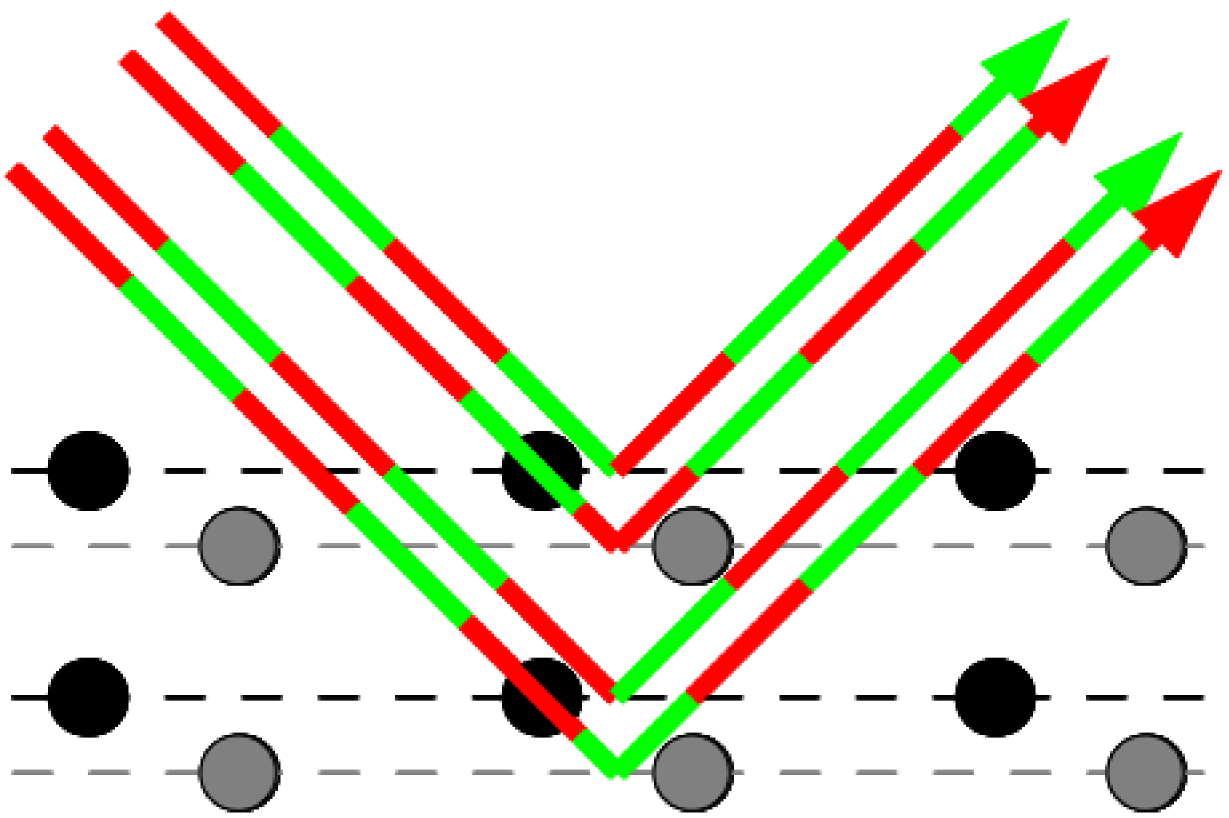



# Structure solution and refinement

Diffraction as a Fourier transform:

$$\rho(x,y,z) = \frac{1}{V_c}\sum\sum_{hkl=-\infty}^{\infty}\sum F(h,k,l)e^{-i2\pi\{hx+ky+lz\}} = \frac{2}{V_c}\sum\sum_{h=0,kl=-\infty}^{\infty}\sum |F(h,k,l)|\cos(2\pi\{hx+ky+lz\}-\alpha_{hkl})$$

The phase problem:



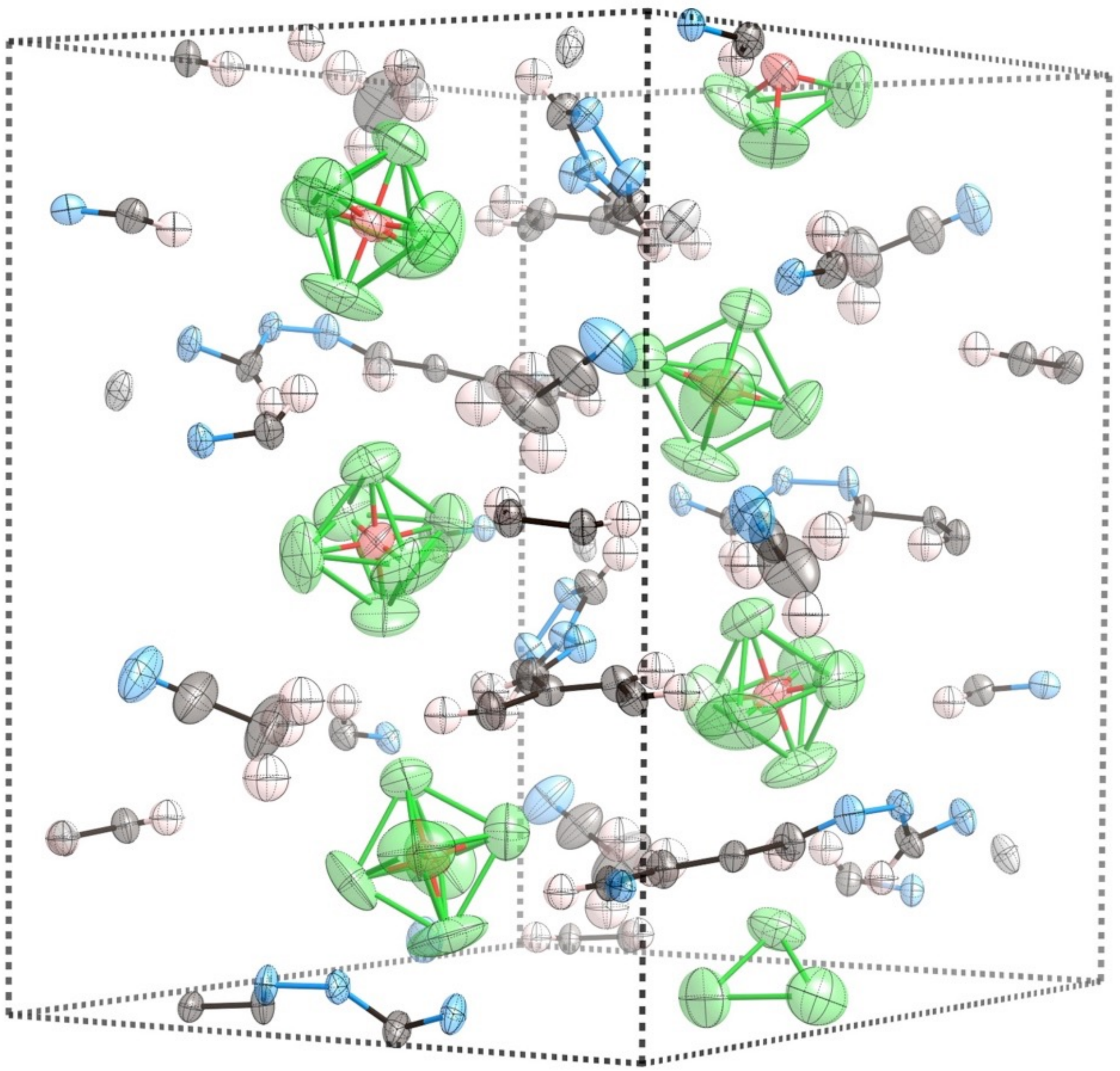
# Structure solution and refinement

After applying various number-crunching statistical methods we expect to be able to solve and refine:

Unit cell and space group symmetry

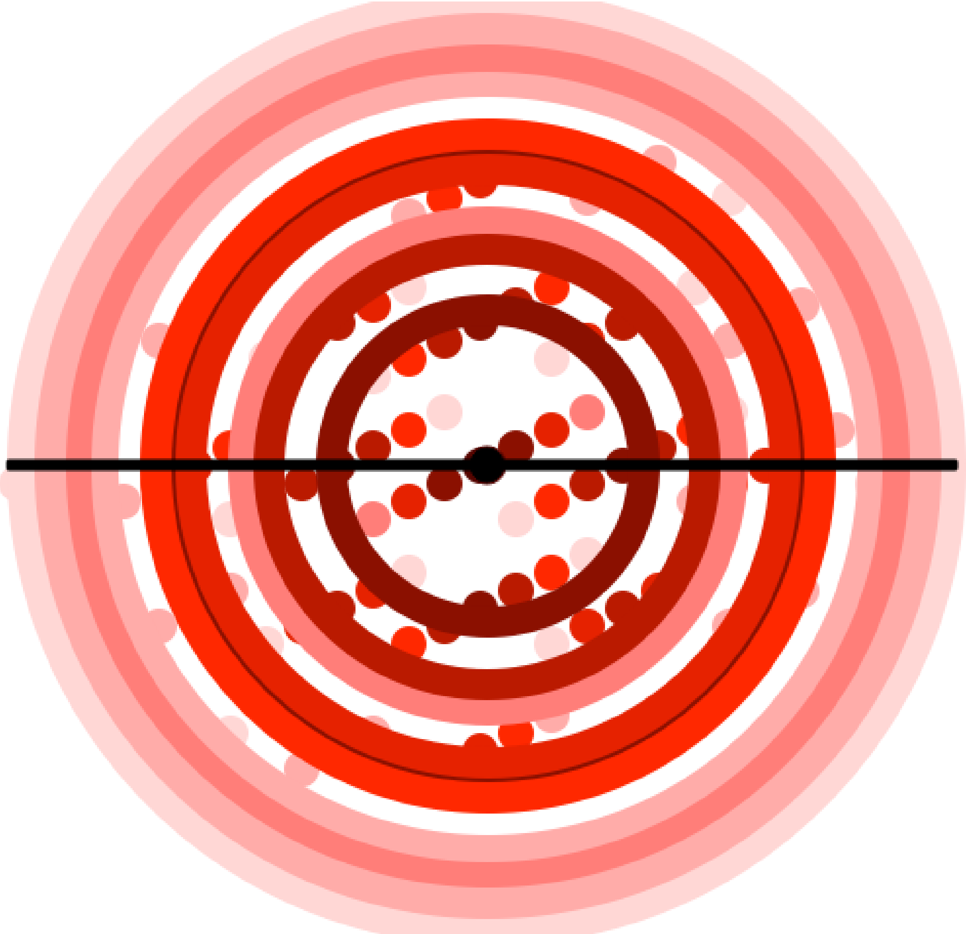
Atomic positions

Anisotropic atomic displacements

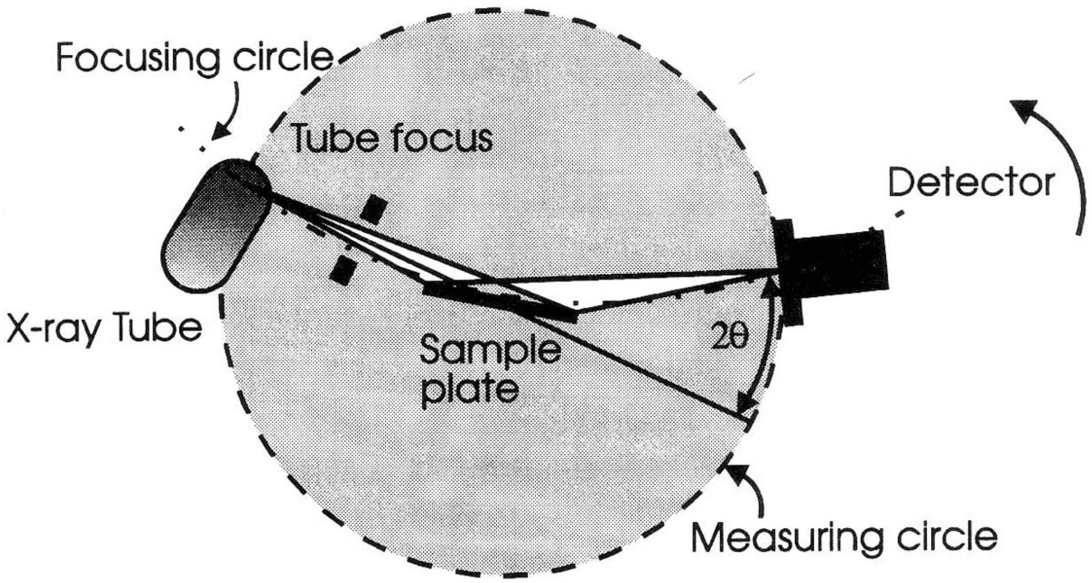


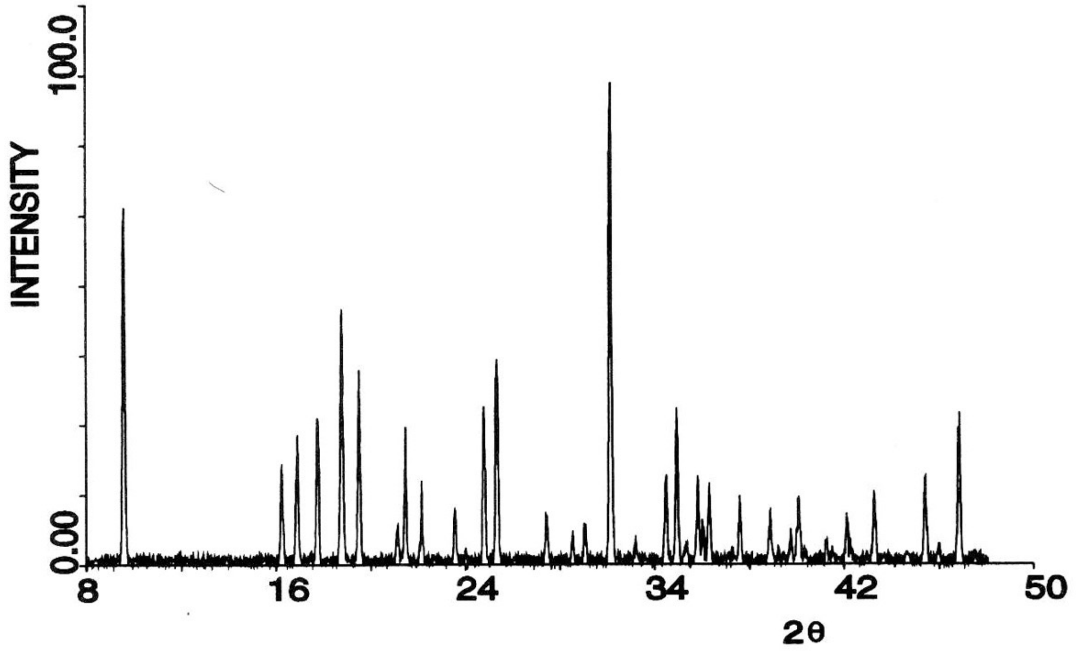
$H_{10}AgF_6N_6P$

# Powder diffraction

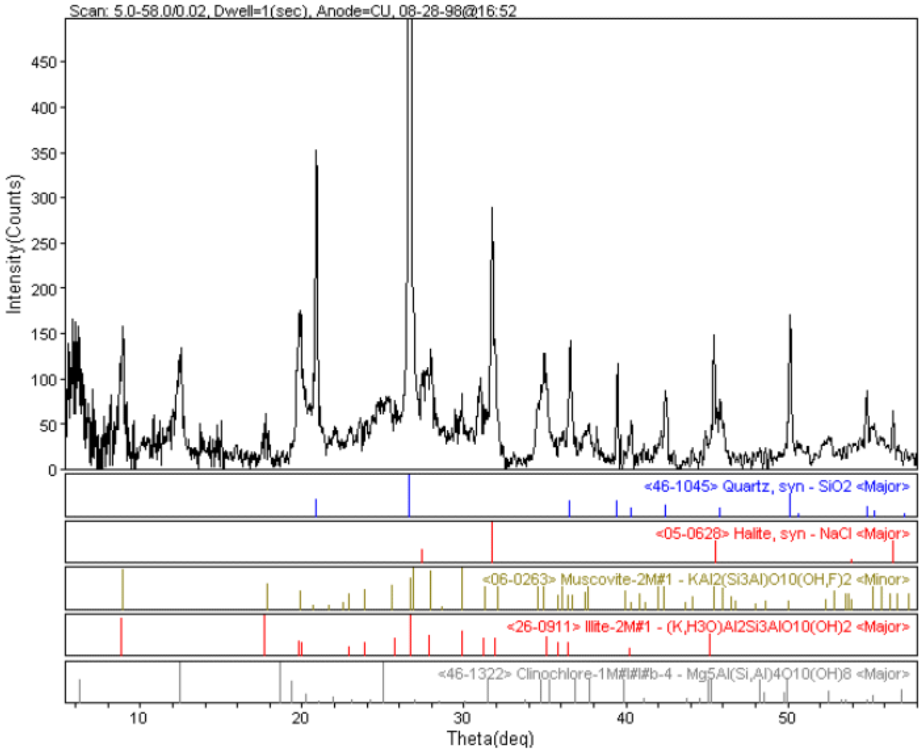


# Powder diffraction







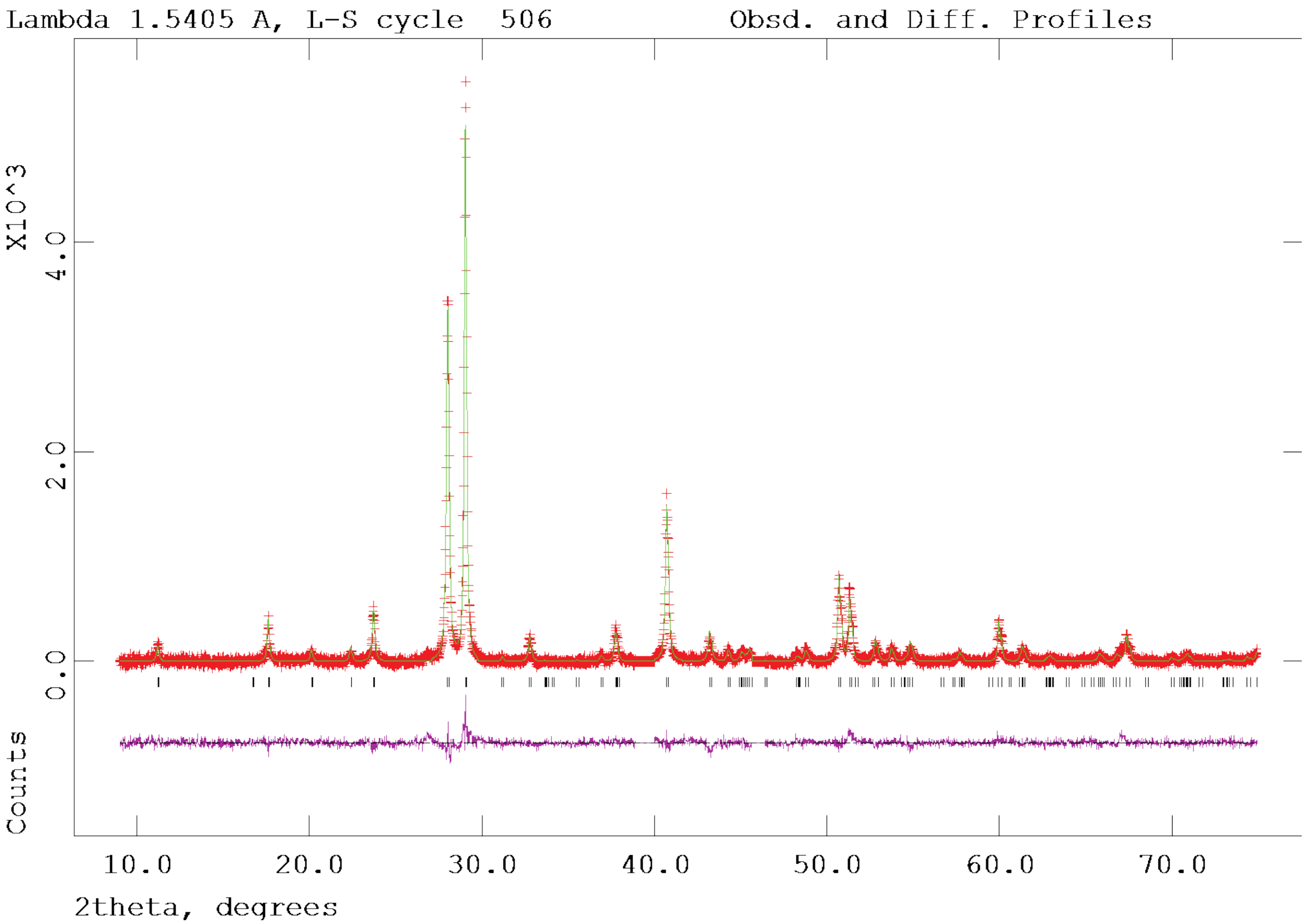
# Structure solution and refinement

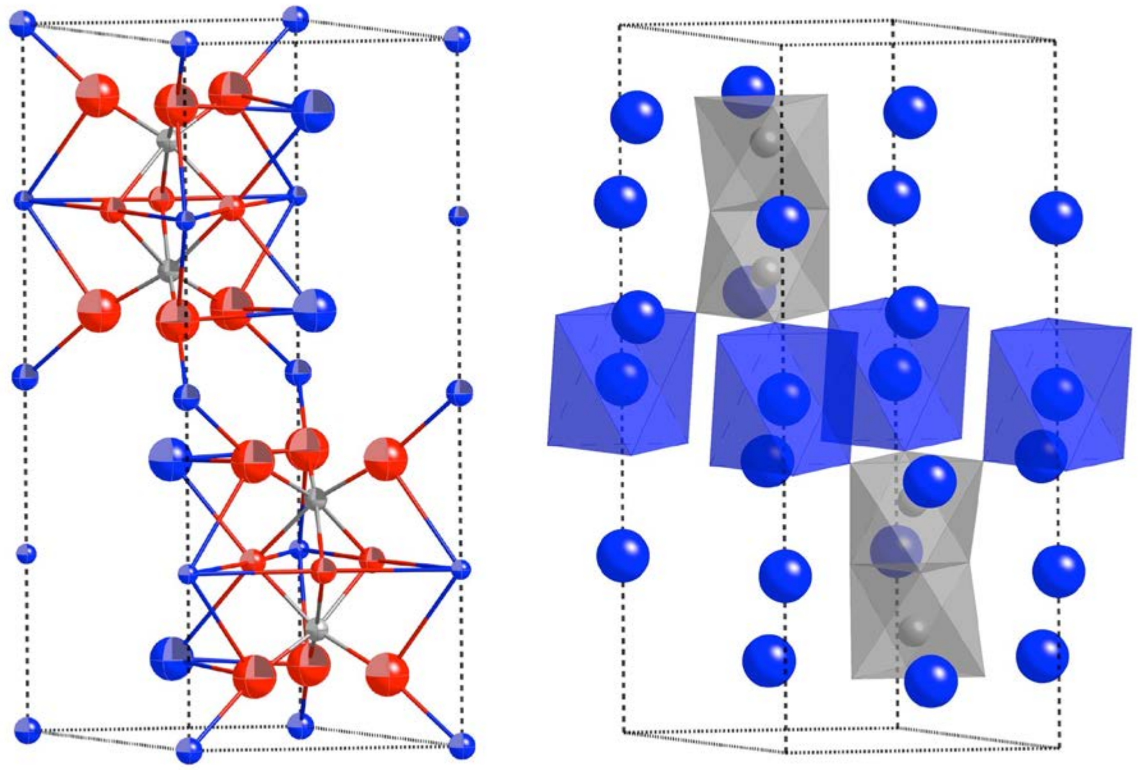
## With full-pattern “Rietveld” methods we expect to refine:

Unit cell and space group symmetry

Atomic positions

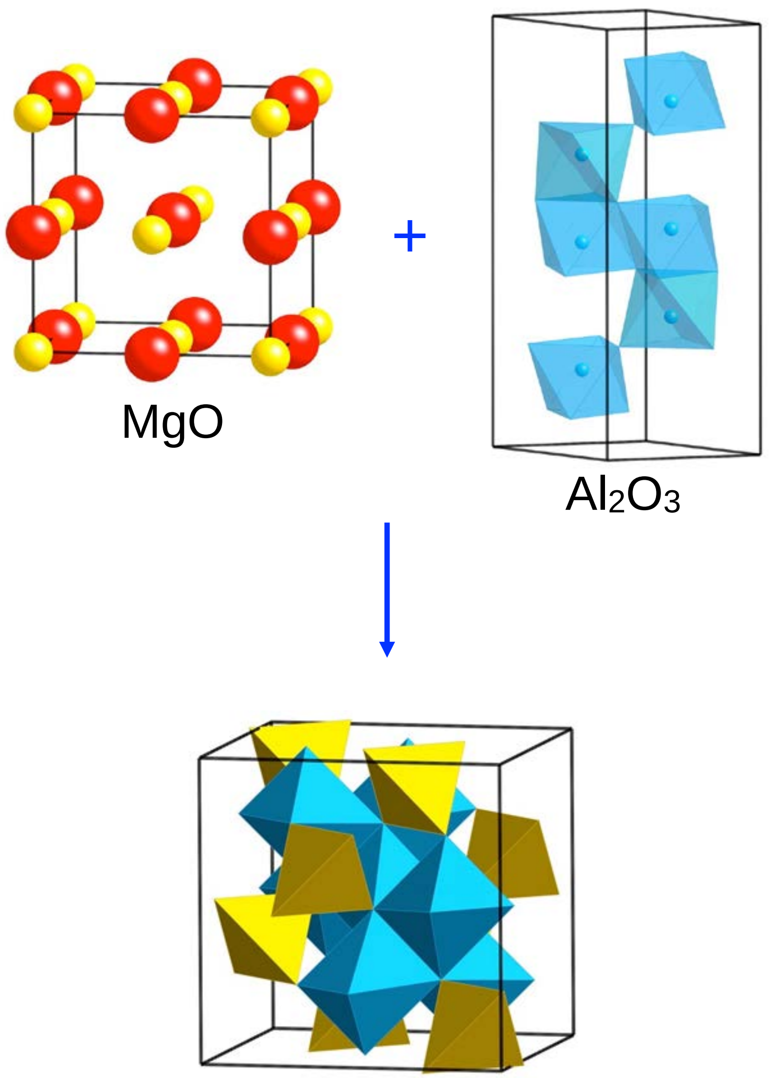
Isotropic atomic displacement parameters



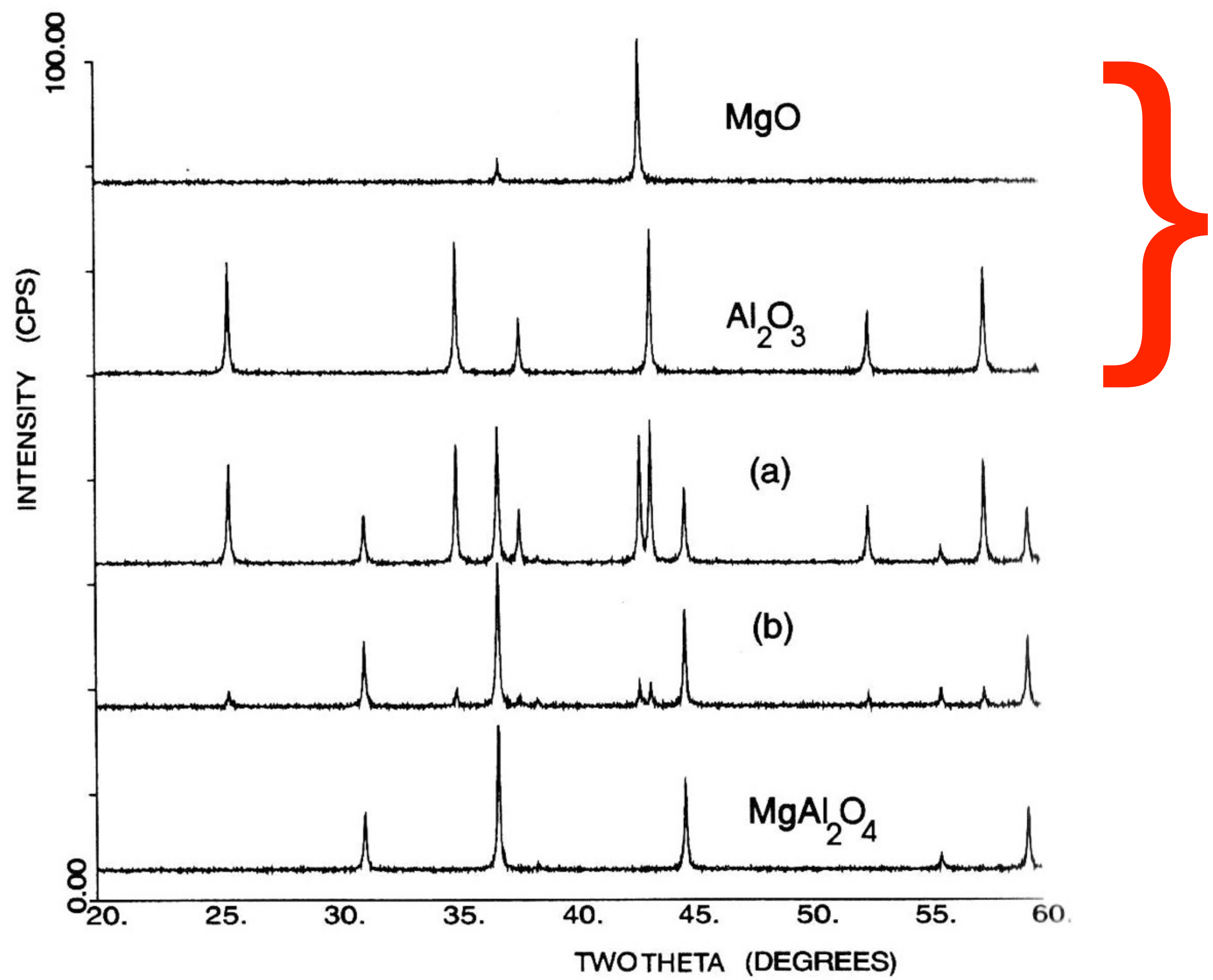



# Phase identification

## Tracking the progress of reactions




MgAl2O4 (spinel)




Reagents

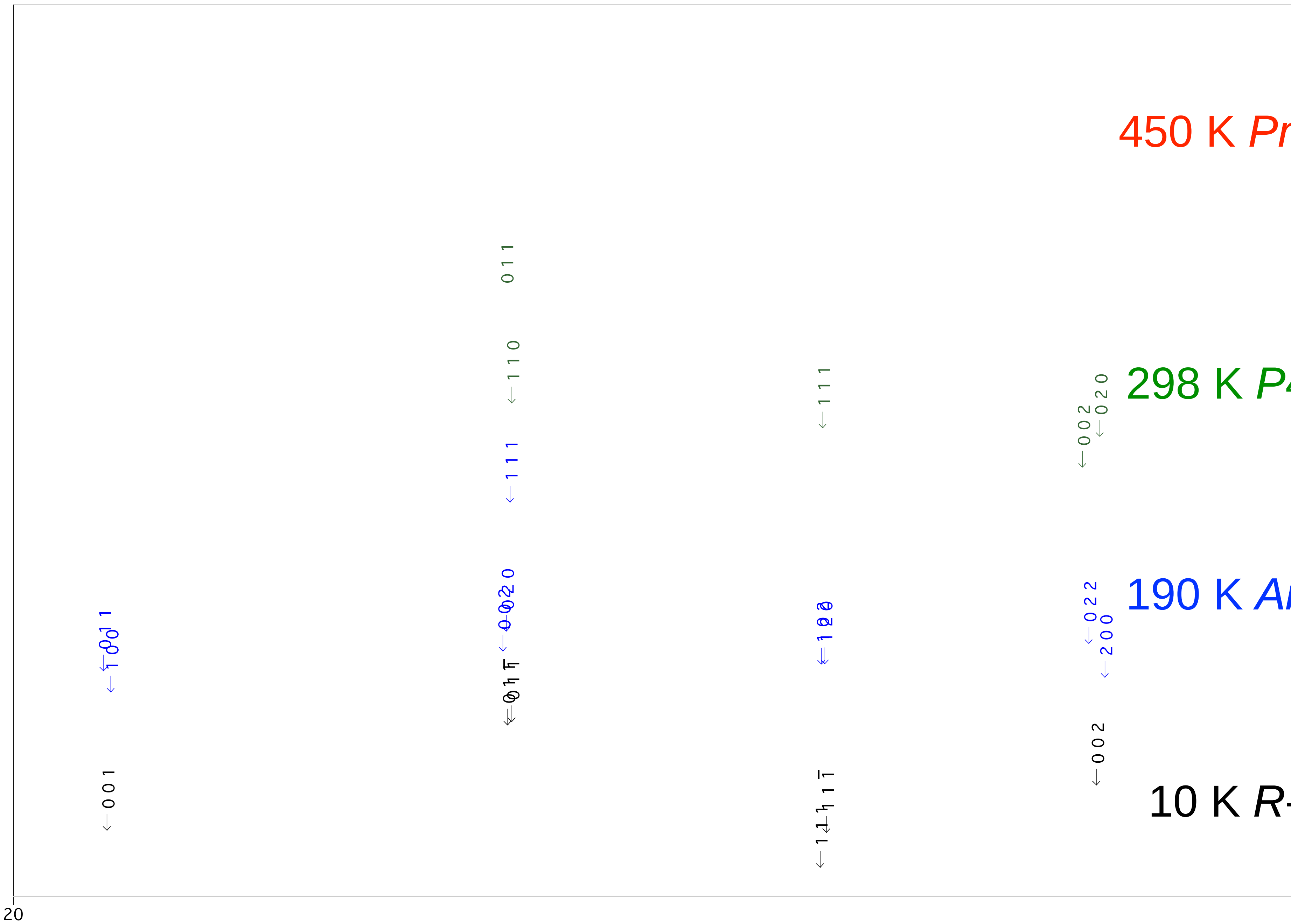
1st firing

2nd firing

3rd firing

# Phase transitions *in situ*

E.g. symmetry-lowering in ferroelectric $BaTiO_3$

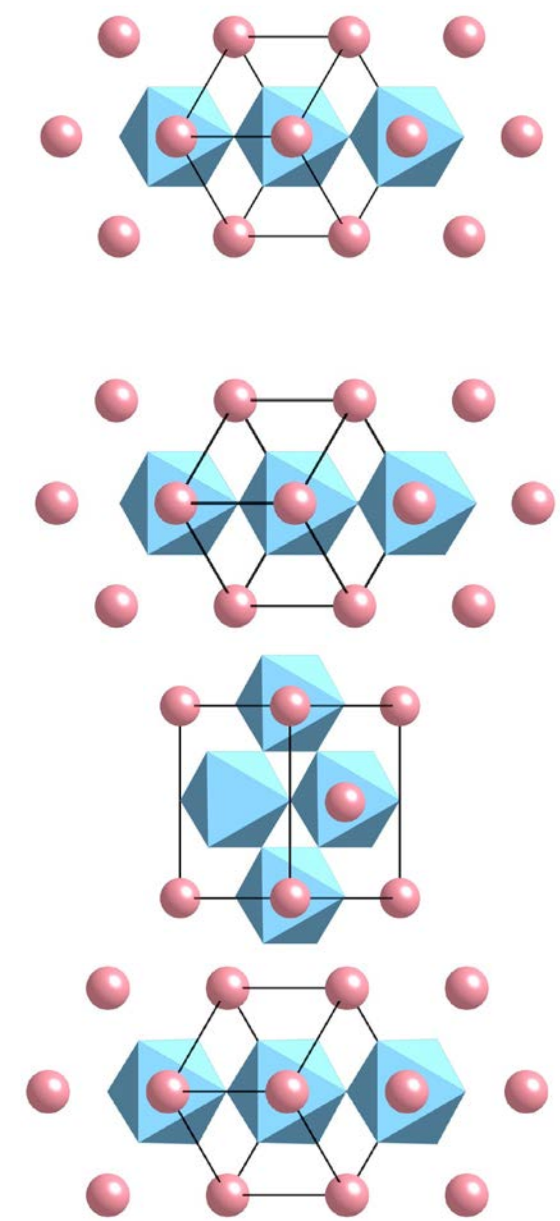



450 K *Pm*-3*m*

298 K *P*4*mm*

190 K *Amm*2

10 K *R*-3*m*



# Conventional X-ray diffraction

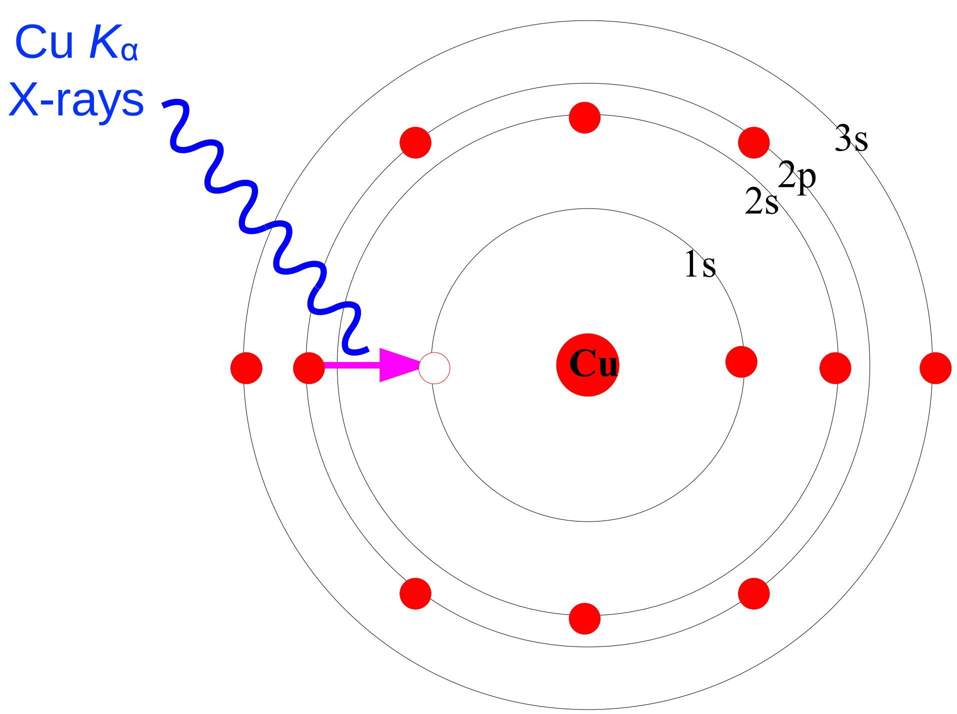
*Cheap, convenient and user-friendly*

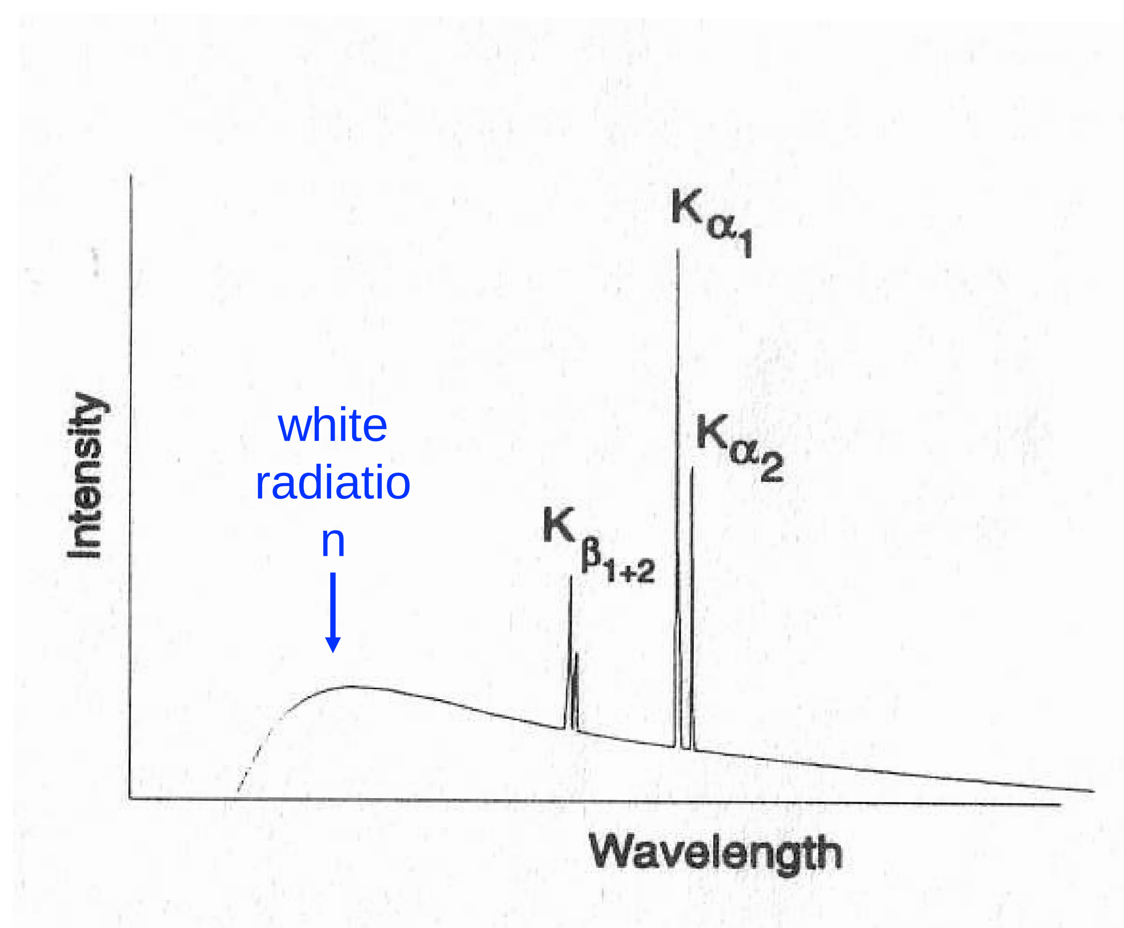
# Laboratory X-ray sources

Laboratory XRD instruments generate X-rays by hitting a pure element with a beam of electrons accelerated through ~30 keV.

Standard sources use sealed tubes

~3× higher fluxes can be achieved using rotating anodes



# Practical limitations of lab sources

## Limited intensity means that:

Requires sample sizes that are not always achievable synthetically (especially single crystals)

Trade-off between divergence and intensity → limited resolution

## Limited minimum wavelength means that:

The accessible $Q$ range is restricted → a limited number of reflections can be collected

Samples are more absorbing → maximum sample size is limited

## Together this means:

The effective maximum dynamic range (weak vs. strong reflections) is limited

# Synchrotron X-ray diffraction

*~~Expensive, inconvenient and frustrating~~*

*Intense, energetic and tuneable*

# Advantages of synchrotron X-rays

## High intensity

Small samples (powder or single crystal)

High speed (fast *in situ* processes, unstable compounds…)

High signal-to-noise → better data

→ weak features (impurities, satellite reflections, diffuse scattering)

High resolution → complex structures with big unit cells

→ fine peak splitting (phase transitions, decomposition)

→ peak shapes defined by sample properties (strain, particle size)

## Tuneable energy

Highlight elements of interest

Minimise absorption

## High energy

High $Q$ → more accurate ADPs, potential for PDF analysis

Compressed patterns → can use restrictive sample environments (pressure, fields)

High penetration → minimise surface effects

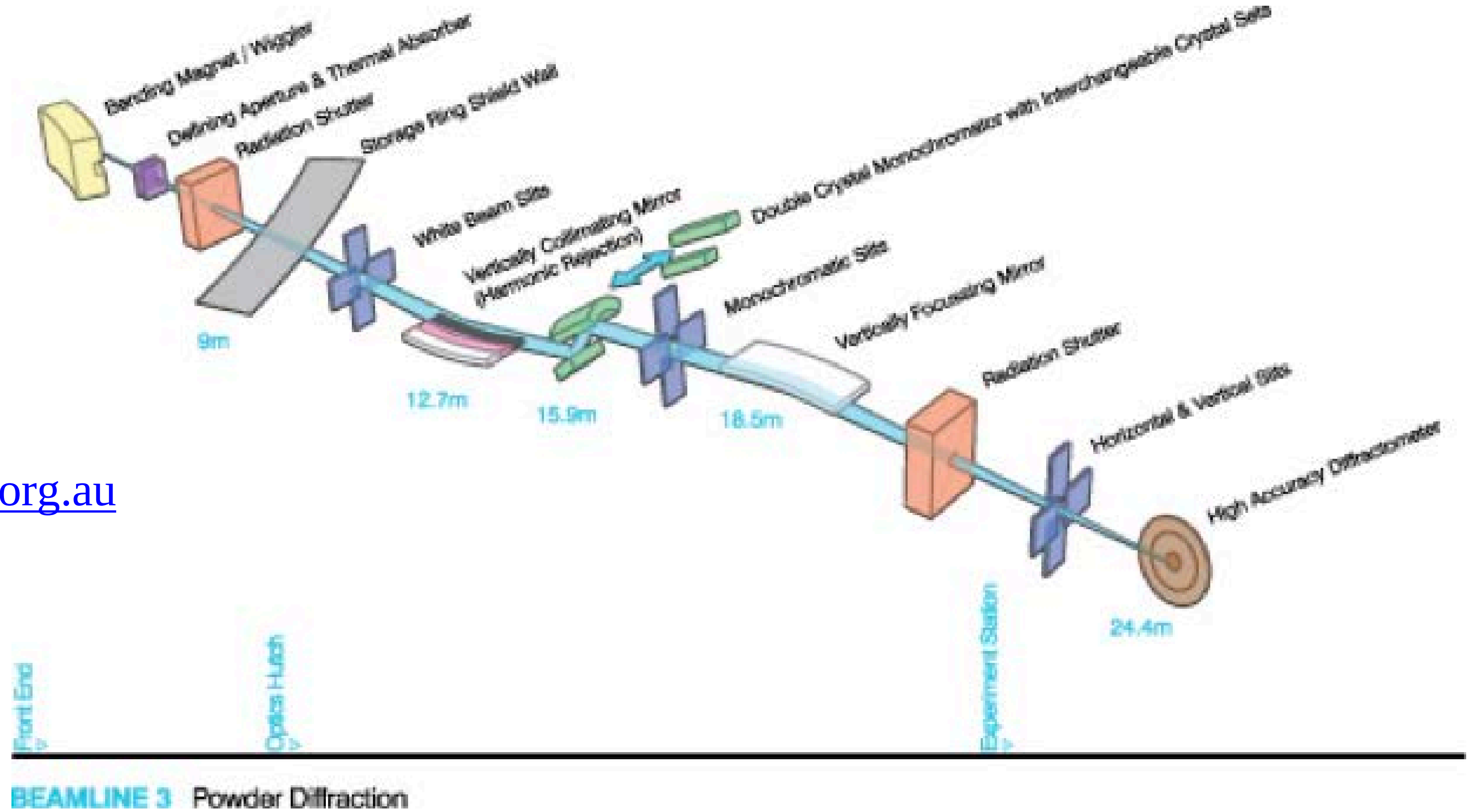
# Diffraction beamline design

## The “white” beam must be monochromated for diffraction

Single-crystal monochromators, typically Si(111), select a single x-ray energy

“Bent” monochromators, mirrors and slits can be used to focus the beam

www.synchrotron.org.au



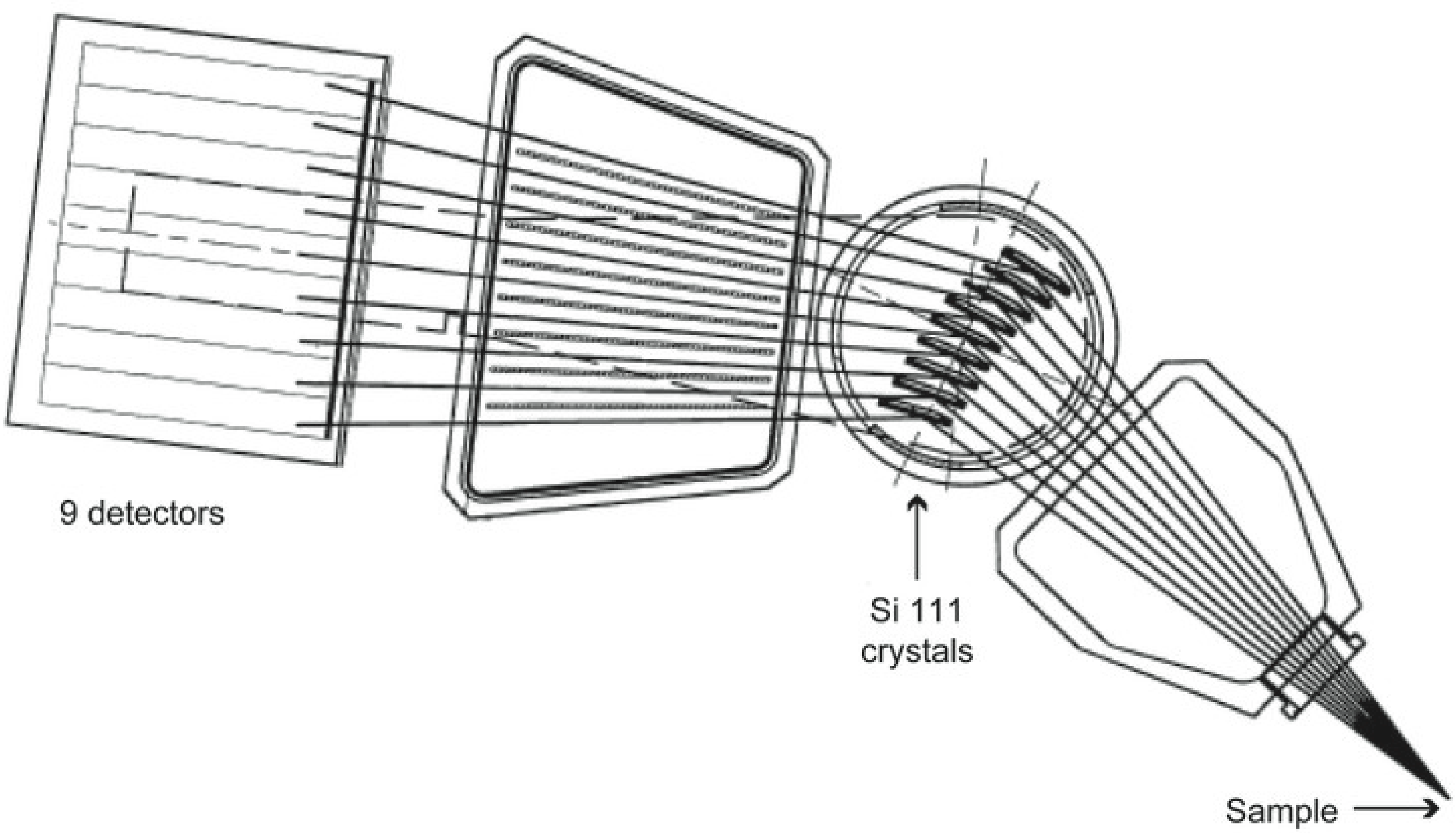

**Typical flux at sample: ~$10^{12}$ – $10^{13}$ photons $mm^{-2}$ $s^{-1}$**

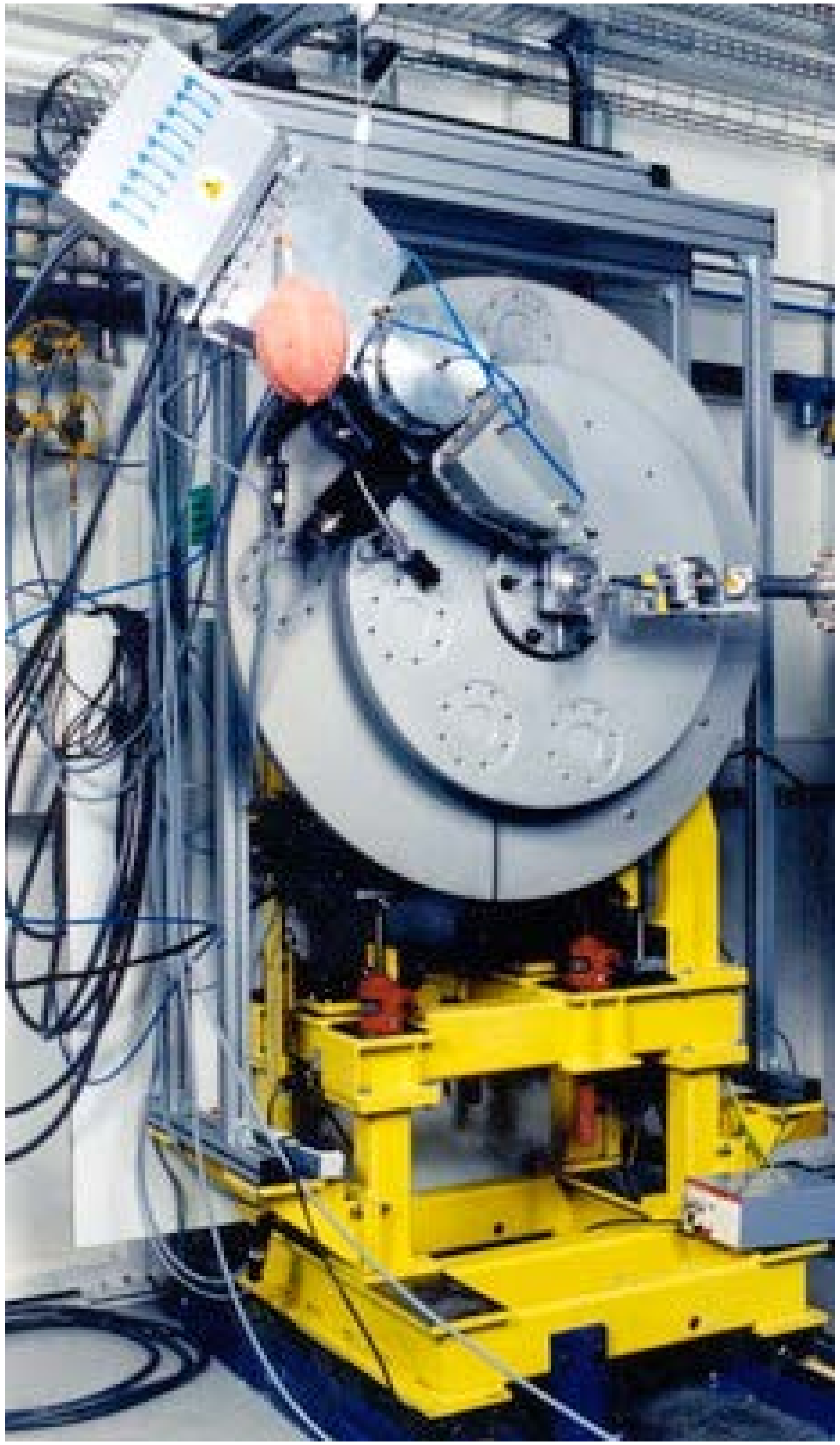
*cf* ~$10^{10}$ – $10^{11}$ photons $mm^{-2}$ $s^{-1}$ (after focussing) from a modern sealed tube (rotating anode) source

# High-resolution detection

## Analyser crystals

Signal-to-noise can be improved further by using a second monochromator crystal to direct only x-rays of the correct energy to the detector.



www.esrf.eu

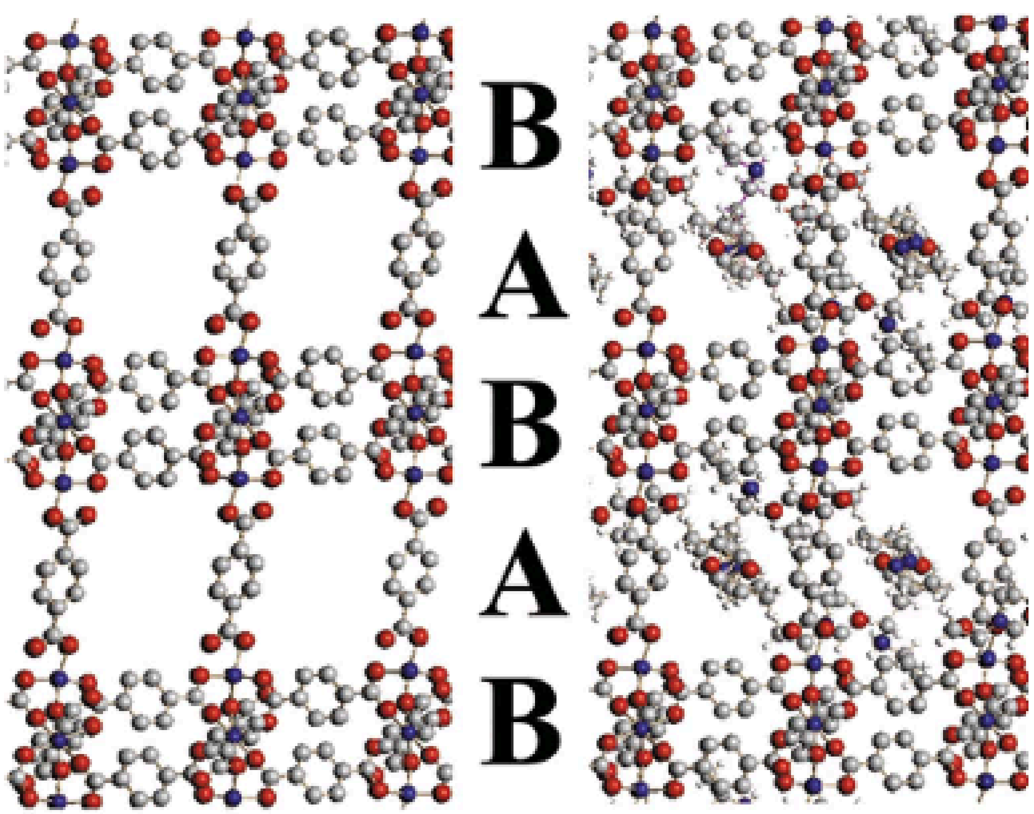
# High Intensity and Coherence

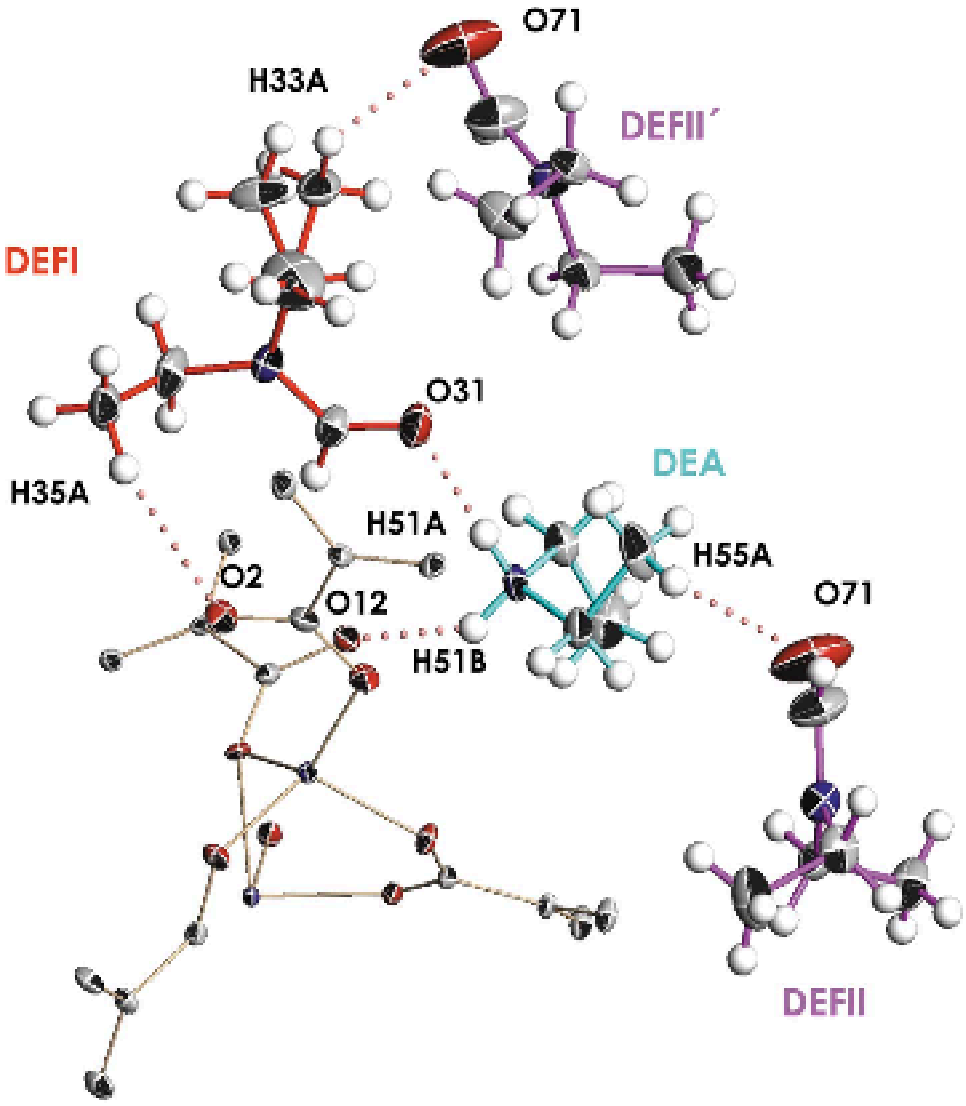
## Smaller samples

Air-sensitive, hygroscopic etc.

Expensive reagents

Difficult to synthesise



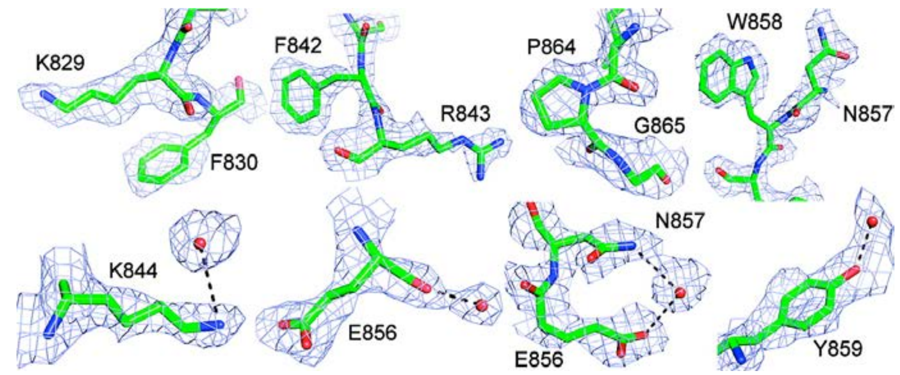

40µm crystal of
$2C_4H_{12}N^+$-$[Co_3(C_8H_4O_4)_4]^{2-}$.$3C_5H_{11}NO$

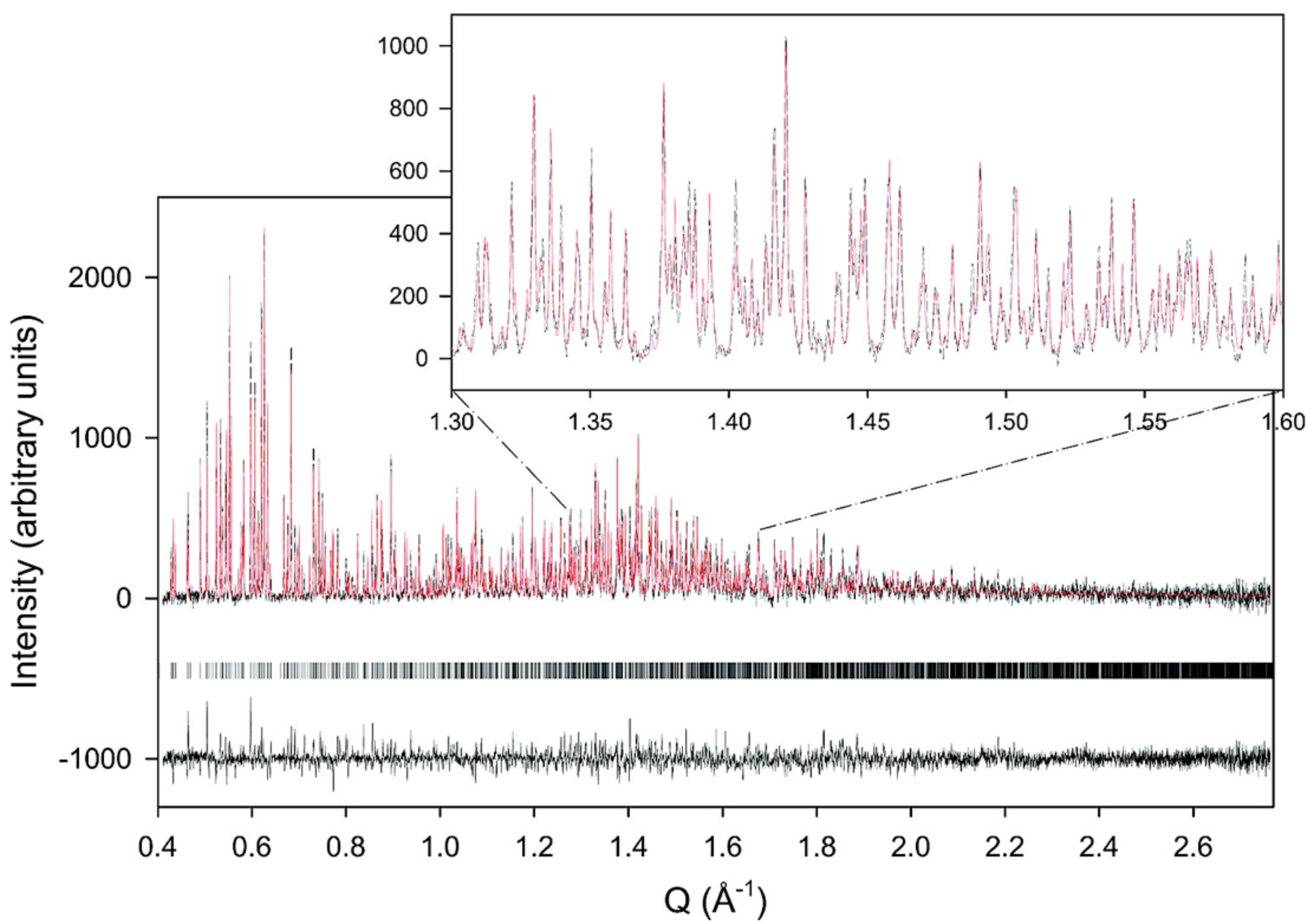
Acta Cryst. (2006). B62, 245–254

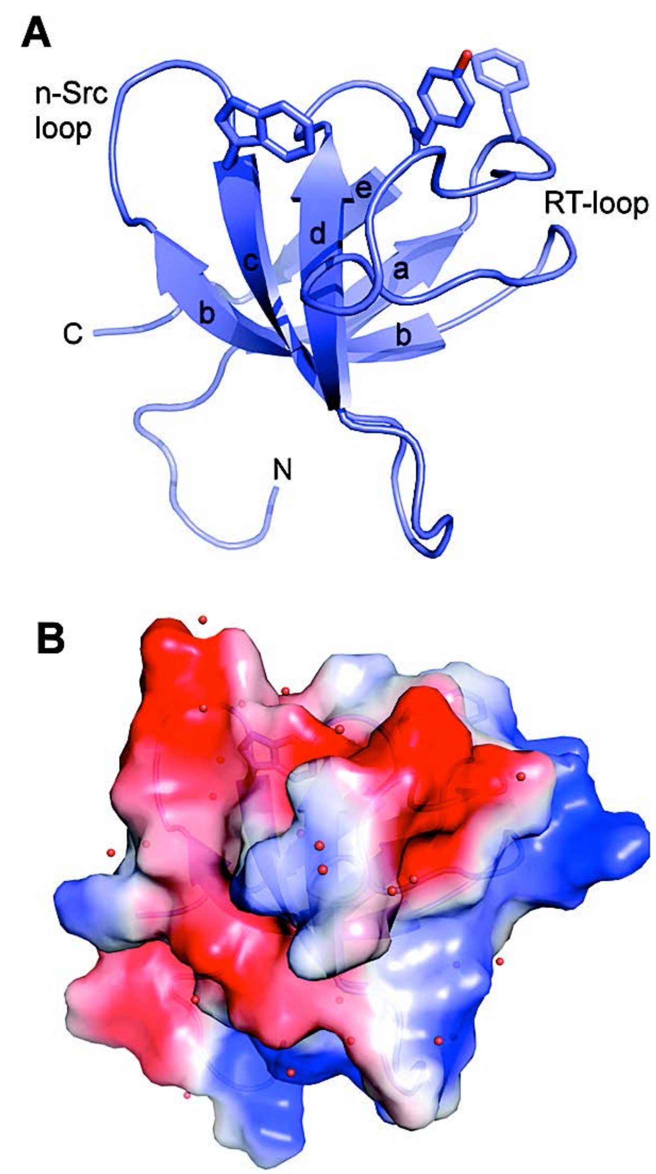
# High Intensity and Coherence

## Complex structures

Rietveld-refinement of a 67-residue protein domain crystal structure with a cell volume of 64 879 Å$^3$



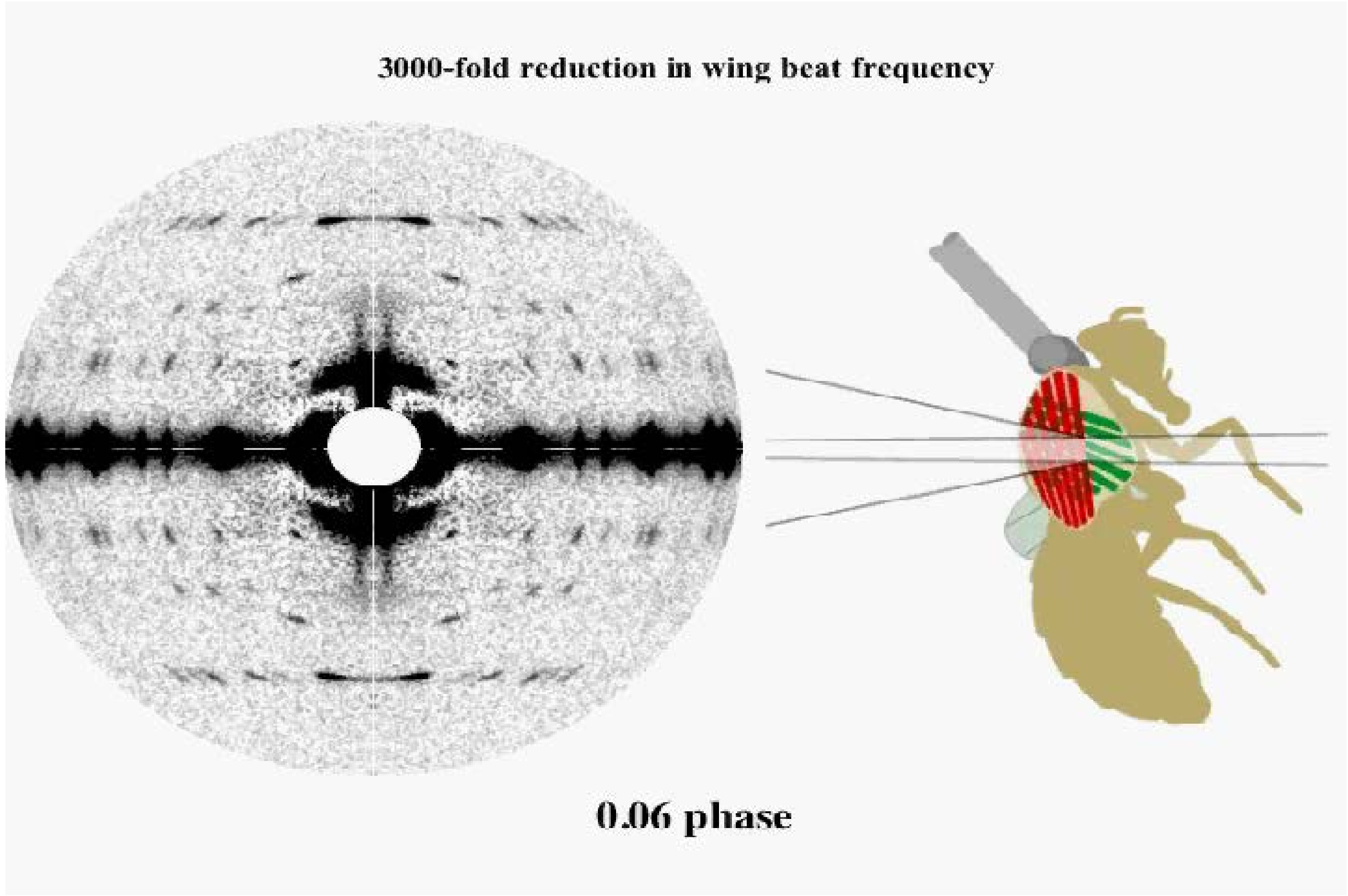



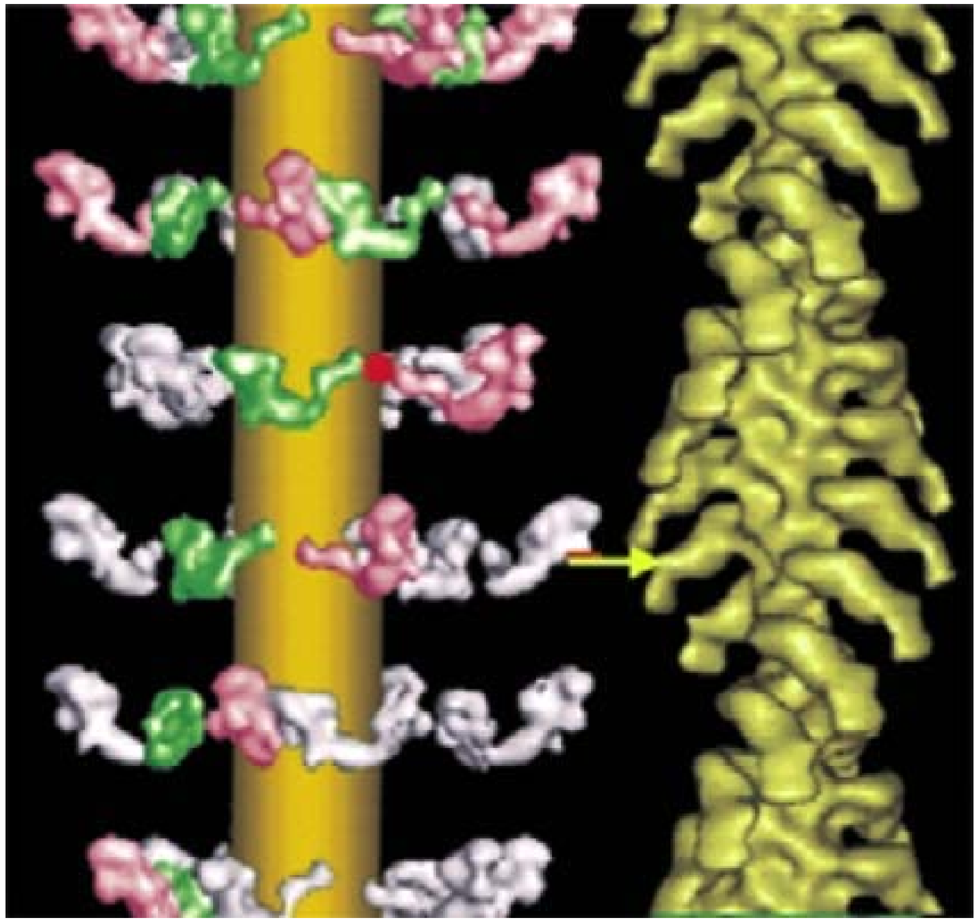

J. Am. Chem. Soc., 2007, 129 (38), pp 11865–11871

# High Intensity and Coherence

## High-speed diffraction

Variable wavelengths permit ultra-fast "white-beam" Laue diffraction



Dickinson *et al.*, *Nature* **433**, 330 (2005).

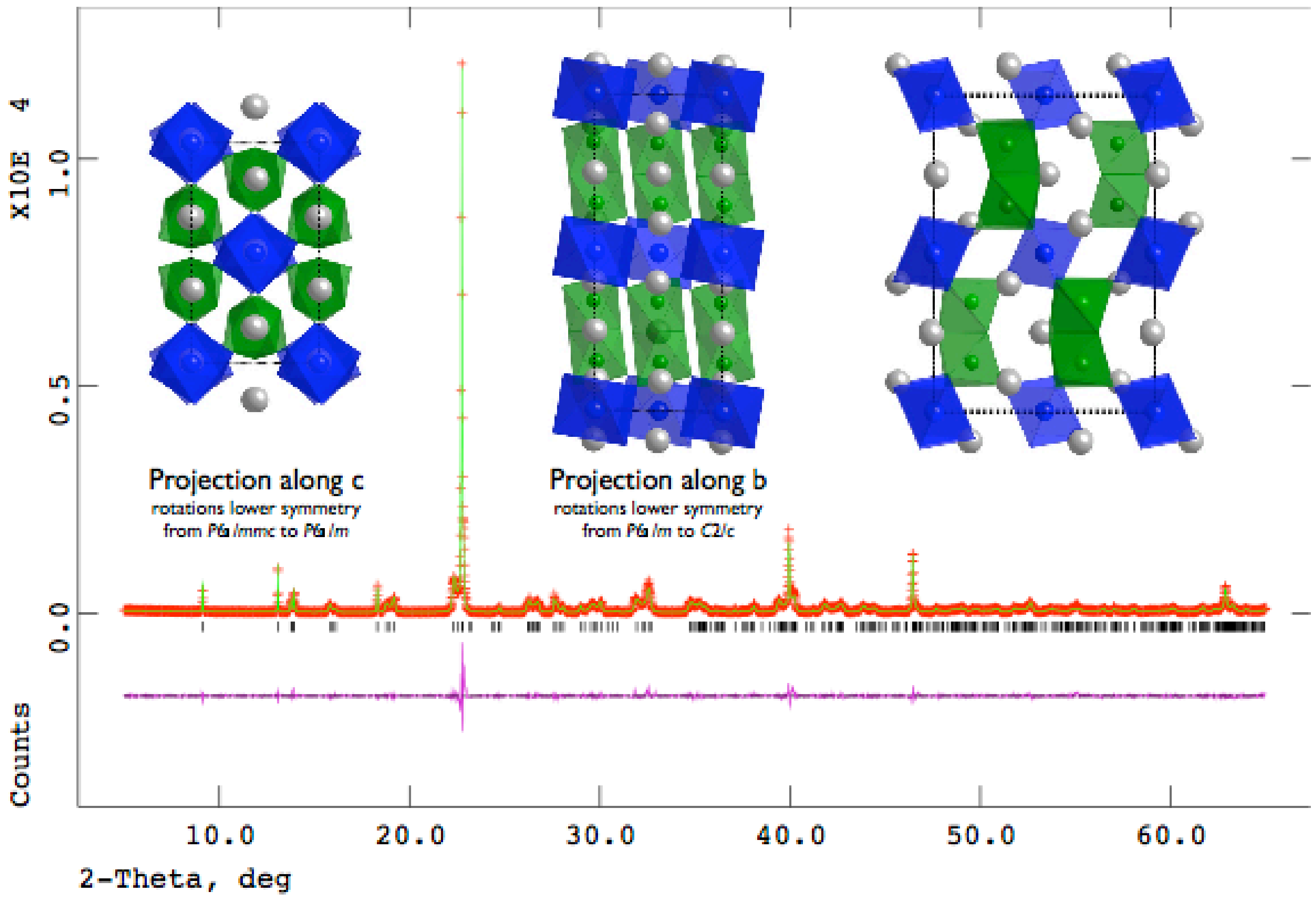
# High Intensity and Coherence

## Lower beam divergence → higher resolution

Large, low-symmetry unit cells

Sample-dependent peak shape functions, e.g., lattice strain

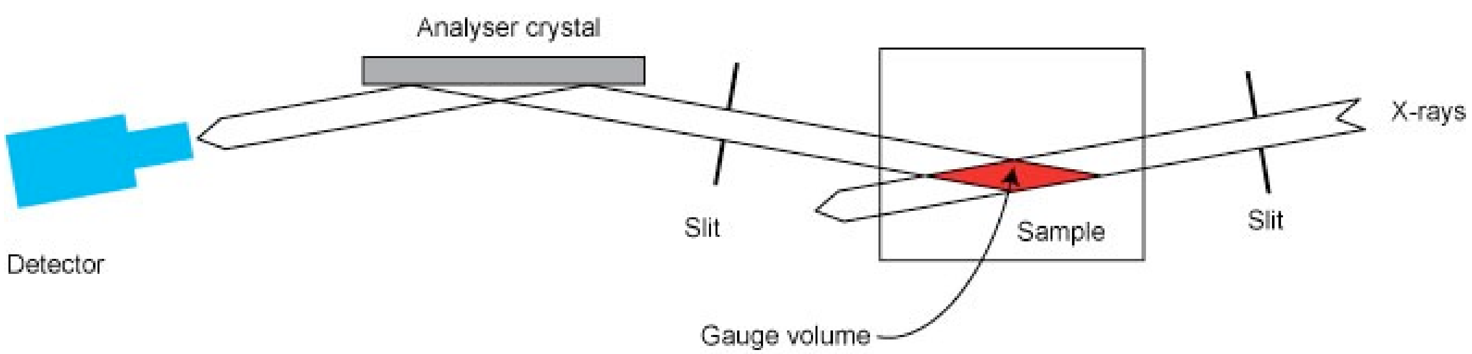
Subtle symmetry lowering



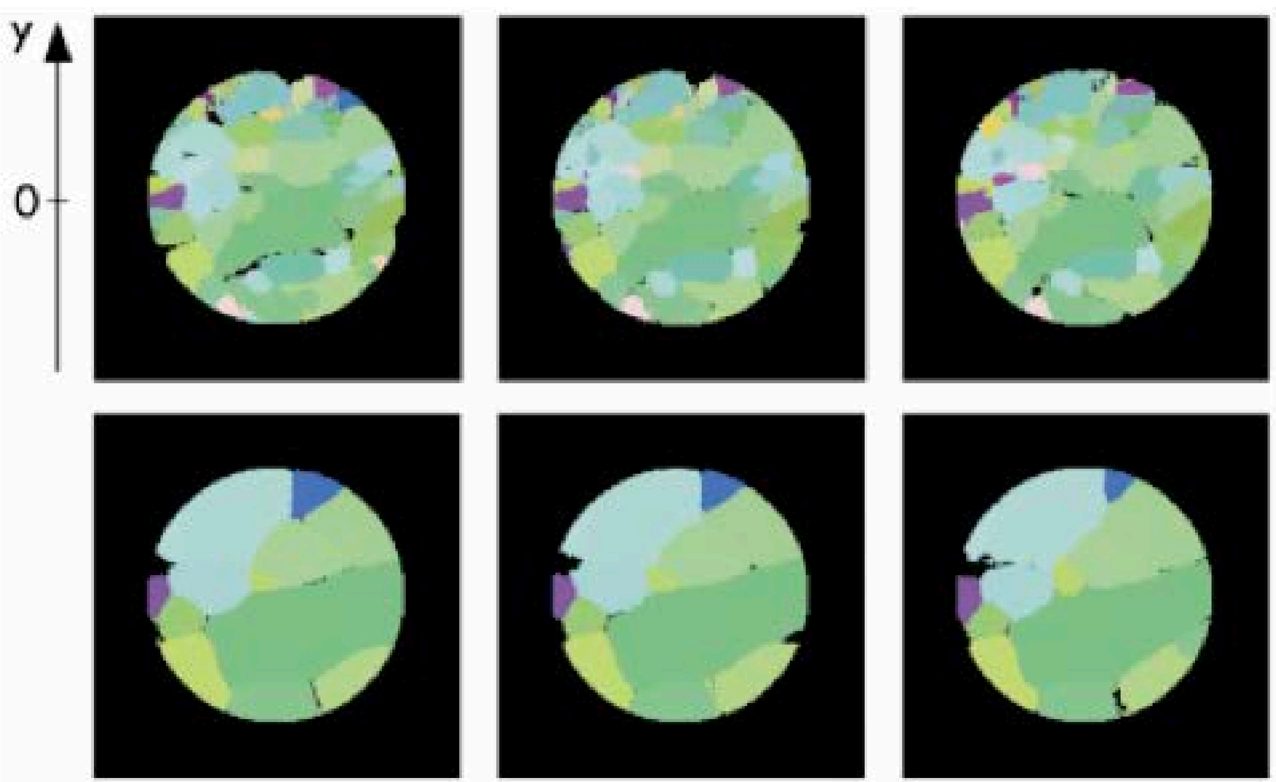

# Tuneable Energy/Wavelength

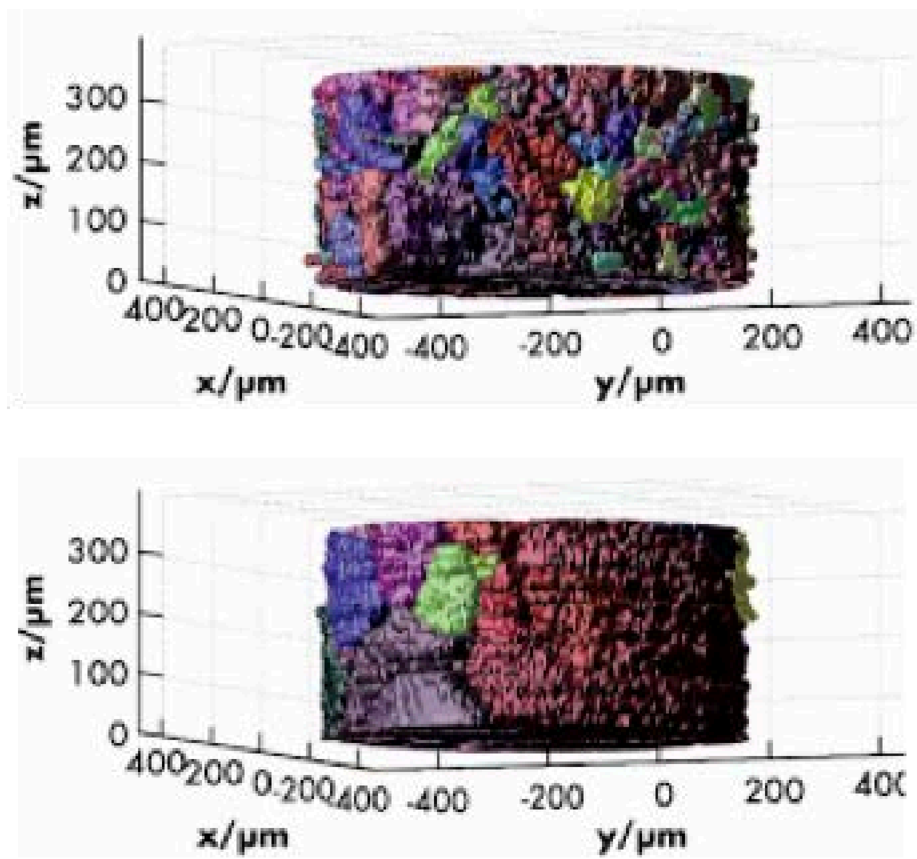
## Higher x-ray energy → higher penetration

3D mapping of crystal orientation and/or strain (peak width) in different gauge volumes




*Al-0.1%Mn alloy before (top)  and after annealing*



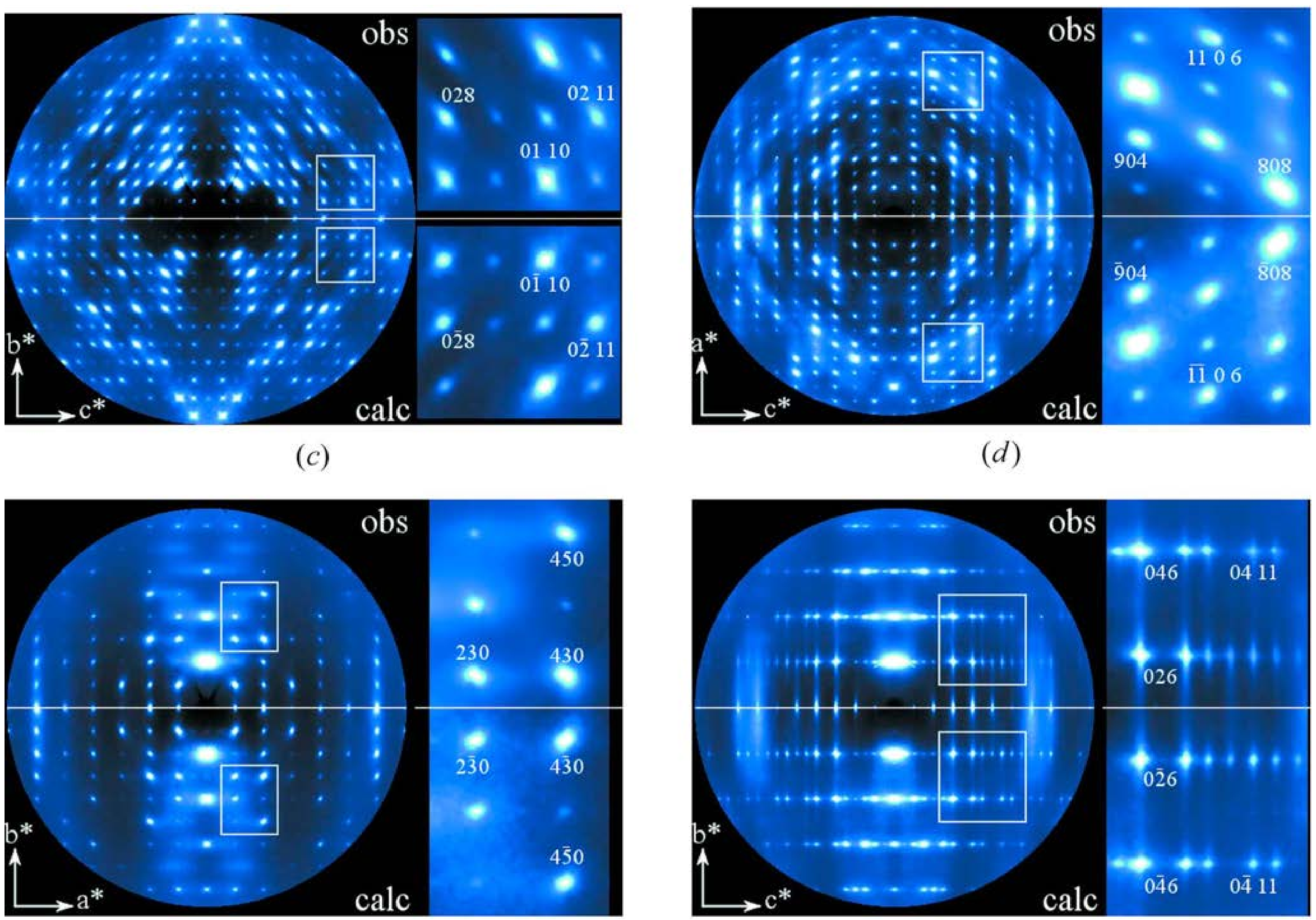

Scripta Mater. **59**, 491 (2008)

# High Intensity and Coherence

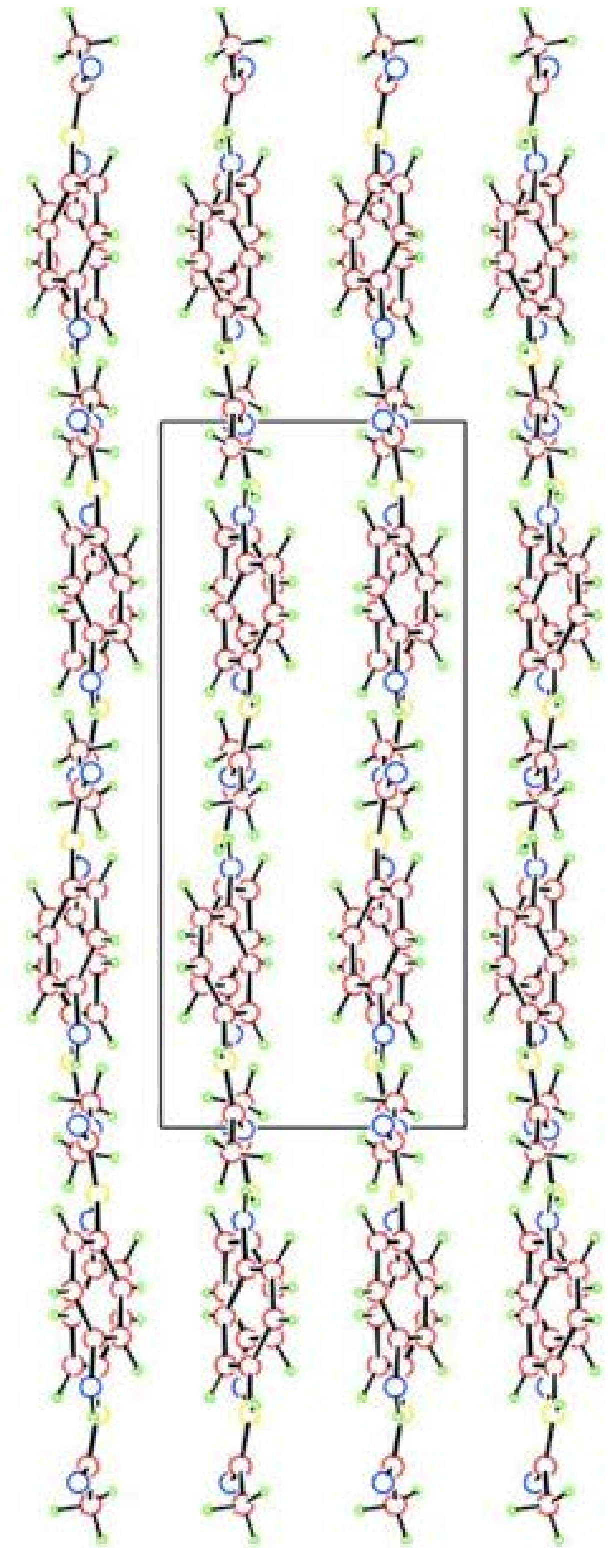
## Greater accessible dynamic range

### Diffuse scattering: structural disorder

### Modulated structures




*Paracetamol*



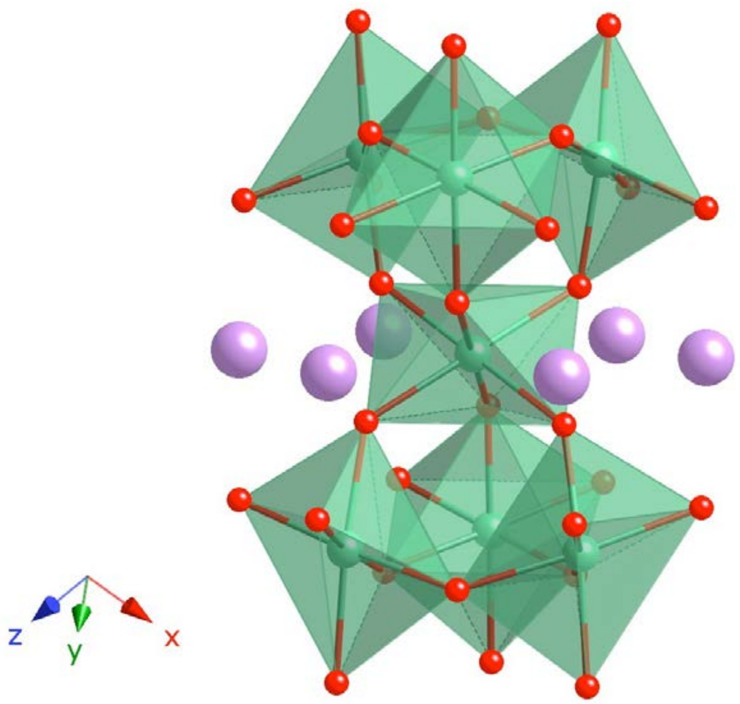
**Acta Crystallographica Section B: Structural Science 68**, 1 (2012) 80-88

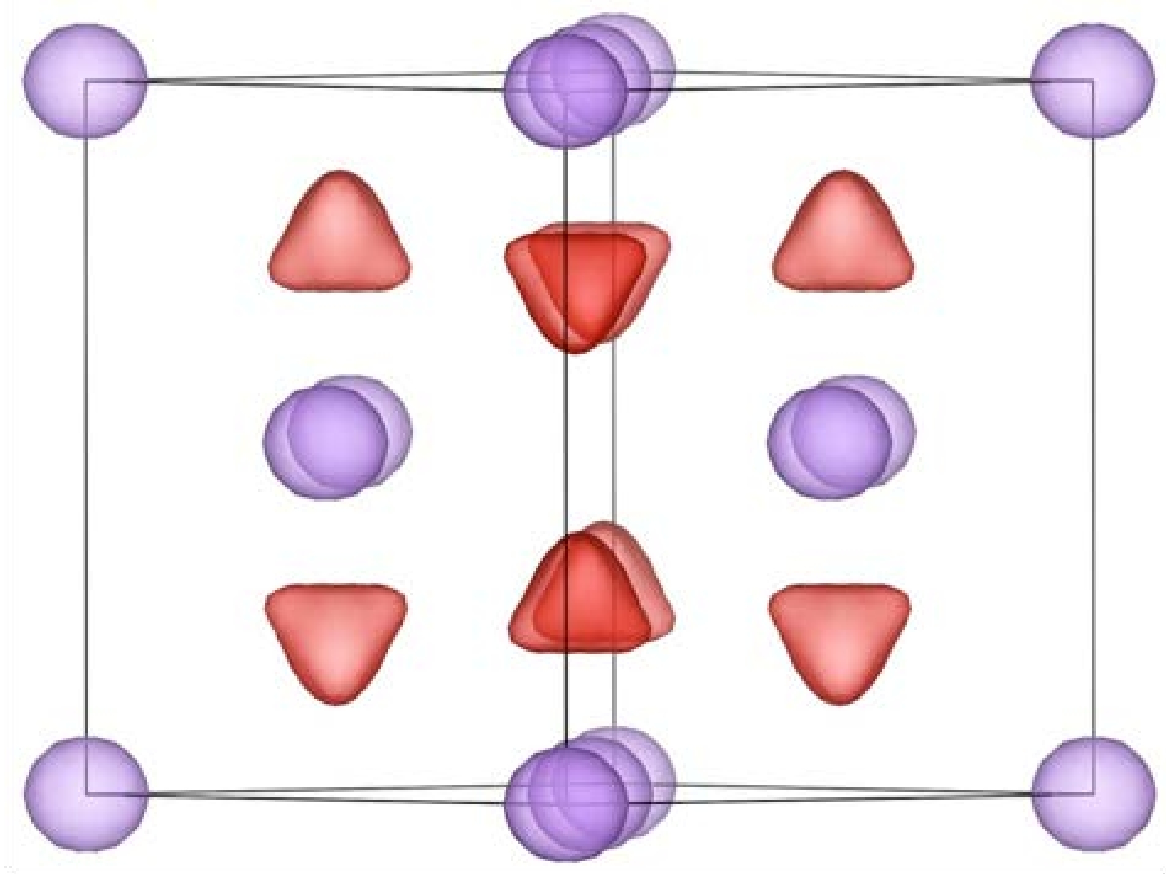
# Tuneable Energy/Wavelength

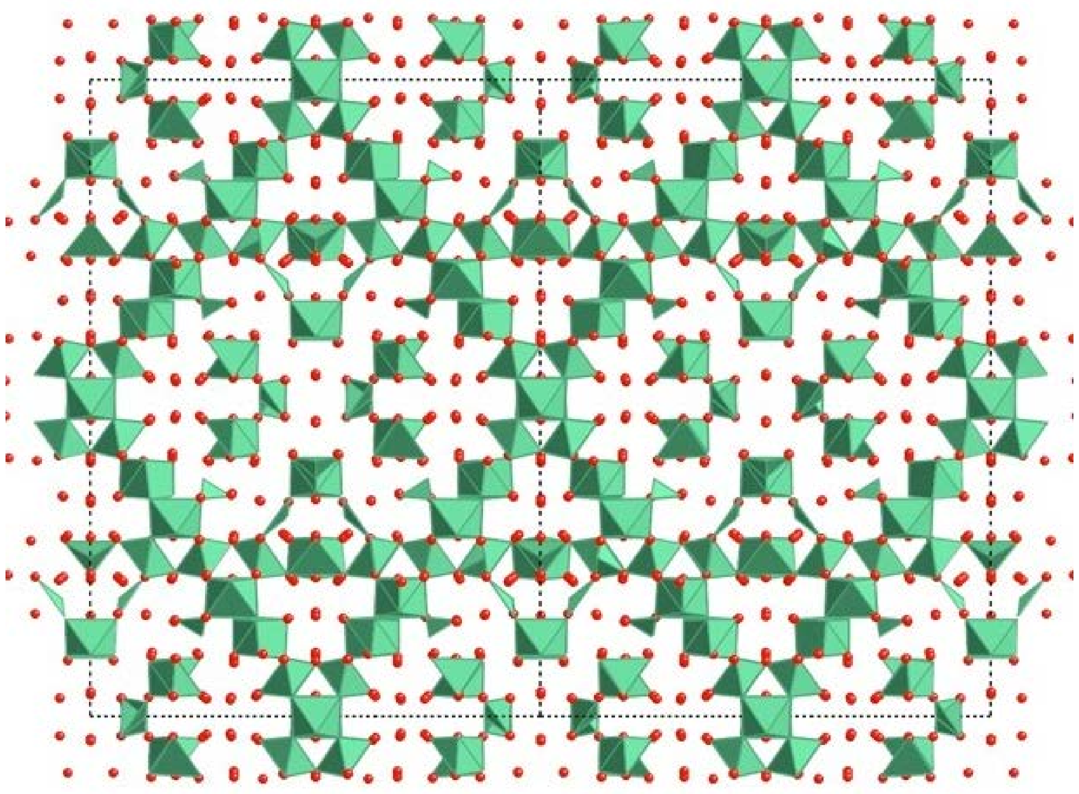
## Greater accessible sinθ/λ range

More information about atomic occupancies

Anharmonic atomic displacement parameters





# Tuneable Energy/Wavelength

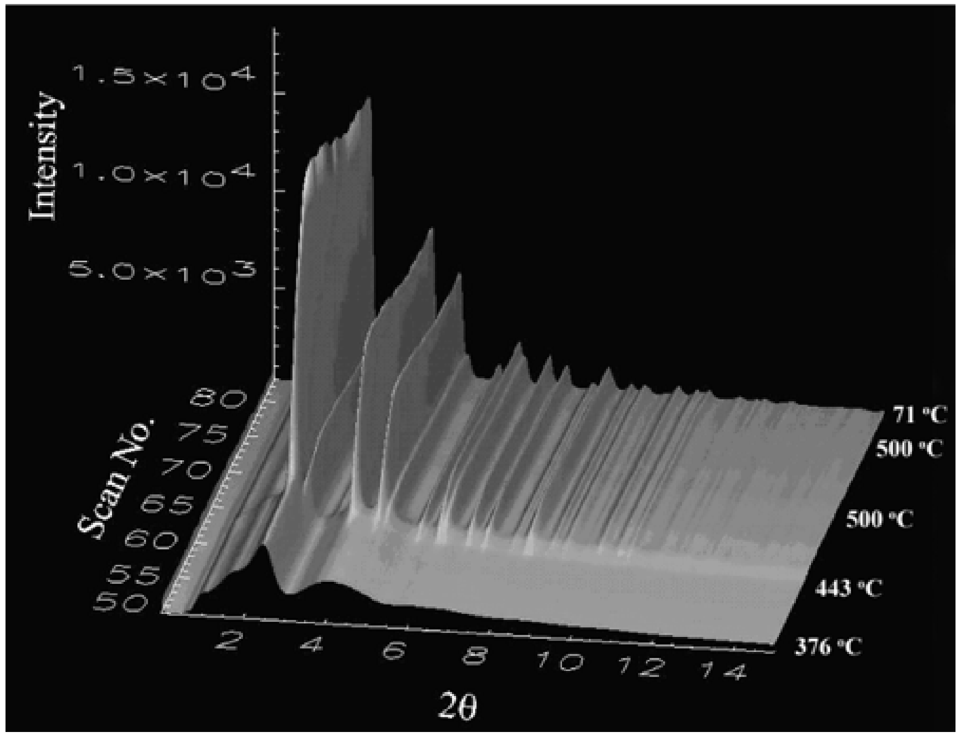
## Greater accessible sinθ/λ range

Site occupancies in disordered structures

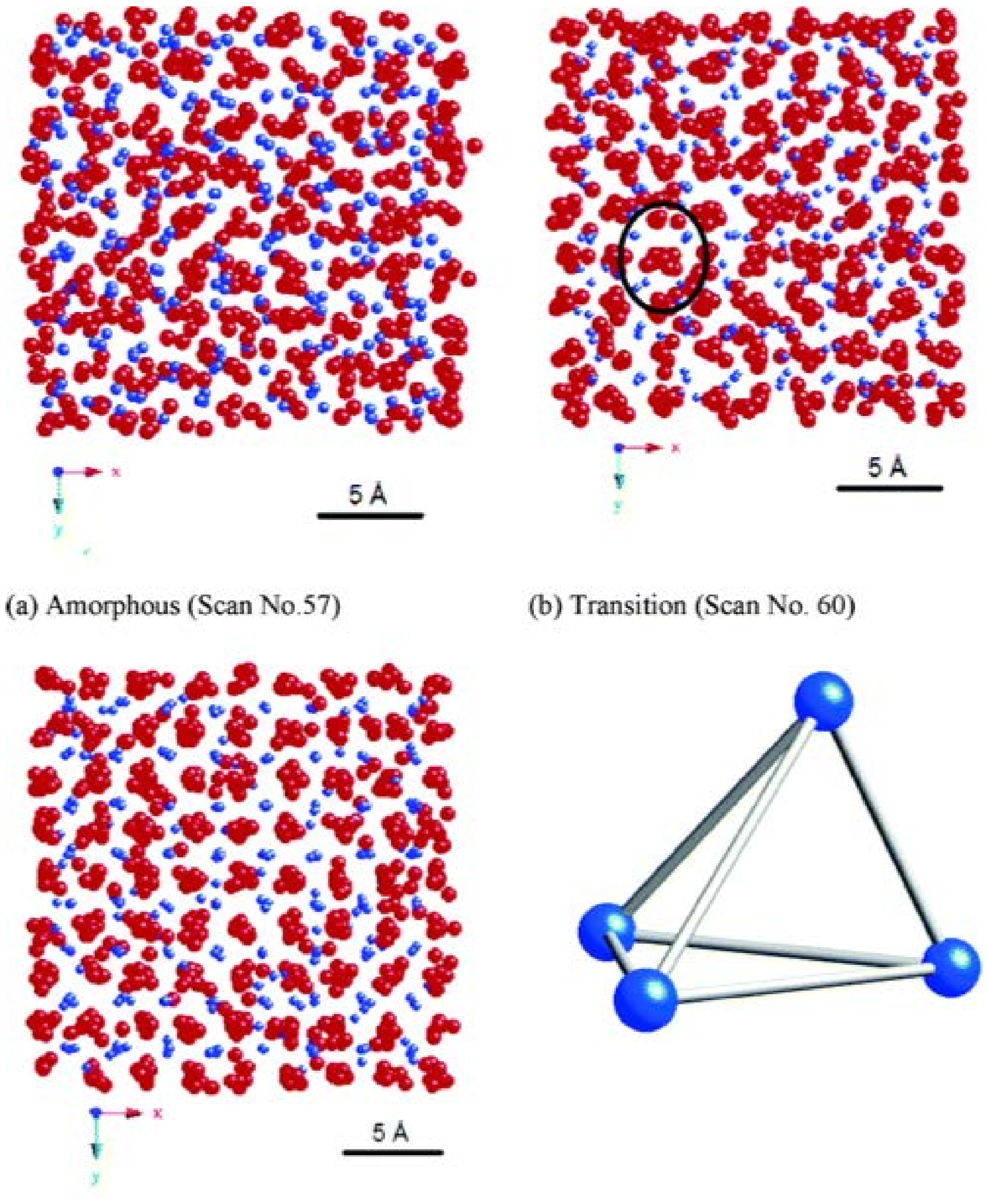
Electron density, maximum entropy (MEM)

Anharmonic atomic displacement parameters

Pair distribution function (PDF) analysis




1-minute S-XRD scans at λ = 0.124 Å of cubic $ZrO_2$ being reduced to an amorphous phase




(a) Amorphous (Scan No.57)

(b) Transition (Scan No. 60)

(c) Cubic 500°C

(d) Zr tetrahedron unit

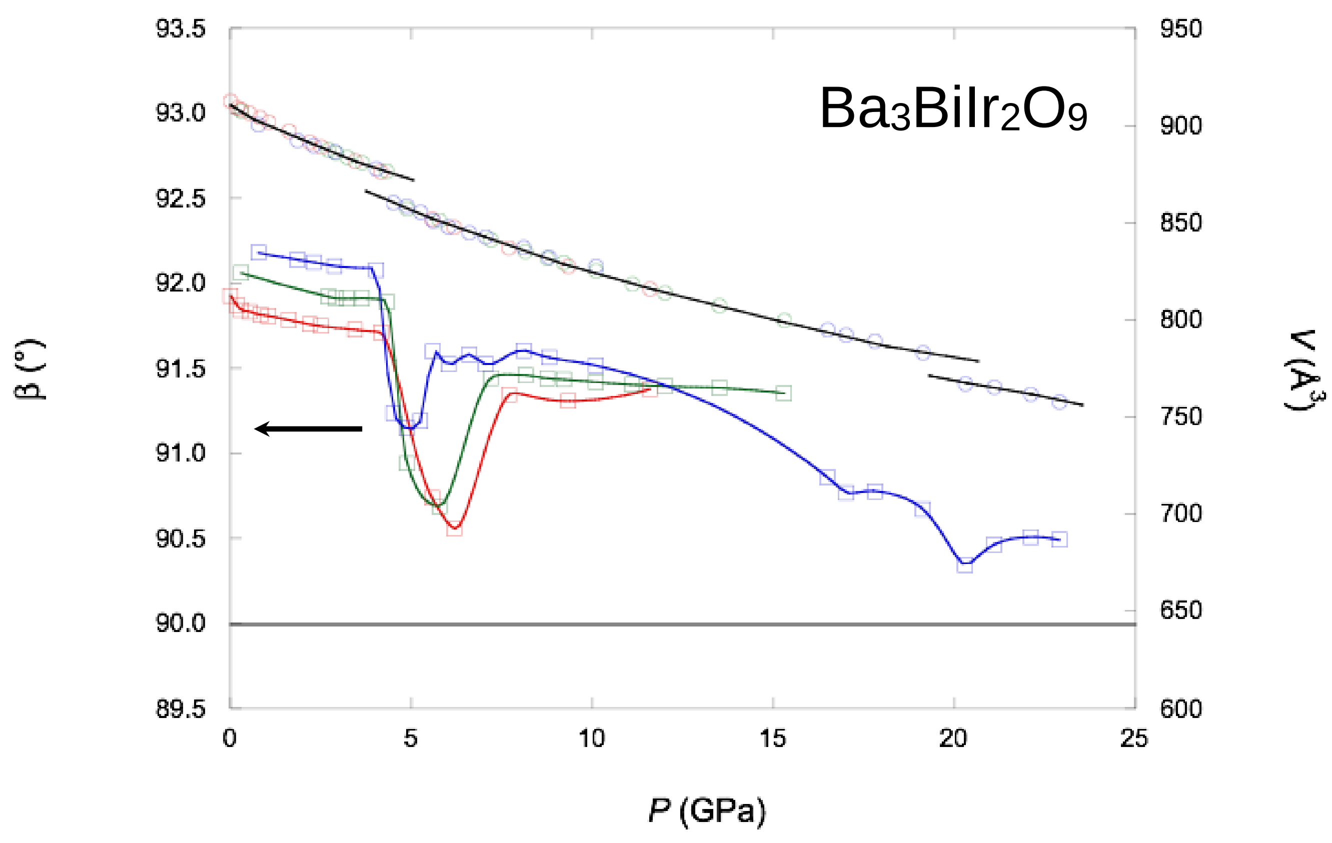
*Chem. Mater., 19 (13), 3118 -3126, 2007*

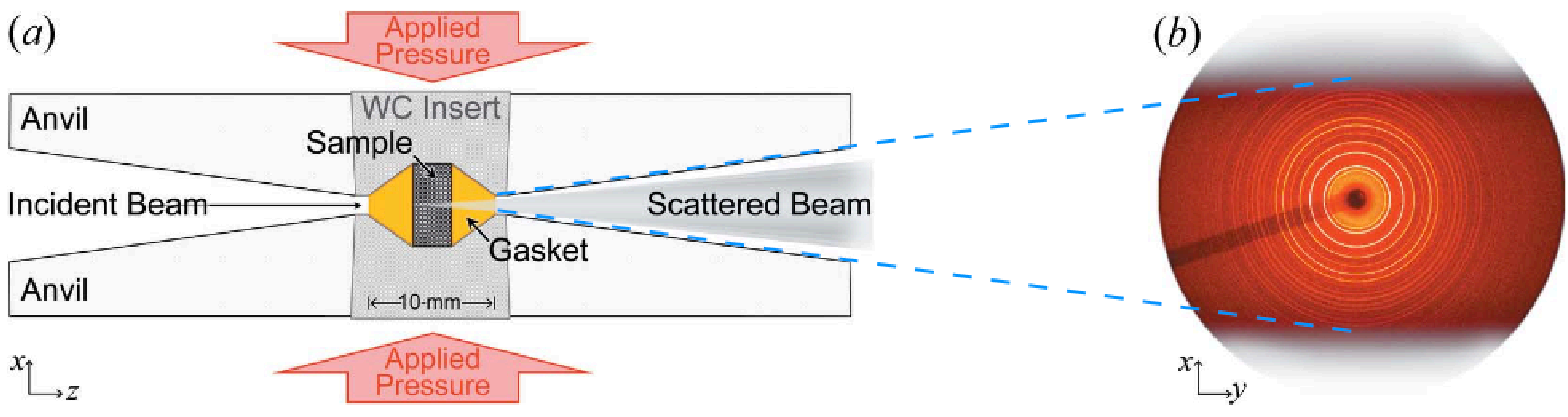
# Tuneable Energy/Wavelength

## Difficult sample environments

Pattern more compressed

Better penetration of gaskets *etc*



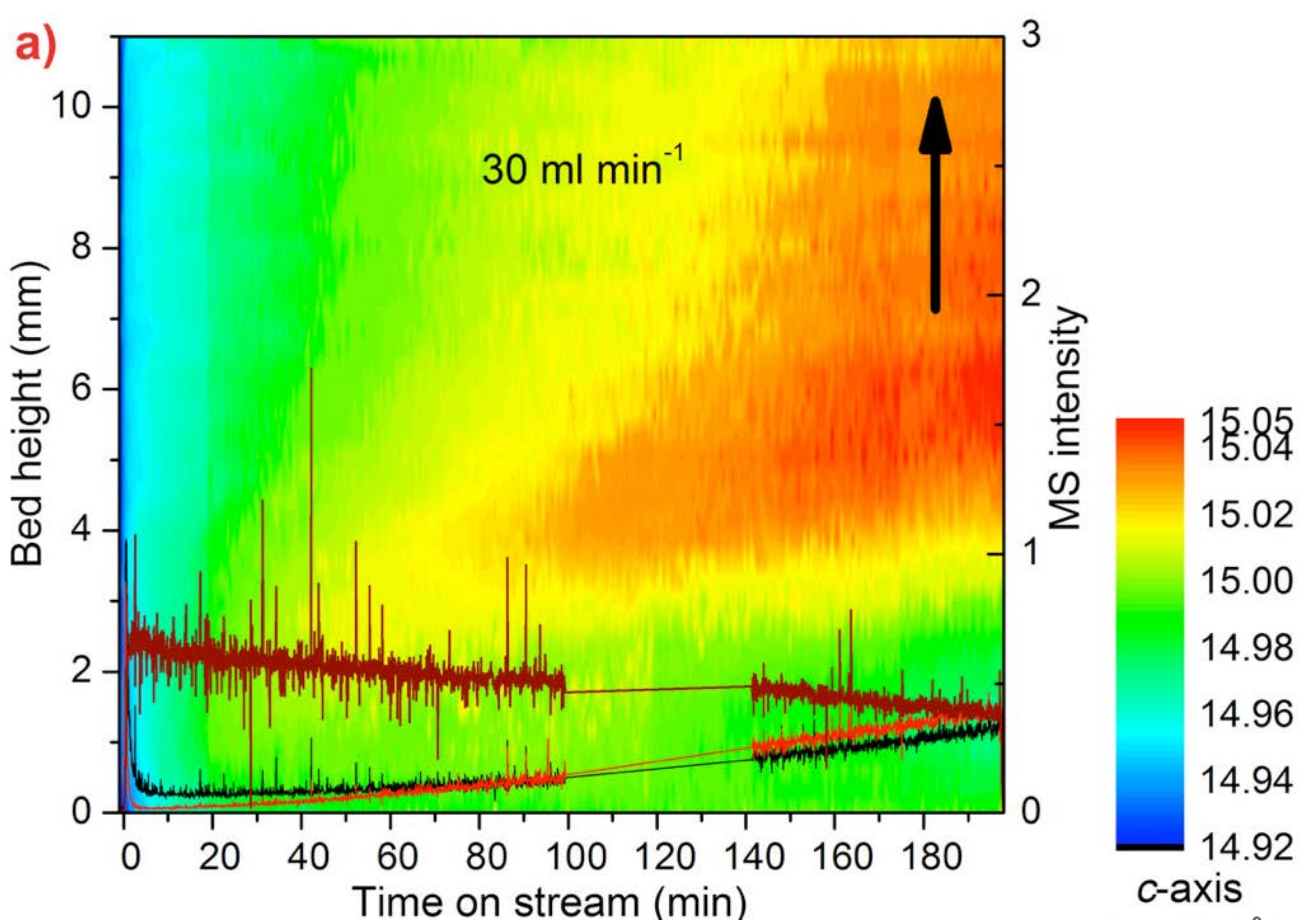



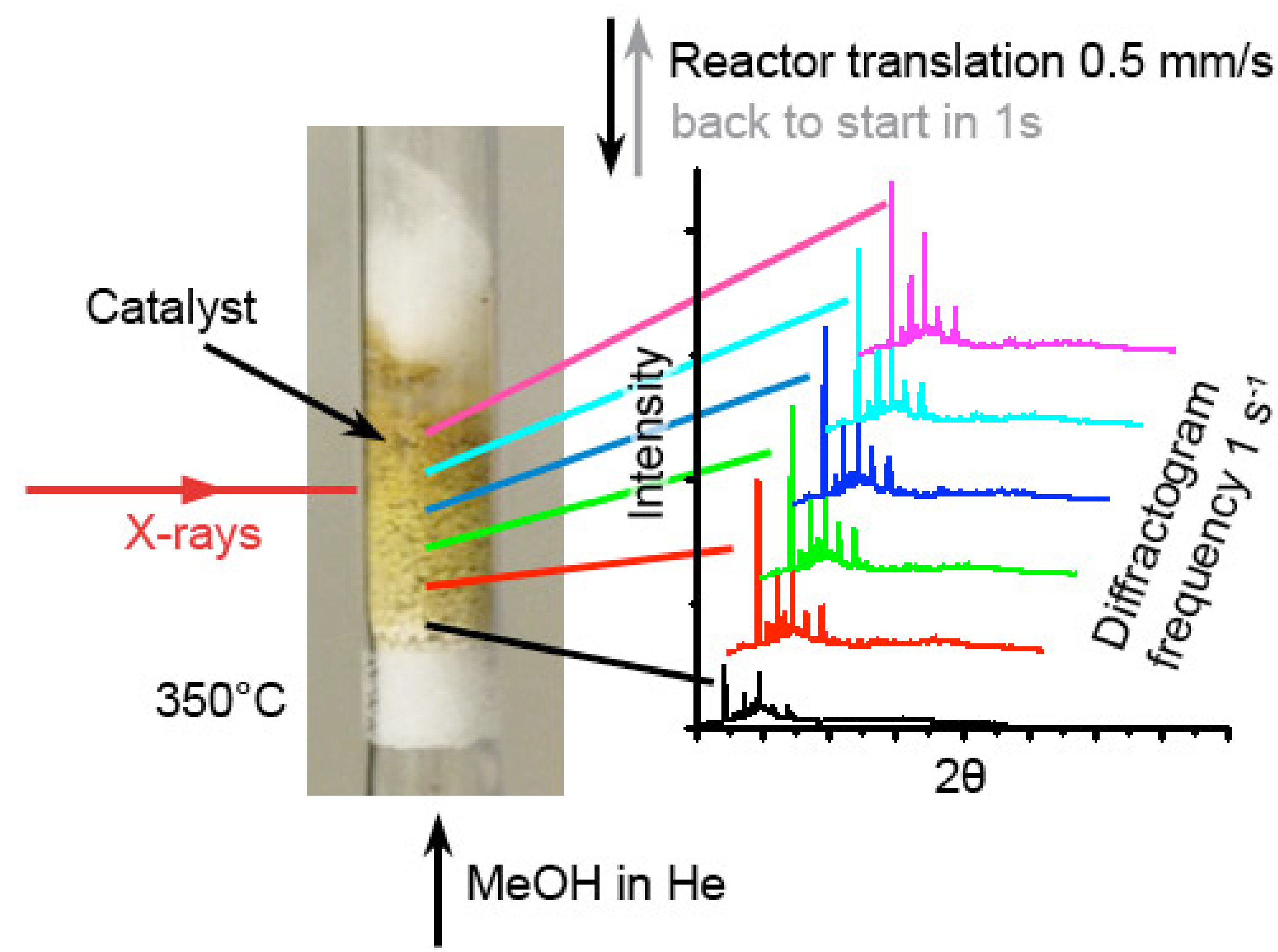
# Tuneable Energy/Wavelength

## *In situ* reactions

High spatial resolution, high data collection speed and high sample penetration allow the study of industrial reactions under “real-world” conditions in real time.

*Lattice expansion of a zeolite catalyst in a methanol-to-olefin reactor, due to coking, mapped in time and space*




Angewandte Chemie International Edition **51**, 7956–7959 (2012).

# Summary: synchrotron killer apps

Small samples

Heavy elements

Big, complex and/or low-symmetry structures

High-resolution ADPs

Modulated structures

Short-range order (PDF)

Medium-range order (diffuse scattering)

Torturing insects


管理区域
BOSS
PEPSI
西棟入口


リーク用