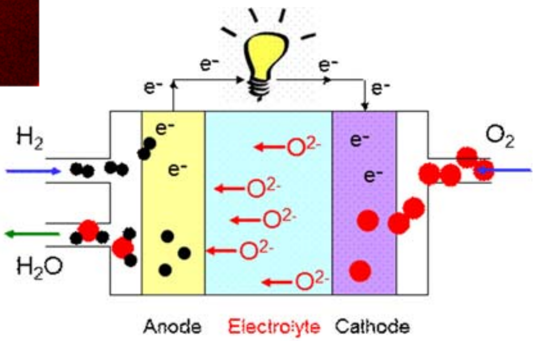
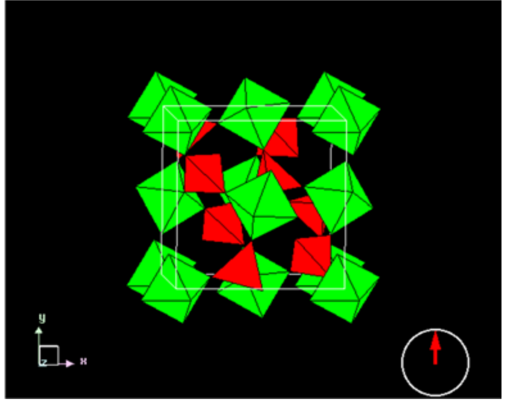
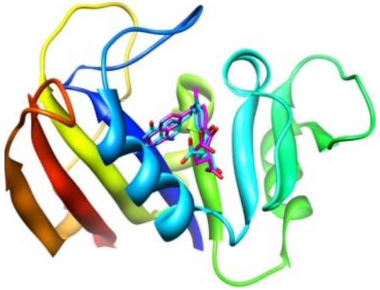




Nove fizickohemijske metode

Metode zasnovane na sinhrotronskom zracenju (Difrakcione metode)



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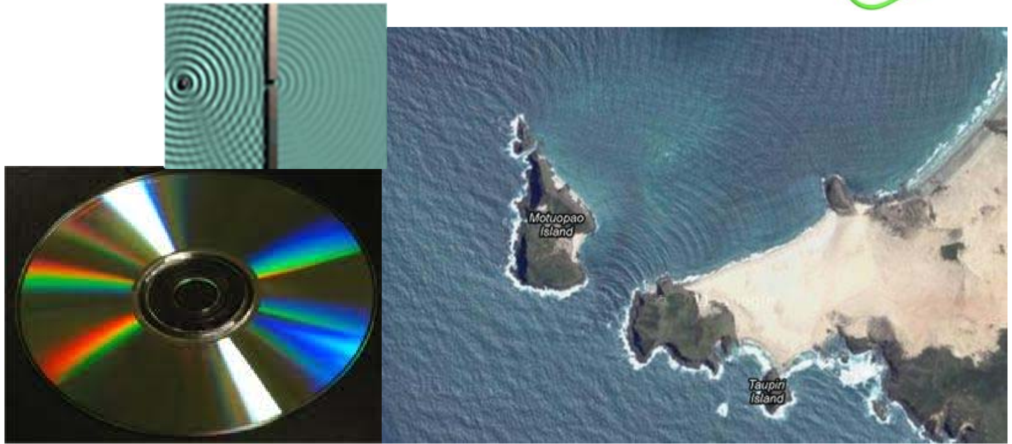

Metode zasnovane na sinhrotronskom zracenju (Difrakcione metode)

- Plan predavanja:
  - Difrakcione metode strukturne karakterizacije materijala
  - Eksperimentalni aspekti difrakcije sinhrotronskog X-zracenja
  - Oblasti primene difrakcije sinhrotronskog X-zracenja
  - Prednosti (i mane) u odnosu na laboratorijski XRD
  - Primeri studija neorganskih funkcionalnih materijala
- Preporuceni prag znanja:
  - Osnovne kristalografske definicije
  - Kristalografska simetrija, prostorne grupe
  - Difrakcija kao fizicka pojava
  - Bragg-ov zakon
  - Rasejanje sa jedinicne celije: strukturni faktor

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Why Study Structures of Solids?

- Proof of molecular structure
  - Quick analytical tool for the synthetic chemist
    - ☐ What molecule have I made?
- Determination of crystal structure
  - Task for the crystallographer
    - ☐ How are the atoms/molecules in this solid arranged in 3D?
- Insight into structure-property relationships
  - Key characterisation method for the materials chemist
    - ☐ Why is my material an ionic conductor?
    - ☐ Why does my material exhibit negative thermal expansion?
    - ☐ How can I make a better superconductor?

Structure Determination: Typical Output

- Table of determined (refined) structural parameters

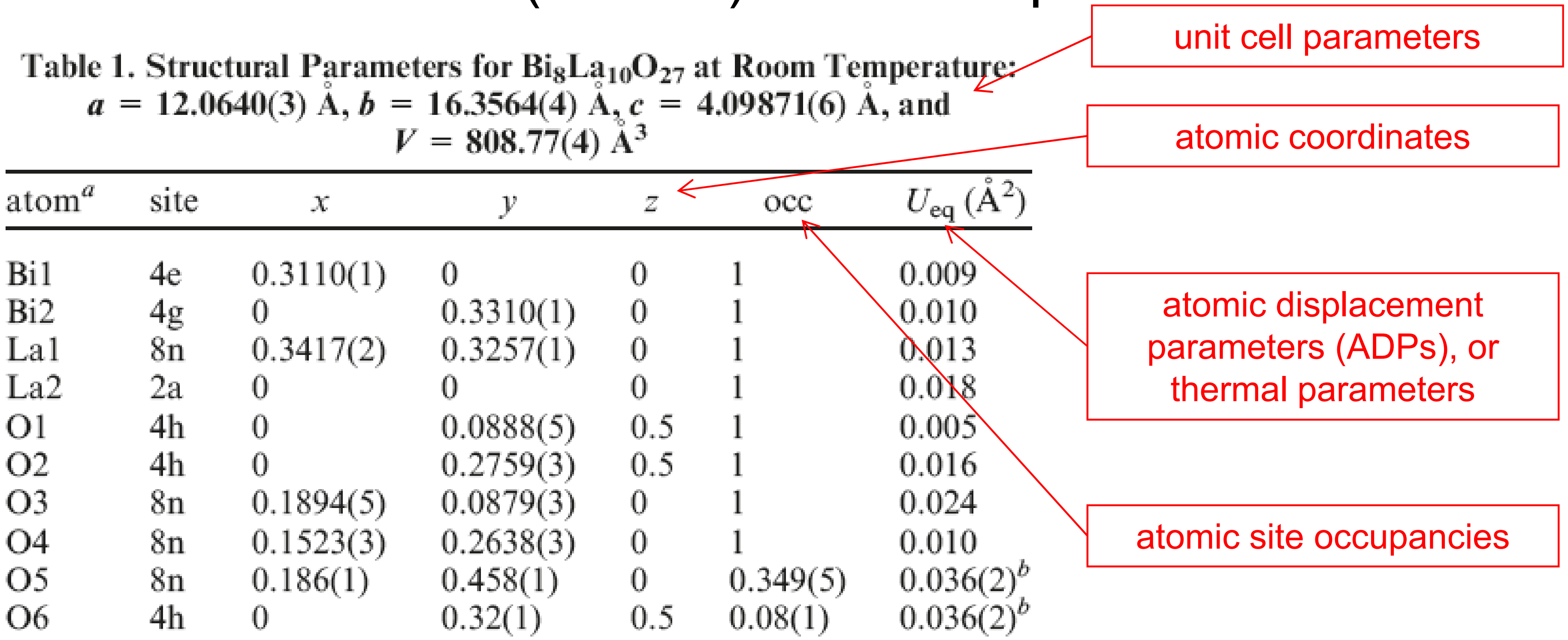


Table 1. Structural Parameters for $Bi_8La_{10}O_{27}$ at Room Temperature: a = 12.0640(3) Å, b = 16.3564(4) Å, c = 4.09871(6) Å, and V = 808.77(4) Å^3

atom[a]	site	x	y	z	occ	U_{eq} (Å^2)
Bi1	4e	0.3110(1)	0	0	1	0.009
Bi2	4g	0	0.3310(1)	0	1	0.010
La1	8n	0.3417(2)	0.3257(1)	0	1	0.013
La2	2a	0	0	0	1	0.018
O1	4h	0	0.0888(5)	0.5	1	0.005
O2	4h	0	0.2759(3)	0.5	1	0.016
O3	8n	0.1894(5)	0.0879(3)	0	1	0.024
O4	8n	0.1523(3)	0.2638(3)	0	1	0.010
O5	8n	0.186(1)	0.458(1)	0	0.349(5)	0.036(2)[b]
O6	4h	0	0.32(1)	0.5	0.08(1)	0.036(2)[b]

unit cell parameters

atomic coordinates

atomic displacement parameters (ADPs), or thermal parameters

atomic site occupancies

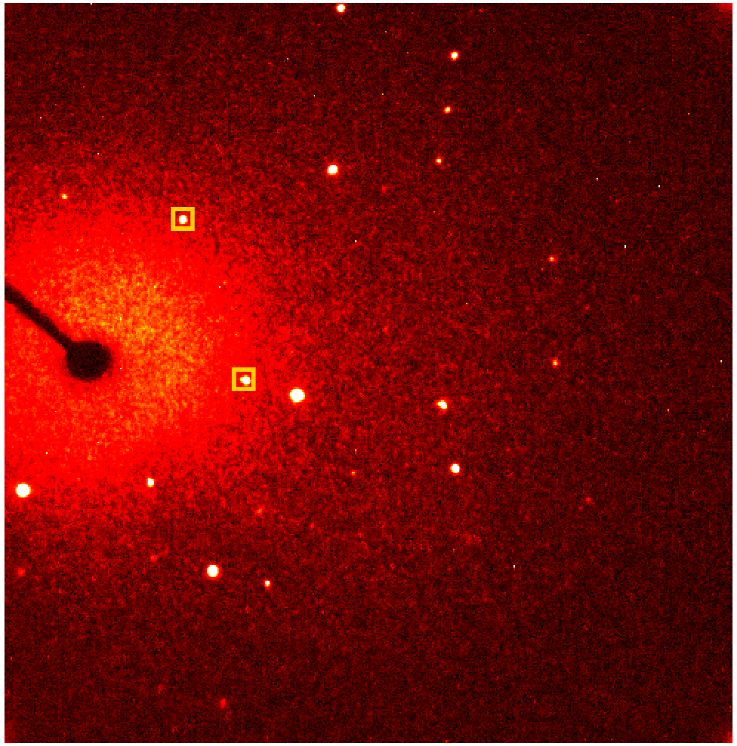
- From these parameters, conclusions about the atomic connectivity and coordination environments (bond lengths and angles) can be drawn

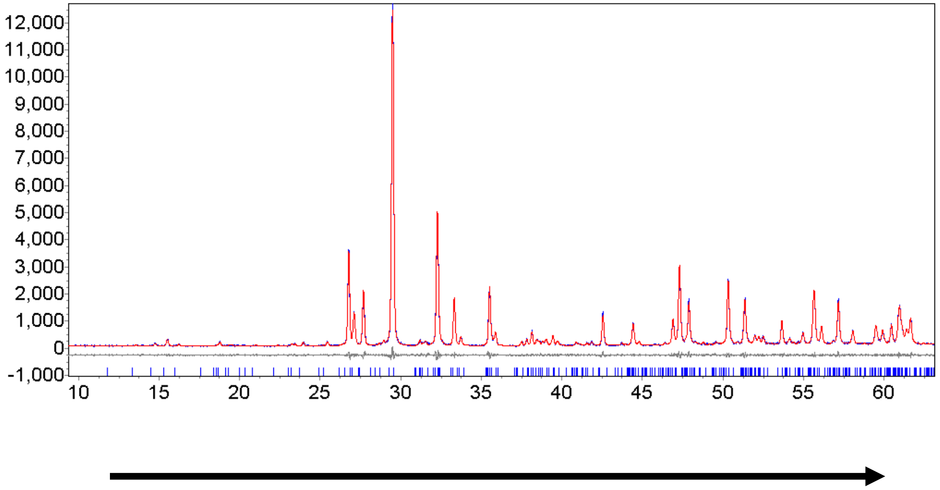
Diffraction Patterns

- Experimentally observed diffraction patterns

Single crystal diffraction

Powder diffraction





2θ (°)

Diffraction by Crystalline Solids

- Crystalline materials = long-range 3D periodic atomic arrays
  - Interatomic distances ~ 0.5 – 2.5 Å

- Waves of comparable wavelengths will be diffracted
  - X-rays = EM radiation, $\lambda \sim 0.1 - 100$ Å
  - Neutrons
  - Electrons

$$\left.\begin{array}{l}\text{Neutrons}\\ \text{Electrons}\end{array}\right\} \quad \lambda = h / mv$$

$$\Downarrow$$

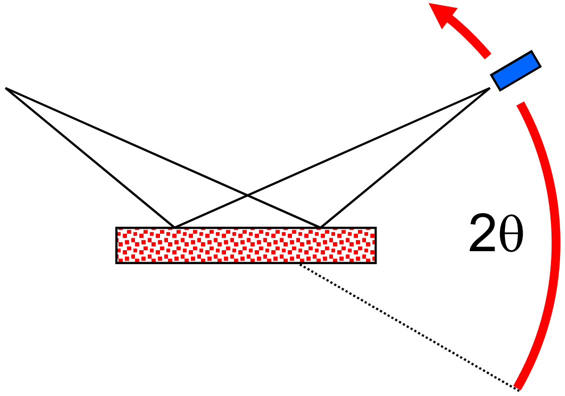
- X-rays, neutrons and electrons are diffracted by crystals

$$\Downarrow$$

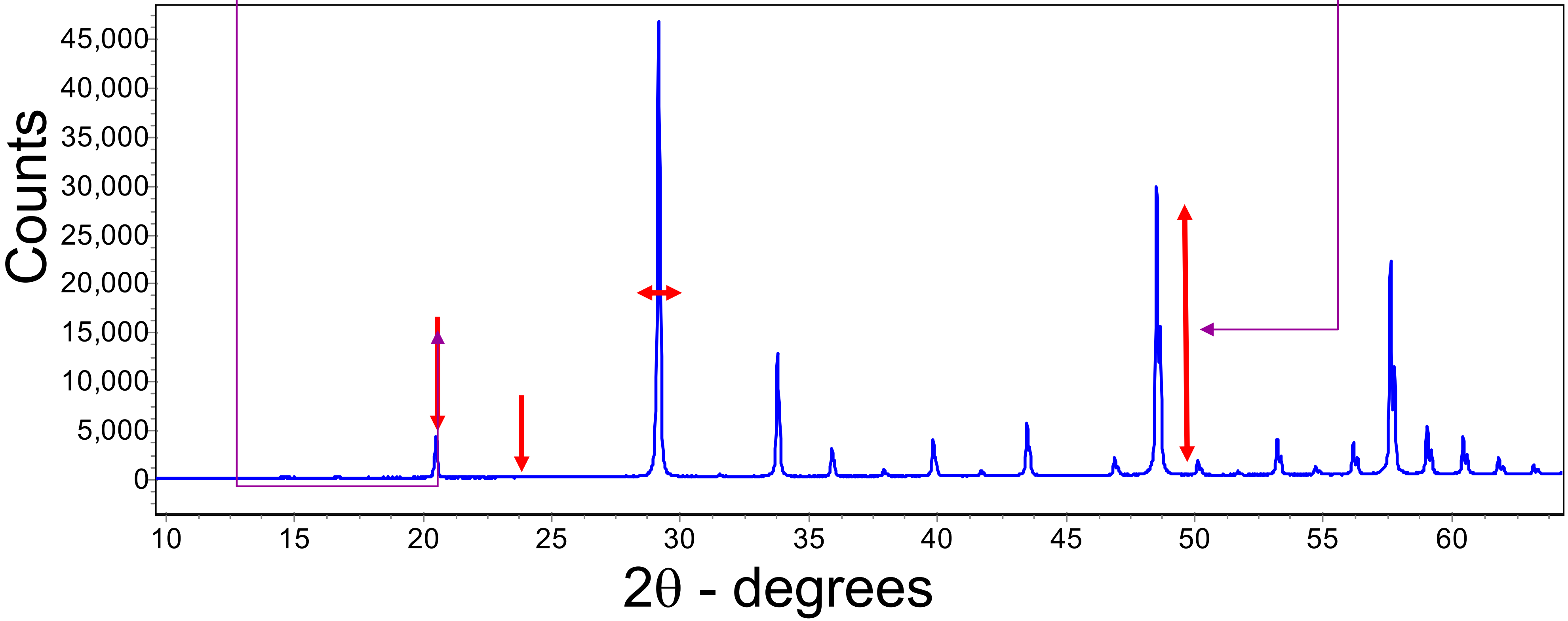
- X-ray, neutron and electron diffraction patterns contain information about 3D arrangement of atoms in crystals

Information in a Powder Pattern

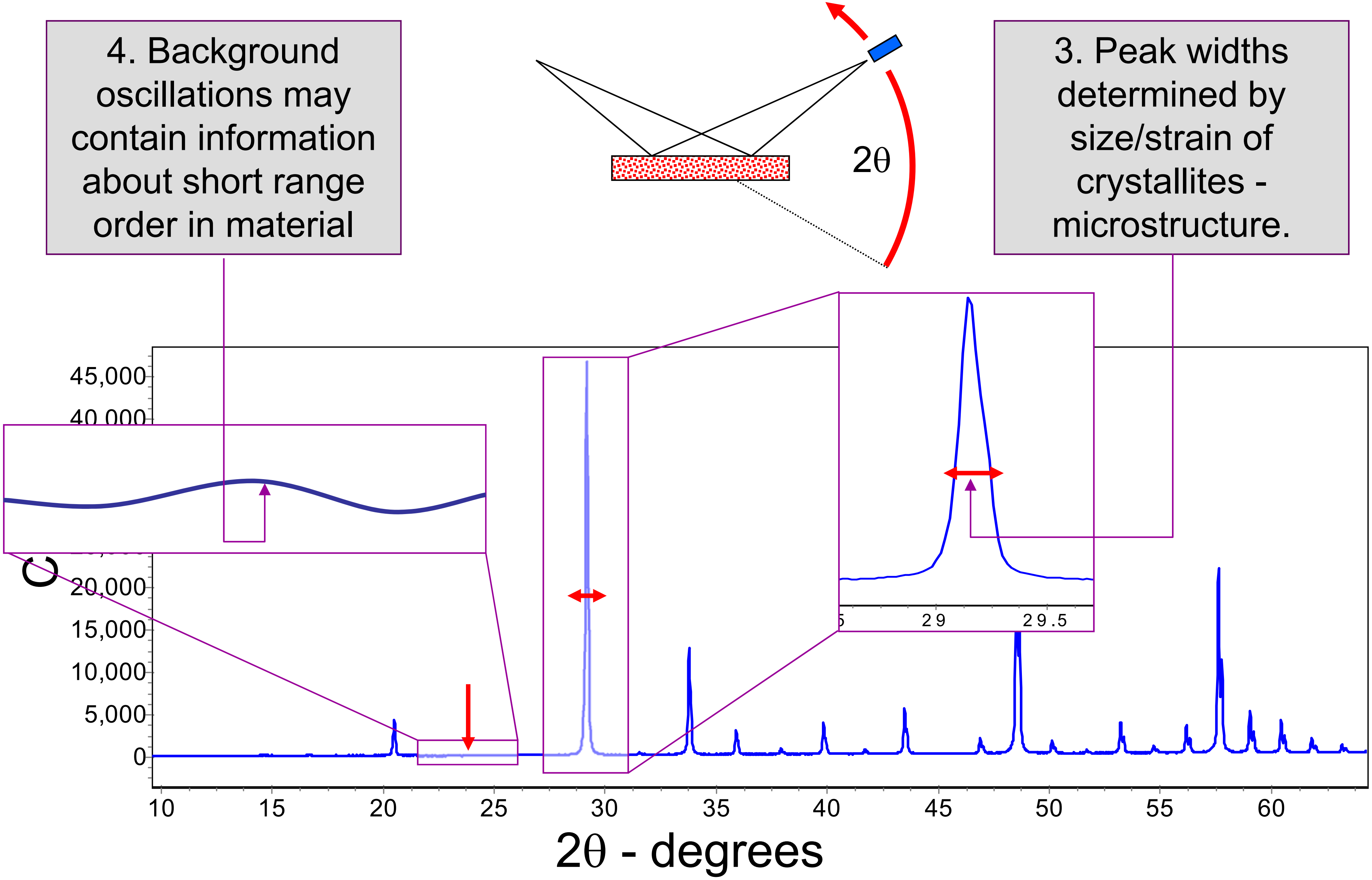
1. Peak positions determined by size and shape of unit cell – internal structure



2. Peak Intensities determined by where atoms sit in unit cell – internal structure



Information in a Powder Pattern

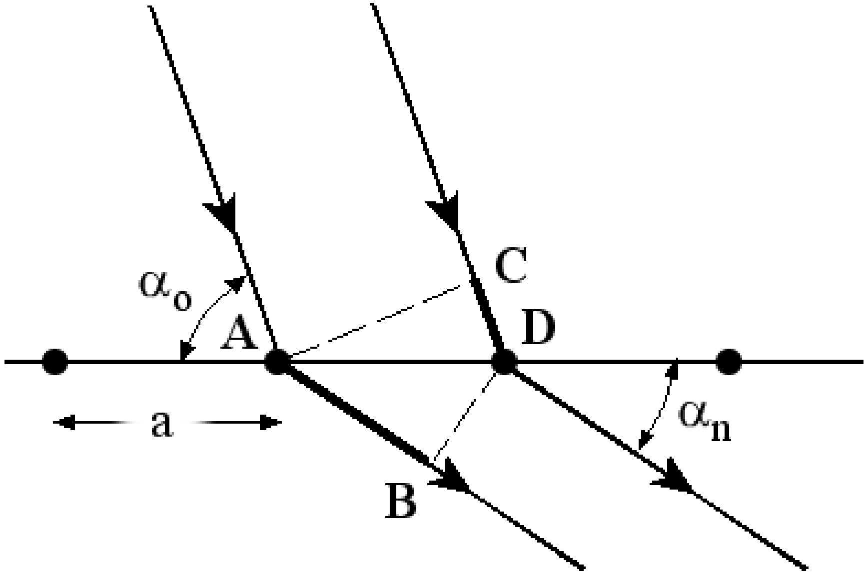


4. Background oscillations may contain information about short range order in material

3. Peak widths determined by size/strain of crystallites - microstructure.

Diffraction by Crystalline Solids

- 1D periodic array of atoms (unit cell parameter a)

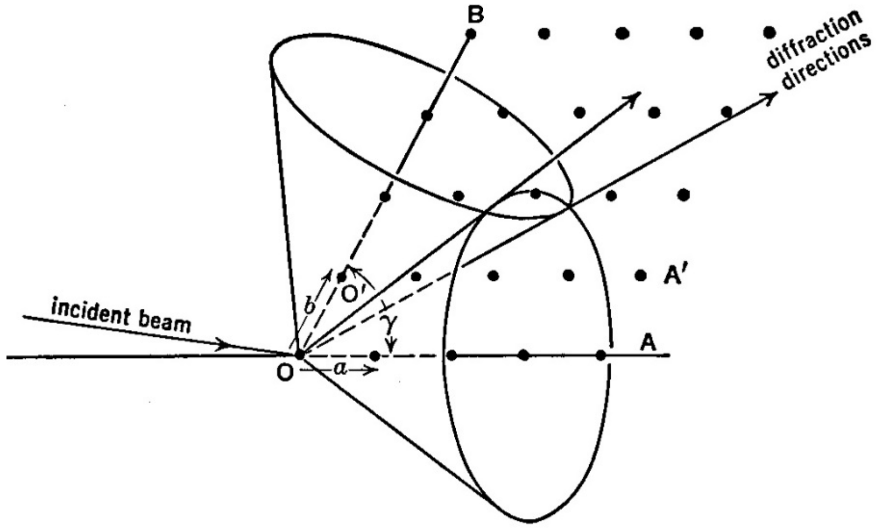


Constructive interference:

$(AB - CD) = a(\cos \alpha_n - \cos \alpha_o) = h\lambda$

Diffraction by Crystalline Solids

- 2D periodic array of atoms (unit cell parameters a, b)
- Maxima in two directions



Constructive interference:

$$a(\cos \alpha_n - \cos \alpha_o) = h\lambda$$

$$b(\cos \beta_n - \cos \beta_o) = k\lambda$$

Diffraction by Crystalline Solids

- 3D periodic array of atoms (unit cell parameters a, b, c)
- Maximum in one direction

Constructive interference:

$a(\cos \alpha_n - \cos \alpha_o) = h\lambda$

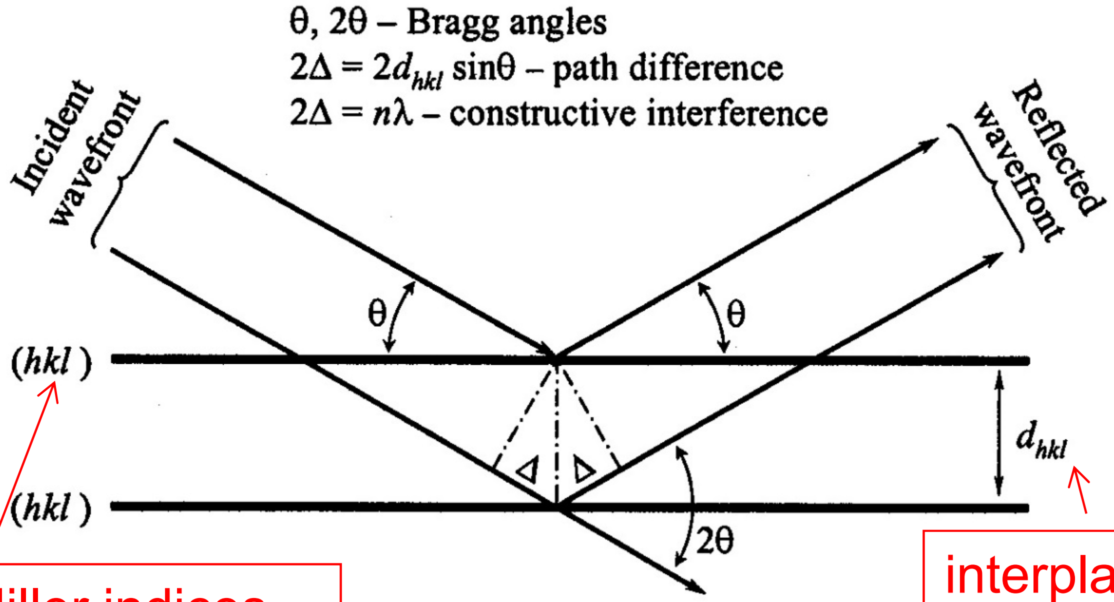
$b(\cos \beta_n - \cos \beta_o) = k\lambda$

$c(\cos \gamma_n - \cos \gamma_o) = l\lambda$

Laue equations

Bragg's Law

- Simplistic, but useful view of diffraction
  - Atoms arranged in parallel planes in a crystal
  - Incident X-rays reflected off the planes
  - Peaks in diffraction patterns referred to as "reflections"



Miller indices

interplanar spacing, d-spacing

$$2\Delta = n\lambda$$

(n=order of diffraction*)

$$2d_{hkl}\sin\theta = \lambda$$

*n=1, because nth order diffraction from (hkl) planes with spacing d can be treated as 1st order diffraction from (nh, nk, nl) planes with spacing d/n

d-spacings and Cell Parameters

- d-spacings in crystals are related to the unit cell parameters a, b and c
- For orthogonal crystal systems:

$$\frac{1}{d_{hkl}^{2}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

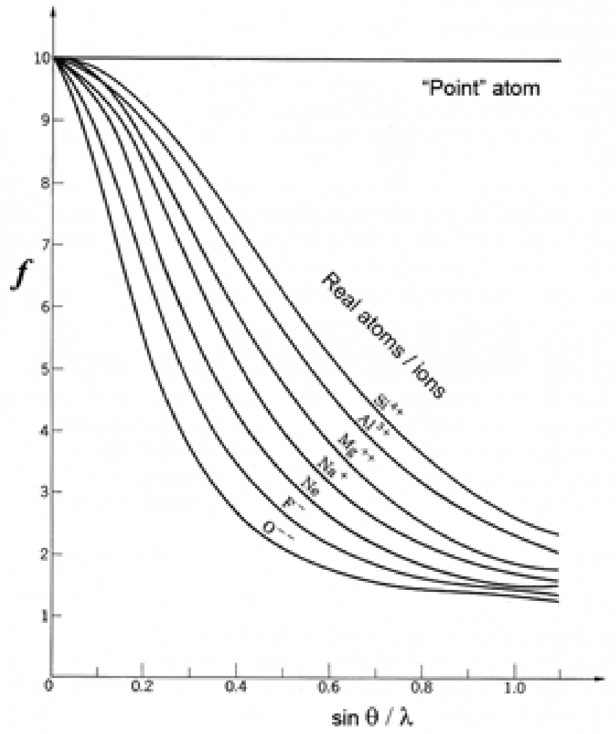
- Applications:
  - From known unit cell parameters, we can predict diffraction patterns (peak positions)
  - From experimentally observed peak positions, we can determine unit cell parameters

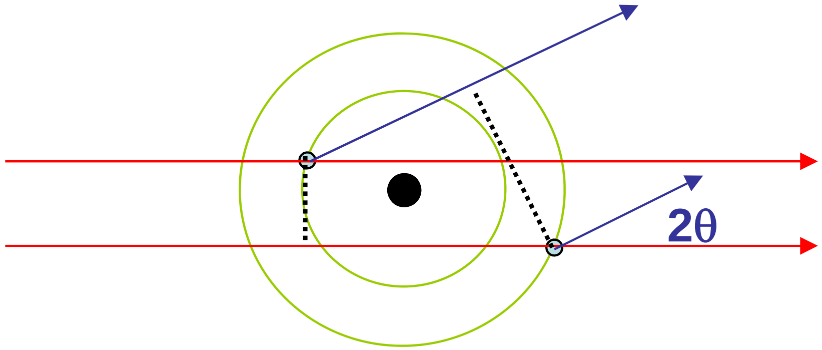
Scattering of X-rays by Atoms

- X-rays are scattered by electrons

$$f = \frac{\text{amplitude of the wave scattered by an atom}}{\text{amplitude of the wave scattered by one electron}}$$

- Thomson (elastic) scattering
- The atomic scattering factor $f = Z$ for any atom in the forward direction ($2\theta = 0$):
- As θ increases f decreases $\rightarrow$ functional dependence of the decrease depends on the details of the distribution of electrons around an atom
- f is calculated using quantum mechanics





Scattering of X-rays by the Unit Cell

- Peak intensities, I_{hkl}: $I_{hkl} \propto |F_{hkl}|^2$
  - $|F_{hkl}|$ ~ the collective scattering power of the atoms in the unit cell
  - Other factors: absorption, thermal vibrations, site occupancies, …

- Structure factor, F_{hkl}

$$F_{hkl} = \sum_{1}^{N} f_n e^{2\pi i\left(hx_n + ky_n + lz_n\right)}$$

Electronic property of the atom
Information about atom types

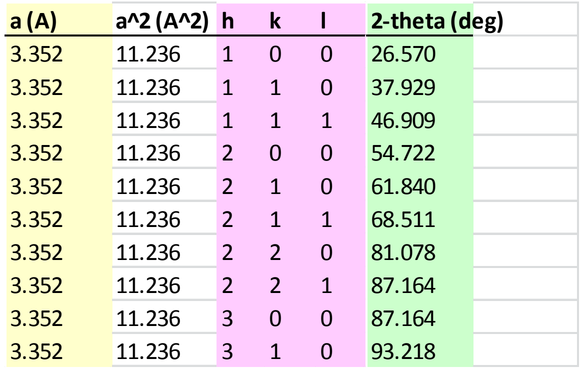
Structural property of the unit cell
Information about atomic positions

- F_{hkl} is a complex number: $F_{hkl} = |F_{hkl}| e^{i\phi_{\mathrm{hkl}}}$

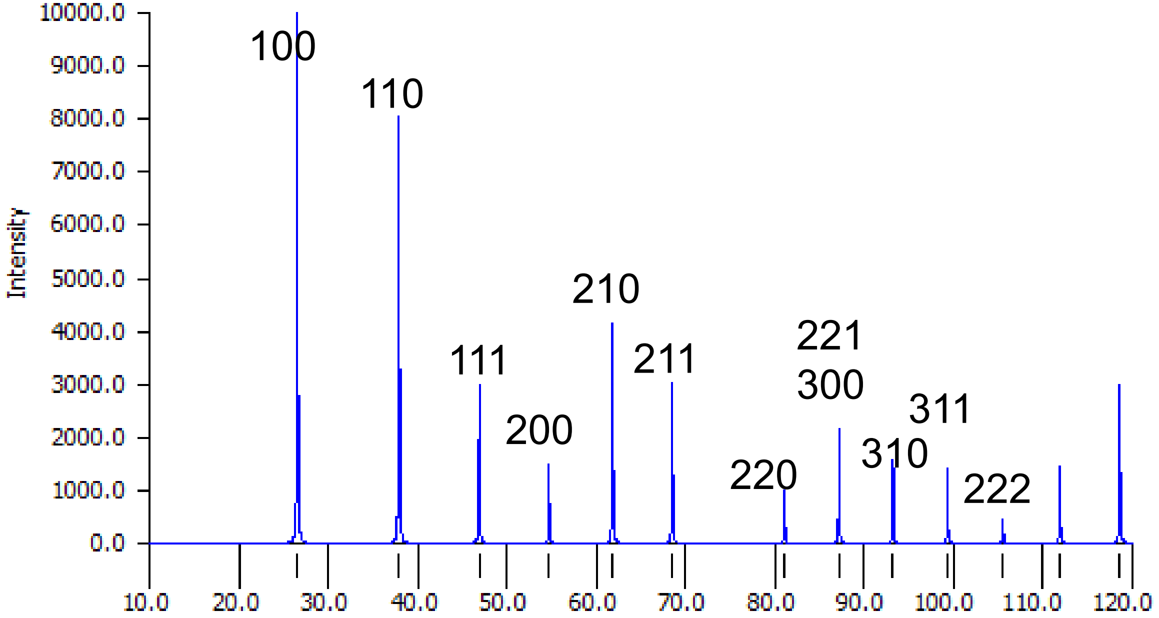
*x_n, y_n and z_n are atomic fractional coordinates: $x_n = x/a$, $y_n = y/b$, $z_n = z/c$

Systematic Absences

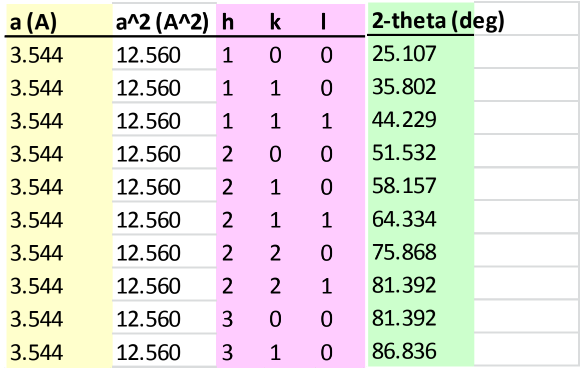
- Example: Po
  - Primitive cubic (*Pm-3m*)
  - a = 3.352 Å



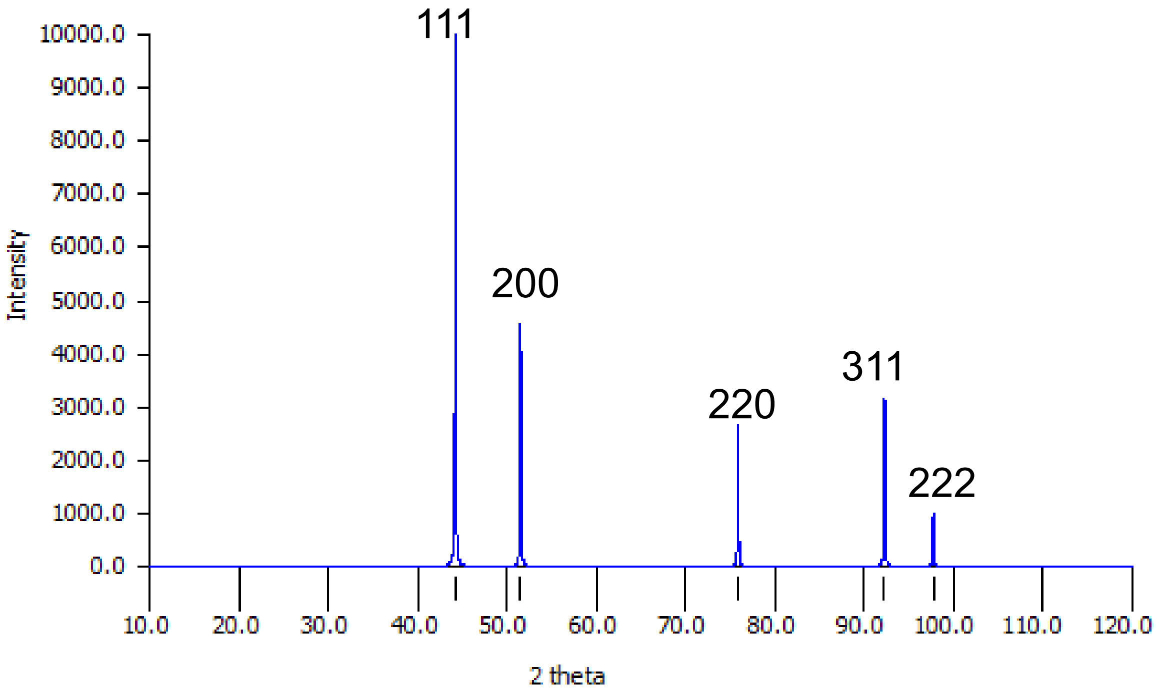
a (A)	a^2 (A^2)	h	k	l	2-theta (deg)
3.352	11.236	1	0	0	26.570
3.352	11.236	1	1	0	37.929
3.352	11.236	1	1	1	46.909
3.352	11.236	2	0	0	54.722
3.352	11.236	2	1	0	61.840
3.352	11.236	2	1	1	68.511
3.352	11.236	2	2	0	81.078
3.352	11.236	2	2	1	87.164
3.352	11.236	3	0	0	87.164
3.352	11.236	3	1	0	93.218



- Example: Co
  - Face-centred cubic (*Fm-3m*)
  - a = 3.544 Å



a (A)	a^2 (A^2)	h	k	l	2-theta (deg)
3.544	12.560	1	0	0	25.107
3.544	12.560	1	1	0	35.802
3.544	12.560	1	1	1	44.229
3.544	12.560	2	0	0	51.532
3.544	12.560	2	1	0	58.157
3.544	12.560	2	1	1	64.334
3.544	12.560	2	2	0	75.868
3.544	12.560	2	2	1	81.392
3.544	12.560	3	0	0	81.392
3.544	12.560	3	1	0	86.836

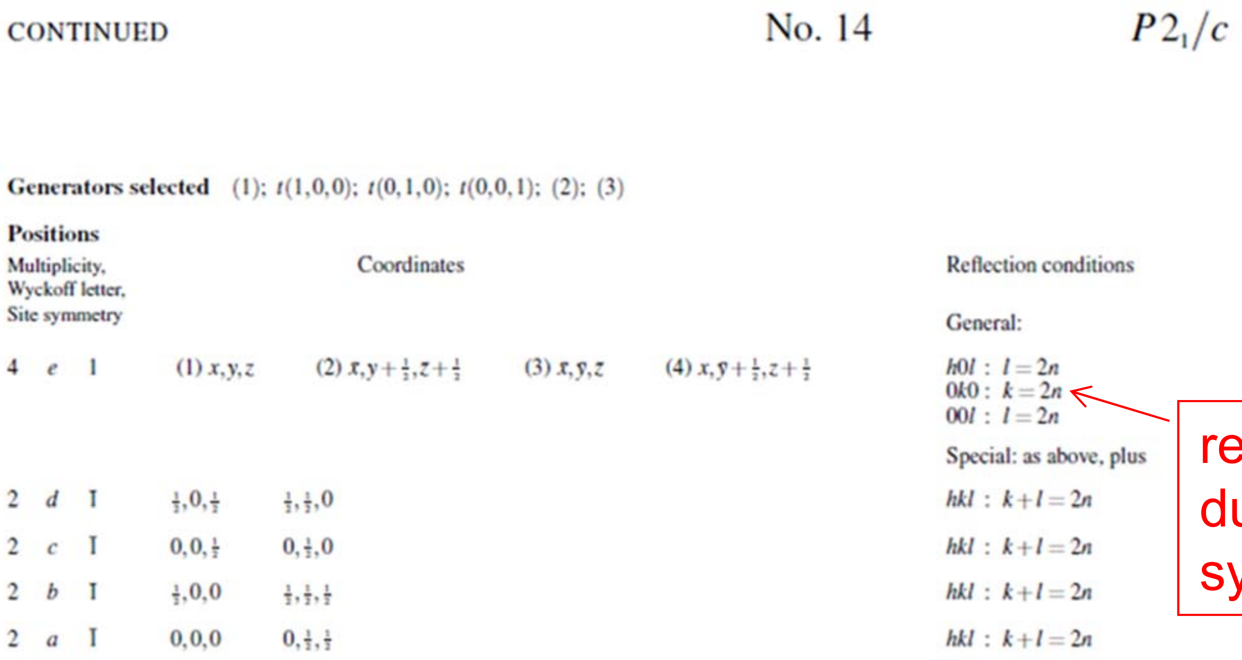


Systematic Absences

- Cell centring:

Centring	Reflection condition
I	$h + k + l = 2n$
F	h , k , l all even/all odd
A	$k + l = 2n$
B	$h + l = 2n$
C	$h + k = 2n$

- Translational symmetry elements:



CONTINUED No. 14 $P2_1/c$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l$: $l=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
							Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			hkl : $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl : $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$

reflection conditions due to translational symmetry elements

Structure Determination

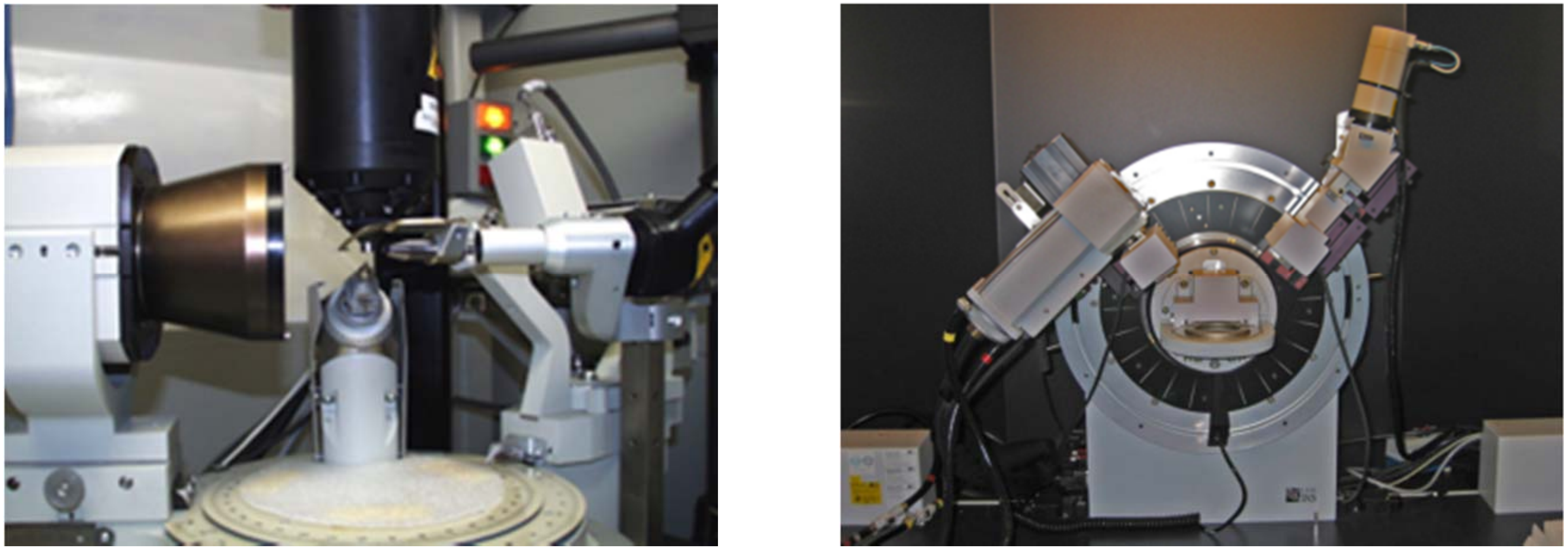
1. Diffraction pattern indexing ⇒ unit cell
2. Systematic absences/ reflection conditions ⇒ space group
3. Structure solution ⇒ finding approximate atomic positions
   - solution of the phase problem (approximate phases)
4. Structure refinement ⇒ final structure
   - iterative improvement of the fit between the observed and calculated intensities (by adjustment of structural parameters)
   - non-linear least squares
   - R-factor (%): measure of the agreement

Experimental Aspects

Source
- X-rays
- Neutrons

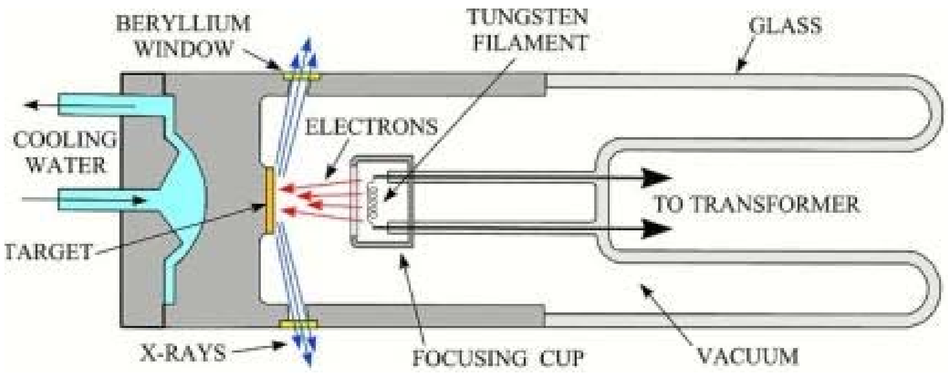
Sample
- Single crystal
- Powder

Detector
- Point detectors
- 2D detectors

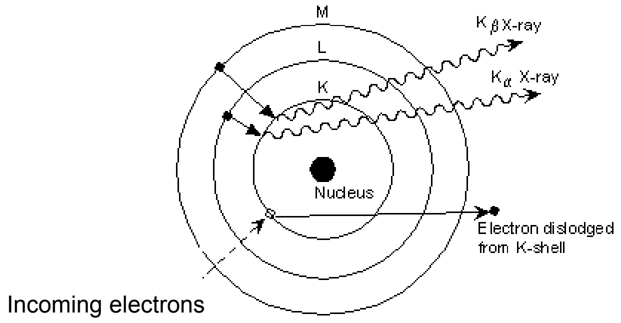


Laboratory X-ray Diffraction

- Laboratory source: X-ray tube

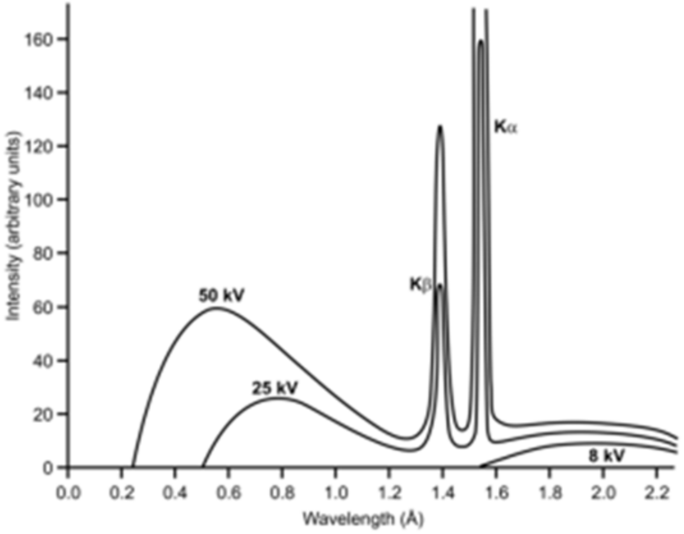


- Electrons accelerated from a filament (W) into a metal target (Cu, Mo)
    - continuous spectrum (bremsstrahlung)
    - characteristic X-rays (electronic transitions)

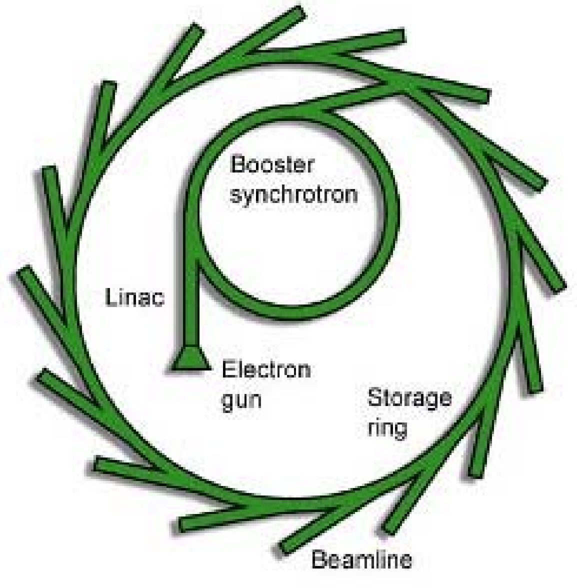


Cu Kα: 1.54184 Å

Mo Kα: 0.711445 Å



Synchrotron X-ray Diffraction (SXRD)

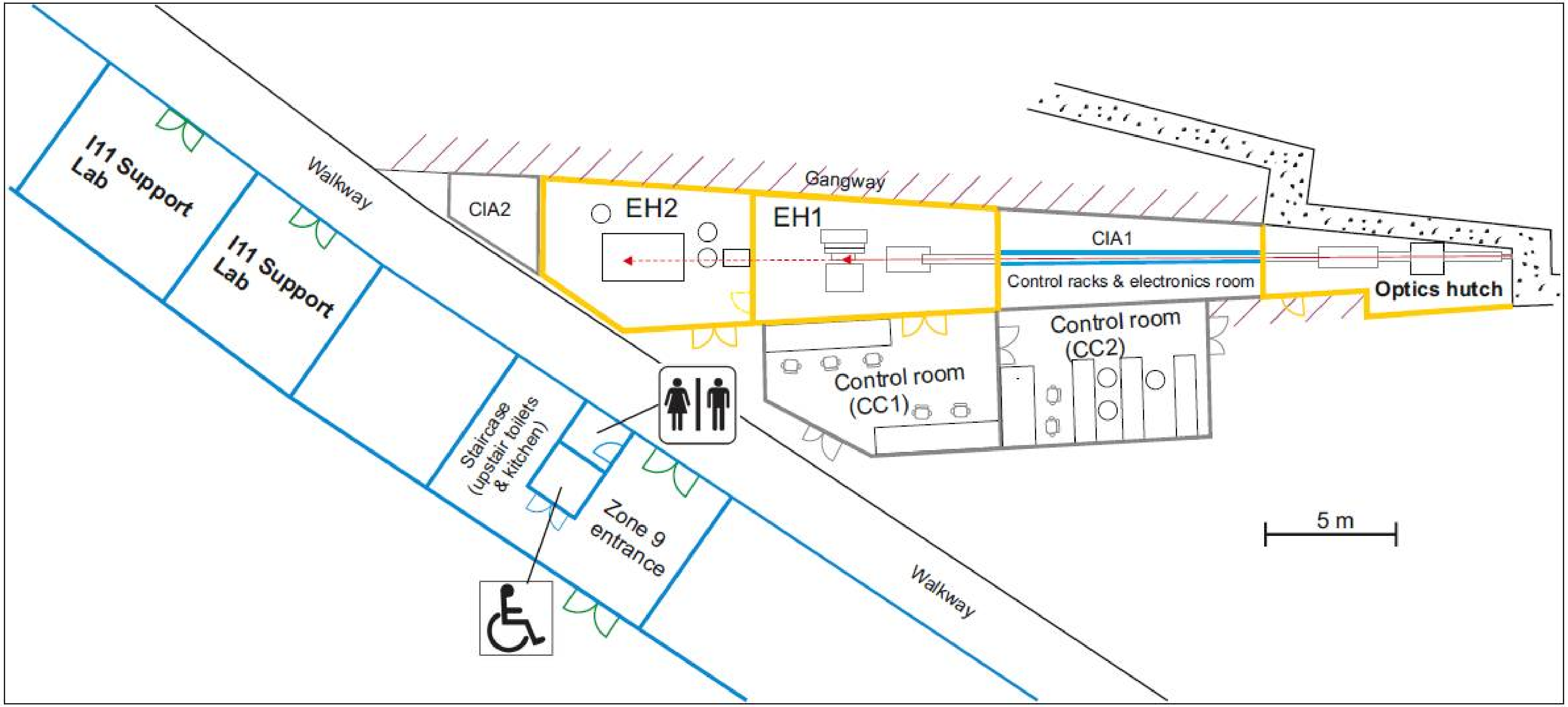


- Synchrotron radiation
  - Electrons moving at relativistic speed along a curved path

- Advantages over lab sources
  1. Tunable λ
  2. High intensity
  3. Highly monochromatic λ and highly collimated beam

Synchrotron X-ray Diffraction (SXRD)

- Powder diffraction beamline I11, Diamond Light Source, UK
  - Layout and area plan

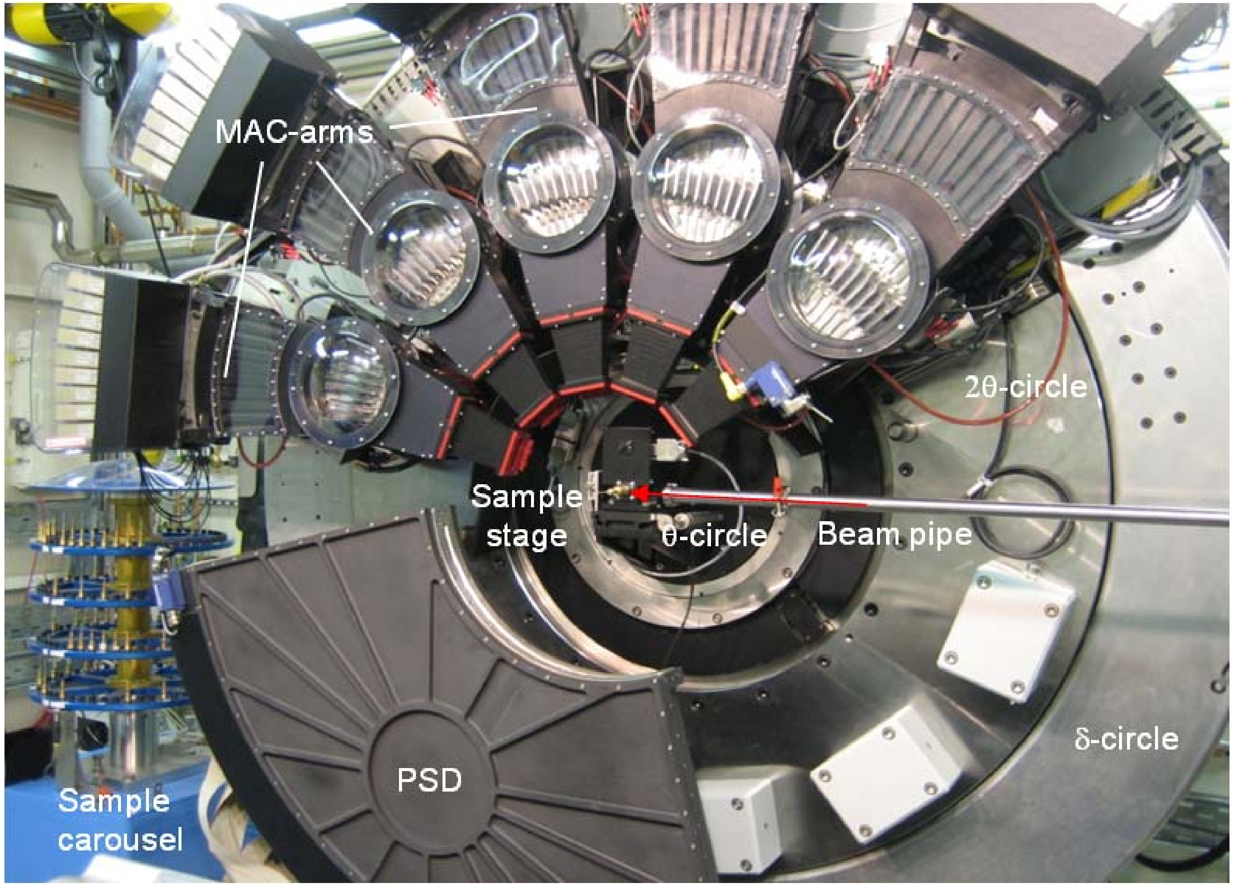


Synchrotron X-ray Diffraction (SXRD)

- Powder diffraction beamline I11, Diamond Light Source, UK
  - Experimental hutch 1 (EH1): the diffractometer

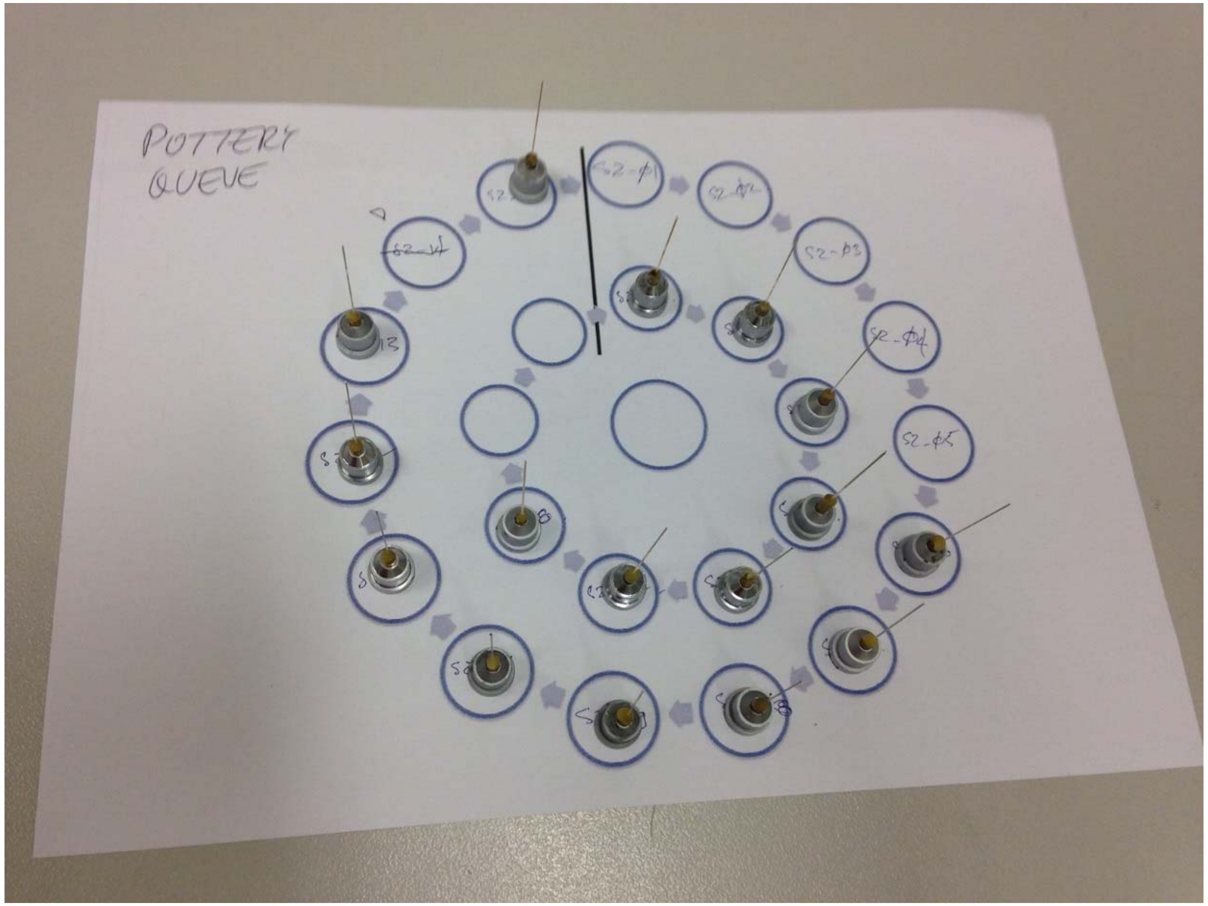
Synchrotron X-ray Diffraction (SXRD)

- Powder diffraction beamline I11, Diamond Light Source, UK
  - Sample stage and detectors



Synchrotron X-ray Diffraction (SXRD)

- Powder diffraction beamline I11, Diamond Light Source, UK
  - Prepared samples in capillaries



Synchrotron X-ray Diffraction (SXRD)

- Powder diffraction beamline I11, Diamond Light Source, UK
  - Operation

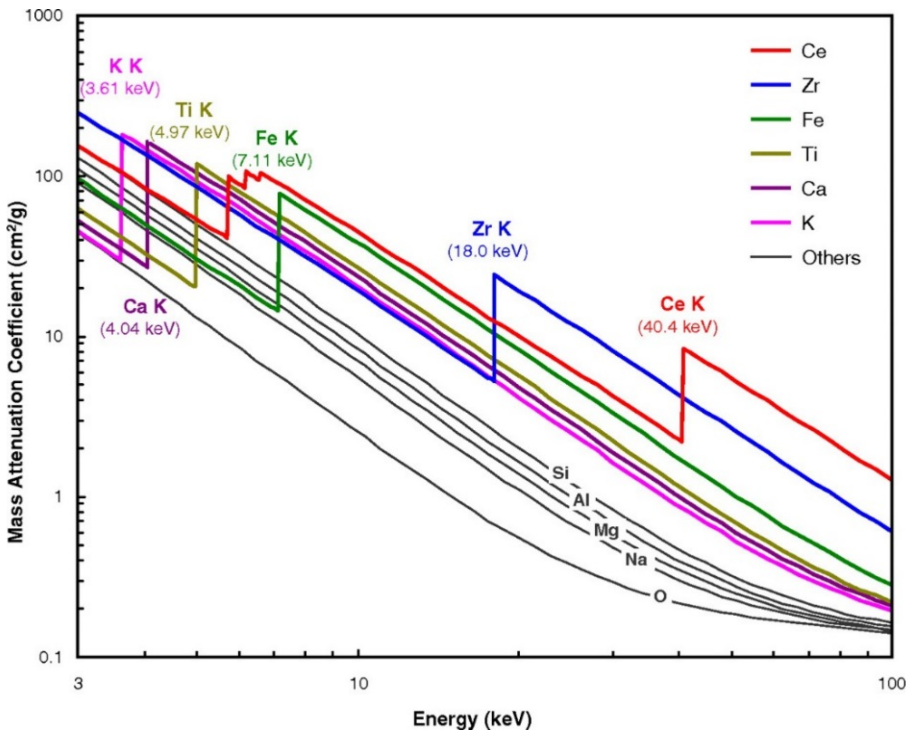
I11_exp_start.mov

SXRD: Tunable Wavelength

- Flux vs. energy
  - I11 at Diamond: 6-25 keV (0.4-2.1 Å), optimised at 15 keV

$I_x \propto I_o e^{-\mu x}$ $\mu = f(E)$

- Optimising absorption
  1. Minimising absorption (hard X-rays)
  2. Experiments away from absorption edges
  3. Experiments at absorption edges



- Applications of resonant (anomalous) scattering
  - Macromolecular xtl: multiple anomalous diffraction (MAD) phasing
  - Physics: exotic magnetism (skyrmions)

SXRD: Tunable Wavelength

- Example 1: Minimising absorption
  - Choose λ and capillary size so that: $\mu^*r < 1.5$
  - What capillary size would you use to measure Bi_2O_3 with $\lambda = 0.410$ Å and 0.825 Å?

    Information: Bi_2O_3 density 8.9 g/cm^3; powder packing density 60%; RMM (Bi_2O_3) = 466.0; mass absorption coefficients for $\lambda = 0.41$ Å: Bi 31.520 cm^2/g, O 0.378 cm^2/g; for $\lambda = 0.825$ Å: Bi 156.000 cm^2/g, O 1.836 cm^2/g.

SXRD: Intensity

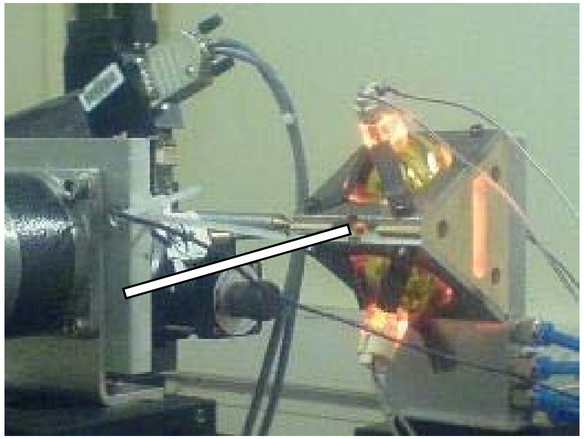
- Intensity ~10^3 lab X-ray source
  - Small samples
  - Rapid data collections
  - Excellent statistics
  - In-situ experiments, complex sample environments

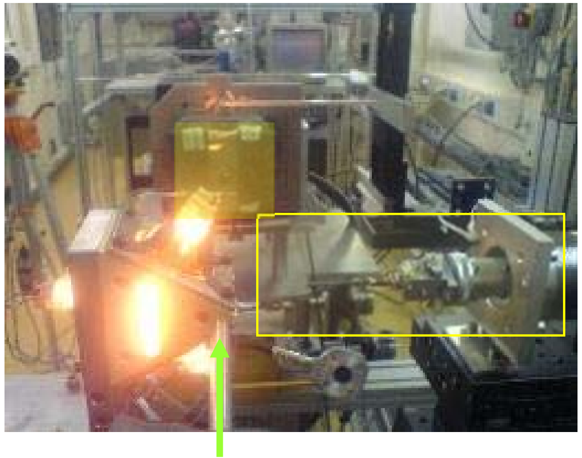
- Example 2: $ZrMo_2O_8$ ultra-rapid synthesis/in-situ SXRD
  - Negative thermal expansion (NTE) material
  - Cubic γ-$ZrMo_2O_8$ shows smooth NTE ($\alpha = -8 \times 10^{-6}$ K^{-1}) over a wide temperature range
  - Previously produced under kinetic control (e.g. dehydration of $ZrMo_2O_7(OH)_2 \cdot 2H_2O$)
  - Metastable

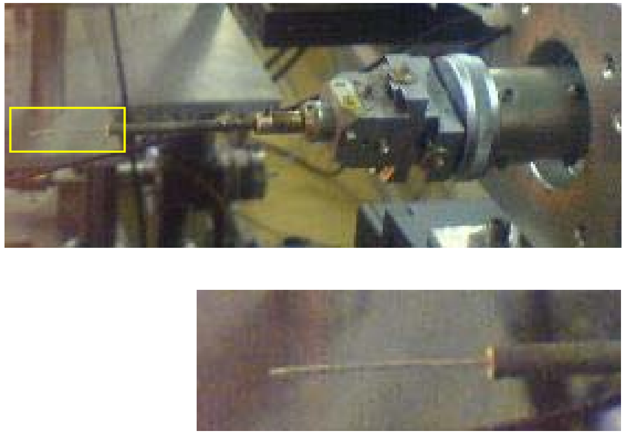
JSO Evans et al., *JACS*, 131, 48, 17560, 2009.

SXRD: Intensity

- Example 2: $ZrMo_2O_8$ ultra-rapid synthesis/in-situ SXRD
  - Beamline ID11 at ESRF, Grenoble
  - λ = 0.19902(2) Å
  - Stoichiometric amounts of ZrO_2 and MoO_3 packed into Pt capillaries (0.57 mm diameter, 0.04 mm wall thickness)



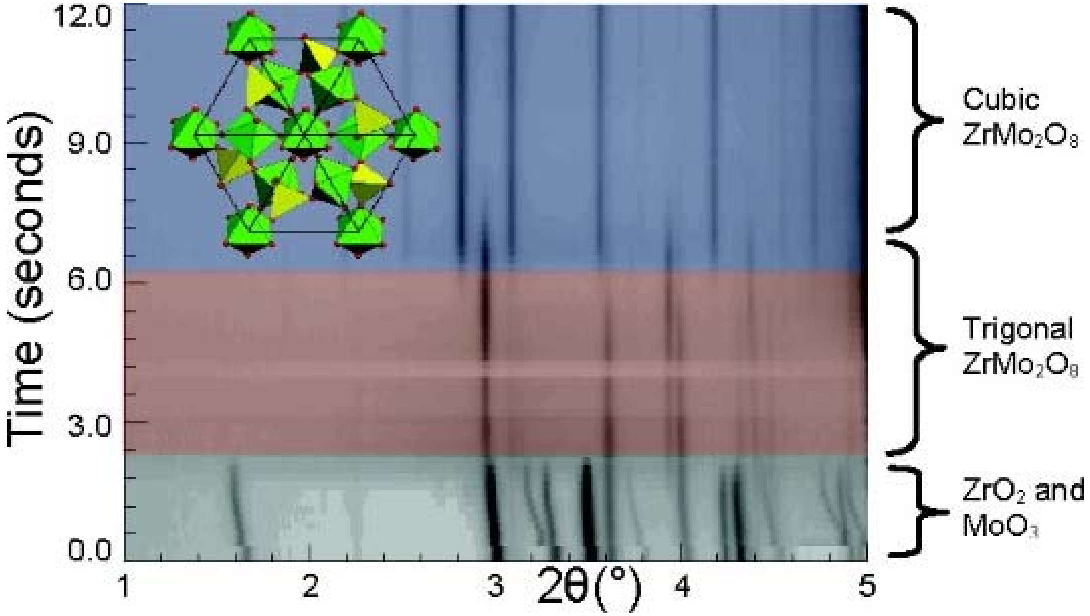




JSO Evans et al., *JACS*, 131, 48, 17560, 2009.

SXRD: Intensity

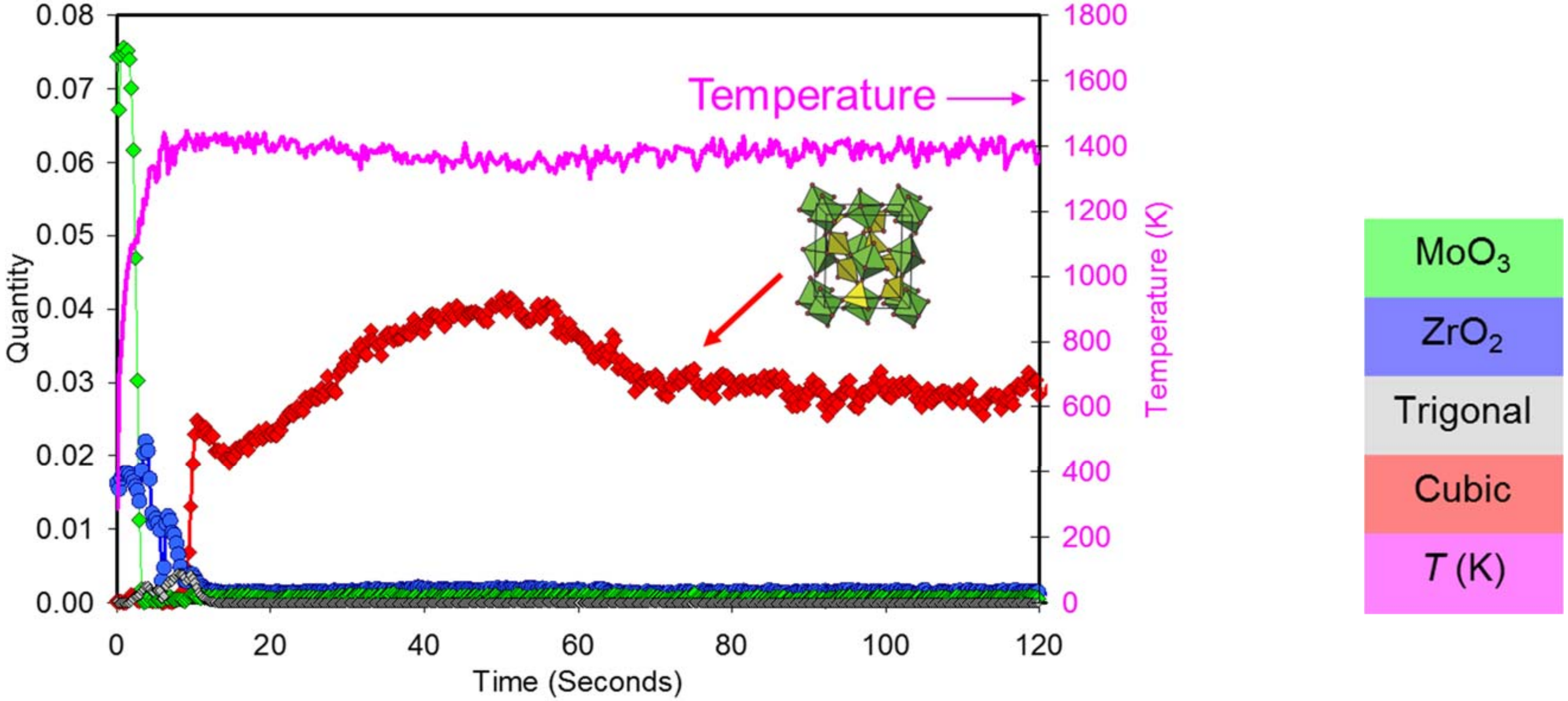
- Example 2: $ZrMo_2O_8$ ultra-rapid synthesis/in-situ SXRD
  - 0.25 s data collections; 480 patterns in 120 s



JSO Evans et al., *JACS*, 131, 48, 17560, 2009.

SXRD: Intensity

- Example 2: $ZrMo_2O_8$ ultra-rapid synthesis/in-situ SXRD
  - Cubic γ-$ZrMo_2O_8$ formed directly from oxides at 1400 K
  - Can be quenched to room temperature
  - Insight into the reaction pathways from quantitative analysis by Rietveld refinement (5 phases)



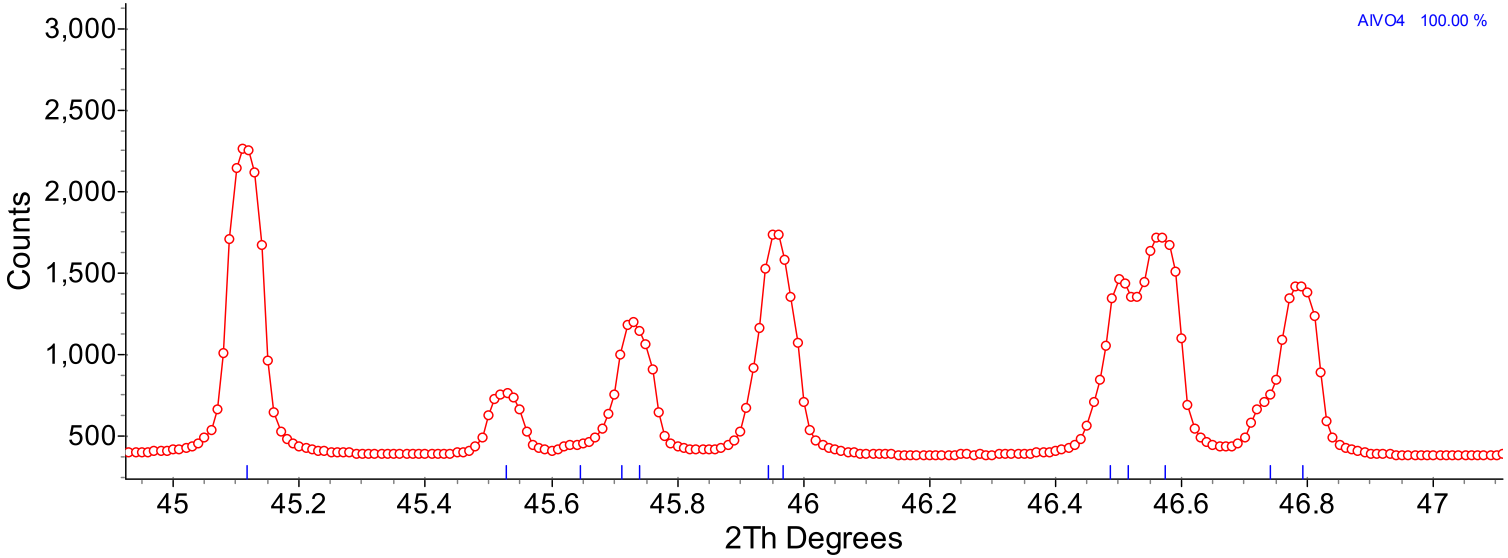
JSO Evans et al., *JACS*, 131, 48, 17560, 2009.

SXRD: High Resolution

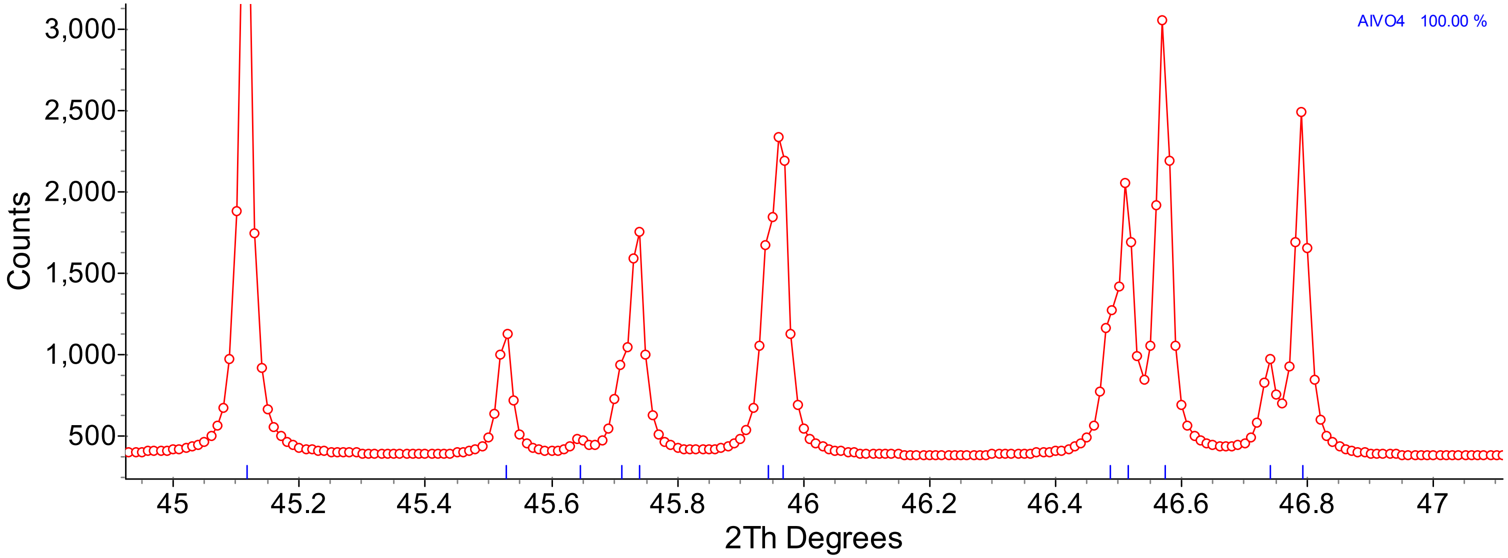
- Resolution: $\Delta d/d$
- Highly monochromatic λ and highly collimated beam
  - Narrow instrumental peak shape
  - Best resolution instruments: $\Delta d/d \sim 10^{-4}$
- Peak widths depend on:
  - Source
  - Instrument (optics)
  - Sample

$$\boxed{\mathrm{Y}(2\theta) = (\mathrm{Source} \otimes \mathrm{Instrument}) \otimes \mathrm{Sample}}$$

High vs Medium Resolution

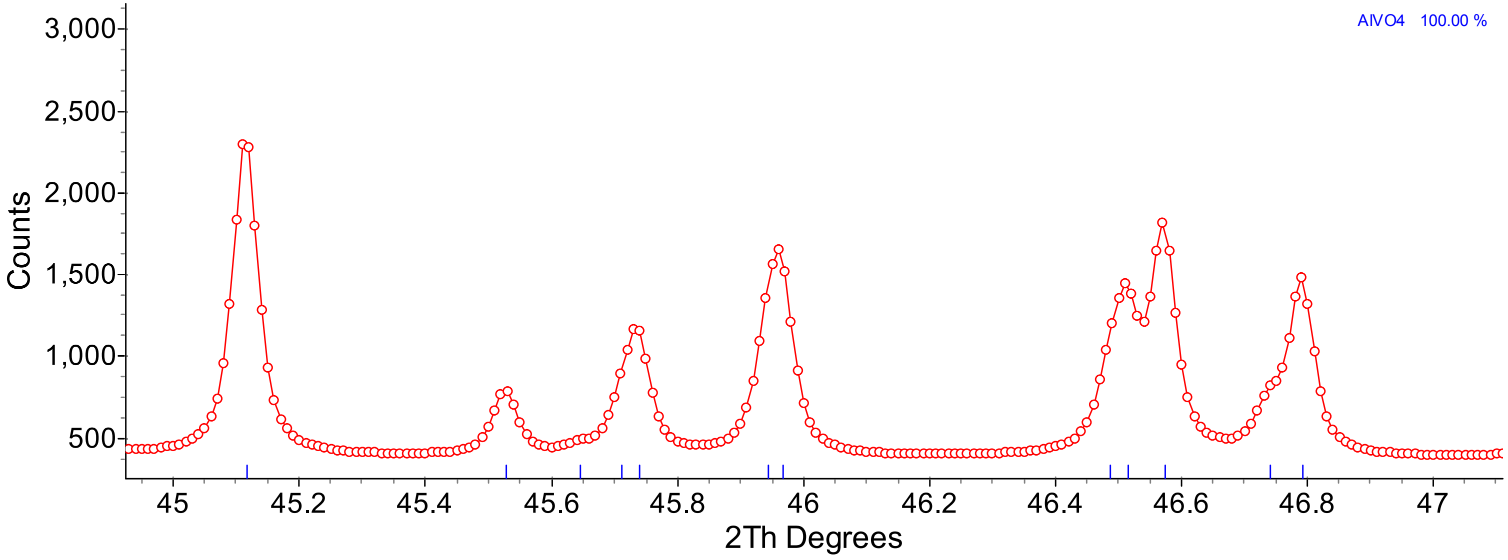


0.20 mm
detector slit



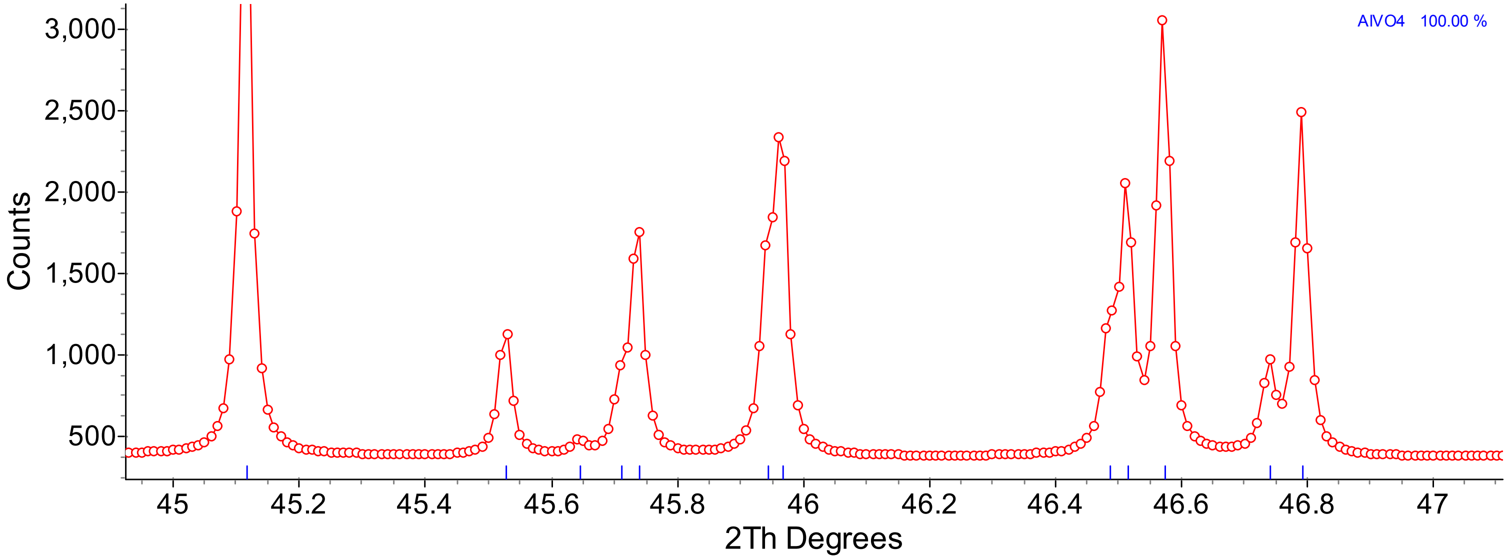
0.05 mm
detector slit

Large vs Small Domains



500 nm domains

0.05 mm detector slit

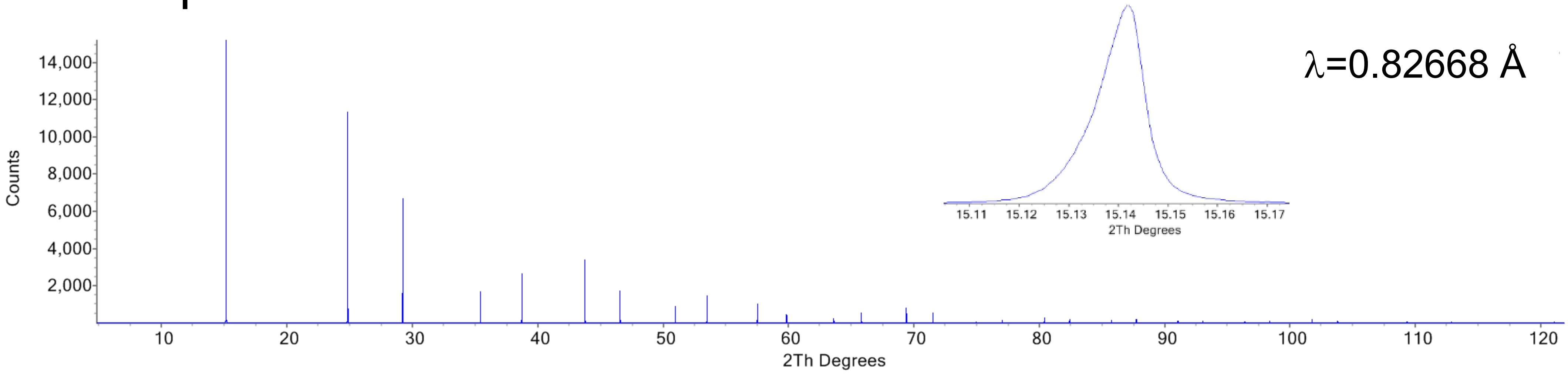


“infinite” domains

0.05 mm detector slit

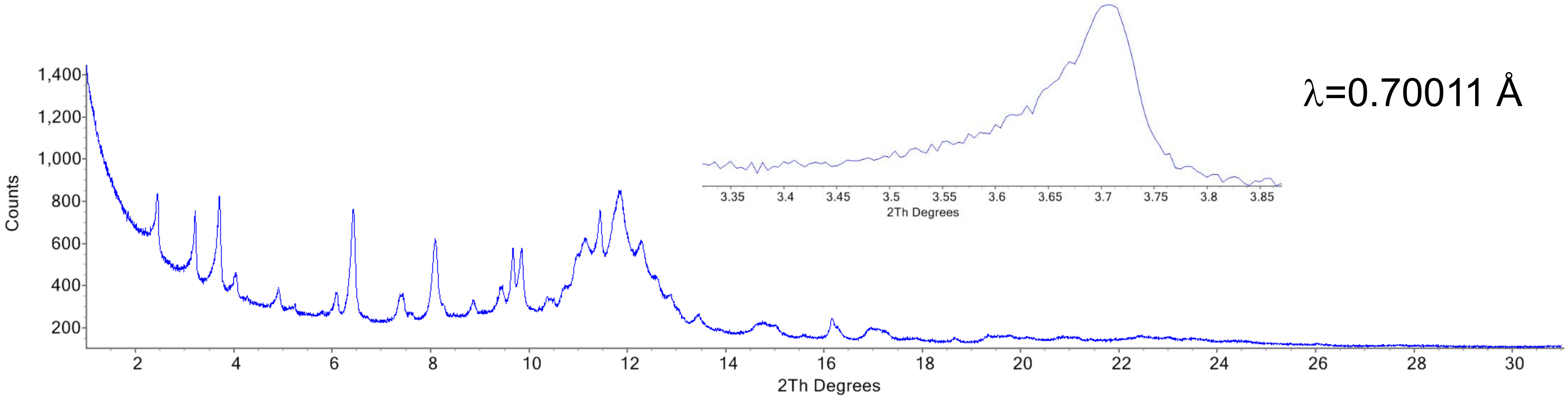
SXRD: High Resolution

- Si pattern



λ=0.82668 Å

- Mechanochemically prepared small organic



λ=0.70011 Å

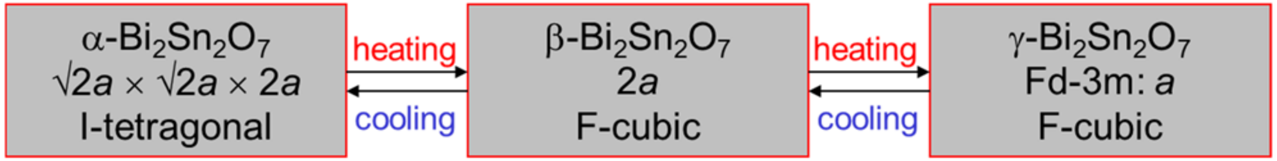
SXRD: High Resolution

- Example 3: Analysis of Egyptian eye make-up (2000 BC)
- Lab XRD suggested:
  - Galena (PbS) and cerussite ($PbCO_3$) – naturally occuring
  - Laurionite (PbOHCl) and phosgenite ($Pb_2Cl_2CO_3$) – very rare in nature
- High-resolution synchrotron XRD used for quantification
  - Laurionite and phosgenite up to 75%
- SEM used for particle morphology analysis
  - Particle morphology consistent with wet chemistry production
- Wet chemistry products
  - Purified (PbO, $NaCl$, Na_2CO_3)$_{aq.}$
  - Multiple solution reactions, filtrations, pH control
- Conclusion: Egyptians used wet chemistry ~2000 BC
  - Chemical technology in Ancient Egypt very sophisticated

Walter et al., *Nature*, 397, 483, 1999.

SXRD: High Resolution

- Example 4: $Bi_2Sn_2O_7$ structure solution
  - Phase diagram (old)



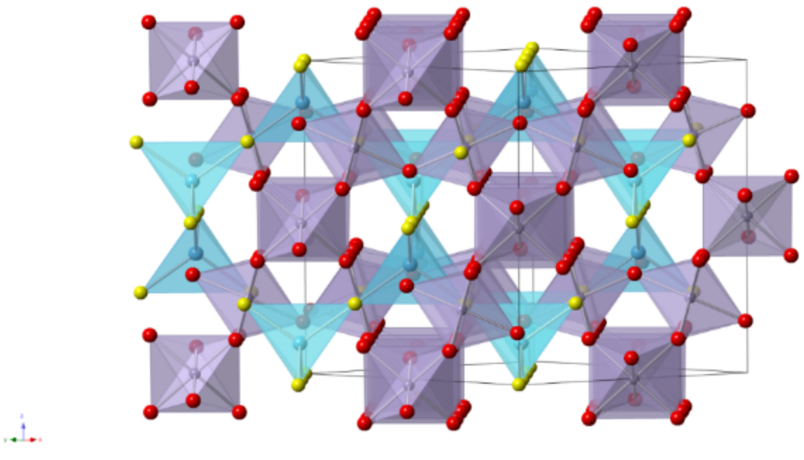
α-$Bi_2Sn_2O_7$
$\sqrt{2}a \times \sqrt{2}a \times 2a$
I-tetragonal

heating →
← cooling

β-$Bi_2Sn_2O_7$
$2a$
F-cubic

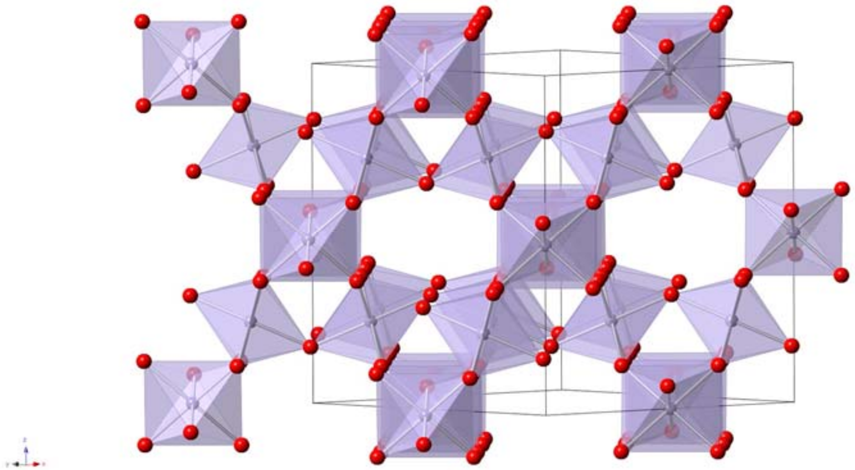
heating →
← cooling

γ-$Bi_2Sn_2O_7$
Fd-3m: a
F-cubic



Cubic γ-$Bi_2Sn_2O_7$

Fd-3*m*
a = 10.72 Å

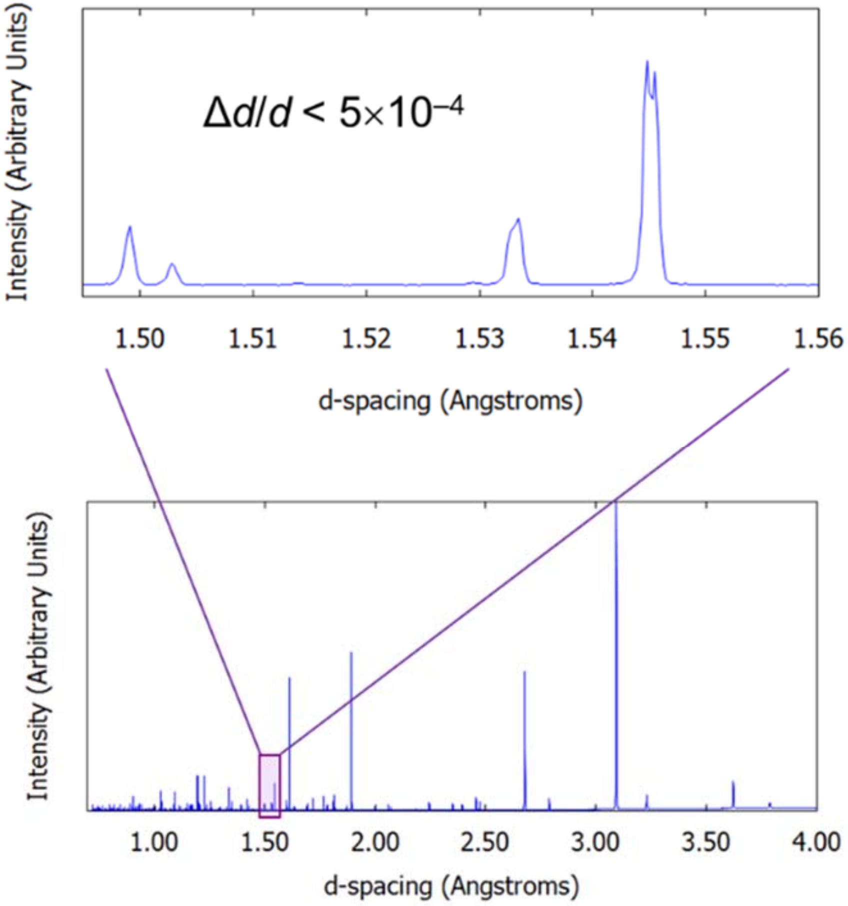


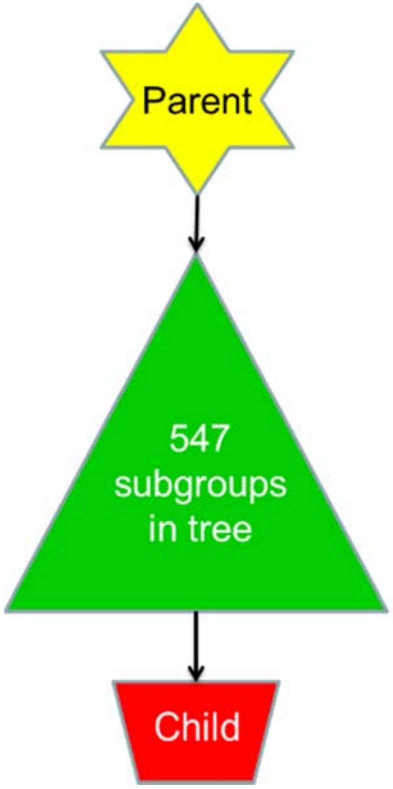
Interpenetrating Sn_2O_6 and Bi_2O' frameworks

IR Evans, JSO Evans et al., *JACS*, 138, 25, 8031, 2016.

SXRD: High Resolution

- Example 4: $Bi_2Sn_2O_7$ structure solution
  - Beamline I11, Diamond Light Source, UK
  - β-$Bi_2Sn_2O_7$ is not cubic
  - Very important for the structure solution methodology used
  - Exhaustive symmetry descent approach





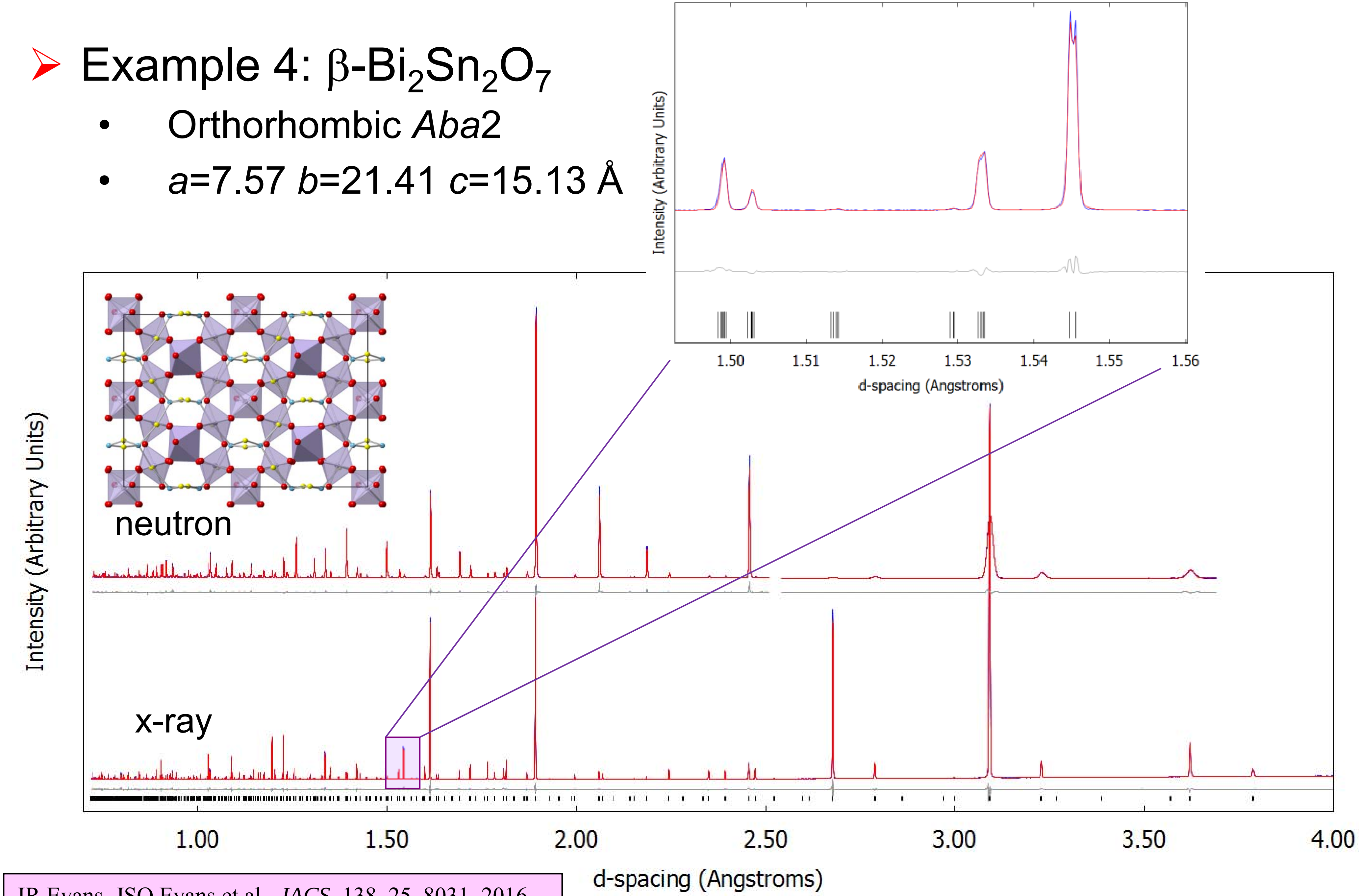
Fd-3m γ parent

P1 $\sqrt{2}a \times \sqrt{2}a \times 2a$ child

IR Evans, JSO Evans et al., *JACS*, 138, 25, 8031, 2016.

SXRD: High Resolution

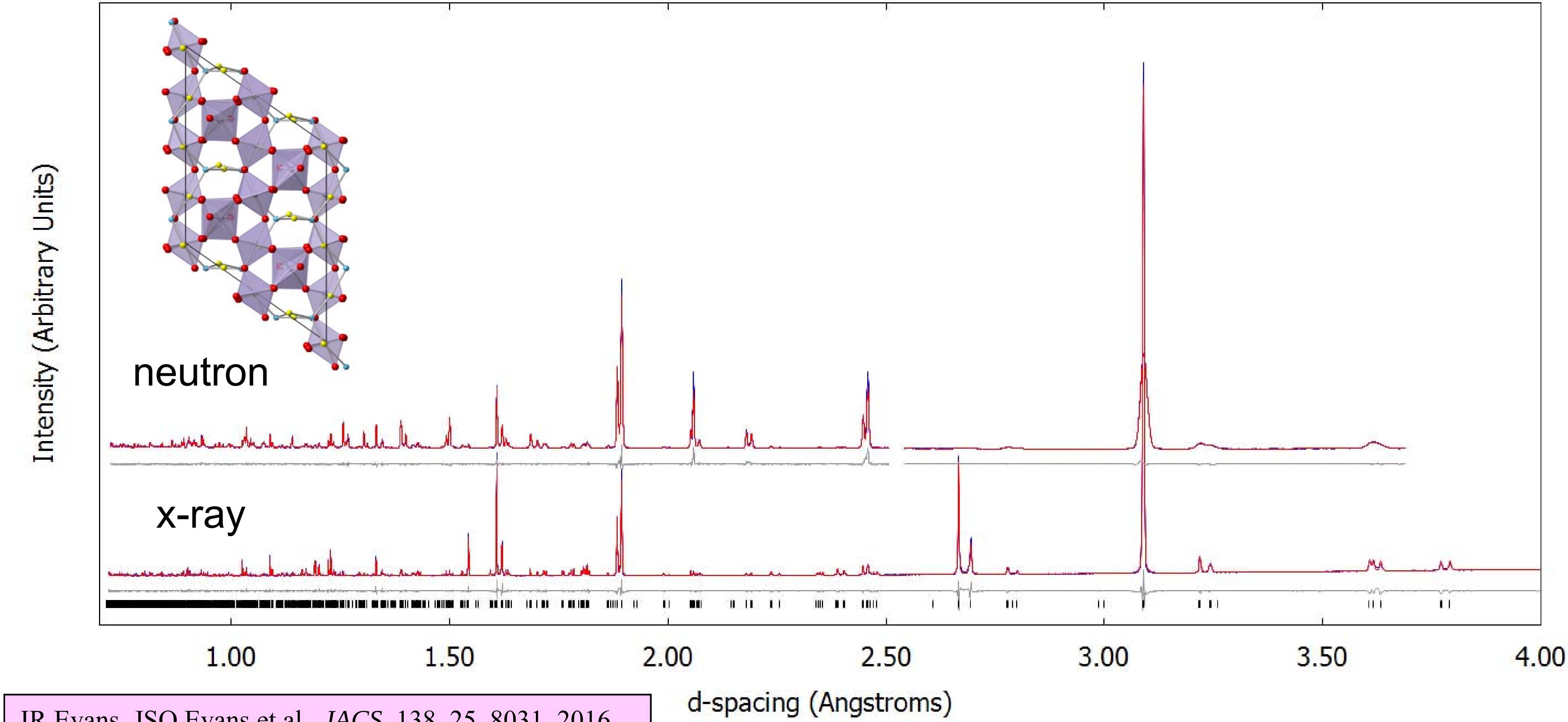
- Example 4: β-$Bi_2Sn_2O_7$
  - Orthorhombic *Aba*2
  - *a*=7.57 *b*=21.41 *c*=15.13 Å



IR Evans, JSO Evans et al., *JACS*, 138, 25, 8031, 2016.

SXRD: High Resolution

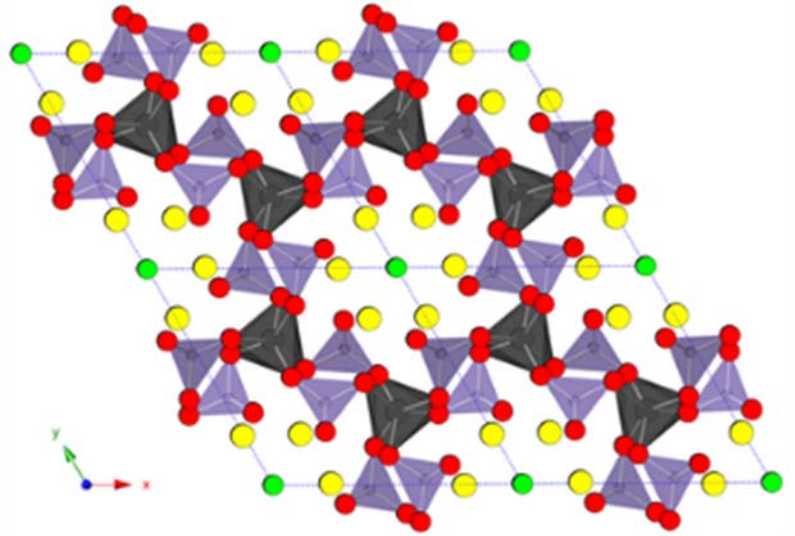
- Example 4: α-$Bi_2Sn_2O_7$
  - Monoclinic *Cc*
  - *a*=7.57 *b*=21.41 *c*=15.13 Å *β*=125°



IR Evans, JSO Evans et al., *JACS*, 138, 25, 8031, 2016.

SXRD: High Resolution

- Example 5: $Bi_2La_8(GeO_4)_6O_3$
  - Oxide ion conductor
  - Apatite structure type (normally hexagonal)
  - $Bi_2La_8(GeO_4)_6O_3$ triclinic at room temperature

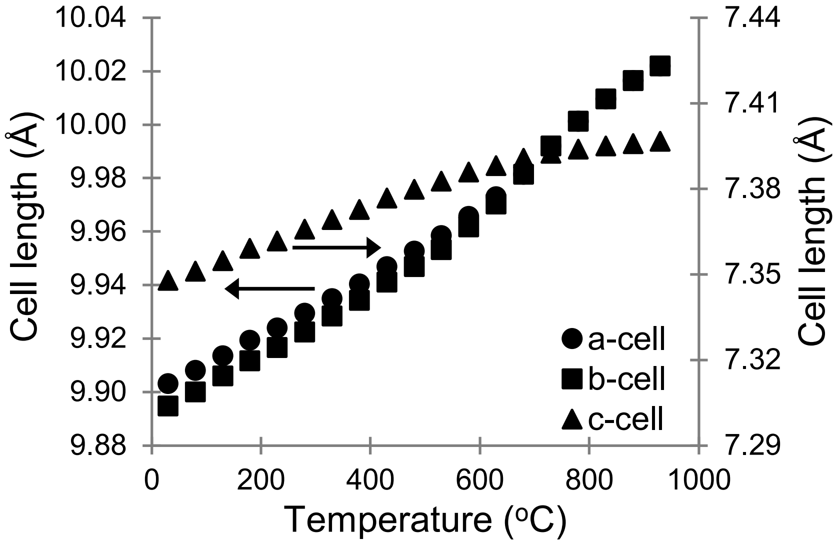


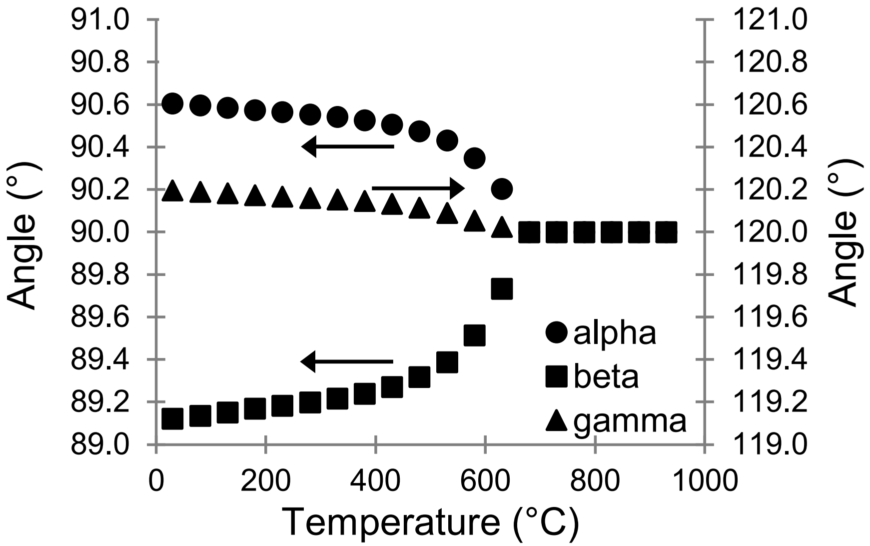
  - Very small unit cell distortions:
    a = 9.90376(10) Å, b = 9.89598(12) Å, c = 7.34622(7) Å
    α = 90.5638(9)^o, β = 89.2007(8)^o, γ = 120.1412(7)^o,

IR Evans et al., *Advanced Functional Materials*, 27, 1605625, 2017.

SXRD: High Resolution

- Example 5: $Bi_2La_8(GeO_4)_6O_3$
  - High-resolution PD beamline, Australian Synchrotron, Melbourne
  - Phase transition to hexagonal above 700°C
  - Unit cell parameters extracted by Rietveld fitting of the data





IR Evans et al., *Advanced Functional Materials*, 27, 1605625, 2017.

Synchrotron X-ray Diffraction (SXRD)

- Advantages over lab sources
  1. Tunable λ
  2. High intensity
  3. Highly monochromatic λ and highly collimated beam

- Disadvantages
  1. Access: proposal, delay, limited beam time, no opportunity to repeat
  2. Lack of control over options and conditions